

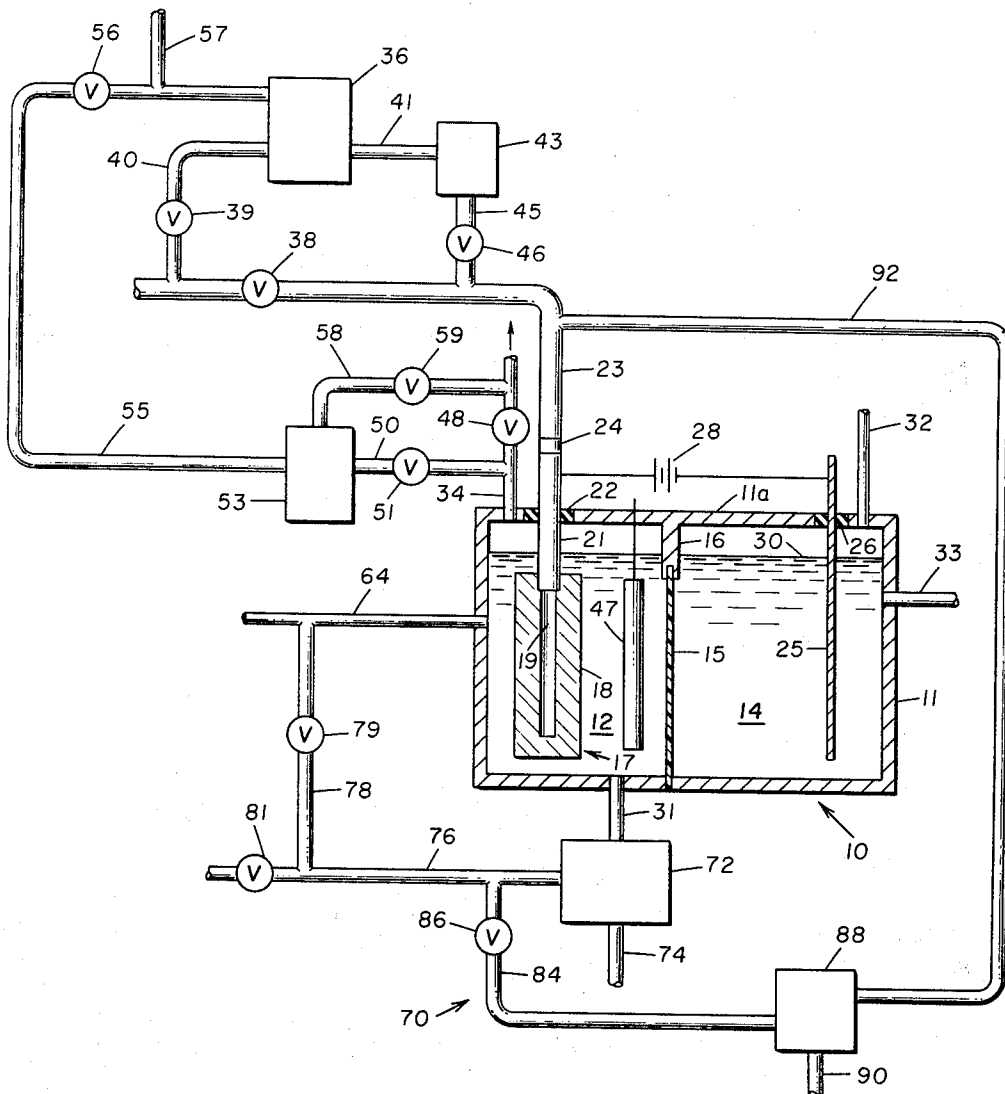
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REMOVAL OF HYDROGEN SULFIDE FROM A HYDROGEN SULFIDE-HYDROCARBON
GAS MIXTURE BY ELECTROLYSIS

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REMOVAL OF HYDROGEN SULFIDE FROM A HYDROGEN SULFIDE-HYDROCARBON GAS MIXTURE BY ELECTROLYSIS

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Continuation-in-part of application Ser. No. 434,533, Feb. 23, 1965. This application Sept. 23, 1965, Ser. No. 489,548

17 Claims. (Cl. 204—101)

This application is a continuation-in-part application of copending application Ser. No. 434,533, filed Feb. 23, 1965, now Patent No. 3,249,522.

This invention relates to the electrolysis of hydrogen sulfide to form free hydrogen and certain valuable sulfur products and particularly to the removal of hydrogen sulfide from a hydrogen sulfide-hydrocarbon gas mixture by electrolysis with the formation of free hydrogen and such sulfur products.

