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PLASMA-CHEMICAL CONVERSION OF HYDROGEN SULFIDE INTO HYDROGEN AND SULFUR

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ABSTRACT

A waste-treatment process that recovers both hydrogen and sulfur from hydrogen-sulfide-contaminated industrial wastes is being developed to replace the Claus technology, which recovers only sulfur. The proposed process is based on research reported in the Soviet technical literature and uses microwave (or radio-frequency) energy to initiate plasma-chemical reactions that dissociate hydrogen sulfide into elemental hydrogen and sulfur. As in the Claus process, liquid sulfur would be recovered and sold. However, in the plasma-chemical process, the remaining gaseous stream would be purified and separated into streams containing the product hydrogen, hydrogen sulfide for recycle to the plasma reactor, and the process purge containing carbon dioxide and water. Since unconverted hydrogen sulfide is recycled to the plasma reactor, the plasma-chemical process has the potential for sulfur recoveries in excess of 99% without the additional tail-gas clean-up processes associated with the Claus technology. Laboratory experiments with pure hydrogen sulfide have confirmed that conversions of over 90% per pass are possible. Experiments with impurities typical of petroleum refinery and natural gas production acid gases have demonstrated that these impurities are compatible with the plasma dissociation process and do not appear to create new waste-treatment problems. Other experiments show that the cyclonic-flow pattern hypothesized by the Russian theoretical analysis of the plasma-chemical process can substantially decrease energy requirements for hydrogen sulfide dissociation while increasing conversion. This process has several advantages over the current Claus-plus-tail-gas-cleanup technology. The primary advantage is the potential for recovering hydrogen more cheaply than the direct production of hydrogen. The difference could amount to an energy savings of 40×10^{15} to 70×10^{15} J/yr in the refining industry, for an annual savings of \$500 million to \$1,000 million. Although the microwave process appears to be especially well suited for the petroleum refining industry, the low capital costs and modular nature of the new process should also make it economically attractive to the natural gas industry for use in small-scale waste treatment technologies.

INTRODUCTION

In 1987, Argonne National Laboratory staff found the first reports in the Western technical literature of Soviet experiments in dissociating hydrogen sulfide with a microwave-induced plasma.[1,2] The small-scale laboratory experiments reported were very similar to those described in several theses prepared at the Massachusetts Institute of Technology in the middle 1960s for the dissociation of various gases.[3-5] Soviet claims for hydrogen sulfide dissociation suggested it should be successful in industrial application, because hydrogen sulfide appeared to be a relatively easy gas to dissociate and modern refineries have significant hydrogen needs. However, the exact value of the energy required to dissociate hydrogen sulfide depends upon the form of the sulfur product. For illustrative purposes, liquid sulfur is assumed in equation (1):

$$H_2S \rightarrow H_2 + S_l \qquad \Delta H^o_{25} = 21.05 \text{ kJ/g·mole} = 5.03 \text{ kcal/g·mole} = 0.24 \text{ eV/molecule.} \qquad (1)$$

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A key feature of the plasma-chemical reaction model hypothesized by the Soviets is the injection of feed gases into the plasma zone tangentially at very high velocities to produce a cyclonic flow pattern.[1] Such a pattern produces rapid separation and cooling of the dissociation products, "freezing" the product composition at the plasma conditions by minimizing the opportunity for the reverse reaction to reform hydrogen sulfide.

A research program was established at Argonne National Laboratory in 1987 by the U.S. Department of Energy, Industrial Waste Reduction Programs. The objective of this research has been to experimentally determine the technical and economic feasibility of dissociating hydrogen sulfide in a microwave-induced plasma. The initial experiments were designed to duplicate the early laboratory results reported by the Soviets. The earliest Argonne laboratory findings were very encouraging.[6-8] The energies of dissociation appeared to be in the same range as reported by the Soviets, while the single-pass yields were generally greater than those reported in the Soviet literature.

