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HYDROGEN AND SULFUR PRODUCTION FROM HYDROGEN SULFIDE WASTES*

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ABSTRACT

A new hydrogen sulfide waste-treatment process that uses microwave plasma-chemical technology is currently under development in the Soviet Union and in the United States. Whereas the present waste treatment process only recovers sulfur at best, this novel process recovers both hydrogen and sulfur. The plasma process involves dissociating hydrogen sulfide in a "nonequilibrium" plasma in a microwave or radio-frequency reactor. After the dissociation process, sulfur is condensed and sold just as is currently done. The remaining gases are purified and separated into streams containing the product hydrogen, the hydrogen sulfide to be recycled to the plasma reactor, and the process purge containing carbon dioxide and water. This process has particular implications for the petroleum refining industry, in which hydrogen is a widely used reagent and must be produced from increasingly scarce hydrocarbon resources. The modular nature of the new process may also offer economic advantages over small-scale waste treatment technologies widely used in the natural-gas industry. Laboratory-scale experiments with pure hydrogen sulfide indicate that conversions exceeding 90% are possible with appropriate reactor design and that the energy required to dissociate hydrogen sulfide is low enough for the plasma process to be economically competitive. In addition, the experiments show that typical refinery acid-gas streams are compatible with the plasma process and that all by-products can be treated with existing technology.

BACKGROUND

In 1987, Argonne staff found the first reports in the Western technical literature of Soviet interest in dissociating hydrogen sulfide with a microwave-induced plasma (#1, #2). These preliminary reports of small-scale laboratory experiments were very similar to several theses prepared at the Massachusetts Institute of Technology in the early 1960s for the dissociation of various gases (#3, #4, #5). However, the Soviet claims for hydrogen sulfide dissociation suggested that it would offer a substantially better opportunity for industrial success since hydrogen sulfide appeared to be a relatively easy gas to dissociate.

$$H_2S \dashrightarrow H_2 + S,\ \Delta H^o = 0.2/eV \text{ (\#1)}$$

In particular, the energy savings opportunities with hydrogen sulfide appeared to be substantial since the U.S. refining industry must generate a substantial volume of hydrogen to desulfurize crude oils. The hydrogen sulfide produced by the desulfurization process is a major waste treatment challenge and cost since sulfur sales does not pay for the total costs of conducting the waste treatment operation. By using the plasma-chemical approach for the treatment of hydrogen sulfide waste, Argonne staff projected energy savings to the U.S. refining industry of $40\text{-}70 \times 10^{12}$ Btu/year in 2010 with significant economic benefits as well (#6).

One key feature of the plasma-chemical reaction model proposed by the Soviets (#1) is that the feed gases should be injected into the plasma zone tangentially and at very high velocities. This procedure produces a rapid separation and cooling of the dissociation products that "freezes" the product composition at their plasma condition, which is characteristic of significantly higher temperatures than would be expected from the bulk-gas temperatures. Since the electronic temperatures of the plasma are on the order of 10 - 50,000 K (#3), the gas temperatures may only be a few hundreds of degrees centigrade. (Gas temperatures in the Argonne experiments have been observed as low as 115°C, which caused the sulfur to solidify and plug the plasma reactor outlet. The reactor outlet is now heat-traced to prevent plugging.)

A research program ("Recovery of Hydrogen and Sulfur from Hydrogen Sulfide Wastes") was established at Argonne National Laboratory in September 1987 by the present-day Office of Industrial Technologies (U.S. Department of Energy, Assistant Secretary for Conservation and Renewable Energy). The objective of this program 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, and the earliest Argonne laboratory findings have been very encouraging (#7, #8). The energies of dissociation appeared to be in the same range reported by the Soviets, while the single-pass yields were generally greater than those reported in the Soviet literature.

