Title: DECOMPOSITION AND REMOVAL OF H₂S INTO HYDROGEN AND SULFUR FROM PETROLEUM GASES

Abstract

The method of removing sulfurous compounds (organic and inorganic) from any fluid (gas or liquid) phase by contacting said fluid (gas or liquid) with a reactive metal to form a metal sulfide (12), recovering said fluid (gas or liquid) free from said sulfurous compounds, and separating electrochemically said reactive metal from said sulfur so as to return said metal and sulfur to elemental form (11), said separating being done at temperatures above the melting point of sulfur.
### FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>AM</td>
<td>Armenia</td>
<td>GB</td>
<td>United Kingdom</td>
<td>MW</td>
<td>Malawi</td>
</tr>
<tr>
<td>AT</td>
<td>Austria</td>
<td>GE</td>
<td>Georgia</td>
<td>MX</td>
<td>Mexico</td>
</tr>
<tr>
<td>AU</td>
<td>Australia</td>
<td>GN</td>
<td>Guinea</td>
<td>NB</td>
<td>Niger</td>
</tr>
<tr>
<td>BB</td>
<td>Barbados</td>
<td>GR</td>
<td>Greece</td>
<td>NL</td>
<td>Netherlands</td>
</tr>
<tr>
<td>BE</td>
<td>Belgium</td>
<td>HU</td>
<td>Hungary</td>
<td>NO</td>
<td>Norway</td>
</tr>
<tr>
<td>BF</td>
<td>Burkina Faso</td>
<td>IE</td>
<td>Ireland</td>
<td>NZ</td>
<td>New Zealand</td>
</tr>
<tr>
<td>BG</td>
<td>Bulgaria</td>
<td>IT</td>
<td>Italy</td>
<td>PL</td>
<td>Poland</td>
</tr>
<tr>
<td>BJ</td>
<td>Benin</td>
<td>JP</td>
<td>Japan</td>
<td>PT</td>
<td>Portugal</td>
</tr>
<tr>
<td>BR</td>
<td>Brazil</td>
<td>KE</td>
<td>Kenya</td>
<td>RO</td>
<td>Romania</td>
</tr>
<tr>
<td>BY</td>
<td>Belarus</td>
<td>KG</td>
<td>Kyrgyzstan</td>
<td>RU</td>
<td>Russian Federation</td>
</tr>
<tr>
<td>CA</td>
<td>Canada</td>
<td>KP</td>
<td>Democratic People's Republic of Korea</td>
<td>SD</td>
<td>Sudan</td>
</tr>
<tr>
<td>CF</td>
<td>Central African Republic</td>
<td>KR</td>
<td>Republic of Korea</td>
<td>SE</td>
<td>Sweden</td>
</tr>
<tr>
<td>CG</td>
<td>Congo</td>
<td>KZ</td>
<td>Kazakhstan</td>
<td>SG</td>
<td>Singapore</td>
</tr>
<tr>
<td>CH</td>
<td>Switzerland</td>
<td>LI</td>
<td>Liechtenstein</td>
<td>SI</td>
<td>Slovenia</td>
</tr>
<tr>
<td>CI</td>
<td>Côte d'Ivoire</td>
<td>LK</td>
<td>Sri Lanka</td>
<td>SK</td>
<td>Slovakia</td>
</tr>
<tr>
<td>CM</td>
<td>Cameroon</td>
<td>LR</td>
<td>Liberia</td>
<td>SN</td>
<td>Senegal</td>
</tr>
<tr>
<td>CN</td>
<td>China</td>
<td>LT</td>
<td>Lithuania</td>
<td>SZ</td>
<td>Swaziland</td>
</tr>
<tr>
<td>CS</td>
<td>Czechoslovakia</td>
<td>LU</td>
<td>Luxembourg</td>
<td>TD</td>
<td>Chad</td>
</tr>
<tr>
<td>CZ</td>
<td>Czech Republic</td>
<td>LV</td>
<td>Latvia</td>
<td>TG</td>
<td>Togo</td>
</tr>
<tr>
<td>DE</td>
<td>Germany</td>
<td>MC</td>
<td>Monaco</td>
<td>TJ</td>
<td>Tajikistan</td>
</tr>
<tr>
<td>DK</td>
<td>Denmark</td>
<td>MD</td>
<td>Republic of Moldova</td>
<td>TT</td>
<td>Trinidad and Tobago</td>
</tr>
<tr>
<td>EE</td>
<td>Estonia</td>
<td>MG</td>
<td>Madagascar</td>
<td>UA</td>
<td>Ukraine</td>
</tr>
<tr>
<td>ES</td>
<td>Spain</td>
<td>ML</td>
<td>Mali</td>
<td>UG</td>
<td>Uganda</td>
</tr>
<tr>
<td>FI</td>
<td>Finland</td>
<td>MN</td>
<td>Mongolia</td>
<td>US</td>
<td>United States of America</td>
</tr>
<tr>
<td>FR</td>
<td>France</td>
<td>MR</td>
<td>Mauritania</td>
<td>UZ</td>
<td>Uzbekistan</td>
</tr>
<tr>
<td>GA</td>
<td>Gabon</td>
<td></td>
<td></td>
<td>VN</td>
<td>Viet Nam</td>
</tr>
</tbody>
</table>
DECOMPOSITION & REMOVAL OF H₂S INTO HYDROGEN AND SULFUR FROM PETROLEUM GASES