Preliminary economic analysis for a commercial-scale system shows that most of the operating costs are for the energy needed to generate the microwaves, although some additional energy is needed to operate pumps and compressors.[7,12,13] The capital costs have been estimated to be less that half the costs of a Claus sulfur recovery unit (CSRU) followed by a tail-gas cleanup unit (TGCU).[7,12] Comparison of the annual operating costs of the plasma-chemical technology with costs for the current CSRU/TGCU technology indicates that the plasma-chemical system might save as much as $4.0 million/yr (assuming a sulfur production of 1.6×10^5 kg/day). This difference is insensitive to the price of sulfur because both processes generate essentially the same amount of sulfur. Because the plasma-chemical technology saves energy, this technology becomes more competitive as the cost of energy increases. The energy savings for the same scale of operation are probably between 550 million and 950 million Btu/day. If it is assumed that 90% of the 30+ year-old plants and the new capacity will use the plasma-chemical technology, the total energy savings for the U.S. refining industry could range from 40×10^{15} to 70×10^{15} J/yr in the year 2010, and the concomitant dollar savings would be $500 million to $1,000 million/yr.

From its inception, the Argonne program has been supported by an Industrial Working Group representing potential users and suppliers of the microwave-plasma technology. Members of this group include Amoco Oil Company, the Electric Power Research Institute, the Gas Research Institute, UOP, Varian, and Wavemat, Inc. The function of the group has been to maintain the industrial focus of the research and to facilitate the transfer of this technology to industry. This group also provides the Department of Energy with immediate feedback about the level of industrial interest in the technology.

STATUS OF THE RUSSIAN RESEARCH PROGRAM

The Hydrogen Energy and Plasma Technology Institute of the Russian Research Centre/Kurchatov Institute (formerly the Kurchatov Institute of Atomic Energy) has expanded its efforts in this field substantially over the years.[9] Their scientists and engineers now operate three separate plasma-chemical facilities in their Moscow laboratories and have a large semi-industrial facility located at a natural gas treatment plant north of Orenburg in central Russia. They have also tested two smaller plasma-chemical units at oil refineries: one near Moscow (5 kW) and the second near L'vov, Ukraine (50 kW). Neither of these latter units is currently operating. Their research and development effort is strongly supported by a theoretical group, as well as by materials and separations research efforts.

The Orenburg natural gas treatment plant currently uses standard technologies (amine purification units followed by a Claus plant) to remove and dispose of the acid gases from the crude natural gas. The plasma-chemical test facility takes a slipstream of acid gas from the amine purification unit and returns gaseous products to the Claus plant. Sulfur produced at the test facility is added to the sulfur product from the Claus plant. In addition to the plasma-chemical facility, the Orenburg test facility has a membrane development laboratory for testing natural gas purification and carbon dioxide recovery, as well as hydrogen/hydrogen sulfide separation.

The Orenburg plasma-chemical test facility was commissioned in 1986 and has been operated at microwave powers up to 1,000 kW with 915-MHz generators. The acid-gas slipstream is dried and filtered before it

enters the plasma reactor, which has been operated at pressures as high as atmospheric pressure. The plasma-product stream is rapidly quenched to minimize the re-formation of hydrogen sulfide and to recover the bulk of the sulfur by condensation. An "electro-filter" (which appears to be an electrostatic precipitator) was recently installed to control sulfur aerosol carryover and, thereby, to increase sulfur recovery. This device is followed by a mechanical filter and finally by a separation unit to recover hydrogen product. The remaining hydrogen sulfide, water, and carbon dioxide are currently returned to the Claus plant, but in commercial practice, the hydrogen sulfide would be recycled to the plasma reactor.

The current plasma reactor (called a plasmatron) at the Orenburg test facility (as shown in Figure 1) is basically a short section (about one meter) of a metallic, cylindrical waveguide. The gas feed enters the reactor through a proprietary feed system to produce the cyclonic flow pattern and flows downward through the plasma zone into the primary sulfur condenser. Microwave energy is injected through one or more ports in the wall of this wave guide. The configuration shown in Figure 1 is that used for the 1,000-kW tests, in which four 250-kW magnetrons were piped to ports located symmetrically about the plasma zone.