Hydrogen sulfide is present as a contaminant in many valuable fluids. For example, in the petroleum industry, hydrogen sulfide is a commonly found contaminant in production fluids such as oil and gas and in processing and product streams attendant to the refining of such production fluids. Perhaps the most troublesome occurrence of hydrogen sulfide is its presence in gaseous hydrocarbon mixtures produced from subterranean formations, either separately or concomitantly with liquid petroleum. Such gaseous hydrocarbon mixtures, commonly termed "natural gas," are usually comprised predominantly of methane and ethane with trace amounts of higher hydrocarbon vapors such as propane, butane, pentane, etc. In addition to hydrocarbons and hydrogen sulfide, natural gas often contains carbon dioxide which may range up to about 30 percent or even higher of the total gas volume.

Because of its corrosive nature and for various other well-known reasons, it usually is necessary or at least preferable to remove hydrogen sulfide when it occurs in admixture with hydrocarbons. Also, where a market exists for certain materials of which hydrogen sulfide is a precursor, it usually will be advantageous for economic reasons to obtain, if possible, such materials as byproducts of the hydrogen sulfide-hydrocarbon gas separation process.

In accordance with the instant invention, there is provided a new and improved method and apparatus for the formation of free hydrogen and certain valuable sulfur products by electrolysis of hydrogen sulfide. In a preferred embodiment of the instant invention, these materials are obtained as byproducts of a novel process of separating hydrogen sulfide from a hydrocarbon gas mixture by electrolysis.

The instant invention utilizes an electrolysis cell having an electrolyte therein and an anode and a cathode in contact with the electrolyte and connected to an external source of electric power. In carrying out the invention, a hydrogen sulfide-hydrocarbon gas mixture is introduced into the electrolysis cell and into contact with the electrolyte and the anode. An externally generated electric current is passed through the electrolyte between the anode and cathode in order to electrolytically oxidize sulfide ions at the anode to a sulfur oxidation product of the sulfide ions. At the same time, the passage of the electric current results in the electrolytic reduction of hydrogen ions to free hydrogen at the cathode. The sulfur product then is withdrawn from the electrolysis cell. The hydrocarbon gas, which is unaffected by the electrolysis reaction at the anode, is withdrawn from the electrolysis cell separately from the sulfur product. The hydrogen gas produced by the cathode reaction also is withdrawn from the cell.

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In one form of the invention, certain polysulfides as well as free hydrogen may be produced by the electrolysis of hydrogen sulfide. In this aspect of the invention, hydrogen sulfide is contacted with a basic cation-furnishing electrolyte in order to neutralize at least a portion of the hydrogen sulfide and form a basic solution of sulfide ions. The resulting solution is subjected to electrolysis in a cell of the type described above by passing an externally generated electric current through the solution. Sulfide ions at the anode are electrolytically oxidized to disulfide ions, and hydrogen ions at the cathode are electrolytically reduced to free hydrogen, the free hydrogen being withdrawn from the cell. The mixture of sulfide and disulfide ions resulting from the primary oxidation of sulfide ions is subjected to further electrolytic oxidation to form trisulfide ions. The mixture of sulfide and trisulfide ions resulting from this step is further oxidized to tetrasulfide ions. The resultant solution of polysulfides of the cation furnished by the electrolyte is withdrawn from the electrolysis cell. The formation of the polysulfide ions requires an electrolyte of a relatively high pH. Therefore, in a preferred embodiment of the invention, basic electrolyte is added to the electrolysis cell at a rate sufficient to maintain the pH of the electrolyte at a level sufficiently high to permit the formation of tetrasulfide ions.

The process of the instant invention may be carried out to produce a sulfur product comprising free sulfur, certain polysulfides, or mixtures thereof. Regardless of the sulfur species desired, it has been found that a tendency exists for some free sulfur to be formed in the electrolyte and deposited on the anode. Such sulfur deposition will lead to concentration polarization of the anode which ultimately will render the process ineffective or at least impractical. Therefore, in a preferred embodiment of the invention, deposition of free sulfur on the anode is restricted by introducing into the electrolysis cell and into contact with the anode a solvent for free sulfur. Preferably, the solvent is introduced at a temperature lower than its boiling point while maintaining the anode at a temperature at least as great as the boiling point of the solvent so that the solvent is vaporized from the anode.

For a better understanding of the instant invention, reference may be had to the following detailed description and the accompanying drawing which is an illustration partly in section of a system for carrying out the present invention.

With reference to the drawing, there is shown an electrolysis cell 10 which is comprised of an outer fluidtight shell or container 11 having top closure plate 11a. Container 11 is divided into an anode compartment 12 and a cathode compartment 14 by a suitable diffusion barrier 15 and a gas impermeable baffle 16. Diffusion barrier 15, which will be described in detail hereinafter, restricts, i.e., impedes or completely prevents, the diffusion of fluid from one electrode compartment to the other while permitting at least some ionic transference.

