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A Modified Electrochemical Process for the Decomposition of Hydrogen Sulfide in an Aqueous Alkaline Solution

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ABSTRACT

An electrochemical process for the decomposition of hydrogen sulfide into its constituents in an aqueous alkaline solution is presented. It essentially consists of presaturation of an alkaline scrubber solution with H₂S. Thereafter, partial neutralization of the presaturated solution provides not only the necessary mass balance for electrolysis, but also creates the optimum conditions under which passivation of the anode, as well as side chemical and electrochemical reactions, are minimized. Finally, the electrolysis stage of the process leads to precipitation of crystalline sulfur at the anode and evolution of hydrogen at the cathode. Regeneration of the alkaline solution via an osmotic effect developed during electrolysis completes the process.

Hydrogen sulfide is present as a contaminant in natural gas wells as well as in other fossil energy resources. With an expected increase of more than 75% on the production of this gas in the next decade (1), removal of hydrogen sulfide from sour gas and subsequent recovery of its constituents will become more important. One widely employed technology for the removal of H₂S from these fuels and the recovery of one of its constituents, sulfur, is the Claus process (2). Although this process with tail gas clean-up units may operate at near 95% efficiency for the removal of H₂S, it still suffers from the disadvantage that the hydrogen is underutilized as steam, instead of being used as a chemical or fuel. In addition, very large plants are required for this process to be economically feasible.

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It has long been realized that hydrogen sulfide can be scrubbed effectively in an alkaline solution and that electrochemical treatment of the stream from such a scrubber will lead to the production of high-purity hydrogen gas and crystalline sulfur at an energy consumption far less than that required for water decomposition. Previous attempts to achieve this goal experimentally have resulted in low yield efficiencies, attributed mostly to anode passivation by the deposition of insulating sulfur on the electrode surface. In some cases, however, addition of organic solvents to the electrolyte and the use of caustic solutions of higher concentrations have been used to attempt to minimize the blocking effect, again achieving only minimal increase in current efficiency.

In this communication, a new approach to recover both hydrogen and sulfur, via electrochemical decomposition

of hydrogen sulfide, with minimal blocking of the anode, is reported. This improved process has the added advantages that no organic solvent for sulfur is required and that side reactions, such as the formation of sulfates and thiosulfates, which might be caused by the incorporation of the higher strength caustic solution, are prevented. The process has also been reproducibly experimentally demonstrated on a laboratory scale.

Analysis of Some Previous Work

Electrolytic decomposition of hydrogen sulfide has received attention since Fetzer (3) showed that precipitation of sulfur on the electrode surface during electrolysis reduced the current to almost zero. Efforts have been focused on the development of either direct or indirect electrolysis schemes that will eliminate the passivating effect of the sulfur.

In the indirect schemes, hydrogen sulfide is first oxidized to sulfur via a chemical reaction with an oxidizer; the reduced oxidizer is then regenerated at the anode with hydrogen evolution at the cathode during electrolysis (4-8). This apparently avoids passivation of the anode, since sulfur is produced by a chemical oxidation reaction. However, not only is the product sulfur in plastic form, which requires further purification and transformation, but the cell voltages of these cells are exceedingly high, resulting in unacceptable energy consumption. For example, the reversible cell voltage estimated from the standard potentials of the anode and cathode reactions for the case where ferricyanide oxidizers are used (4) is at least 1.288 V (9). Also, the potentials of the redox couples are usually high enough to electrochemically oxidize any sulfur or sulfide species into sulfites and thiosulfates (10). At the same time, thermodynamic incompatibility between sulfides and oxidizers in an alkaline environment may easily lead to the formation of sulfites via chemical oxidation reactions of the type (11)



Interdiffusion of the redox couples must be prevented, otherwise regeneration of the oxidizer is not possible. Finally, dissolution of sulfur in the alkaline sulfide solution can occur to form polysulfide, which can further be electrochemically oxidized to a sulfur film at the anode, thus passivating the process.

Several direct electrolysis schemes have also been proposed to solve the problem of anode passivation. Since any mechanical method is ineffective (12), Bolmer (13) proposed to use organic vapor to remove the sulfur on the electrode surface. In this approach, hot organic vapor in a stream of hydrogen sulfide containing gas is passed through a porous carbon anode, where H_2S is dissolved in the alkaline electrolyte and oxidized to sulfur at the electrode. To the best of our knowledge, no experimental results have been reported so far from such a scheme.