LABORATORY EXPERIMENTS

The experimental apparatus used in the experimental program at Argonne originally was patterned after the system described in the first Soviet publication.[1] The original system was designed to (1) determine the degree of dissociation for pure hydrogen sulfide and to estimate its dissociation energy, (2) determine the effects of typical refinery acid-gas compositions on the dissociation process, (3) test plasma-reactor design features, and (4) evaluate potential process enhancements. Most recently, after the original waveguide applicator was replaced with a resonant-cavity model and extensive modifications were made to the feed system to permit atmospheric pressure operations, this apparatus (shown in Figure 2) was used to study acid gases with carbon dioxide contents up to 65%.

The gas-feed system uses mass-flow controllers to meter hydrogen sulfide, carbon dioxide, and either a "pipeline" natural gas or argon from gas cylinders. These gases are mixed in a heat-traced feed manifold. Water is metered in by a peristaltic pump from a burette and vaporized in the feed manifold. For safety, and as an aid in igniting a plasma, argon can also be added separately through a rotometer-controlled purge line. The manifold and the entire feed-transfer line are heat-traced with an electrical resistance heater.

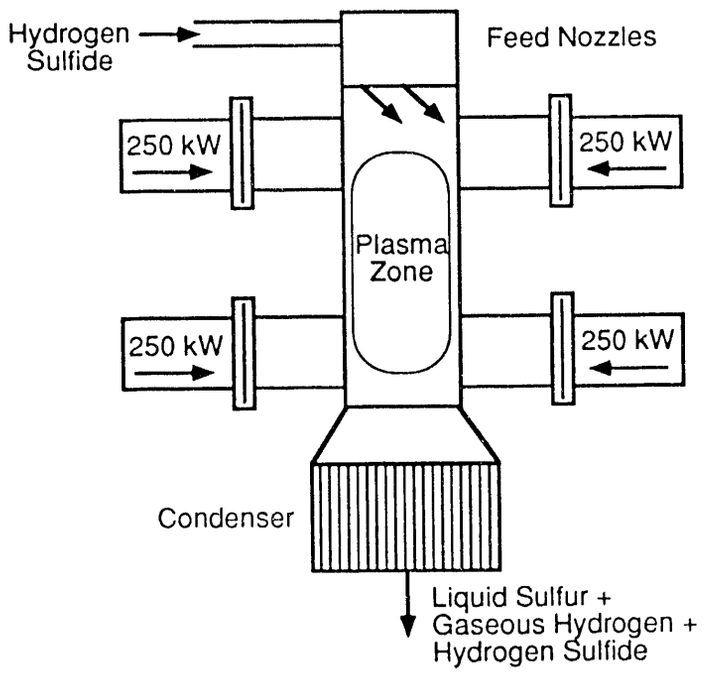

Fig. 1. 1,000-kW plasmatron (plasma-chemical reactor) used at Orenburg.