Disposed in compartment 12 is an anode 17 comprising a porous and permeable cylindrical member 18 having an inner passage 19. Anode member 18 is supported on a tube 21 formed of a suitable electrically conductive material such as steel which extends exteriorly of the electrolysis cell through an insulator 22 of rubber or other suitable dielectric material. Electrode tube 21 is connected to an inlet pipe 23 by means of a nonconductive collar 24 formed of a suitable dielectric such as plastic. Disposed in compartment 14 is a cathode 25 which extends exteriorly of the cell through an insulator 26. The anode and cathode are connected to the positive and negative poles, respectively, of a suitable direct current source 28. The direct current source may take the form of a battery, as shown, or may comprise other suit-

able means such as a DC generator or rectified alternating current.

The anode member 18 preferably is a porous cylindrical body of the type shown, that is, one having a central passageway which opens at one end thereof to provide for the introduction of gas into the passage so that it diffuses laterally through the wall of the anode member. It will be understood, however, that the anode member may take various shapes including such as provided for by spaced discs or plates. For example, the anode member may be formed of two spaced permeable plates extending transversely of the anode compartment such that gas introduced into the area between the plates diffuses laterally through the plates. While an anode of the flow-through type, i.e., one having a permeable member through which the injected gas diffuses, is preferred, it will be recognized that the anode may be formed of a single plate in which case the injected gas merely flows along the surfaces of the plate or is dissolved in the electrolyte and then carried to the anode by the solution.

The anode member 18 may be formed of any suitable material. Porous carbon is a preferred material, although the anode may be formed of other structures such as screens, gauzes, and the like of materials such as titanium, nickel, stainless steel, etc. The anode member 18 may have disposed on or impregnated therein a suitable catalyst such as platinum.

The cathode 25 is shown as comprising a single plate, although it will be recognized that numerous other electrode structures may be employed. For example, the cathode may comprise a porous structure or a plate having numerous fins extending laterally thereof in order to increase the surface area thereof. The cathode may be formed of any materials such as those noted above with regard to the anode. Also, it will be recognized that the cathode may be provided with a suitable catalyst such as platinum for the electrolytic reduction reaction.

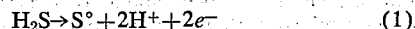
The electrolysis cell is provided with an electrolyte 30 in contact with the anode and cathode. In most cases, the electrolyte in anode compartment 12 (the anolyte) and the electrolyte in cathode compartment 14 (the catholyte) will be the same. However, different electrolytes may be used. For example, the anolyte may be an aqueous solution of sodium hydroxide and the catholyte an aqueous solution of ammonium carbonate, or vice versa.

The anolyte is maintained at a level above the uppermost point of egress of gas from the anode member 18 such that all of the gas diffusing therethrough contacts and passes through the electrolyte. This is accomplished most expeditiously by maintaining the top of the anolyte well above the top of the permeable anode member 18, as shown. Also, electrolyte is maintained above the bottom of baffle 16, thus preventing direct gaseous communication between compartments 12 and 14.

The operation of the electrolysis cell and the attendant system is as follows. A hydrogen sulfide-hydrocarbon gas mixture is conducted from a suitable source such as a gas-oil separator (not shown) through line 23, collar 24, and tube 21 into the porous anode member 18. The hydrogen sulfide-hydrocarbon gas mixture flows into the passageway 19 of the anode member and diffuses through the porous walls thereof into the electrolyte 30. As the gas mixture diffuses through the anode, a three-phase contact zone is formed which comprises the anode surfaces, the adjacent electrolyte, and the gas itself. As the hydrogen sulfide contacts the electrolyte, it becomes ionized to form a solution of hydrogen and sulfide ions in the electrolyte. Sulfide ions are electrolytically oxidized to a sulfur oxidation product of the sulfide ions which may include free sulfur and/or one or more ionic sulfur species, as described in detail herein-after, and hydrogen ions are electrolytically reduced at the cathode to form free hydrogen. The sulfur product is withdrawn from the anode compartment of the cell through an outlet 31 and free hydrogen gas is withdrawn

from the cathode compartment through an outlet 32. The cathode compartment also is provided with a suitable inlet line 33, for the introduction of such make-up catholyte as may be necessary. The hydrocarbon gases in the mixture pass upwardly through the anolyte and are withdrawn from the anode compartment through a second outlet 34 therein. It will be understood that as baffle 16 extends transversely of the space above electrolyte 30, intermingling of the hydrocarbon gas and hydrogen will not occur.