Shih and Lee (14) reported a scheme in which addition of either toluene or benzene (as sulfur solvents) to the anolyte in a continuously stirred electrochemical reactor led to an average 60% conversion efficiency for sulfur production. The purity of the sulfur product was reported to be about 95%. In addition to the low sulfur conversion efficiency reported, an increase in cell resistance, which is easily attributable to the organic solvent added, was observed. The low purity of the product also implies that further purification is required before commercialization.

Direct schemes excluding organic solvents for sulfur have also been reported (15-18). In the work of Dandapani *et al.* (15, 16), a rapid increase in current was reported if the operating temperature of the cell was raised to at least 60°C. Their experimental conditions require continuous passage of the H_2S gas into a one-compartment cell. Under these conditions, not only will polysulfides formed at the anode be reduced back to sulfide at the cathode, but any sulfur formed will passivate the electrode, since it is insoluble in the low-pH electrolyte which results from continuous bubbling of H_2S . Nygren *et al.* (17) reported an enhancement of current density when an activated glassy

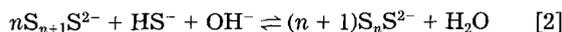
carbon electrode was used. This normally has low catalytic activity for sulfide oxidation.

Recently, Winnick (18) proposed two processes utilizing alkaline polysulfide solution for the absorption of hydrogen sulfide. In one, H_2S is absorbed at the catholyte and reduced to hydrogen gas and polysulfide ions. The polysulfide ions then migrate through a membrane to the anode where oxidation to sulfur takes place. In the other, H_2S is oxidized to sulfur at the anode, with subsequent regeneration of OH^- at the cathode. The exact conditions for sulfur precipitation without passivation of the anode were not stated, and no experimental work has been reported on these processes. An inherent difficulty is the fact that the cathodic reaction is the reduction of polysulfides, rather than hydrogen evolution.

Further development of a direct scheme for the decomposition of hydrogen sulfide is therefore required. The process should demonstrate the conditions for high current efficiency conversion of hydrogen sulfide into hydrogen and sulfur with minimal, if any, blocking of the anode. This is addressed in this paper.

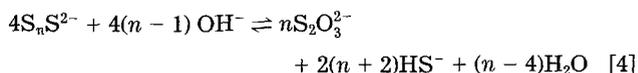
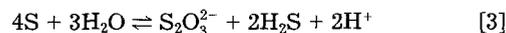
Chemical Reactions

Sulfur and polysulfide species are thermodynamically unstable in alkaline aqueous solutions (19), and chemical dissolution of sulfur in sulfide-containing aqueous solutions increases with alkalinity of the solution (19-22). The dissolution process proceeds by several reaction equilibrium steps (23-25), generally expressed as



where n varies from 1 to 5. As a consequence, there is a marked increase in the ratio of polysulfide sulfur to sulfide sulfur, in equilibrium with elemental sulfur, as alkalinity increases. The average chain length of polysulfide species therefore increases with alkalinity, while the concentrations of higher polysulfides vary inversely with alkalinity (24, 26).

In highly alkaline solutions, more significantly at temperatures over 150°C, sulfur and polysulfides have been reported to disproportionate into thiosulfate and sulfite ions (23, 24, 26-28) via the reactions



Also, polysulfide species are unstable in acidic environments, so dissolved sulfur in an alkaline sulfide solution will precipitate when the pH of the solution is lowered (23, 29).

Successful electrolysis will therefore be strongly affected by the chemical solubility of sulfur in the solution. In solutions with a pH in the acidic range, sulfur is insoluble and any precipitated sulfur will block the electrode. As the pH increases into the alkaline region, sulfur becomes soluble and therefore electrolysis will result in sulfur precipitation when the solution is saturated with sulfur. Solutions of high alkalinity are not desirable, especially at elevated temperatures, since these lead to the formation of sulfur oxyanions.

Electrochemical Reactions

Table I is a summary of possible electrochemical reactions that have been reported during electrolysis of H_2S in an aqueous alkaline solution. Sulfide ions are easily oxidized to either elemental sulfur, polysulfides (S_x^{2-}), sulfates (SO_4^{2-}), sulfites (SO_3^{2-}), thiosulfates ($\text{S}_2\text{O}_3^{2-}$), or dithionates ($\text{S}_2\text{O}_4^{2-}$). Hence, electrolytic conditions become critical if some of these reactions are to be avoided, as is the case for efficient decomposition of H_2S into hydrogen and sulfur. The reactions in Table I can be divided into two distinct groups (30-33). The first group constitutes reversible reactions involving sulfides and polysulfides, while the second group of reactions are irreversible and involve polysulfides and oxyanions of sulfur species.