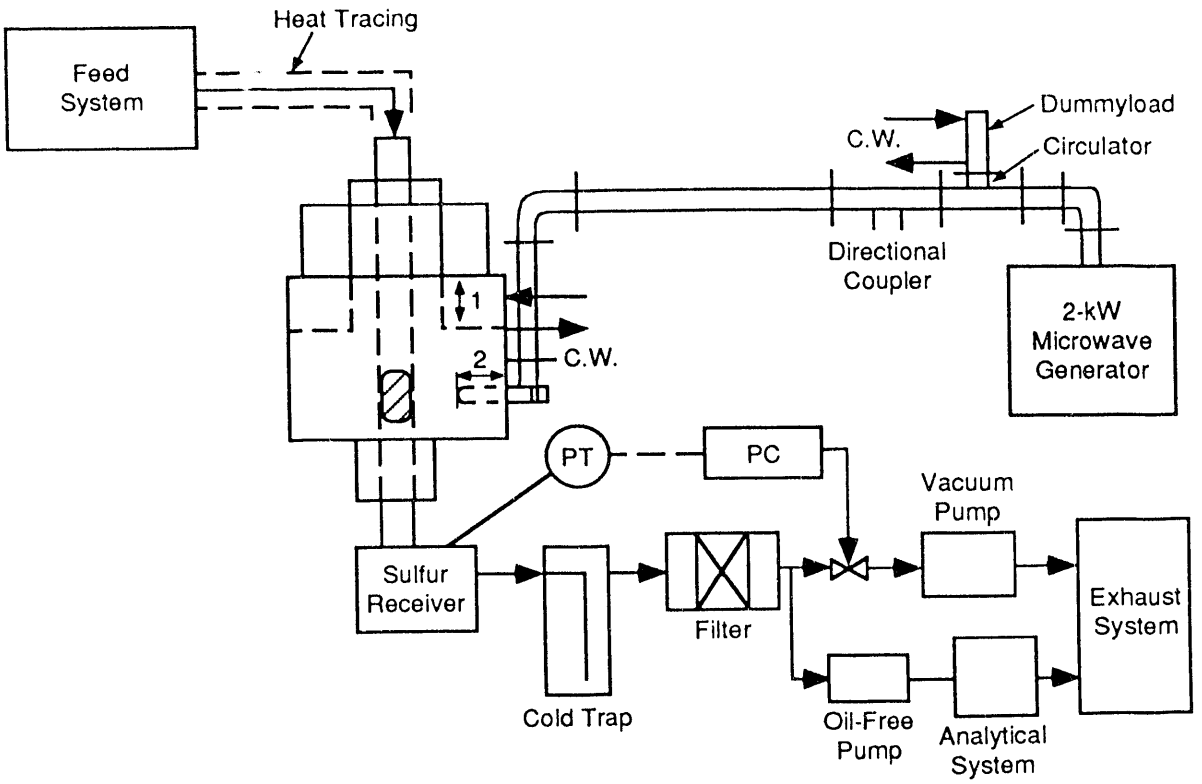

Figure 2. Argonne experimental system.

The current reactor (see Figure 3) uses a metal coupling to connect the feed manifold to the reactor, which is just a straight section of quartz tubing. This coupling holds a metallic insert with nozzle(s) machined into it, which is designed to produce the cyclonic flow pattern. The quartz section of the reactor extends well into the chokes on both sides of the resonant cavity of the applicator, so quartz is the only material exposed to either the microwave radiation or the plasma. This microwave applicator is a tunable, resonant cavity and, in these experiments, was operated in the "TM_{012}" resonant mode. This mode produces an electric field with cylindrical symmetry centered on the plasma zone in the quartz-tubular reactor. In all the experiments reported here, the microwave generator is a continuously variable 2.2-kW magnetron (2.45 GHz).

The lower section of the quartz reactor and the entrance of the sulfur receiver are heat-traced to 125°C. In order to condense some of the sulfur product without having it solidify, the body of the sulfur receiver is cooled with laboratory water to solidify the bulk of the sulfur produced. Finally, the gas stream is chilled to −10°C in a glycol-cooled cold trap to remove additional sulfur as a solid. However, invariably some sulfur reached and even passed through a 6-in.-deep glass-wool filter. In the laboratory system, this sulfur carryover has required regular maintenance on the pressure-control valve and the sample pump in the analytical system. It may be less of a problem in a commercial-scale system, but it should not be ignored (the process proposed by Argonne includes a catalytic reduction step to control sulfur carryover[10]). The cold trap also condenses a significant fraction of the water contained in the product stream, which causes some problems in interpreting the data (see the results section). The cooled gases pass through the primary vacuum pump to iron-sponge scrubbers to remove residual hydrogen sulfide and then are vented. Analytical gas samples are compressed by an oil-free pump into the analytical system. Gases leaving the analytical system pass through a separate iron-sponge scrubber and then are vented into the laboratory exhaust system.