BACKGROUND OF THE INVENTION

Field of Invention: This invention relates to the recovery of elemental sulfur and hydrogen from hydrogen sulfide generally contained in hydrocarbon fluids such as petroleum or natural gas. Further, the invention also relates to the removal and decomposition of H₂S from a natural gas stream via an electrochemical process.

State of the Art: Generally, hydrogen sulfide is removed from a hydrocarbon stream by solvent extraction followed by distillation. The separated H₂S gas is then converted to elemental sulfur by the widely used Claus process. The Claus process comprises a combustion stage, catalytic conversion stage, and tail gas clean up treatment. The process involves the following three reactions:

\[ \text{H}_2\text{S} + \frac{3}{2} \text{O}_2 \rightarrow \text{SO}_2 + \text{H}_2\text{O} \]  
(1) Combustion Stage

\[ 2\text{H}_2\text{S} + \text{S}_0 \rightarrow 2\text{S} + 3\text{H}_2\text{O} \]  
(2) Catalytic Stage

\[ 3\text{H}_2\text{S} - \frac{3}{2} \text{O}_2 \rightarrow 2\text{S} + 3\text{H}_2\text{O} \]  
(3) Overall

Recently, the National Chemical Laboratory for Industry in Japan together with Idemitsu Kosan announced development of a hybrid process, which recovers both sulfur and hydrogen from hydrogen sulfide in a hydrocarbon stream produced from oil refineries. The Idemitsu hybrid process involves two major operations. Initially, hydrogen sulfide is absorbed into a ferric chloride solution where a redox reaction occurs to convert H₂S and FeCl₃ into sulfur, ferrous chloride and hydrochloric acid as follows:

\[ \text{H}_2\text{S} (g) + 2 \text{FeCl}_3 \text{ (aqueous)} \rightarrow 2\text{FeCl}_2 + \text{S} (s) + 2\text{HCl} \text{ (Aqueous)} \]  
(4)

After separation of sulfur through filtration, the solution of ferrous chloride (FeCl₂) and hydrochloric acid (HCl) is electrolyzed to regenerate ferric chloride in the anodic chamber and produce hydrogen in the cathodic chamber as follows:

\[ 2\text{FeCl}_2 \text{ (Aq.)} + 2\text{HCl} \text{ (Aq.)} \rightarrow 2\text{FeCl}_3 + \text{H}_2 \text{(g). \hspace{1cm} (Aq.)} \]  
(5)

The overall reactions of (4) and (5) can be written as

\[ \text{H}_2\text{S} (g) \rightarrow \text{H}_2 (g) + \text{S}(s) \]  
(6)

Thus, the Idemitsu-hybrid process gives hydrogen as a byproduct which has chemical and fuel value and hence makes the process economically advantageous.
over the Claus process. The Idemitsu process is described in SRI international’s
document. (PEP Review No. 88-2-1).

However, both the above described processes involve several cumbersome
steps to recover sulfur from hydrogen sulfide. In the Claus process, the reactions
generate another hazardous chemical, SO_2, as an intermediate product and also does
not give hydrogen as a byproduct as the Idemitsu hybrid process does. In any
event, both of these processes are expensive from energy and capital cost point of
view.

Therefore, there is a need in the industry for an improved one-step process
for recovering sulfur from H_2S and preferably directly from natural gas and other
petroleum products.

SUMMARY OF THE INVENTION

A process and system have been invented for decomposing and removing
H_2S from hydrocarbon fluids such as petroleum products and natural gas.

This process is based on solid electrolyte electrochemical cell technology. A
natural or petroleum gas containing H_2S is contacted with a sulfide-forming metal
generated via a solid state electrochemical process. The metal ions react with H_2S,
forming metal sulfide and hydrogen. The metal sulfide so formed is then
electrolytically reconverted to the base metal preferably in situ by the same
electrolytic means by reversing the applied potential polarity on the cell.