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From its inception, this 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, Paton Tek, UOP, Varian, and Wavemat, Inc. The function of the group has been to maintain an industrial focus of the research and to facilitate the eventual transfer of the technology to industry. This effort also provides the Department of Energy with immediate feedback about the level of industrial interest in the technology.

STATUS OF THE SOVIET RESEARCH PROGRAM (#9)

The Kurchatov Institute has expanded its efforts substantially over the years. Scientists at Kurchatov now operate three separate experimental facilities at their Moscow laboratory and have at least three installations operating at industrial sites: Orenburg, Moscow, and L'vov in the Ukraine. Their experimental effort is strongly supported by a theoretical group, as well as by materials and separations research efforts.

The Kurchatov program has advanced to the point of demonstrating the plasma-chemical process at a natural gas processing facility in the Orenburg gas fields (located in the Russian Republic near the European/Asian border). The Orenburg gas facility currently uses fairly standard technology to remove acid gases from the crude natural gas-amine purification units followed by a Claus plant. Figure 1 shows a block flow sheet for the plasma-chemical demonstration unit. The 1.0-MW "semi-industrial" plant uses a slip-stream of acid gas from the amine purification unit. The Kurchatov scientists described the plasma reactor at the Orenburg demonstration unit as being the same as the "Povod" unit located at Kurchatov. These units, sketched in Figure 2, use four 250-kW magnetrons operating at 915 MHz. Another 250-kW unit is used for experimental work on carbon dioxide dissociation. This stream has some of its water removed and is filtered before it reaches the plasma reactor, which operates at or close to atmospheric pressure. The product stream is rapidly quenched to recover the bulk of the sulfur by condensation. Scientists at Kurchatov are currently installing an "electro-filter" (which appears to be an electrostatic precipitator) to control sulfur aerosol