The analytical system includes a binary gas analyzer and a station for collecting 125-mL gas samples in glass sample tubes. The binary gas analyzer uses a pair of thermal conductivity cells to determine the gas composition by comparing the thermal conductivity of the sample stream to a reference stream of pure hydrogen. The instrument reading is converted into a mole percent concentration for hydrogen sulfide by means of a calibration curve (0 to 100 % H_2S). This method provides a direct measure of conversion only

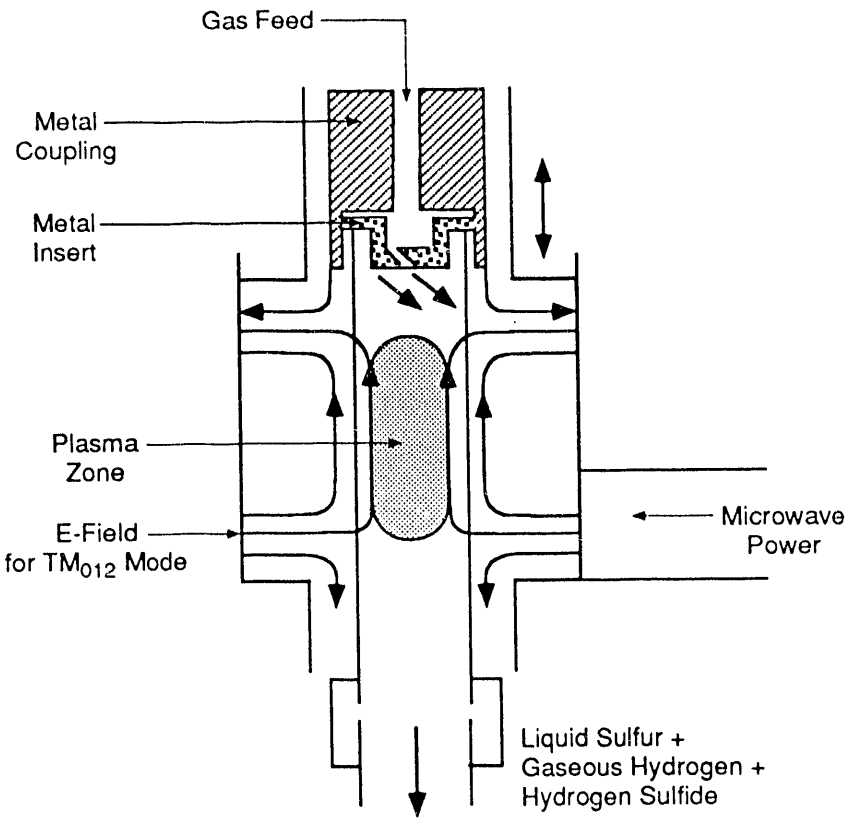

Figure 3. Resonant-cavity applicator with new feed injectors.

for experiments when pure hydrogen sulfide is fed to the plasma reactor, and hydrogen and hydrogen sulfide are the only gaseous species to reach the binary gas analyzer. When gas mixtures are fed to the plasma reactor, the binary gas analyzer is only used to determine when an experiment has reached steady state; in these cases, gas samples are collected and conversions are calculated from the results of off-line, mass-spectrographic analyses of both the feed and product gas samples.

EXPERIMENTAL RESULTS

Previous experimental results[13] showed that, for a fixed volumetric feed rate, higher linear velocities with greater cyclonic effects yielded higher conversions with lower energies of dissociation, as hypothesized by the Russians.[1] However, as the volumetric feed rate increased, the conversion decreased, which indicated that residence time in the plasma zone is also an important variable for hydrogen sulfide conversion.

Previously, acid-gas compositions typical of refinery operations had been tested. The most recent set of experiments studied the effects of carbon dioxide over the range of 30.0 to 65.0% on the conversion of hydrogen sulfide in an acid-gas stream more typical of recent natural gas discoveries than refinery conditions. These experiments used a factorial design in three variables — the concentrations of carbon dioxide, water, and natural gas in hydrogen sulfide. The gas compositions for these two series of experiments are compared in Table I. In Series I, pure methane was used to represent the hydrocarbons present in refinery acid gases, while in Series II, a "pipeline" natural gas mixture prepared by the Institute of Gas Technology (Chicago, Illinois) was used to represent the hydrocarbons present in the gas industry's acid gases. Series I used the waveguide applicator and internal-diaphragm reactor, while Series II used the resonant-cavity reactor with the newer nozzle feed system. In Series II, the plasma reactor pressure was held at 6.67 kPa to ensure a stable plasma in the current apparatus with a total gas flow rate of 6.0 SLPM (L/min at standard conditions), while the input microwave power was 1.0 kW. In Series I, the reactor pressure was 2.67 kPa, with a gas feed rate of 1.0 SLPM and 1.0 kW input microwave power.