Table I. Possible electrochemical reactions with corresponding standard potentials in aqueous sulfide solutions.

Group One		
$\text{HS}^- + \text{OH}^- \rightleftharpoons \text{S} + \text{H}_2\text{O} + 2e^-$		-0.478 ^a
$\text{S}_n^{2-} \rightleftharpoons \text{S}_n + 2e^-$		-0.508 ^a
$\text{S}_n^{2-} + \text{S}_{n-1}^{2-} \rightleftharpoons \text{S}_n^{2-} + 2e^-; 2 \leq n \leq 5$		(-0.466--0.520) ^{a,b}
Group Two		
$\text{S}_n^{2-} + 6 \text{OH}^- \rightarrow \text{SO}_3^{2-} + 3\text{H}_2\text{O} + 6e^-$		-0.597 ^b
$\text{S}_n^{2-} + 6 \text{OH}^- \rightarrow \text{S}_2\text{O}_3^{2-} + 3\text{H}_2\text{O} + (n-2)\text{S} + 6e^-$		(-0.647--0.667) ^b
$2\text{HS}^- + 8 \text{OH}^- \rightarrow \text{S}_2\text{O}_3^{2-} + 5\text{H}_2\text{O} + 8e^-$		-1.131 ^b
$\text{SO}_3^{2-} + 2 \text{OH}^- \rightarrow \text{SO}_4^{2-} + \text{H}_2\text{O} + 2e^-$		-0.930 ^a

^a From Ref. (9, 10, 19).

^b Calculated from data in Ref. (9, 10).

During H₂S electrolysis, therefore, sulfur is either precipitated after the solution is saturated with polysulfide or is further oxidized into oxyanion species. Accordingly, while reactions in Group 1 are desirable, those in Group 2 are undesirable. Further, the reversibility of reactions in Group 1 implies that oxidation products at the anode can be reduced at the cathode if a one-compartment cell is used for electrolysis. Electrolysis of H₂S should therefore be conducted at an appropriate temperature in a two-compartment cell, where the mass input and pH of the anolyte and catholyte are appropriately adjusted.

Conditions for H₂S electrolysis

For a successful H₂S electrolysis scheme in an aqueous sulfide solution, the following conditions appear to be necessary (i) the anolyte should be saturated with polysulfide or sulfur, so that sulfur can precipitate; (ii) a two-compartment cell is essential to prevent polysulfide reduction at the cathode; (iii) precipitation of sulfur must take place in the bulk electrolyte or near the electrode; and (iv) chemical and electrochemical disproportionation of polysulfides into oxyanion of sulfur species must be eliminated. As a consequence, continuous bubbling of H₂S into the anode compartment electrolyte should be avoided, since polysulfide saturation will not be achieved under these conditions. Both hydroxide ion concentration and temperature should be kept at optimum values to allow sulfur precipitation at high polysulfide concentrations.

The change in solution pH during electrolysis, as well as the ratio of zero valent sulfur as polysulfides to total sulfide ions in the solution, must be carefully controlled. One way to follow these changes is to analyze the mass balances in electrolysis cells with different initial electrolyte solutions. For simplicity, it is assumed that a two-compartment cell, separated with an ideal cation-selective membrane is used. The anolyte is assumed to contain α M NaOH and β M NaHS, while the catholyte contains (α + β)M NaOH. It is also postulated that during electrolysis, sulfide or bisulfide species are oxidized to polysulfides at the anode, and water is reduced to hydrogen gas and hydroxide ions at the cathode. Consequently, sodium ions will migrate through the membrane, from the anodic compartment to the cathodic compartment, to preserve charge neutrality. Concentrations of sulfide and sodium ions therefore decrease in the anolyte while that of hydroxide ions increase in the catholyte. These postulates can be expressed quantitatively as follows: In the anodic compartment

