

HYDROGEN SULFIDE AS A SOURCE OF HYDROGEN

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Abstract—We suggest that hydrogen sulfide (that which is removed from fossil fuels as an unwanted waste product, as well as that which might be sought as a mineral in its own right), should be considered as a source of hydrogen. We discuss several techniques by means of which hydrogen sulfide might be thus exploited. We address, very briefly, the apparent problem of finding materials of construction for use in such processes.

INTRODUCTION

A source of hydrogen which should be given serious consideration is hydrogen sulfide. It is usually considered to be simply a disagreeable industrial waste product recovered in large quantities from the sweetening of fossil fuels. Some gas wells in western United States and elsewhere are so rich in hydrogen sulfide that they are not now used for the production of natural gas. Although hydrogen sulfide itself has a reasonably high heating value, 16.55 kJ g^{-1} if it is burned to sulfur dioxide and liquid water [1], its use as a fuel is obviated by the unpleasant environmental effects that that would entail as well as by the fact that sulfur is much more valuable as a commodity than it is as a fuel. We suggest that it might be worthwhile to explore the possibility of seeking and using hydrogen sulfide itself as a mineral and as a previously untapped source of hydrogen.

At the present time, the Claus process is the most widely used means of disposing of hydrogen sulfide. In this process, hydrogen is oxidized to water to furnish low-grade process heat at a place where the low grade process heat has little value [2] and sulfur is recovered as the element. In 1979, in the United States, 1.76 million tons of sulfur was thus recovered from natural gas, and 2.31 million tons was recovered from petroleum. In Canada, 6.1 million tons was recovered. Most of the sulfur was first retrieved as hydrogen sulfide [3].

The associated hydrogen might have been used to fix 2.5 million metric tons of atmospheric nitrogen as ammonia. Its heating value, $9.1 \times 10^{16} \text{ J yr}^{-1}$, 2900 MW, had it been recovered, would have been, in a year, equivalent to that of 17 million barrels of gasoline [3, 4]. Alternatively, the hydrogen might have been used to hydrogenate 1 million tons of coal to produce 59 million barrels of high-grade liquid hydrocarbon, about 3% of the number of barrels of petroleum imported into the United States in 1980.

One estimate of the organically bound sulfur in recoverable fossil fuels in the United States alone places

it at least at 40 billion metric tons [3, 4]. The associated hydrogen would come to approx. 2.7 billion tons. Regardless of exactly how much is actually there to be recovered, there will be a lot of hydrogen sulfide in the future. Such an important potential source of hydrogen must certainly attract the attention of the hydrogen-energy community.

We recently reported the results of two preliminary studies [3, 5] of techniques which might be used to recover both hydrogen and sulfur from waste hydrogen sulfide. This paper was written to call them to the attention of the hydrogen-energy community and, perhaps, to stimulate additional interest and research on this fascinating problem.

The idea of recovering both hydrogen and sulfur from hydrogen sulfide was considered by Raymont [6] who suggested that platinum or palladium hydrogen-permeable membranes be used to separate hydrogen from dissociating hydrogen sulfide as it forms at elevated temperatures. Fukuda *et al.* [7] studied sudden cooling as a means of freezing the composition of high-temperature dissociated mixtures of its decomposition products. They also tried to use a microporous Vicor effusion membrane to effect the separation [8]. These studies presumed that such processes would be limited to temperatures below approx. 1000 K, perhaps because most combustion processes are quite limited in the upper temperatures at which they can be used to provide process heat [9, 10] or possibly because they were concerned that chemical attack upon the materials of construction would preclude operation at higher temperatures.

However, the sun is a 6000 K heat reservoir. Highly concentrated sunlight is potentially an excellent source of high-temperature process heat [3, 10]. We therefore believe that high-temperature solar thermochemical processing provides one mechanism by which this most attractive source of hydrogen might be profitably tapped.

Another takes advantage of the fact that, from a thermodynamic standpoint, hydrogen sulfide itself is much less stable than is its homologue, water. By spending a small fraction of the hydrogen we can, in principle, design a device which uses existing technology to pro-

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duce from hydrogen sulfide; sulfur and pipeline pressure hydrogen. Such a device need not use any external energy source.