Table I. Comparison of test acid-gas compositions.

Gas Component[a]	Series I		Series II	
	Low	High	Low	High
CO_2	0.0%	16.1%	30%	65%
H_2O	0.0%	6.3%	0.0%	7.0%
Methane	0.0%	0.1%	-	-
"Pipeline" gas	-	-	0.0%	0.2%

[a] H_2S was the balance gas in both series.

Table II compares the amounts of hydrogen sulfide converted and by-products in the product stream for these two series of experiments. The major differences between these two series are the much wider range of hydrogen sulfide and carbon dioxide conversions in the second, most recent work (simulated natural gas acid-gas stream). While the second series also showed a slightly greater amount of sulfur dioxide in the gaseous product stream, the other by-product concentrations were surprisingly similar. Furthermore, because the second series used a much higher flow rate (6.0 versus 1.0 SLPM), the hydrogen sulfide residence time in the plasma zone was six times greater in the first series of experiments. This increased residence time probably accounts for the higher average hydrogen sulfide conversions and the narrower range of conversions for the first series.

Table II. Summary of results for acid-gas experiments.

Dependent Variables	Series I	Series II
	%	%
H_2S conversion	81.4–95.6	53–99
CO in product	0–12	3–35
COS in product	0.0–0.6	0.1–0.8
CS_2 in product	0.05–0.58	0.04–0.70
SO_2 in product	0.0–1.4	0.0–2.1

The practically insignificantly small differences between the production of carbonyl sulfide and carbon disulfide in these two series suggests that the reaction mechanisms for their formation are weakly related, if at all, to the carbon dioxide concentration. The production of sulfur dioxide would seem to be more dependent upon the carbon dioxide concentration, since carbon dioxide is the major source of oxygen in these gas mixtures. However, the variations in sulfur dioxide concentration were significantly smaller than the range of carbon dioxide concentrations studied.

A statistical analysis of the Series II results indicated that hydrogen sulfide conversion is directly proportional to the carbon dioxide concentration and that no other variable had a significant effect. However, the primary mechanism for this relationship appears to be a simple dilution effect, as shown in Figure 4. Here the conversion of hydrogen sulfide increases as its concentration decreases. This is the classical profile of a limiting reagent situation; at the highest hydrogen sulfide concentrations studied here, a linear, inverse relationship is observed, which levels out and becomes insensitive to changes in concentration as the concentration continues to decrease. In other words, since the input microwave power was constant (1.0 kW) for all of these experiments, the energy available per molecule of hydrogen sulfide increased to the point that it no longer limited the dissociation process — hydrogen sulfide became the limiting reagent.

High carbon dioxide concentrations had a serious negative impact on hydrogen production, as is shown in Figure 5. As the carbon dioxide concentration in the feed to the plasma reactor increased, the fraction of the hydrogen sulfide converted to hydrogen decreased. The remaining hydrogen reacted with carbon dioxide to produce water and carbon monoxide — as in the water-gas-shift reaction. However, the precise mechanism for the oxidation of the hydrogen could also be the dissociation of carbon dioxide to carbon monoxide and an oxygen atom, which then reacted with a hydrogen molecule to form water. The overall result is the loss of a significant fraction of the potential hydrogen production. In order to maximize hydrogen production, the carbon dioxide content in the feed to the plasma-chemical reactor must be kept low.