In an alternative embodiment, H_2S removal and decomposition from natural
and petroleum gas may be achieved in two stages. In a first stage, the extraction
(removal) of H_2S is done by a commercially available solvent and distillation
process. In a second stage, H_2S is decomposed via a solid electrolytic cell. In this
stage H_2S is contacted with a sulfide-forming metal to convert the metal into metal
sulfide, thereby releasing hydrogen gas. The reaction when the sulfide-forming
metal is sodium (e.g.) occurs as follows:

\[ 2Na + H_2S \rightarrow Na_2S + H_2 \]  

The sulfided sodium is then converted to essentially pure sodium and sulfur
in an electrolytic cell (Fig. 1) as per the following reaction.

\[ Na_2S \rightarrow 2Na + 1/2 S_2 \]
It is especially convenient to have an $\text{H}_2\text{S}$ decomposition unit constructed as an electrolytic cell so that the metal sulfide, e.g., sodium sulfide, may be regenerated in situ to sodium metal. It is desirable, therefore, to employ two $\text{H}_2\text{S}$ decomposition cells in parallel whereby the units are used alternatingly, i.e. so that the system could be run continuously (Figure 1).

The $\text{H}_2\text{S}$ decomposition unit is preferably one which employs a metal ion conductor in which the metal ion has an affinity for sulfur. Sodium, lithium, silver and copper ion conductive materials are the preferable solid electrolytes for $\text{H}_2\text{S}$ decomposition for two reasons: Firstly, these metals readily form sulfides, and; Secondly, these metal ion conductors are fast ion conductors leading to very efficient device. Preferred operating temperatures are from 100°C to about 1100°C depending on the metal ion conductor. The examples of metal ion conductors include sodium and silver conducting Beta and Bet aluminas, Nasicon, Lisicon, silver iodide, lithium iodide and the like.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic illustration of a pair of electrochemical cells operating in parallel to decompose $\text{H}_2\text{S}$ and recover sulfur and hydrogen;

FIG. 2 is a schematic illustration of a solvent extraction system used to remove $\text{H}_2\text{S}$ from a petroleum gas and to decompose the $\text{H}_2\text{S}$ and recover sulfur and hydrogen via a pair of electrochemical cells;

FIG. 3 illustrates a single solid electrolytic cell for decomposition of $\text{H}_2\text{S}$ and recovery of sulfur and hydrogen;

FIG. 4 illustrates an electrolytic cell similar to the cell of FIG. 3 wherein the cell is powered by an alternating current;

FIG. 5 illustrates a molten sodium scrubber to convert $\text{H}_2\text{S}$ to $\text{Na}_2\text{S}$ and an electrolytic cell to decompose $\text{Na}_2\text{S}$ and recover sulfur and sodium; and

FIG. 6 illustrates a single electrochemical cell for recovering sulfur and hydrogen from a petroleum gas contaminated with $\text{H}_2\text{S}$.

DETAILED DESCRIPTION OF INVENTION

The process and apparatus of the instant invention are especially suited for removal of $\text{H}_2\text{S}$ from liquids or gases, particularly hydrocarbon liquids or gases.
Liquids contaminated with H₂S are preferably heated to form a vapor to facilitate processes according to the instant invention.

A process for removing H₂S, as a contaminant, from a gas stream is illustrated in FIG. 1. The figure illustrates direct removal and decomposition of H₂S from petroleum based gases. The figure shows that two identical cells work in alternate fashion. Cell No. 2 is decomposing H₂S to generate metal sulfide and petroleum gases containing H₂. At the same time, Cell No. 1 is in charging mode generating active metal from metal sulfide and sulfur is collected from anode compartment. A petroleum based gas is introduced to the system via conduit 10. A pair of electrochemical cells 11 and 12 are positioned in parallel. Each cell is capable of decomposing H₂S and of being regenerated. Cell 12 is illustrated in a decomposition mode wherein the contaminated gas flows through a tee connection and into a pipe with its valve 14 open to permit the gas to enter cell 12. Meanwhile, cell 11 is in a regeneration mode, being sealed off from the gas stream by closed valve 13.

The decomposition process illustrated in Figure 1 is thermally self sustaining since joule heating of the cell via decomposition current flow will keep it at operating temperature without additional heat input from external sources. Typical current densities range from 10 mA/cm² to 1 Amp/cm² while applied voltages range from 0.5 volt to 3 volts, depending on the metal used for sulfidation.

The instant invention has many advantages over Claus and Idemitsu hybrid process; namely, (1) single step process, (2) no additional raw materials, (3) lower capital and operating cost, (4) solid state process and hence longer durability and reliability, (5) hydrogen is recovered as by-product.