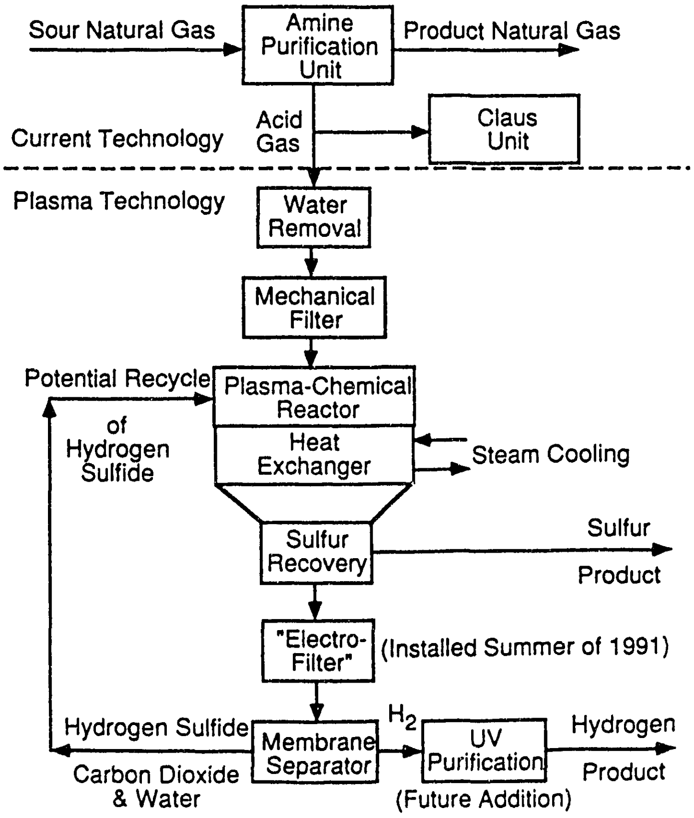

Figure 1 Orenburg "Semi-Industrial" Plasma-Chemical Plant

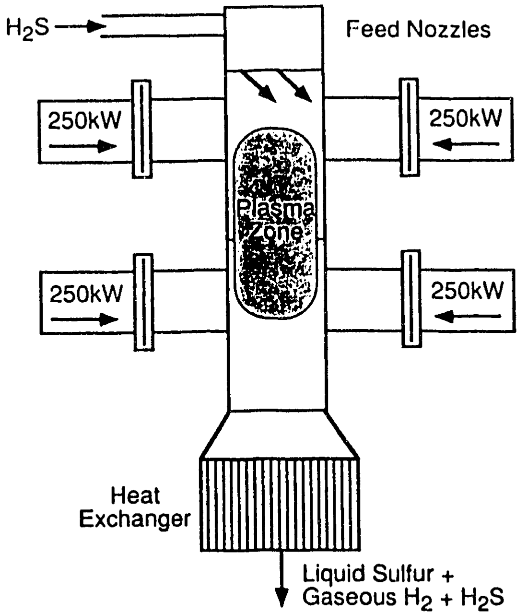

Figure 2 1-MW Orenburg Configuration

carryover and, thereby, increase sulfur recovery. This is followed by a mechanical filter and, finally, a hollow-fiber separation unit to recover the hydrogen product. The remaining hydrogen sulfide, water, and carbon dioxide are currently purged, although the hydrogen sulfide could, in theory, be separated for recycle to the plasma reactor.

The microwave energy is generated by a single magnetron. The output of the magnetron is split between two rectangular waveguides that, in turn, feed a cylindrical waveguide tangentially from opposite sides of the waveguide preceding the plasma reactor proper. The transition sections from the rectangular waveguide into the cylindrical section look like giant whistles in profile (axial view). The gas flow is 90 normal m^3/h of carbon dioxide and runs at atmospheric pressure with about 100 kW power input. All of the Kurchatov microwave generators are continuously variable (no chopping to obtain less than full power levels). The gas is also fed tangentially through the left waveguide transition section (a second port may also have been located on the right section but was not noticeable) in order to obtain the desired centrifugal flow profile as it passed into the feed section.

The plasma reaction zone was downstream of the second microwave port and appeared to be in an enlarged section of pipe. However, part of the increased diameter may also have been due to an integral cooling jacket. The primary heat exchanger was located immediately downstream of the plasma zone. Its shell and tube configuration defined that end of the resonant cavity, which is designed for an H_{10} resonance. A video camera, looking down the axis of the reactor, provided a clear view of the plasma start-up and confirmation of stable operation. The desired condition is a plasma centered in the reactor as illustrated in Figure 3.

Kurchatov's second laboratory system included a 10-kW, 2.45-GHz microwave plasma reactor and a radio-frequency, inductively coupled plasma reactor. The two reactors were connected in parallel to the same feed system and downstream sulfur recovery and hydrogen purification equipment. These reactors were both constructed from straight sections of quartz tubing and achieve centrifugal flow by passing the hydrogen sulfide feed stream through nozzles above the plasma zone. This laboratory appears to be used primarily for the testing and development of the downstream equipment.

The original laboratory apparatus has been extensively redesigned since the 1982 paper. In particular, the microwave applicator is now a resonant cavity using the same H_{10} mode as "Povod." This apparatus is much more highly instrumented than was originally described in that paper, and it is more highly instrumented than either of the other two Kurchatov laboratory plasma systems. It appears to be primarily used for testing gas compositions and other more fundamental aspects of their modeling efforts. For example, one of their recent papers (#10) showed how the energy distribution between the vibrational and translational modes of a gas molecule was affected by the nonequillibrium nature of the plasma. This analysis was performed with an on-line infrared spectrometer.