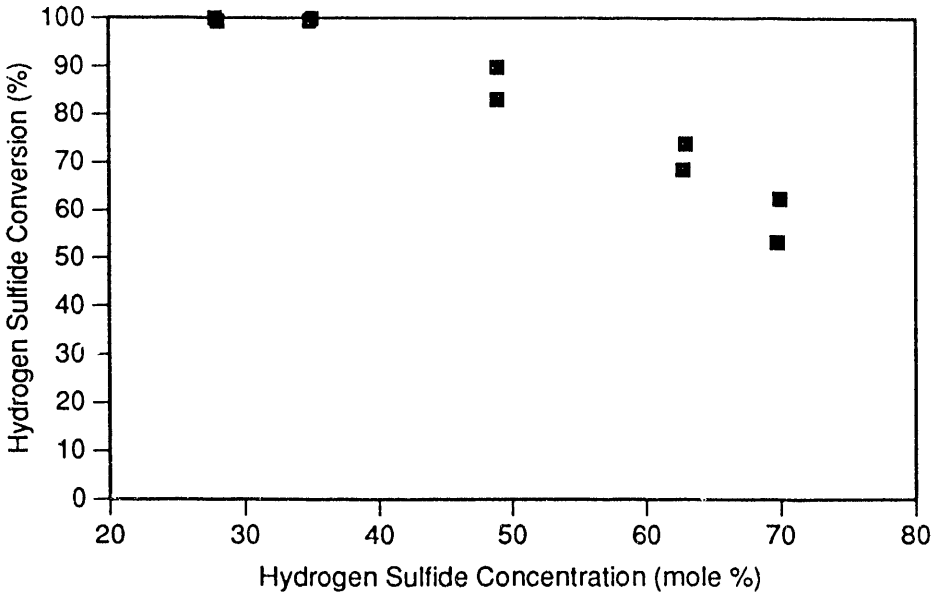

Figure 4. Hydrogen sulfide conversion as a function of hydrogen sulfide concentration.

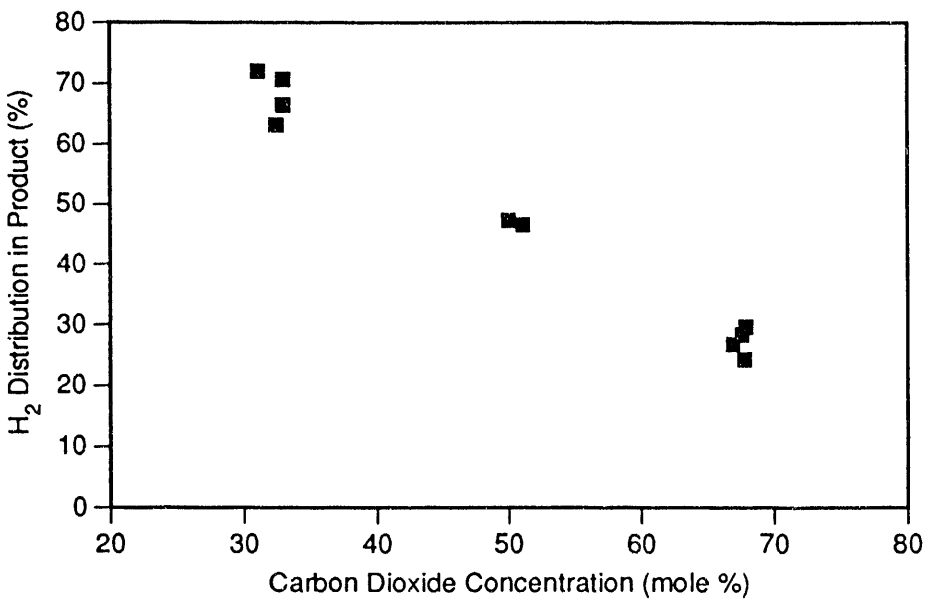

Figure 5. Hydrogen distribution in product as a function of carbon dioxide concentration.

CONCLUSIONS AND FUTURE RESEARCH

The research to date has shown that an H_2S waste-treatment process based on plasma-chemical dissociation technology is compatible with refinery and high-carbon-dioxide acid-gas streams. The minor amounts of impurities produced in the plasma-chemical reactor should be treatable by an internal catalytic reduction step. However, to maximize hydrogen production in this process, a significant fraction of the carbon dioxide should be removed from the gas feed to the plasma reactor. Future research should determine the maximum acceptable carbon dioxide concentration in the feed to the plasma-chemical reactor.

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