This invention has many facets. H₂S from petroleum gas products can be removed directly through a one step solid electrolyte process without going through solvent extraction and distillation steps even if H₂S exists in trace quantities in petroleum based gases. Figures (1-5) illustrate the various configurations of solid electrolytic cell used for decomposition and removal of H₂S from petroleum gases.

The system illustrated in FIG. 1 uses a pair of solid electrolyte electrochemical cells in parallel. One cell is utilized to remove hydrogen sulfide from a gas stream while the other cell is being regenerated. The sodium sulfide formed by reaction with hydrogen sulfide is decomposed during regeneration to
return sodium metal to its reactive condition and to release sulfur which is
recovered as a liquid at temperatures above the melting point of sulfur (119°C).

The solid electrolyte electrochemical cell shown in FIG. 1 has a construction
as illustrated in FIG. 6. The cell 15 comprises a first chamber 16 containing
sodium metal available for reaction with hydrogen sulfide gas passed through the
first chamber to form sodium sulfide and to release hydrogen. Thus, a gas
contaminated with $\text{H}_2\text{S}$ is passed through the first chamber to have the $\text{H}_2\text{S}$ removed
from it. Thus, the first chamber will accumulate sodium sulfide as the reaction
proceeds until substantially all the sodium in the first chamber is converted to
sodium sulfide.

Once Cell 11 of FIG. 1 is exhausted of sodium, then the $\text{H}_2\text{S}$ contaminated
gas is switched to the second Cell 12 wherein fresh sodium is available for reaction.
While the second Cell is operational, the first Cell is set in the regeneration mode.
During regeneration, Na$_2$S in the first Cell gets converted to sodium metal and
elemental sulfur by imposing an applied potential greater than 2 volts. The
elemental sulfur is collected from chamber 16 of Cell during regeneration as a
liquid at temperatures above the melting point of sulfur (119°C). The active
sodium metal formed in chamber 17 of Cell 15 is then ready for reaction with $\text{H}_2\text{S}$
contaminated gas after the second Cell has been exhausted of sodium metal. Thus
Cell 11 and Cell 12 can be operated alternatively; while one is being active in terms
of removing $\text{H}_2\text{S}$ from the gas, the other is regenerating sodium metal and removing
sulfur simultaneously.

Cells 11 and 12 are identical in construction as are chambers 16 and 17 of a
typical Cell 15. Cell 11 and Cell 12 are structured in the manner of Cell 15.

Chamber 16 removes $\text{H}_2\text{S}$ by its reaction with a reactive metal, e.g. sodium,
to form $\text{H}_2\text{S}$. Hydrogen gas and purified petroleum gas exit chamber 16 during the
purification stage. During the regeneration stage, the flow of petroleum gas to
chamber 16 is ceased. A d.c. current is applied to the electrodes (not shown)
adherent to opposed faces of the sodium ion conducting electrolyte. The current is
applied so that the electrode in chamber 16 is positive (anode) and the electrode in
chamber 17 is negative (cathode).

As current is applied, metal ions (Na$^+$) flow through the electrolyte from
chamber 16 to chamber 17. At the cathode, the Na$^+$ ions combine with electrons to
form molten sodium metal in chamber 17. The cell is operated above the melting points of sodium. In chamber 16, sulfur ions (S\(^{2-}\)) are released from sodium sulfide. The sulfur ions give up their electrons to the anode and form molten sulfur which may be drawn from the bottom of chamber 16. Once substantially all of the Na\(_2\)S has been converted to sodium metal (in chamber 17) and the molten sulfur recovered from chamber 16, the current is turned off and the regenerated cell is ready to be used again to purify (decontaminate by removal of H\(_2\)S) a petroleum gas stream by introducing it to chamber 17, which is identical in construction to chamber 16. To regenerate chamber 17, the polarity of the d.c. power source is switched so that the electrode of chamber 16 becomes the cathode and metal ions may be transported from chamber 17 to chamber 16. Appropriate valving is used so that both chambers 16 and 17 can be operated in either a purification (decomposition) mode or a regeneration mode.

The system illustrated in FIG. 2 is very similar to that illustrated in FIG. 1 except that the carrier gas, i.e., illustrated as a petroleum gas containing hydrogen sulfide as a contaminant, has first gone through a solvent extraction and distillation system of the type being currently commercially utilized, wherein hydrogen sulfide is released as substantially pure gas as from the distillation stage. FIG. 2 illustrates H\(_2\)S decomposition through a solid electrolytic cell after H\(_2\)S was removed from commercially available solvent extraction and distillation stage. The substantially pure hydrogen sulfide is then directed toward a pair of electrochemical cells utilized alternatively as in FIG. 1. The cells of the type similar to FIG. 1 may be utilized in this system.