In this paper we first review, for the hydrogen-energy community, the results of some of the work that we have done with hydrogen sulfide. Then we describe some preliminary experiments which suggest that the materials-of-construction problems, which may have deterred previous researchers from considering very high temperatures in thermochemical studies, may not be so serious as one might have anticipated.

THERMOCHEMICAL HYDROGEN PRODUCTION FROM HYDROGEN SULFIDE

The hydrogen-sulfur system

At low and moderately high temperatures, the hydrogen-sulfur system gives rise to a host of molecular species. They include, as well as H_2S , H_2 and S_2 , S_3 - S_8 and the sulfanes such as H_2S_2 - H_2S_9 . If the temperature is low enough and the pressure high enough the various condensed phases of sulfur may also be present. At higher temperatures HS appears, and at very high temperatures the monatomic species are present. Figure 1 gives the calculated equilibrium composition of hydrogen-sulfur mixtures having various overall compositions at 1 atm over the temperature range 0–2000 K. It is noteworthy that in the range 1000–2000 K the only substances present in significant quantities are H_2 , S_2 and H_2S . The calculated values are in good agreement with the experimental observations of Raymont [11] whose experiments went to 1400 K. Moreover, Raymont observed that at temperatures above 1250 K equilibrium was achieved very quickly, even in the absence of catalysts. Hydrogen sulfide is thus a good candidate for effusional separation studies such as those we made in connection with the separation of water into hydrogen and oxygen [12–19], and possibly for the potentially more economical ROC-type diffusional separations [20]. We have also done some preliminary experiments in which we have found it possible to quench the recombination reaction. In this system, in contrast with water, quenching is unlikely to yield hazardous products. Quenching, as well, thus deserves experimental study as a device for recovering hydrogen and sulfur from hydrogen sulfide.

Effusional separation

Effusional separation has been most widely used for the separation of uranium isotopes [21]. It relies on the fact that, when a mixture of gases is permitted to effuse through openings in the Knudsen flow regime, i.e. when the mean-free-paths are comparable to the diameters of the openings, the lighter molecules effuse faster, in relation to their concentrations, than do the heavier ones; a partial separation is achieved. The effectiveness of a separation goes as the square root of the ratio of the molecular weights of the species being separated.