$$C_{\text{S}^{2-}} = C_{\text{S}^{2-}}^0 - \frac{Q}{2V_a} \quad [5]$$

$$C_{\text{Na}^+} = C_{\text{Na}^+}^0 - \frac{Q}{V_a} \quad [6]$$

$$C_{\text{OH}^-} = C_{\text{OH}^-}^0 - \frac{Q}{2V_a} \quad [7]$$

and in the cathodic compartment

$$C_{\text{NaOH}} = C_{\text{NaOH}}^0 + \frac{Q}{V_c} \quad [8]$$

where $Q = \int_0^t |I|/F dt$, I is the current passing through the cell during electrolysis, F is the Faraday constant, $C_{\text{S}^{2-}}$ represents the concentration of sulfide ions including bisulfide ions and the sulfide ions in forms of polysulfides. The superscript “o” denotes initial values, while V_a and V_c are the volumes of the anolyte and catholyte, respectively. Because of the dependence of sulfur solubility in sulfide solutions on the concentration of sulfide species, one can also express the total amount of sulfur as a ratio, X , where

$$X = \frac{C_{\text{S}^{2-}}^0 - C_{\text{S}^{2-}}}{C_{\text{S}^{2-}}} = \frac{C_{\text{S}^{2-}} + \frac{Q}{2V_a}}{C_{\text{S}^{2-}}} \quad [9]$$

Hence, both solution pH of the anolyte and total amount of sulfur, X , may be expressed quantitatively as a function of sulfide ions conversion to sulfur, M_s^t , where

$$M_s^t = \frac{C_{\text{S}^{2-}}^0 - C_{\text{S}^{2-}}}{C_{\text{S}^{2-}}^0} \quad [10]$$

Figure 1 shows the pH – M_s^t relationship in three separate solutions with different initial NaOH:NaHS ratios. In the solution of ratio 1.5, the pH barely deviates from its initial value even when S^{2-} species are completely consumed. Hence, polysulfides formed during electrolysis by the oxidation of sulfide species will be further oxidized to oxyanion species according to one or more of the reactions in Table I. When this ratio is lowered to 0.5, the solution becomes acidic when only about half of the sulfide ions have been oxidized. Thus, any sulfur formed will block the electrode, because of the low sulfur solubility in acidic media. However, when $C_{\text{NaOH}}^0/C_{\text{NaHS}}^0 = 1$, a rapid change in the solution pH is observed only when about 85-90% of S^{2-} ions have been oxidized. This high value of M_s^t corresponds to polysulfide saturation; thus, a further decrease in the pH will result in precipitation of sulfur in an amount corresponding to the difference in solubility (i.e., amount of sulfur oversaturation), as is depicted in Fig. 2. In addition, the conditions for further oxidation of the sulfur are completely eliminated.

Figure 3 shows the dependence of the ratio of the total sulfur (including zero valent sulfur and sulfide ions) to sulfide ions, X , on the conversion of sulfide ions to zero valent sulfur including polysulfides, M_s^t . X increases rapidly when the conversion is greater than about 0.7. This value signifies the point of polysulfide near-saturation. Further oxidation therefore results in rapid changes in X , as well as pH, for a solution with an initial NaOH:NaHS ratio of unity, enhancing sulfur precipitation.

In the above analysis, the transport of solvent from the anodic compartment to the cathodic compartment has been neglected. As mentioned earlier, the total solute molarity in the anodic compartment decreases with electrolysis, while the concentration of sodium hydroxide increases in the cathodic compartment. A solute-concentration difference will occur, which becomes increasingly

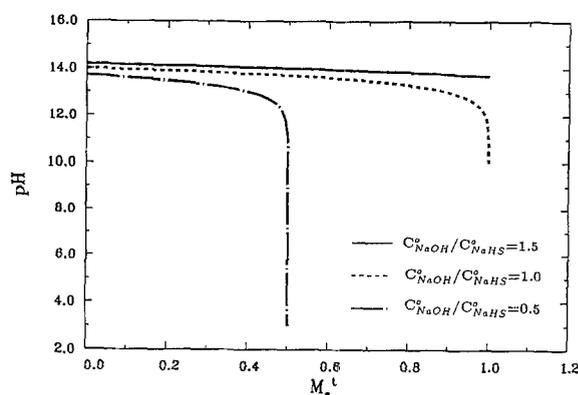


Fig. 1. The relationship between pH and the conversion of sulfides to sulfur, M_s^t for electrolyte solutions where $C_{\text{NaOH}}^0 = 1.0M$.