FIG. 3 illustrates a single cell which is used continuously for removal of hydrogen sulfide, carrier gas such as a natural gas or petroleum gas. Construction of the cell is similar to that of FIG. 6; however, the cell sizing must be such that sodium is recovered at about the same rate that it is consumed in the hydrogen sulfide removal process. FIG. 3 illustrates a single solid electrolytic cell construction for decomposition of H\(_2\)S into hydrogen and sulfur. Initially, H\(_2\)S is contacted to porous electrode in compartment A whereby Na is generated continuously via decomposition of Na\(_2\)S in compartment B. Once Na\(_2\)S is exhausted from compartment B, the H\(_2\)S is then flowed through compartment B and the applied potential on the cell is reversed. In this case, Na\(_2\)S is decomposed in
compartment A and Na is reacted with H$_2$S in compartment B, generating hydrogen and Na$_2$S. Alternate strategy like this could utilize only one cell. More specifically, in the first compartment of the cell (FIG. 3), the hydrogen sulfide containing gas is reacted with sodium to form hydrogen sulfide. Sodium ions are continually fed through the solid electrolyte from compartment 2 which is separate from compartment one. The reaction is:

$$2 \text{Na}^+ + \text{H}_2\text{S} + 2 \text{e}^- \rightarrow \text{Na}_2\text{S} + \text{H}_2.$$

In the second compartment, sodium sulfide is decomposed to yield two sodium ions, one mole of sulfur and two electrons. The sodium ions are directed through the solid electrolyte through compartment 2 to compartment 1, which in this phase of operation is the cathode compartment. Sodium ions must be pumped through the solid electrolyte at substantially the same rate as hydrogen sulfide is introduced. That is, for every mole of hydrogen sulfide coming into the first compartment, that is, the cathode compartment, two moles of sodium ions must become available through the solid electrolyte for reaction purposes. When the first compartment has been significantly filled with the sodium sulfide, the valving is reversed and the current is reversed so that the second compartment becomes the cathode compartment and the sodium sulfide, which has accumulated in the first compartment, is then decomposed to produce sodium ions. The process continues for removal of hydrogen sulfide, which is now being directed to the second compartment. Thus, in this system, the cathode compartment is the hydrogen sulfide decomposition compartment, and generates hydrogen and sodium sulfide. The hydrogen carries over with the carrier gas being treated. In the anode compartment, sodium ions and liquid sulfur are produced from sodium sulfide since the electrochemical cell is maintained above the melting point of sulfur. Thus, a single cell may be used in a continuous operation.

Another system for utilizing a single cell in a continuous operation is illustrated schematically in FIG. 4. FIG. 4 illustrates H$_2$S decomposition solid electrolytic cell utilizing A.C. power supply. In this case, sodium is transported alternately between two electrodes via decomposition of Na$_2$S (generating sulfur), while H$_2$S reacts with fresh sodium on either side generating and Na$_2$S and H$_2$. Since H$_2$ and S so formed alternately at temperatures between 100°C and 300°C do not back react, they can be separated via condenser to collect sulfur and H$_2$. The
porous electrodes could be from graphite, molybdenum, tungsten, titanium, etc. FIG. 4 involves a sodium ion conductor sandwiched between a pair of porous electrodes. The electrodes are attached to an alternating current power supply and the whole electrode ion-conductor sandwich is contained in a glass-type enclosure in which a hydrogen sulfide containing gas is introduced. Preferably, the gas must pass though the porous electrodes before it is discharged at an outlet from the system enclosure. Hydrogen sulfide containing gases are introduced into the cell while exiting it are the carrier gas, hydrogen and sulfur as a vapor or liquid. A condenser is positioned in the discharge line and operated at a temperature below the boiling point of sulfur to condense all sulfur vapor and recover it as a liquid.

The electrochemical cell is operated at a temperature above the melting point of the sulfur. The electrodes act alternatively as a cathode and then an anode. The AC power supply may be a conventional 60 hertz power supply wherein the cycling of current direction reverses 60 times per second. Hydrogen sulfide reacts with sodium on the surface of the electrolyte (sodium ion-conductor) to form sodium sulfide. Hydrogen is released. Upon reversal of the current, sodium sulfide is decomposed to again form sodium and sulfur. Since hydrogen and sulfur do not react with one another at temperatures less than about 300°C, they can be separated by this type of system.

The sulfur is maintained in the molten state by operating the temperature of the electrochemical cell at above the melting point of sulfur. Preferably the cell operates at a temperature between about 100°C and 300°C. Sulfur liquid is carried over with the carrier gas into the discharge system, along with the hydrogen that has been generated by the cell. A condenser in the discharged line is operated at a temperature below the boiling point of sulfur to condense sulfur vapor. The porous electrodes in such an electrochemical cell may be graphite, molybdenum, tungsten, iron, titanium and the like.