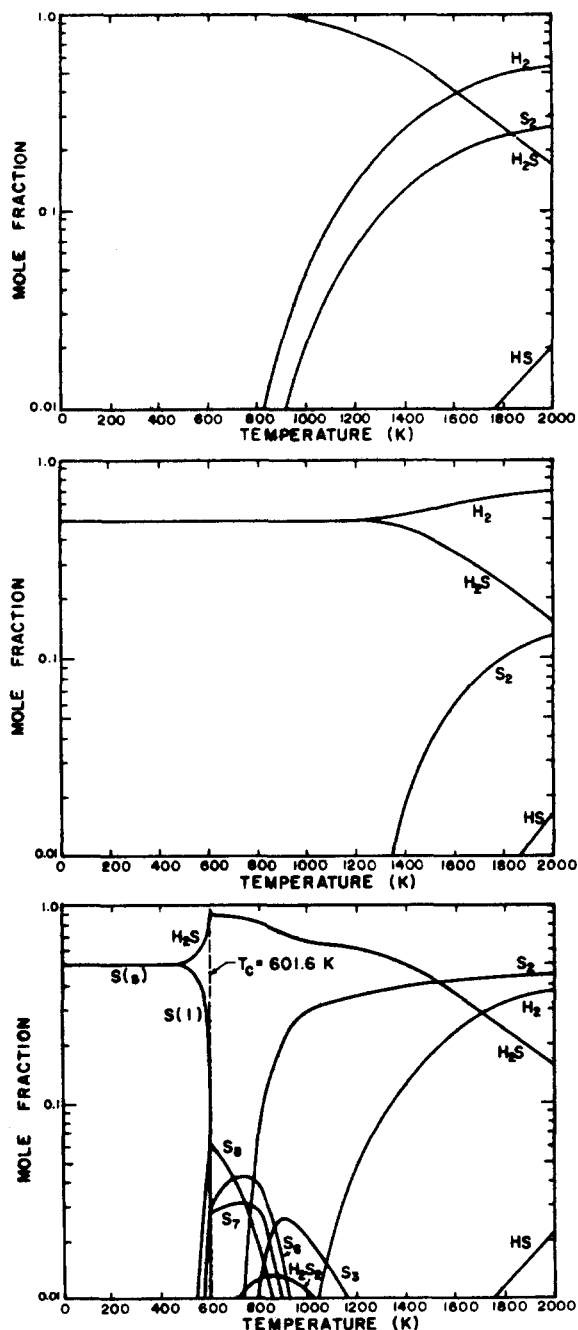


Fig. 1. Variation of the equilibrium mole-fractions of H-S mixtures at 1 atm with temperature; top, $(\text{H}/\text{S}) = 2$ (stoichiometric); middle, $(\text{H}/\text{S}) = 4$ (excess hydrogen); bottom, $(\text{H}/\text{S}) = 1$ (excess sulfur), [3].

Previous studies with water have shown that, provided the system can be made to work, the capital cost of a hybrid solar facility for simultaneously generating electric power and producing hydrogen would not be out-

rageous [17]. It is to be expected that hydrogen sulfide would be a better candidate for solar-thermal effusional separation than would water; the operating temperature would be about 1000 K lower and the molecular weight ratio twice as great. Accordingly, we conducted an analytical study of the process. We have described an archetypal device for producing hydrogen and sulfur from hydrogen sulfide and reported its operational characteristics over a wide range of temperatures and pressures elsewhere [3].

Using cost-of-component estimates we had made in a previous study of an archetypal water splitting device [17] we estimated capital costs of the major components of a solar plant for making hydrogen and sulfur from hydrogen sulfide. The major components are the solar collector (concentrator), pumps, a zirconia reactor-separator, a heat exchanger and a cooler. The capital costs for a device which operates at 1600 K, with an upstream-of-the-membrane pressure of 0.5 atm and a downstream-of-the-membrane pressure of 0.1 atm, with a minimum temperature difference across a heat exchanger tube of 50 K, is shown in Fig. 2. In this figure the capital cost, per 4 mol s^{-1} of hydrogen produced,

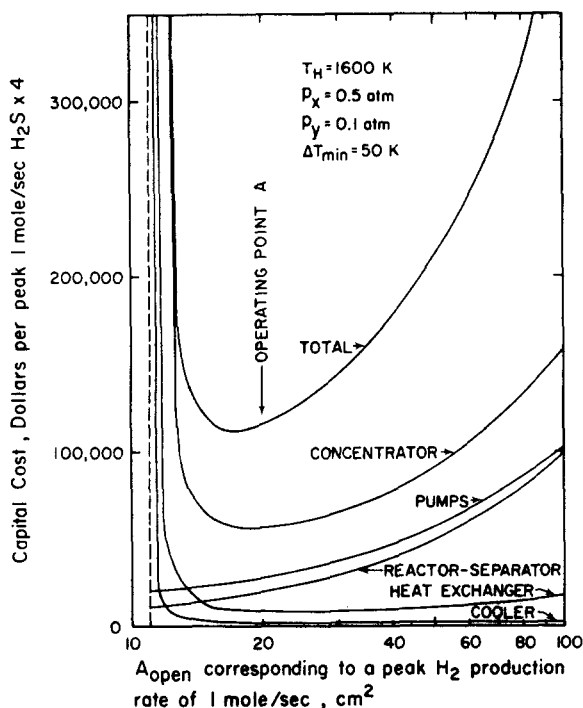


Fig. 2. Variation of the estimated capital costs associated with the time average production rate of 1 mol s^{-1} each of hydrogen and of sulfur, with the open area of the reactor-separator, for the following reactor operating conditions: temperature, 1600 K; upstream pressure, 0.5 atm; downstream pressure, 0.1 atm; minimum heat exchanger temperature drop, 50 K. The peak production rate for such a plant would be 4 mol s^{-1} . We quadrupled the cost of the 1 mol s^{-1} plant to take into account night time and cloudy days [3].

of each of the major components, as well as the total cost, is shown as a function of the open area of the separation membrane, around which the size of the reactor-separator can be scaled. Allowing for 75% down time to compensate for the time when the sun is not shining, the ordinate on this figure gives the capital cost, per mol per s of hydrogen and of sulfur produced, of a plant which operates continuously, night and day, in fair weather and in foul.