PROPOSED AMERICAN PROCESS

The process flowsheet proposed by Argonne for the United States has several differences from the process installed at Orenburg. The major difference is an internal purification step to remove plasma by-products observed in the Argonne laboratory experiments with gas mixtures of hydrogen sulfide, carbon dioxide, water, and methane. (#8) A block flow diagram is shown for this process in Figure 3. The acid gas containing hydrogen sulfide, carbon dioxide, water, and traces of hydrocarbons from a sulfur removal system (such as the amine purification system shown here) is injected into the microwave plasma reactor to produce a product stream containing hydrogen and sulfur, plus unconverted hydrogen sulfide, carbon dioxide, and water. This stream also contains low levels of some undesirable by-products, including carbon monoxide, sulfur dioxide, carbonyl sulfide, and carbon disulfide. (The Soviets also saw these by-products in their original experiments but

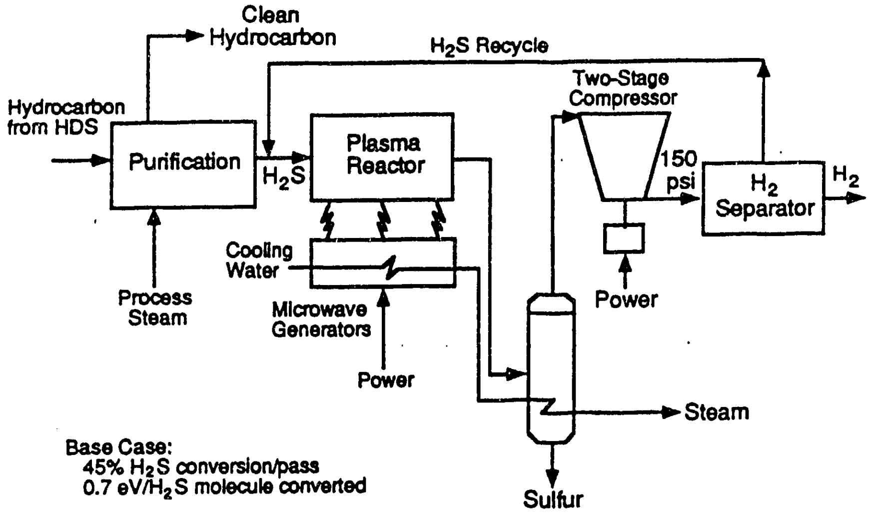

Figure 3 Proposed Plasma-Chemistry for Converting Hydrogen Sulfide to Sulfur and Hydrogen

say that they have not been a problem in their larger-scale tests.) (#9)

After treatment in the plasma reactor, the sulfur would be condensed out of the gaseous product stream and recovered for sale. The uncondensed gases would then pass through a catalytic reduction step to convert the undesired sulfur-containing by-products (less than 1% of the hydrogen sulfide dissociated) and residual gas-phase sulfur back into hydrogen sulfide for recycle to the plasma reactor. The carbon monoxide would be converted back into carbon dioxide via the shift reaction with residual water in the plasma product stream. Although some hydrogen would be consumed in this unit operation, the net loss to the overall process would be very minor, since the hydrogen sulfide produced in the reduction step would be recycled and re-dissociated in the plasma reactor. The final step in the process would be the separation of the products of this reduction step into the product hydrogen stream, the hydrogen sulfide recycle stream, and a purge stream containing carbon dioxide and water plus any residual byproducts.

LABORATORY EXPERIMENTS

The experimental apparatus was designed to accomplish the following: (1) determine the dissociation energy and degree of dissociation for pure hydrogen sulfide, (2) determine the effects of typical sour-gas compositions on the dissociation chemistry, (3) test plasma reactor design features, and (4) evaluate potential process enhancements. The results from the first two objectives have already been reported (#7, #8), while results from the latter objectives are reported here. The apparatus in Figure 4 has been described in detail (#8) but will be briefly reviewed here for the features germane to the experimental results presented in this paper.

The gas feed system uses mass-flow controllers to meter hydrogen sulfide, carbon dioxide, and either methane or argon from gas cylinders. These gases are mixed in a heat-traced 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 is heat traced with an electrical resistance heater. The maximum preheat temperature was 400°C (limited by a graphite ferrule in the metal-to-quartz union at the inlet of the quartz-tubular reactor).