In other continuous methods of removing hydrogen sulfide from a carrier gas, such as natural gas or petroleum gas, is illustrated in FIG. 5, wherein hydrogen sulfide is contacted with molten sodium in a scrubbing unit. Sodium sulfide is formed in the scrubber and removed from the bottom of the scrubber and transported, i.e., by gravity flow or by a pump, to an electrochemical cell containing a sodium ion conductor (electrolyte) wherein the sodium sulfide is
decomposed into sulfur liquid or vapor by operation of the electrochemical cells above the melting point of sulfur. Sodium ions are transported through the electrolyte into a cathode compartment wherein molten sodium is recovered and transported via a pump back to the top of the scrubber unit. Exiting from the top of the scrubber unit is the carrier gas.

In order to remove all the hydrogen sulfide, it is as generally preferred to operate with an excess of sodium, that is, above stoichiometric requirements, in the scrubbing units so that some sodium in recycled along with sodium sulfide to the electrode chemical cell. Systems of the type just described may be operated in a manner to remove upwards of 100 tons a day of hydrogen sulfide from a carrier gas system. Also, the above systems may be made in small sizes to remove very small amounts of hydrogen sulfide from a carrier gas at a point-of-use site or at a production facility in the event that the quantity of hydrogen sulfide was small in comparison to the volume of the gas stream.

The invention is described herein primarily with reference to its use as a system for purifying a gas. That is, undesirable hydrogen sulfide is removed from a carrier gas stream in which hydrogen sulfide in considered a contaminant. However, it should be understood that the instant invention may be utilized as a method of producing hydrogen and sulfur from a hydrogen sulfide feed stock and that the system may work very effectively with a gas stream which is 100% hydrogen sulfide. The exact structure of a system designed to decompose 100% hydrogen sulfide could be the same or differently structured than one which was designed to remove hydrogen sulfide as a contaminant in a carrier gas. Also, the systems in the invention may be utilized in relation to one another, i.e., an electrochemical cell of the type described in FIGS. 3 or 4, which are continuous operation cells, could be used in conjunction with one another in series. The sodium scrubber process illustrated in FIG. 5 could be used in conjunction with the electrochemical cells of FIG. 3 or FIG. 4, wherein one system is used as a rough removal system, i.e., designed to remove up to perhaps 50% of the hydrogen sulfide present, while the other unit is used as a final or finish clean-up unit wherein the presence of hydrogen sulfide may be at a value close to zero.

Although not illustrated in all the figures hereinabove, it is generally recognized that at high gas flow rates through a particular system that there is some
probability that sodium vapors or liquid droplets of sodium are carried over into the
discharge stream. Thus, it is generally desirable to have a condenser in any
discharge stream in which a vaporized molten reactive metal, such as sodium, may
exist.

The detailed description of the invention considered only Na ion conductors.
However, the instant invention compasses use of silver, copper and lithium ion
conductors.

The system of the invention may also be utilized to remove such noxious
gases, such as oxides of nitrogen, (NO₂, NO, N₂O) or sulfur (SO₂, SO₃) from
various types of gas streams. For example, the system of FIG. 5 may be utilized
when the reactive metal in place of sodium may be lithium which is quite reactive
with nitrogen and especially in the absence of oxygen. Nitrous oxide, for example,
may be contacted in a scrubbing unit with molten lithium to form both lithium oxide
and lithium nitride. The lithium nitride and lithium oxide may be decomposed to
lithium, nitrogen gas and oxygen gas by electrochemical cells similar to that shown
in FIG. 5. At typical temperatures of operation of such cells, i.e., generally below
500°C and frequently below 400°C or even 300°C, nitrogen and oxygen do not
react with one another so that what had been a noxious gas, N₂O, can be
decomposed via such a system to the majority components of air, that is, nitrogen
and oxygen.

The system of this invention can be also utilized to decompose CO₂ gas into
oxygen and CO or oxygen and CO₂. This has direct application in converting the
Lunar and Mars CO₂ environment into useful oxygen production. This oxygen will
be used as the propellant for the return leg of the mission. CO₂ will react with
metals like sodium and lithium to form sodium oxide and carbon or sodium oxide
and carbon monoxide depending on the chemical conditions. The sodium oxide so
formed can be regenerated into metal by solid electrolyte process using sodium ion
conducting electrolyte generating pure oxygen in the process.