The anode reaction, and therefore the nature of the sulfide oxidation product formed, depends upon the type of electrolyte used. In the broadest aspect of the invention, the electrolyte may be either an acid such as one molar sulfuric or hydrochloric acid or a base. While the use of an acid electrolyte would in theory require a minimum decomposition potential, it appears to lead to severe activation polarization of the anode. In addition, the only sulfur oxidation product obtainable by electrolysis of hydrogen sulfide in an acid electrolyte is free sulfur as indicated by the anode reaction:



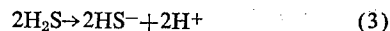
Free hydrogen is formed at the cathode by the electrolytic reduction of hydrogen ions as indicated by the cathode reaction:



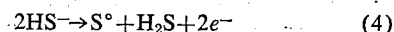
With the use of a basic electrolyte, on the other hand, a wider selection of sulfur products may be obtained and the anode is not subject to the severe activation polarization which is encountered with the use of an acid electrolyte. As a practical matter, therefore, and in the preferred embodiment of the invention, a basic electrolyte is used.

Suitable basic electrolytes for carrying out the present invention include aqueous solutions of compounds such as sodium sulfide, sodium carbonate, sodium phosphate, sodium mono- or di-hydrogen phosphate, sodium hydroxide, sodium bicarbonate, sodium bisulfide, and the like. Ammonium or potassium compounds corresponding to the foregoing sodium compounds are also of value. While numerous other basic electrolytes may be used, either aqueous or nonaqueous, it usually will be preferred to use electrolytes which furnish sodium, potassium, or ammonium ions, since it usually will be desired to form polysulfides of these cations. It is preferred to utilize an aqueous solution of a hydroxide with the cation being selected from the class consisting of sodium, potassium, and ammonium ions.

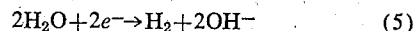
A number of products may be recovered at the anode, depending upon the alkalinity of the electrolyte. With an electrolyte of relatively low alkalinity, e.g., a pH on the order of 7.5 to 8, free sulfur is produced at the anode. In this case, hydrogen sulfide is ionized in the basic electrolyte to form bisulfide ions according to the following reaction:



The bisulfide ions are in turn electrolytically oxidized to free sulfur, the anode reaction being:



Free hydrogen is formed at the cathode by reaction (2) above and/or by the reduction of water according to the following reaction:



Reaction (5) will likely predominate, but in either case the cathode reaction is the electrolytic reduction of hydrogen ions to free hydrogen and will tend to balance the oxidation reaction at the anode. When reduction at the cathode follows reaction (2), the ionic current flow in the cell will be by the migration of hydrogen ions to the cathode. When it follows reaction (5), the current flow will be by migration of hydroxide ions to the anode.

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When, as in the case of electrolysis of hydrogen sulfide in a mildly alkaline electrolyte, free sulfur is formed as a product, it is likely that the finely divided precipitated sulfur may enter the pores of the porous anode member 18, causing an increase in anode polarization and an increase in the resistance across the anode-electrolyte interface. In order to restrict such deposition, and in accordance with a preferred embodiment of the instant invention, a solvent for free sulfur is introduced into the electrolysis cell and into contact with the anode.

With reference to the drawing, this leaching of the anode surfaces with the sulfur solvent may be accomplished in the following manner. The incoming stream in line 23 is diverted to a solvent reservoir 36 by closing or partially closing a valve 38 in line 23 and opening a valve 39 in a bypass line 40 leading to the reservoir. Reservoir 36 contains a suitable solvent for free sulfur, such as benzene. As the gas stream flows through reservoir 36, it picks up the benzene or other solvent and forms an aerated mixture of gas and benzene, the benzene being in the form of dispersed, liquid-phase droplets which may have some hydrogen sulfide and hydrocarbon dissolved therein. The resulting mixture leaves reservoir 36 and flows through a line 41 to a heater 43 where it is heated to a temperature less than the boiling point of the solvent. Thereafter, the mixture flows through a line 45 and an opened valve 46 therein into inlet line 23 and tube 21 and thence into the passage 19 of anode member 18.

The anode and the electrolyte adjacent thereto are maintained at a temperature at least as great as the boiling point of the solvent but suitable temperature control means. As shown in the drawing, this temperature control means preferably takes the form of a heat exchanger 47 immersed in the electrolyte near the anode. Heat exchanger 47 may be simply a conventional electric heater provided with suitable thermostatic means (not shown) for automatically regulating the temperature. It will be understood, however, that other temperature control means could be used. For example, the temperature of the anolyte and anode could be regulated by continuously introducing anolyte at a desired temperature into the anode compartment.