Operating point A in Fig. 2 is a near-optimum capital cost operating point, which, for this particular membrane Knudsen number and heat-exchanger temperature difference, makes use of a near minimum cost solar collector, and operates with a near maximum thermal efficiency. (It is not possible to optimize all of the operating variables at the same time. Noring *et al.* [3] gives information which indicates what kinds of trade-offs are possible.)

It is still too early in the development of this fascinating new technology to make economic evaluations in which we have a great deal of confidence. Even if we were to find, now, that it is more cost advantageous than any existing technology for dealing with hydrogen sulfide, it could not be immediately implemented. Current techniques for handling hydrogen sulfide are tightly linked to the giant chemical complexes which they now serve. Changing existing plants would probably be prohibitively costly. Nevertheless, since hydrogen sulfide will be with us in increasing amounts for many years to come, it is appropriate that we explore new techniques for exploiting it. With that in mind, we have prepared Fig. 3, which provides some perspective for the information given in Fig. 2. Figure 3 is a map, on membrane-open-area vs downstream-pressure coordinates of the capital cost, per mol per s, of a continuously operating processing plant. Operating point A of the previous example is shown on the plot. It can be seen that we might have reduced the capital cost of the plant somewhat by having used a smaller reactor and having operated at a somewhat lower pressure downstream of the membrane.

Figure 3 shows that our lowest capital cost, about \$105,000 mol $^{-1}$ s is within a factor of 2.5–10 times that of a current continuous Claus process plant which handles the same amount of hydrogen sulfide but produces no hydrogen [2, 22]. Knowing whether we could actually operate at such a condition will depend on the results of experiments.

One of the objectives of our research, besides accumulating basic knowledge which will be of interest in many other respects, is to accumulate information which will make a reliable economic evaluation possible. We have not yet acquired such information. Nevertheless, it is possible to compare, with some degree of confidence, solar-thermal effusional separation with existing technology.

At the present time in the Claus process hydrogen is burned to water to provide low grade process heat. At the same time, possibly even in the same industrial complex, hydrogen is being manufactured by one of

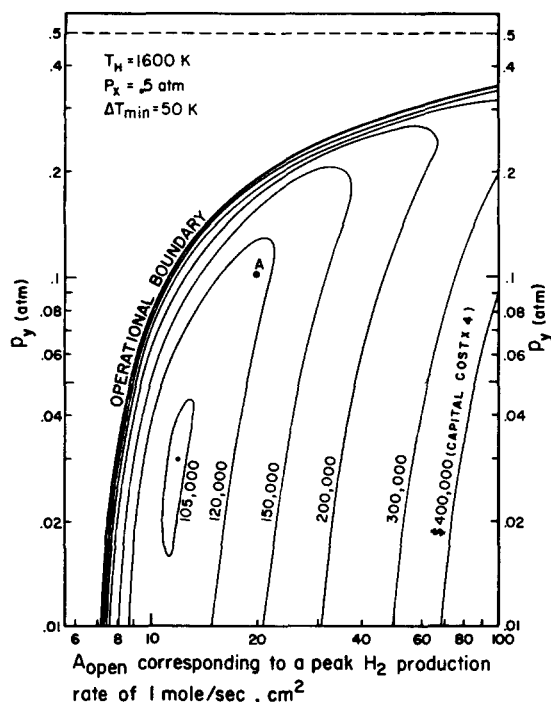


Fig. 3. Capital cost ($\times 4$) of a plant whose peak production rate is 1 mol s^{-1} each of hydrogen and sulfur [3].

several processes such as methane reforming, coal gasification, or catalytic steam reforming, depending on the nature of the plant in which removal of hydrogen sulfide is one of the operations. By far, the largest fraction of all the hydrogen manufactured is used near the site of its manufacture. It is much more valuable as a raw material in the manufacture of ammonia, for example, or in the hydrogenation, conversion and upgrading of fuels than it is as a source of low grade process heat in a refinery.

Hydrogen thus has intrinsic value as a commodity, raw material, or even as a fuel that is much greater than that achieved by burning it to produce low grade heat. As pipeline gas, its price in 1980 was \$3.00 per 100 cubic feet, delivered. Sold as a liquid at the plant in 13 000 gallon lots, its price was \$9.80 per 1000 standard cubic feet. Its price as a by-product gas was lowest, 1 cent per 1000 cubic feet, which reflects the very low value that is placed on it in present-day processing complexes which are ill equipped or unable to take advantage of its intrinsic value. If hydrocarbon fuel were to be assigned a value based on its energy content in a comparable way, its value would be <1.5 cent per gallon.