The reactor was fabricated from 35-mm quartz tubing in the Argonne Chemistry Glass Shop. The feed gases flowed down the reactor and through a hole drilled tangentially in an internal diaphragm. This design yielded the high-velocity, cyclonic flows cited by the Soviets as being instrumental in obtaining high conversions with low energies of dissociation. The plasma zone was located immediately below the diaphragm, on the centerline of the waveguide from the microwave generator, which is a continuously variable 2.2-kW magnetron (2.45 GHz). The gaseous product exiting the plasma zone was allowed to cool to 125°C to condense some of the sulfur product and then chilled to -10°C to trap additional sulfur. However, some sulfur invariably reached and even passed through a 6-in.-deep glass-wool filter. The gases either passed through the main vacuum pump to the final scrubbers or was compressed to the analytical system.

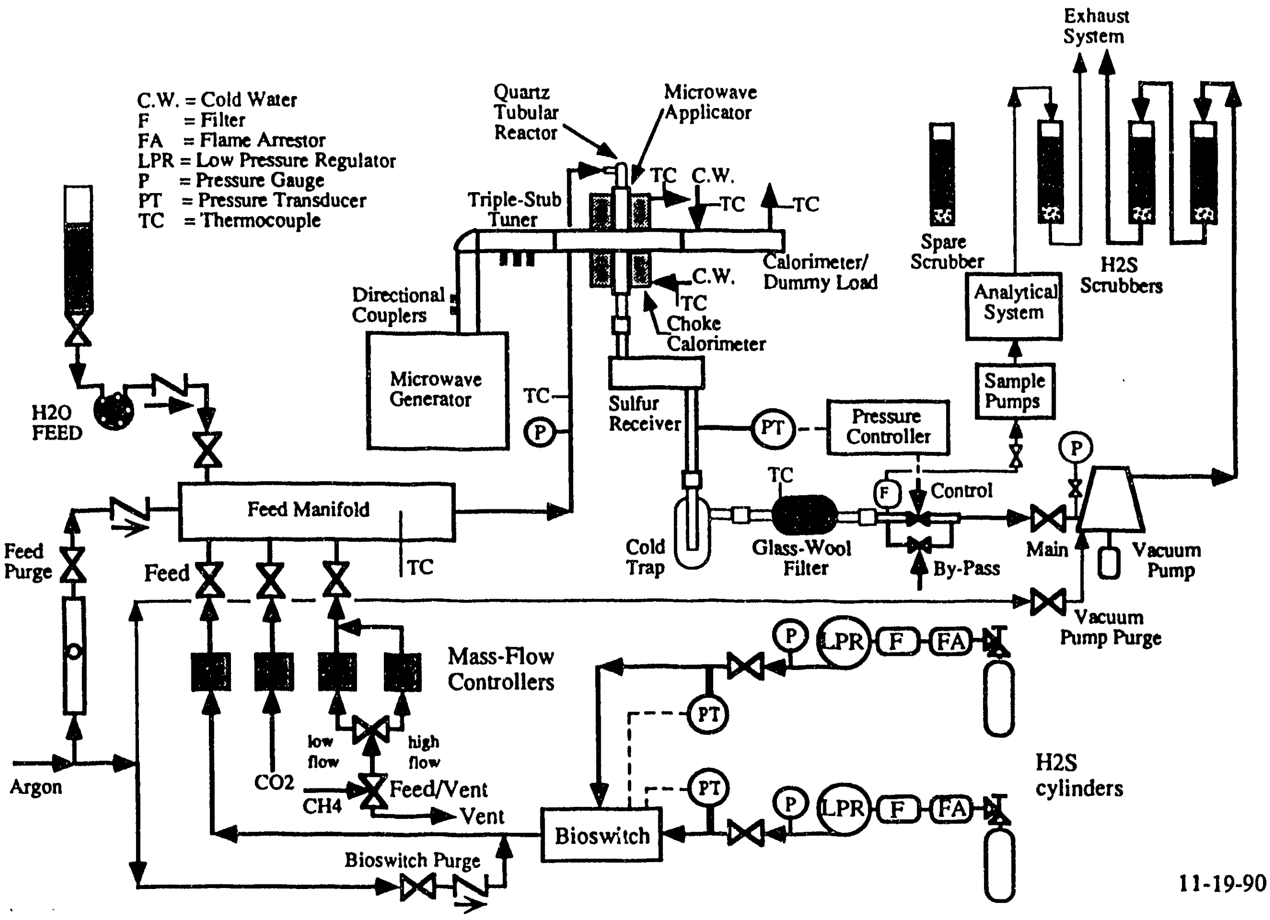

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Figure 4 Experimental Apparatus

The analytical system included a binary gas analyzer that provided a direct measure of conversion for experiments where pure hydrogen sulfide was fed to the plasma and where hydrogen and hydrogen sulfide were the only gaseous species to reach the analyzer system. When gas mixtures were used, the binary gas analyzer was only used to determine when an experiment had reached steady state. In these cases, gas samples were collected and conversions were calculated from the results of off-line mass-spectrographic analyses of both the feed and product gas samples.