As the gas-solvent mixture enters the pores of anode member 18 and diffuses therethrough, the solvent is vaporized by the heat of the anode and boils off from the outer surfaces thereof into the adjacent electrolyte, concomitantly retarding the deposition of sulfur on the anode and removing any sulfur so deposited. The solvent is unaffected by the electrochemical oxidation reaction at the anode. However, any hydrogen sulfide which may have been entrained in the liquid solvent is evolved therefrom and undergoes electrochemical oxidation as the solvent vaporizes. The free sulfur dissolves in the electrolyte or precipitates out, depending upon the saturation of the electrolyte, and the solvent vapors thus free of sulfur bubble up through the anolyte and are withdrawn with the hydrocarbon gas from the anode compartment through outlet line 34. With a valve 48 in line 34 closed, the hydrocarbon gas-solvent effluent is diverted through a line 50 and an opened valve 51 therein to a gas-solvent separation chamber 53. The solvent is separated from the gas as by cooling and condensation and the condensed solvent is recirculated through a line 55 and an opened valve 56 therein to the solvent reservoir 36. Such make-up solvent as may be necessary is introduced into the reservoir by way of a line 57. The gaseous effluent from separator 53 is passed through a line 58 and an opened valve 59 therein into line 34. In the unlikely event any free sulfur is entrained in the effluent withdrawn from the anode compartment, such sulfur may be separated from the gaseous solvent and hydrocarbons, for example, by filtration, prior to condensation of the solvent.

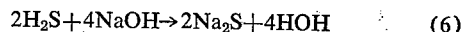
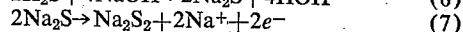
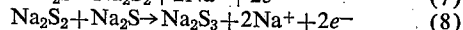
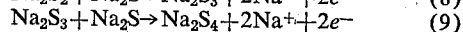
As noted above, the anode is maintained at a temper-

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ature at least equal to the boiling point of the solvent. Preferably, the temperature of the anode will be maintained at a temperature higher than the boiling point of the solvent in order to insure rapid and relatively complete vaporization of the solvent as it leaves the anode. Where benzene, having a boiling point of about 80° C., is utilized as a solvent, the anode and the adjacent electrolyte may be maintained at a temperature of about 85° C.

As noted previously, the instant invention may be carried out to produce polysulfides. In this form of the invention, a strongly alkaline electrolyte, e.g., one having a pH on the order of 14, is used. In this case, a feed gas comprising hydrogen sulfide is introduced into the electrolysis cell in the manner described beforehand. The hydrogen sulfide is neutralized in the strongly alkaline electrolyte to form a basic solution of sulfide ions which are electrolytically oxidized by the passage of current through the electrolyte to disulfide ions. The mixture of disulfide ions and sulfide ions resulting from the above oxidation step and the continuous introduction of hydrogen sulfide may be further electrolytically oxidized to form trisulfide ions which may in turn be oxidized to form tetrasulfide ions. In addition, free sulfur formed at the anode will dissolve in the solution to form polysulfides. Depending upon the residence time of the anionic sulfur species in the cell and upon the current flowing through the anode, electrolytic oxidation at the anode may be carried out to produce disulfide, trisulfide, or tetrasulfide ions, or mixtures thereof, or even free sulfur. Also, in some instances as, for example, where the anolyte comprises a potassium compound, the product formed at the anode may include pentasulfide ions. Generally, an increase in the residence time of the ions within the cell or an increase in current density will tend to produce a predominant amount of the higher polysulfides and ultimately free sulfur. The cathode reaction in any case will be the reduction of hydrogen ions to free hydrogen as indicated by reactions (2) and/or (5) and the hydrogen will be withdrawn through outlet 32.

The degree of oxidation permitted to take place at the anode will of course depend upon the desired sulfur product. One valuable product obtainable by the process of the present invention is sodium tetrasulfide. In the production of this material, a preferred electrolyte is an aqueous sodium hydroxide solution having a molar concentration in the range of 1 to 10 and maintained at a pH of about 14 or greater. By way of illustration, the reactions at the anode attendant to the production of sodium tetrasulfide by the electrolysis of hydrogen sulfide in an aqueous sodium hydroxide solution are as follows:



In reactions (8) and (9) the sodium sulfide reactant is the result of the neutralization (as indicated by reaction (6)) of the continuously introduced hydrogen sulfide.

Reactions (7), (8), and (9) are sequential in the sense that one will not proceed until the sulfide or polysulfide reactants are available as the result of the previous reactions. However, it will be recognized that in the actual operation of the process various reactions will occur simultaneously. For example, while reaction (9) is taking place, neutralized sulfide ions will be undergoing electrolytic oxidation in accordance with reaction (7).

In addition to the reactions noted above, free sulfur will be formed in the anolyte. For example, some bisulfide ions may be formed, some of which may in turn be oxidized to free sulfur in accordance with reaction (4). Also, free sulfur may result directly from the electrolytic oxidation of some sulfide ions. Unless the anolyte is saturated, the free sulfur will tend to dissolve therein to form

polysulfides. For example, free sulfur will dissolve in a sodium sulfide solution to form sodium polysulfides which in turn may be converted to higher polysulfides by further combination with additional free sulfur or by electrolytic oxidation.