The real economic value is thus very hard to define. Even merchant hydrogen sells at prices which can vary by 1000%. It seems reasonable to suppose, however, that its value will increase in the future as we seek to use fossil fuels with greater and greater efficiency. In this paper we shall use a price of \$1.00 per 1000 cubic

feet, which is one third of the 1980 price of the pipeline gas.

The important economic respect in which our processes differ from the Claus process is that we recover hydrogen as a commodity, in addition to sulfur. We may thus compare the relative economic costs of the two processes by asking the question, "What are we paying for the hydrogen we get from our process, and what is it worth?"

The capital cost of an existing Claus unit at a refinery near Minneapolis was, several years ago, \$15 million. The plant handles 1000 tons/day of hydrogen sulfide, and produces 941 tons of sulfur [22]. Our process, operating near the least capital cost position shown on Fig. 3 of our proposal would have a capital cost of \$105 000 for an average hydrogen sulfide processing rate of 1 g mol s^{-1} . This capital cost estimate assumes that the plant would not be operating when the sun is not shining, estimated to be 75% of the time. Our capital cost for a plant which handles the same amount of hydrogen sulfide in a year, and thus produces 21 535 tons of hydrogen, in addition to the 343 500 tons of sulfur that each of the plants produces in 1 year, is thus \$32.55 million. The difference between the cost of the two plants is thus \$17.55 million.

In other words we are paying \$17.55 million for a hydrogen manufacturing plant which produces 21 535 tons per year of hydrogen. At \$1.00 per 1000 cubic feet, the value of the hydrogen is \$358 per ton. The value of the hydrogen produced in our plant is thus \$7.71 million per year. Thus, in approx. 2 years and 3 months the plant would have produced an amount of hydrogen whose value equals the capital cost of the plant. It is hard to imagine any way in which the operating costs of the two different kinds of plants would be very different, thus, the 'operating cost' attributable to the hydrogen plant alone would be essentially zero.

It is now pertinent to examine the cost of a hydrogen producing plant. An important source of hydrogen today is its production from coal. The following quotation is from the *Encyclopedia of Chemical Technology* [23]:

The . . . coal-gasification system is one of those used for raw-gas generation . . . The energy requirement . . . is 108 000 kJ/mol hydrogen . . . This corresponds to a thermal efficiency of 50.7% on a LHV basis or 58.1% on a higher heating value basis. This conversion efficiency is 20% higher than that reported for atmospheric gasification systems . . . (which are worse—my comment) . . . A typical . . . plant producing 2.83 million cubic meters per day of contained hydrogen requires . . . 2041 short tons per day of coal feed, 83.4% of which is process coal . . . The estimated capital investment requirement, based on third quarter 1978 prices is about \$231 million.

The cost of the plant referred to above includes many components which we have not included in the cost of our plant, such as construction interest and start-up costs, and coal preparation units, which our plant will not have. The net capital cost of the coal-using plant

was about \$189 million. This works out to \$129000 (mol s^{-1})⁻¹ hydrogen production, compared to the net capital cost of our hydrogen-and-sulfur producing plant of \$105000 (mol s^{-1})⁻¹ of hydrogen produced. The cost of the hydrogen producing component alone of our plant is \$57 million. The cost of a plant of comparable capacity which uses 2041 short tons of process coal per day in the production process is more than three times as great, \$189 million.

It thus appears that if our process can be made to work, it will be more cost-effective, as well as energy-effective than current state-of-the-art for the manufacture of hydrogen. Moreover, the difference can be expected to become more important as the need for energy economy grows in the future, and as our infant technology experiences the kinds of improvements that operating experience and development will make possible.

Finally, in connection with effusional separation it behoves us to add that, although we are partial to sunlight because the heating value of the hydrogen obtained is substantially greater than the solar energy needed to effect the separation and the process thus serves as an amplifier for storing sunlight, effusional separation may be attractive in non-solar applications as well, such as the use of nuclear reactors as sources of process heat.

ELECTROLYTIC PRODUCTION OF HYDROGEN AND SULFUR FROM HYDROGEN SULFIDE

We are intrigued by the use of solar energy for the recovery of both hydrogen and sulfur from hydrogen sulfide, and the concomitant storage of solar energy. However, the electrolysis of hydrogen sulfide, using the resulting hydrogen with atmospheric oxygen in a fuel cell to provide electric power for the electrolysis, is also a tantalizing option.