Other nitrogen carbon compounds in gaseous form could be similarly
30 treated, as well as other sulfur compounds in gaseous form. Various types of beta-
alumina electrolytes may be utilized such as sodium beta"-alumina or lithium beta"
alumina or silver beta"-alumina and the like. Also, such lithium and sodium
conductors such as Nasicon and Lisicon, which are of the sodium zirconium silicon
phosphate oxide family may be utilized. Other conductors such as silver halides and iodide, and cuprous halides such as cuprous iodides, cuprous chloride, silver and cuprous bromide, may also be utilized. The Nasicon materials, in which the sodium may be replaced by lithium or another alkaline metal, are represented by the formula Na$_{1+x}$Zr$_{2}$P$_{3}$Si$_{12}$O$_{12}$, wherein the maximum conductivity is achieved around a composition of $x=2$, which gives Na$_{3}$Zr$_{2}$PSi$_{2}$O$_{12}$. Other lithium conductors may be used. Other lithium conductors include lithium iodide, especially if lithium iodide contains calcium iodide, also lithium aluminum chloride (Li Al Cl$_{4}$), LiII-Al$_{2}$O$_{3}$ composites containing 35 to about 40% alumina, that is, lithium iodide, wherein the percentage is in mole percent. The electrolyte characteristics should be such that the reactive ion is a very mobile ion and that the electrolyte is thermodynamically stable and has sufficient structural integrity to endure in an electrochemical cell operated at temperatures up to about 500°C.
What is claimed is:

1. A method of removing and decomposing \( \text{H}_2\text{S} \) as a contaminant in a carrier gas stream comprising contacting said carrier gas with a solid metal ion conducting electrolyte wherein said metal is a sulfide forming metal under metal ion conducting conditions to react said metal with \( \text{H}_2\text{S} \) from said carrier gas under metal sulfiding conditions, recovering \( \text{H}_2\text{S} \) free carrier gas containing \( \text{H}_2 \), electrolytically converting said metal sulfide to reform said metal and recovering sulfur.

2. The method of claim 1, wherein said electrolytically converting of said metal sulfide is done in situ.

3. The method of claim 2, wherein said electrolytically converting of said metal sulfide to regenerate said sulfide forming metal is done concurrently with reaction of \( \text{H}_2\text{S} \) with said metal resulting in the formation of metal sulfide.

4. The method of claim 1, wherein said electrolyte is maintained at a temperature up to about 500°C.

5. The method of claim 1, wherein said solid electrolyte exists in the electrochemical cell.

6. The method of claim 1, wherein sulfide forming metal is selected from the class consisting of sodium, lithium, copper and silver and their alloys and composites.

7. The method of claim 1, wherein metal ion conducting electrolyte is a sodium, lithium, copper or silver ion conducting electrolyte.

8. The method of decomposing \( \text{H}_2\text{S} \) contained in a carrier gas comprising contacting said \( \text{H}_2\text{S} \) directly with a sulfide forming metal under metal ion conducting conditions.
sulfide forming conditions to form a metal sulfide and hydrogen and electrolytically converting said metal sulfide to reform into metal.

9. The method of claim 1, wherein said carrier gas can be any hydrogen and hydrocarbon gas containing H₂S.

10. The method of claim 1, wherein said reaction of H₂S with metal and said electrolytically converting of metal sulfide to metal is done concurrently, by means of alternating current power supply, decomposing H₂S into H₂ and sulfur simultaneously.

11. The method of claim 1, wherein the electrochemical cell consists of porous electrodes made of either carbon, graphite, nickel, molybdenum, titanium, tungsten or Fe-chromium alloys.

12. The method of claim 1, wherein the electrochemical cell consists of preferably the following solid electrolytes:
Sodium ion conductors are chosen from either Na-β alumina or Nasicon type of sodium ion conductors; or sodium conducting glasses.

Lithium ion conductors are chosen from either LiCl-KCl-LiBr-MgO or LiX-Al₂O₃ (X=Cl,Br & I) type composite electrolytes;
Silver ion conductors are chosen either from AgX (X=Cl, Br or I) - Al₂O₃ composite, and Ag β'Alumina materials or RbAgI₃ type super ion conducting materials; and

Copper ion conductors are chosen from either Rb₂Cu₃Cl₄ type of materials or Cu-β' Alumina type materials or CuX (X=Cl, Br or I) - Al₂O₃ composite type of materials.

13. The method of claim 1, wherein the hydrocarbon gas can be replaced by hydrocarbon fluid.

14. The method of claim 1, wherein the H₂S can be replaced by sulfur containing organic and inorganic compounds.
15. A method of removing a contaminant gas from a fluid stream wherein said contaminant gas is a halide, oxide, hydride or chalcogenide compound containing an anion of an elemental gas comprising:

contacting said contaminant gas containing fluid with a reactive metal to form a metal cation which combines with said anion elemental gas;

recovering said fluid substantially free of said contaminant gas and containing said elemental gas; and

separating electrochemically said reactive metal from said gas anion by passing cations of said metal through a solid ion conducting electrolyte to return said metal to elemental form and to release elemental anions of said gas, said separating being conducted at a temperature above wherein the said anion element is a liquid.