In the utilization of the instant invention to produce sodium tetrasulfide (or other polysulfides), the process preferably is carried out as a continuous operation. That is, anolyte containing the desired polysulfide is withdrawn through line 31 while at the same time hydrogen sulfide feed is introduced through tube 21 and make-up sodium hydroxide (or other cation-furnishing electrolyte) is introduced through an inlet line 64. The make-up electrolyte will be introduced in a concentration and at a rate sufficient to maintain the pH of the anolyte at the desired level.

As noted above, the particular sulfur product formed will depend upon the residence time of the oxidized sulfide products in the anode compartment and the current density at the anode as well as of course the rate of hydrogen sulfide feed to the cell. The desired product can be obtained by testing the effluent from line 31 and adjusting one or more of the above factors accordingly. For example, should a test of the anolyte withdrawn show a predominance of sulfides, disulfides, and trisulfides with only a small amount of tetrasulfide, the residence time in the cell can be increased (while holding the current density and hydrogen sulfide feed constant) in order to obtain a greater proportion of the higher polysulfides. The residence time can be increased simply by decreasing the rate of withdrawal through line 31 and correspondingly decreasing the input of electrolyte through line 64 in order to achieve a balance with withdrawal and maintain a relatively constant amount of electrolyte in the anode compartment. Alternatively, the current density at the anode can be increased or the rate of hydrogen sulfide feed to the anode decreased while holding the residence time unchanged.

The embodiment of the instant invention utilizing a strongly alkaline electrolyte may be carried out to form free sulfur in the electrolysis cell. This may be accomplished by increasing the residence time in the cell past the point at which the predominant product is a tetrasulfide. The sulfur thus formed initially will dissolve in the anolyte to form polysulfides as indicated above, but as the anolyte becomes saturated, sulfur will begin to precipitate out of the solution. The precipitated sulfur may be recovered through line 31 as is the case with the other sulfur products produced in accordance with the instant invention.

Regardless of the product desired, in carrying out the invention with a strongly alkaline electrolyte it is likely that some sulfur will form and tend to be deposited on the anode. Therefore, in accordance with this embodiment of the invention, as well as where a relatively weak base is used, the invention preferably is carried out utilizing solvent extraction at the anode as described above.

To summarize briefly, the nature of the sulfur product will depend upon the basicity or acidity of the anolyte. In an electrolyte that is an acid or a relatively weak base, the product will be free sulfur while in a strongly alkaline electrolyte the product will comprise free sulfur or certain polysulfides, or mixtures thereof. It is preferred in carrying out the invention to utilize a basic electrolyte in view of the above-noted disadvantages attendant to the use of an acid.

In the production of free sulfur, the electrolyte preferably will be at a pH in the range of about 7.5 to 8 with a pH of about 7.7 being particularly preferred, it having been found that operations at this value give very good results. However, the production of free sulfur by the electrolytic oxidation of bisulfide ions may be carried out in a basic electrolyte having a pH up to about 12. It will be recognized that as the pH of the electrolyte approaches 12, there will be an increasing tendency toward the pro-

duction of polysulfides in accordance with reactions (6), (7), (8), and (9).

In order to form polysulfides, the process of the instant invention is carried out in an electrolyte having a pH preferably of 14 or greater and, in any case, at least greater than 12.

As noted previously, free sulfur can be formed by utilizing a strongly alkaline electrolyte. However, this embodiment of the invention cannot as a practical matter tolerate feedstreams having material amounts, i.e., greater than about two percent, of carbon dioxide therein since the carbon dioxide makes it difficult to maintain the pH of the electrolyte at the desired level. Therefore, where the feedstream contains appreciable carbon dioxide, as is many times the case with natural gas, the instant invention preferably will be carried out in the lower pH range with the predominant byproduct being free sulfur.

In instances where the feedstream contains little or no carbon dioxide, free sulfur can be obtained by carrying out the invention utilizing a strongly alkaline electrolyte to form polysulfide in the anode compartment, withdrawing the polysulfide from the cell, and decomposing it to obtain a product including free sulfur. In this embodiment of the invention, an ammonium compound such as an aqueous solution of ammonium hydroxide is used as the anolyte and the residence time in the cell is controlled to produce a product comprised predominantly of ammonium polysulfide and including as little free sulfur as practical. The product then is withdrawn from the cell and heated in order to decompose the ammonium polysulfide to form free sulfur. This embodiment of the invention offers the advantage of keeping the formation of free sulfur within the cell at a minimum, thus lessening the tendency toward polarization of the anode due to deposition of sulfur thereon.