EXPERIMENTAL RESULTS

In one set of experiments, the gas velocity entering the plasma zone was varied in order to test the Soviet hypothesis that a high-velocity, cyclonic flow was required to obtain high conversions and low energies of dissociation. This was accomplished by varying the diameter of the hole drilled tangentially through the reactor diaphragm from 0.8 mm to 5.1 mm in a sequence of reactors. The hydrogen sulfide conversion was determined at flow rates of 0.75, 1.25, and 1.75 (partial data set) SLPM (standard liters per minute) as shown in Figure 5 for a power level of 1.0 kW and a reactor pressure of 20 Torr.

The highest flow rate, 1.75 SLPM, gave the lowest conversion, even though this flow rate would be expected to have the highest gas velocities exiting the orifices in the reactor diaphragm. As the flow rate decreased to 1.25 SLPM and then to 0.75 SLPM, the hydrogen sulfide conversion increased and was consistently greater than 90% for the lowest flow rate and orifices greater than 2.0 mm in diameter. Simply calculating a Mach number on the basis of geometric diameter suggests that the best conversions were obtained for subsonic gas velocities. However, this conclusion neglects the fact that a flow exiting an orifice actually has an effective diameter smaller than the geometric diameter — the "vena contracta." The ratio of the vena contract area to the geometric area is called the discharge coefficient. While these coefficients have been determined for some nozzle