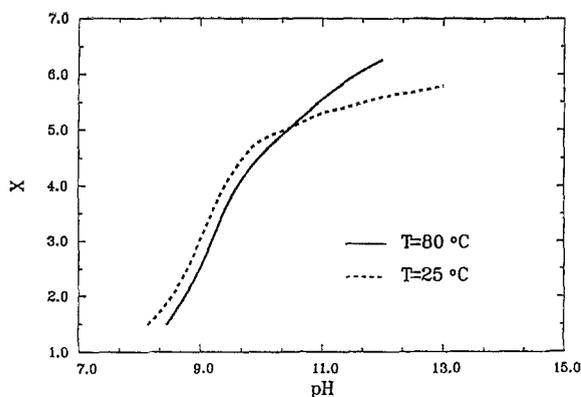


Fig. 2. Ratio of dissolved sulfur and sulfide concentrations to sulfide concentration, X , vs. alkalinity, pH, for aqueous polysulfide solutions in equilibrium with elemental sulfur (i.e., solubility vs. pH plot). Data taken from Ref. (23).

larger with electrolysis. This concentration difference between the two compartments is reduced by electro-osmotic transport of the solvent from the anodic compartment through the membrane to the cathodic compartment. It is therefore expected that the level of the anolyte will fall and that of the catholyte will rise during electrolysis.

The Modified Electrochemical Process and the Preferred Electrolysis Conditions

It follows from the above analysis that the scrubbing and electrochemical decomposition of hydrogen sulfide should be carried out separately in different units. The relative amounts of each species in the anolyte should be properly adjusted prior to electrolysis. A modified electrochemical process which satisfies these requirements is presented here. The flow diagram representation of the process is shown in Fig. 4. It consists of a compartment for presaturation of NaOH with H_2S , (H_2S scrubber), a compartment where partial neutralization of the HS^- species in solution from the scrubber takes place, and an electrolytic cell where the electrochemical separation of hydrogen and sulfur is carried out by the passage of a desired current.

The scrubber contains a solution capable of reacting with H_2S and is at the same time chemically stable and thermodynamically inactive with respect to the other constituents of the inlet gas stream. An aqueous alkaline solution of sodium hydroxide is therefore employed. The basic process in the scrubber is therefore a chemical reaction which is represented, upon H_2S saturation, by the reaction



The H_2S -saturated solution is then pumped into the mass balance (neutralization) compartment, where the addition of more caustic solution not only neutralizes the HS^- species in solution to partially form S^{2-} , but also provides the

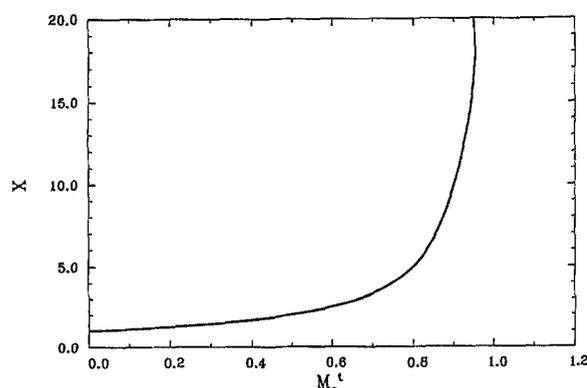


Fig. 3. The relationship between the ratio of total sulfur (including zero valence sulfur and sulfide concentrations) to sulfide concentration, X , and the conversion of sulfides to sulfur, M_s^t .

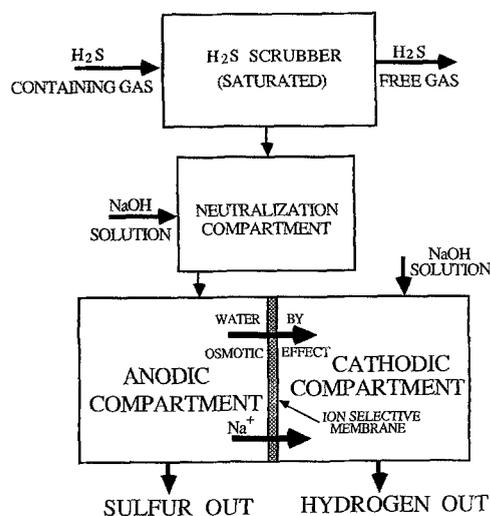


Fig. 4. Step-wise flow diagram for batch production of hydrogen and sulfur by electrochemical decomposition of hydrogen sulfide in an aqueous alkaline solution.

optimum pH balance required for electrolysis. The critical factor in the neutralization is the ratio of $HS^-:S^{2-}$ species, or $OH^-:HS^-$, which should be in the equimolar range to satisfy the necessary and sufficient conditions for electrolysis.