The effluent from anode compartment 12 is passed through line 31 to a suitable separation system 70. Regardless of the particular material or materials desired as a byproduct of the electrolysis process, the effluent through line 31 will in all likelihood contain some free sulfur. Therefore, as a first step in the separation process, the anolyte withdrawn from the anode compartment is passed to a suitable sulfur-separation zone 72. Separation zone 72 may conveniently comprise a filtration chamber. The sulfur is filtered out of the withdrawn anolyte and dispensed through line 74 to a suitable terminal zone (not shown) and the filtrate is withdrawn through line 76. If the sulfur thus separated is the only desired product, the fluid in line 76 may be recycled to the anode compartment through a line 78, an opened valve 79 therein, and line 64. Where a soluble sulfur product such as sodium tetrasulfide is desired, the anolyte may be passed to a suitable terminal station (not shown) by closing valve 79 and opening a valve 81 in line 76.

In the above-described embodiment of the invention in which free sulfur is formed from ammonium polysulfide, the filtrate from chamber 72 is passed through a line 84 and an opened valve 86 therein (valves 79 and 81 being closed) to a suitable heating zone 88. In zone 88, the withdrawn anolyte containing ammonium polysulfide is heated to a temperature sufficient to decompose the polysulfides and precipitate sulfur and evolve hydrogen sulfide and ammonia. The sulfur is withdrawn from zone 88 through line 90. The ammonia and hydrogen sulfide are withdrawn through line 92 and may be passed to inlet line 23 as shown.

As noted previously, the diffusion barrier 15 restricts the diffusion of fluid from one electrode compartment to the other. While such a barrier is not strictly a necessity and the invention may be carried out without a diffusion barrier separating the anolyte and catholyte, one usually will be preferred since it tends to prevent the intermingling of the anolyte with the catholyte with the resulting migration of sulfide and polysulfide ions to a location remote from the anode. As such, the diffusion barrier may take a

number of forms. The diffusion barrier may be comprised of a conventional cation selective membrane which permits the transference of cations therethrough but restricts such transference of anions. Such a membrane may be formed from a cation exchange resin by casting the resin into the form of a sheet or membrane or by incorporating granules of the resin in a matrix comprising a binder such as polyethylene. The cation exchange membrane may have a permselectivity of about 0.9 and a conductivity of about 100 milliohms per square centimeter or more. However, it will be recognized that these values are illustrative only and that membranes of lower permselectivity and conductivity may be used in the instant invention.

In addition to cation exchange membranes, the diffusion barrier 15 may be formed of an electrically neutral member having a relatively low permeability which impedes the diffusion of fluid from one compartment to another. In most instances, a nonselective membrane will be preferred, particularly in those cases where the predominant cathode reaction is reaction (5). By way of illustration, the barrier may be formed of an electrically neutral porous carbon plate of relatively low permeability which allows without selectivity the migration of anions and cations therethrough under the influence of the electrical bias produced at the anode and cathode but which prevents or at least strongly impedes fluid movement between the anode and cathode compartments. The term "diffusion barrier" as used herein and in the appended claims therefore designates a barrier which extends transversely of the electrolysis cell between the anode and cathode and restricts, i.e., prevents or at least impedes, diffusion of electrolyte from one electrode compartment to the other while permitting at least some ionic transference.

Having described specific embodiments of the instant invention, it will be understood that further modifications thereof may be suggested to those skilled in the art, and it is intended to cover all such modifications as fall within the scope of the appended claims.

What is claimed is:

1. In the removal of hydrogen sulfide from a hydrogen sulfide-hydrocarbon gas mixture with the formation of sulfur product and free hydrogen by electrolysis in an electrolysis cell having an electrolyte therein and an anode and a cathode in contact with said electrolyte and connected to an external source of electric power, the method of:

(a) introducing a hydrogen sulfide-hydrocarbon gas mixture into said electrolysis cell and into contact with said electrolyte and said anode;

(b) passing an externally generated electric current through said electrolyte between said anode and said cathode to electrolytically oxidize at said anode sulfide ions to a sulfur oxidation product of said sulfide ions and electrolytically reduce at said cathode hydrogen ions to free hydrogen;

(c) separately withdrawing said hydrocarbon gas and at least a portion of said sulfur product from said electrolysis cell; and

(d) withdrawing said hydrogen gas from said electrolysis cell.

2. The method of claim 1 wherein said sulfur product includes free sulfur which tends to deposit on said anode and further comprising introducing into said electrolysis cell and into contact with said anode a solvent for free sulfur whereby deposition of free sulfur is restricted.