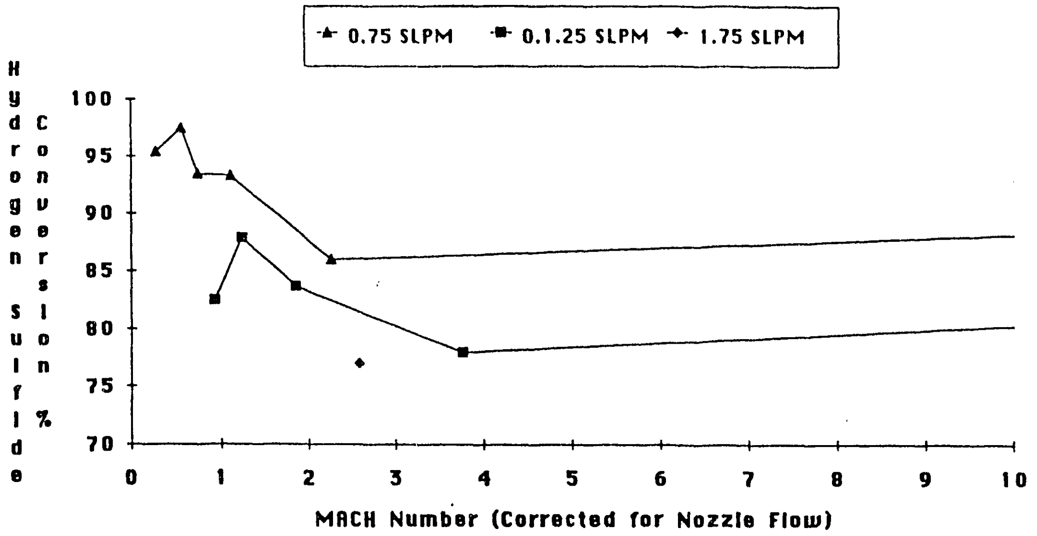

Figure 5 Sonic Flow Conditions and H_2S Conversion (correcting for nozzle effects shows that best conversion occurs close to sonic flow rates)

configurations, we have not yet found a satisfactory method for estimating it for the particular geometry in the situation described here.

However, this does mean that the actual Mach numbers would be higher than those calculated, probably giving sonic velocities for orifices between 3 mm and 4 mm for the 0.75 SLPM case and supersonic velocities for the 3.5-mm orifice for the 1.25 SLPM case. (These values more or less coincide with the maximum conversions observed for the two hydrogen sulfide flow rates.) This suggests that the gas velocities for the smaller orifices were supersonic, which is not very likely since their shape is so far from the proper profile for supersonic flow. More likely, the flow pattern exiting these orifices was turbulent and was rapidly slowed to velocities less than sonic values. Clearly, an orifice larger than one with sonic velocity will always have a subsonic flow. Thus, the optimal conversion appears to occur at, or close to, the conditions which will produce near-sonic velocities entering the plasma zone.

The advantage of maintaining a cyclonic flow pattern with as great a gas velocity in the plasma zone as possible can be explained two ways. First, the centrifugal forces generated by the cyclonic pattern would tend to remove the higher-molecular-weight sulfur product preferentially from the plasma zone. Second, the higher velocities at the reactor surface would increase heat transfer and, thereby, speed sulfur condensation. In both cases, the net effect is to remove one of the products from the reaction zone and, thereby, minimize the rate of back reaction — recombining to form hydrogen sulfide. This is supported qualitatively by the observation that, with reactors having little or no cyclonic flow, sulfur clouds were observed in the center of the quartz tubes, but when better reactor designs generated and maintained a cyclonic pattern, all the visible sulfur condensation occurred at the reactor wall.

The inverse relationship between conversion and the gas feed rate over the wide range of gas velocities studied here also indicates that the residence time in the plasma zone is an important variable for hydrogen sulfide conversion.

Another set of experiments varied the argon concentration in the hydrogen sulfide feed gas. These experiments were designed to determine whether or not a chemically inert but easily ionized gas could either increase the hydrogen sulfide conversion or lower the microwave power required to maintain a given conversion. The argon concentrations ranged from 0% to slightly over 1%, with a hydrogen sulfide flow rate of 1.25 SLPM. In all of the experiments, the reactor orifice was 3.6 mm, the reactor pressure was 20 Torr, and the microwave power was 1.0 kW. The low-flow methane mass-flow controller was used to regulate the argon feed rate by resetting the gas constant on the mass-flow controller for argon. The results are summarized in Table I.

The data show that, within the experimental error, the argon addition was ineffective over this relatively narrow range of concentration. If much greater concentrations were to be used, the expense of handling the inert gas load in the process would have to be considered.

Table I Effect on Argon on Hydrogen Sulfide Conversion

Argon Concentration (%)	Hydrogen Sulfide Conversion (%)
0.0	81.0
1.2	78.5
1.3	79.1

The final set of experiments to be reported here was designed to determine whether or not preheating the gas feed would decrease the microwave power needed to dissociate hydrogen sulfide. The feed-gas temperature was varied from 25°C to 350°C, while the hydrogen sulfide flow rate was decreased proportionately in order to maintain a constant gas velocity into the plasma zone.