The emf required to electrolyze a substance in a reversible electrolytic cell, or the emf produced by a reversible fuel cell is given by [24]:

$$E = \pm \Delta G/nF \quad (1)$$

where ΔG is the change in Gibb's function of the overall reaction which occurs in the cell, n is the number of moles of electrons transferred in the external circuit during the course of the reaction, and F is the Faraday constant. The + sign applies to an electrolysis cell: the - sign applies to a fuel cell.

The change in Gibb's function of a chemical reaction,

$$\sum a_i M_i = 0 \quad (2)$$

where M_i is a reactant or product, and a_i is its coefficient in the chemical equation is given to a good approximation by;

$$\Delta G = \Delta G^0 + RT \ln \prod P_i^{a_i} \quad (3)$$

where P_i is the fugacity of gaseous species i , assumed

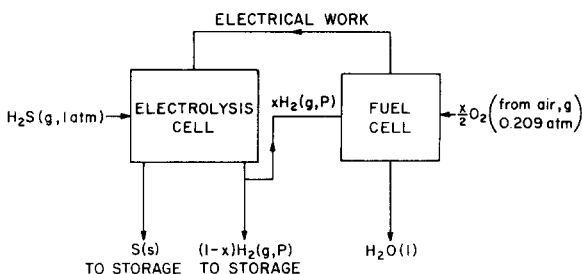
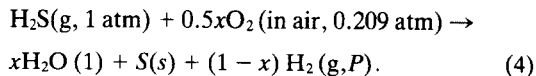


Fig. 4. Schematic representation of the device. Hydrogen sulfide from a source at 1 atm is introduced to the electrolytic cell, which produces hydrogen and sulfur at some higher pressure (P). In practice, the hydrogen sulfide might be pumped into the electrolysis cell as a liquid or gas or in solution in an appropriate solvent. For our purpose, it is necessary only to note that it has become available to us at 1 atm and that our analysis need not consider the details of the mechanisms by which the components of the system operate. A fraction of the hydrogen (x) at pressure P , is fed to the fuel cell, and the rest is stored. Hydrogen at pressure P and oxygen at 0.209 atm [27] are the reactants of the fuel cell, which rejects liquid water at 1 atm [26].

here to be ideal and therefore equal to its pressure, and is very nearly 1 for condensed phases.

Hydrogen-oxygen fuel cells are well known [25]. There exists a patent [26], for the production of hydrogen and sulfur from hydrogen sulfide by electrolysis. We can easily imagine a coupling in which hydrogen and sulfur are produced in an electrolysis cell with electric power from a hydrogen-air fuel cell. One intriguing feature of the process is that, once hydrogen sulfide has been introduced into the cell at its operating pressure, perhaps as a liquid or in a liquid solution, electrolysis can supply the work of pumping the hydrogen to an arbitrarily high pressure. That pressure might be a pipeline pressure. There would be no need for additional pumps. The wasteful process of pumping a gas would have been eliminated. In this connection, it should be pointed out that the same statement might be made with respect to hydrogen production by the electrolysis of water, as well as many other processes.

The thermodynamics of the reversible process is straightforward. A schematic representation [5] of the process is given in Fig. 4. The temperature is 298.15 K. The overall reaction is;



When $\Delta G = 0$,

$$(1-x)RT \ln P + x\Delta G_{\text{H}_2\text{O}}^0 - 0.5RT \ln 0.209 - \Delta G_{\text{H}_2\text{S}}^0 = 0. \quad (5)$$

Using equation (5) we can calculate the fraction of the hydrogen in hydrogen sulfide, x , needed to effect the electrolysis and compress the remaining hydrogen to pressure P in a reversible device. The results are shown