16. A method of removing H₂S from a hydrocarbon gas and/or vapor comprising:

contacting said H₂S with a reactive metal to form a metal sulfide and hydrogen;

recovering said hydrocarbon gas and/or vapor free from H₂S and containing hydrogen; and

separating electrochemically said reactive metal from said sulfur to return said metal to elemental form and to release elemental sulfur, said separating being done at temperatures above the melting point of sulfur.

17. A method of decomposing CO₂ or SO₂ comprising:

contacting said CO₂ or SO₂ gas with a reactive metal which forms metal oxide and carbon or sulfur under metal oxide forming conditions and electrolytically converts said metal oxide to reform it into said reactive metal while recovering oxygen.
PETROLEUM GASES + H₂S → \text{SOLVENT EXTRACTION AND DISTILLATION OF H₂S}

\text{CELL NO. 1 - REGENERATION CELL}

\text{SOLID ELECTROLYTIC CELL IN CHARGING MODE}

\[ \text{Na}_2\text{S} \rightarrow 2\text{Na} + \frac{1}{2}\text{S}_2 \]

\text{OFF}

\text{CELL NO. 2 - ACTIVE CELL}

\text{SOLID ELECTROLYTIC CELL IN DISCHARGING MODE}

\[ 2\text{Na} + \text{H}_2\text{S} \rightarrow \text{Na}_2\text{S} + \text{H}_2 \]

\text{ON}

\rightarrow \text{SULFUR}

\rightarrow \text{H}_2

\text{Fig. 2}
Fig. 3

2Na⁺ + H₂S + 2e
→ Na₂S + H₂

Na⁺

SULFUR TO CONDENSER

H₂

2Na⁺ + 1/2S₂ + 2e
→ Na₂S

H₂S

SOLID ELECTROLYTIC

POROUS ELECTRODE

2e

ON
Fig. 5

S (GAS)

Na₂S + Na⁺ → Na

MOLTEN SODIUM

H₂S + Na → Na₂S

H₂ + CARRIER GAS → H₂S

H₂S CONTAINING GAS (CARRIER GAS)
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C25B 1/00, 1/02
US CL : 205/341, 412, 444, 494, 560, 617, 637, 663

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 205/341, 412, 444, 494, 560, 617, 637, 663

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category *</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A P</td>
<td>US, A, 5,391,278 (Honma et al) 21 February 1995. See Abstract.</td>
<td>1, 8, 15</td>
</tr>
<tr>
<td>A P</td>
<td>US, A, 5,433,828 (van Velzen et al) 18 July 1995, see Abstract.</td>
<td>1, 8, 15, 16</td>
</tr>
<tr>
<td>A</td>
<td>US, A, 4,443,424 (Olson) 17 April 1984. See Abstract.</td>
<td>1, 8, 15</td>
</tr>
<tr>
<td>A</td>
<td>US, A, 4,069,117 (Cooper) 17 January 1978. See Abstract.</td>
<td>1, 8, 15</td>
</tr>
<tr>
<td>A</td>
<td>US, A, 4,038,366 (Fukuda et al) 26 July 1977, see Abstract.</td>
<td>1, 8, 15</td>
</tr>
<tr>
<td>A</td>
<td>US, A, 4,772,366 (Winick) 20 September 1988, see Abstract.</td>
<td>1, 8, 15</td>
</tr>
</tbody>
</table>

X Further documents are listed in the continuation of Box C. □ See patent family annex.

* Special categories of cited documents:
"A" document containing the general state of the art which is not considered to be of particular relevance
"E" earlier document published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is combined with one or more other such documents, each combination being obvious to a person skilled in the art
"A" document member of the same patent family

Date of the actual completion of the international search
26 FEBRUARY 1996

Date of mailing of the international search report
02 APR 1996

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231
Facsimile No. (703) 305-3230
Authorized officer: Donald R. Valentine
Telephone No. (703) 308-3327

Form PCT/ISA/210 (second sheet) (July 1992)
### DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>US, A, 4,544,461 (Venkatesan et al) 01 October 1985, see Abstract.</td>
<td>1, 8, 15</td>
</tr>
<tr>
<td>A</td>
<td>US, A, 3,409,520 (Bolmer) 05 November 1968, see see cols. 3-4.</td>
<td>1, 8, 15</td>
</tr>
</tbody>
</table>