Figure 6 plots the hydrogen sulfide conversion versus the mass flow rate entering the plasma zone for the preheat experiment and the conversions for a control experiment. In the control experiment, the same range of mass flow rates was tested but the gas temperature was constant at 25°C. This graph shows that preheating the hydrogen sulfide feed had no discerible effect on conversion.

CONCLUSIONS AND FUTURE RESEARCH

The discussions at the Kurchatov Institute and the experimental results on the dissociation of hydrogen sulfide in a microwave nonequilibrium plasma presented here (and in the earlier publications) show the following:

1. Hydrogen sulfide dissociation in a microwave-induced plasma is technically feasible and will produce marketable hydrogen and sulfur.
2. Hydrogen sulfide can be dissociated at high enough conversions and low enough energy inputs to be economically competitive with the current hydrogen sulfide waste-treatment technologies.
3. Proper reactor design will yield hydrogen sulfide conversions in excess of 90% in a single pass.
4. The hydrogen sulfide residence time in the plasma zone appears to be the second most important variable for dissociation — conversion was observed to be directly proportional to residence time.
5. Preheating the hydrogen-sulfide feed showed no effect over the temperature range studied here (25-350°C).

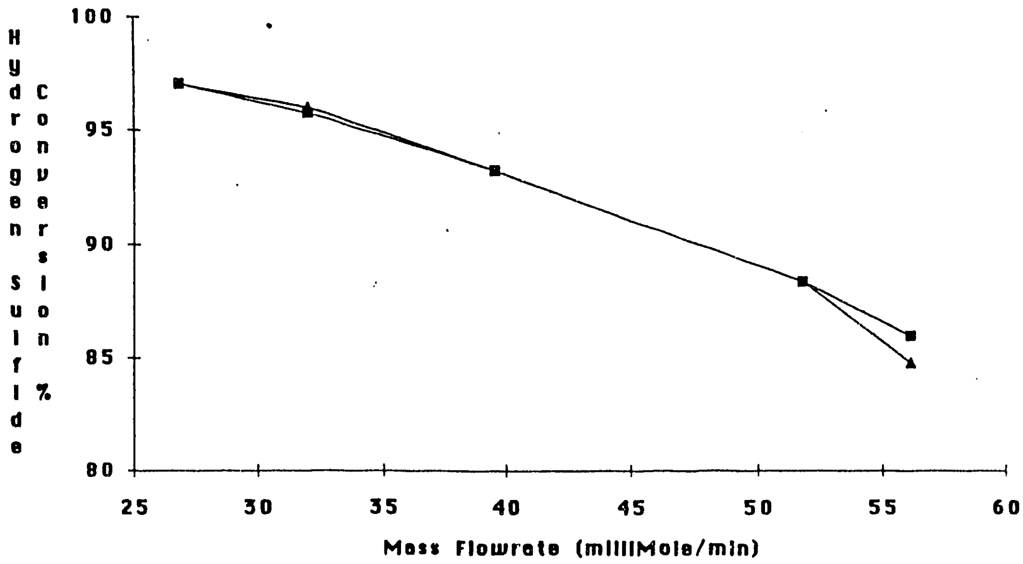

Figure 6 H_2S Conversion vs. Residence Time for the Feed Gas

The immediate laboratory objective is to obtain plasmas at atmospheric pressures with hydrogen sulfide since the Argonne Industrial Working Group has placed its highest priority on this goal. Once that objective is achieved, the next step proposed for the DOE program is to build a field experiment to test the plasma-chemical reactor on an industrial hydrogen sulfide waste stream at a scale large enough (probably one-quarter to five long tons of sulfur per day) to obtain the energy and material balance data required for a final analysis of the commercial potential of this technology. The Field Experiment appears to be equivalent to the Soviet's Orenburg "semi-industrial" facility. Assuming a favorable result from the field experiment, the final step proposed for the development of this technology is to build a fully-integrated plant at a scale of 50-150 long tons of sulfur per day.

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