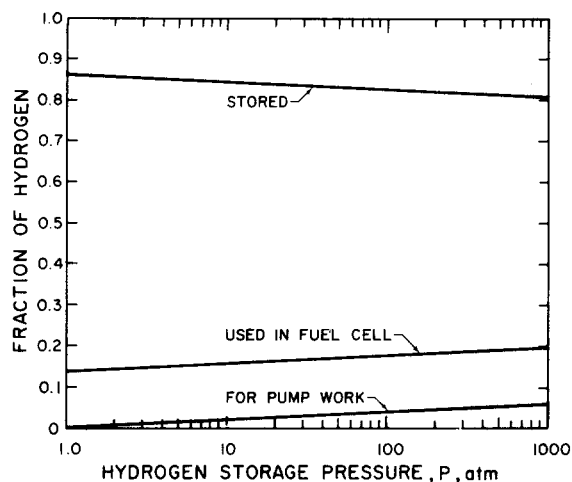


Fig. 5. Variation, with storage pressure, of the fraction of hydrogen consumed, stored and used to provide the work of compressing that which is stored [5].

in Fig. 5. Figure 5 also shows the fraction of the hydrogen which is used solely for performing pump work. Only a tiny fraction need be sacrificed to bring the remainder to very high pressure.

Incidentally, we would like to note that electrolytic pumping may be applicable to other processes in which a gaseous product, which is to be produced by electrolysis of a condensed phase, is wanted at a high pressure. Thus, the often wasteful process of compressing gases may be replaced by pumping condensed phases first, or by resorting to batch processing, in which a completely unpumped system, initially in a condensed phase at ambient pressure, is brought to high pressure by the electrolytic evolution of the gas itself.

MATERIALS OF CONSTRUCTION

The suggestion that one wishes to work with sulfur containing substances at high temperatures usually evokes the response that the problem of finding materials of construction for the equipment will be difficult to solve. We have done some preliminary thermodynamic calculations which suggest that one's initial response to the materials problem may possibly be unnecessarily pessimistic. The refractory oxides may well be stable to attack by sulfur at high temperatures. Accordingly, we did a few preliminary exploratory experiments. Our objective was to see if hydrogen sulfide would produce a catastrophic result with some candidate materials of construction; quartz, type 304 stainless steel, inconel, alumina and zirconia, before we actually went to the trouble of doing more extensive testing in a solar furnace.

We did two kinds of experiments. In one set we heated the material in the flame of a Meker burner in which methane-air was being burned. Then we gradu-

ally replaced the methane with hydrogen sulfide and observed the result. In the second set, we used a methane-oxygen glassblowing torch to achieve higher temperatures. We heated the samples from below as we impinged hydrogen sulfide onto them from above, and observed the change in appearance and weight of the samples. These preliminary tests usually lasted for several minutes.

Within a few minutes inconel and type 304 stainless steel showed evidence of chemical attack in the form of the build-up of sulfide layers at temperatures in the range 1100–1250 K. Inconel blistered and built up a thick, porous layer; the stainless steel's layer was thinner and flaky. Both metals gained weight. Black steel pipe, at 1100 K developed a thin, apparently adherent scale.

The nonmetals fared much better. We were able to heat a zirconia honeycomb on its bottom surface to 1720 K with a methane-oxygen torch while impinging a jet of hydrogen sulfide on its upper surface, which was at 1120 K. There was no weight change of the zirconia, and no apparent adverse effect. Alumina spark-plug electrode insulators, which contain silica, were unaffected by hydrogen sulfide at 1150 and 1440 K, although the material began to melt at the higher temperature. Pure alumina heated from below to 1700 K and exposed to a jet of hydrogen sulfide on its upper surface at almost 1400 K was completely unaffected in the test. The commercial ceramic insulating material, Fiberfrax was unaffected up to the temperature at which it began to melt, 1640 K. A quartz tube, heated by a brush burner burning methane-air, through which hydrogen sulfide flowed and was pyrolyzed, was unaffected by the experience. It thus appears that the ceramic oxides will be the preferred materials of construction for high-temperature thermochemical processing of hydrogen sulfide.

CONCLUSION

Hydrogen sulfide, now an undesirable waste product in fossil fuel technology, should be explored as a source of hydrogen, as well as a source of sulfur. The possibility of using naturally occurring hydrogen sulfide itself as a valuable fuel and mineral source should be investigated. It is likely that ceramic oxides will be useful materials of construction for high-temperature processes.

Hydrogen sulfide itself might be a useful fossil fuel if it were not for the disastrous environmental problems its use would entail. It might nevertheless be so used in a process which makes use of existing devices to convert it into hydrogen and sulfur, electrolytically, with no immediately evident serious environmental problems, with only a slight loss of its inherent thermodynamic value.

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