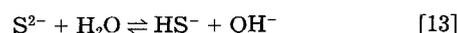
In the electrolytic cell, the anodic compartment contains the solution from the neutralization compartment. The catholyte is a pure alkaline solution. The two compartments are separated from one another by a cation-selective membrane, which impedes migration of sulfide or polysulfide species. At the anode, sulfide ions are oxidized to elemental sulfur. As sulfur begins to precipitate out, the anolyte will become more dilute, thus less conducting. A practical system may therefore require a supporting electrolyte, or otherwise, to avoid IR losses.

The formation of sulfur by the oxidation of HS^- (and S^{2-}), and its subsequent chemical dissolution in the sulfide-containing alkaline solution to form polysulfides, and eventually crystalline sulfur, results in the migration of cations (Na^+) from the anodic compartment through the membrane to the cathodic compartment to preserve charge neutrality. The consumption of OH^- species coupled with water formation will result in a decrease of the pH in the anode compartment, while the concentration of OH^- builds up at the cathode, where H_2O is reduced, producing hydrogen.

The above process has been tested in the laboratory under the preferred conditions, and the results were found to be highly reproducible (34). Experiments were carried out at temperatures of $80 \pm 5^\circ C$. At desired current densities (e.g., 200 mA/cm^2 at a voltage of about 0.9 V in an unoptimized cell), crystalline sulfur was produced at the anode, while hydrogen gas was evolved continuously at the cathode. During electrolysis, the pH of the anolyte progressively decreased from an initial value of 13.2 for the partially neutralized solution in the mass balance compartment to about 9.6 toward the end of electrolysis. From these pH values, less than 20% of the total sulfur content in solution initially occurred as S^{2-} species, decreasing to 0.5% at the end of electrolysis. These fractions are given by the relationship (35)

$$HS^- \rightleftharpoons S^{2-} + H^+; \quad \log \frac{[S^{2-}]}{[HS^-]} = -13.9 + \text{pH} \quad [12]$$

Because of the low second dissociation constant of hydrogen sulfide, S^{2-} ions are converted to HS^- according to the equation



at pH values below 13.9. The dominant sulfide species in this process is therefore believed to be HS^- .

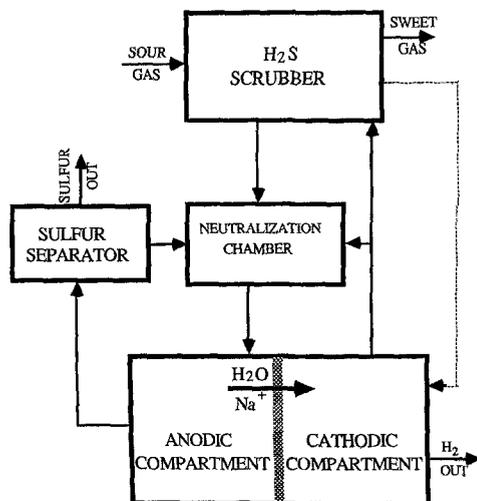


Fig. 5. Schematic of the extended process flow diagram for continuous H_2S electrolysis in an aqueous alkaline solution.

The process that is described above has been shown to produce both sulfur and hydrogen by the decomposition of hydrogen sulfide in an alkaline aqueous solution. However, if it is carried out as indicated, it will be a batch process. To become commercially viable, the process must be made continuous. One proposition for achieving this is illustrated in the extended flow diagram of Fig. 5. Here, a portion of the sulfur that is produced in the anodic compartment is recycled into the neutralization unit. The input solution from the neutralization chamber will then always be polysulfide at the correct pH. In addition, regenerated caustic solution from the cathodic compartment can be fed into the scrubbing and neutralization units for further utilization.

Conclusions

In this work, the relevant chemical and electrochemical reactions in aqueous sulfide solutions have been reviewed and analyzed for the purpose of electrochemically decomposing hydrogen sulfide into hydrogen and sulfur. On the basis of the analysis, an improved electrochemical process for the electrolysis of hydrogen sulfide is given. This modified process differs from previous ones in that sulfur precipitation is carried out via a sequence of steps in different units. This way, conditions are properly controlled so that all unwanted side reactions are eliminated, and sulfur precipitation takes place in the bulk solution or near the electrode surface, thereby minimizing electrode passivation. Analysis of the mass balances in the modified process leads to the requirement that an equimolar solution of NaOH and NaHS should be used as the anolyte. This requirement fixes the solution pH at an optimum value, so that electrode passivation is delayed by sulfur dissolution. This pH value also prevents oxidation of polysulfide species to sulfur oxyanions.

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