3. In the removal of hydrogen sulfide from a hydrogen sulfide-hydrocarbon gas mixture with the formation of sulfur product and free hydrogen by electrolysis in an electrolysis cell having a basic electrolyte therein and an anode and a cathode in contact with said electrolyte and connected to an external source of electric power, said anode including a gas-permeable member, the method of:

(a) introducing a hydrogen sulfide-hydrocarbon gas mixture into said permeable member and diffusing said mixture through said permeable member and

into contact with said electrolyte whereby a basic solution of sulfide ions is formed at said anode;

(b) passing an externally generated electric current through said electrolyte between said anode and said cathode to electrolytically oxidize at said anode sulfide ions to a sulfur oxidation product of said sulfide ions and electrolytically reduce at said cathode hydrogen ions to free hydrogen;

(c) separately withdrawing hydrocarbon gas and electrolyte containing a sulfur product from said electrolysis cell;

(d) withdrawing hydrogen gas from said electrolysis cell; and

(e) simultaneously with steps (a), (b), (c), and (d) introducing basic electrolyte into said electrolysis cell.

4. The method of claim 3 wherein said electrolyte is introduced at a rate sufficient to maintain the level of the electrolyte adjacent said anode above the uppermost point of egress of said mixture from said permeable member.

5. The method of claim 3 wherein said sulfur product includes free sulfur which tends to deposit on said permeable member and further comprising introducing into said permeable member and diffusing therethrough into said electrolyte a solvent for free sulfur whereby deposition of free sulfur is restricted.

6. The method of claim 5 wherein said solvent is introduced into said permeable member at a temperature lower than its boiling point and said permeable member is maintained at a temperature at least as great as the boiling point of said solvent whereby said solvent is vaporized from said anode.

7. The method of claim 3 wherein said electrolyte is an aqueous solution of a base having a cation selected from the class consisting of sodium, potassium, and ammonium ions.

8. The method of claim 7 wherein said base is a hydroxide.

9. In the formation of sulfur products and free hydrogen by electrolysis of hydrogen sulfide, the method of:

(a) contacting hydrogen sulfide with a basic, cation-furnishing electrolyte to neutralize at least a portion of said hydrogen sulfide and form a basic solution of sulfide ions;

(b) in an electrolysis cell having a cathode and an anode therein, passing an externally generated electric current through said solution between said cathode and anode to electrolytically oxidize at said anode a portion of said sulfide ions to disulfide ions and electrolytically reduce at said anode hydrogen ions to free hydrogen;

(c) continuing to pass said electric current through said solution to electrolytically oxidize at said anode a mixture of sulfide and disulfide ions resulting from step (b) to trisulfide ions;

(d) continuing to pass said electric current through said solution and oxidizing at said anode a mixture of sulfide and trisulfide ions resulting from step (c) to tetrasulfide ions;

(e) continuously repeating steps (a), (b), (c), and (d) while withdrawing free hydrogen from said electrolysis cell at the cathode and withdrawing a solution of polysulfides of the cation furnished by the basic electrolyte from said electrolysis cell at said anode; and

(f) simultaneously with steps (a), (b), (c), (d), and (e) adding basic electrolyte to said electrolysis cell at a rate and in a concentration sufficient to maintain the basicity of said electrolyte in said cell at a level sufficiently high to permit the formation of tetrasulfide ions.

10. The method of claim 9 wherein the electrolyte in said cell is maintained at a pH greater than 12.

11. The method of claim 9 wherein the electrolyte in said cell is maintained at a pH of at least 14.

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12. The method of claim 9 wherein said electrolyte is an aqueous solution of a base having a cation selected from the class consisting of sodium, potassium, and ammonium ions.

13. The method of claim 12 wherein said base is a hydroxide.

14. The method of claim 9 wherein said cation furnished by said basic electrolyte is ammonium and comprising the further steps of withdrawing a solution of ammonium polysulfides from said electrolysis cell and heating said solution to a temperature sufficient to decompose said ammonium polysulfides and form free sulfur.

15. The method of claim 14 wherein said electrolyte is an aqueous solution of ammonium hydroxide.

16. In the formation of sulfur products and free hydrogen by electrolysis of hydrogen sulfide, the method of:

(a) contacting hydrogen sulfide with a liquid electrolyte to form a solution of sulfide ions in said electrolyte;

(b) in an electrolysis cell having a cathode and an anode therein, passing an externally generated electric current through said solution between said cathode and anode to electrolytically reduce at said cathode hydrogen ions to free hydrogen and to electrolytically oxidize at said anode sulfide ions to a sulfur oxidation product of said sulfide ions includ-

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ing free sulfur which tends to deposit on said anode;

(c) introducing into said electrolysis cell and into contact with said anode a solvent for free sulfur whereby deposition of free sulfur on said anode is restricted;

(d) withdrawing free hydrogen from said electrolysis cell at said cathode; and

(e) withdrawing sulfur product from said electrolysis cell at said anode.

17. The method of claim 16 wherein said solvent is introduced into said electrolysis cell at a temperature lower than its boiling point and said anode is maintained at a temperature at least as great as the boiling point of said solvent whereby the solvent is vaporized from said anode.

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