EXPLOSIVE NATURE OF HYDROGEN IN PARTIAL-PRESSURE VACUUM

Despite the widespread commercial use of hydrogen, not all of the flammability limits of the gas are known. Experiments were performed to determine hydrogen reaction limits in a partial pressure vacuum to allow the design of a vacuum furnace system having the necessary safeguards.

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Hydrogen is a stable gas in seclusion, but in air, is very unstable. The flammability properties of such a mixture are well-known at atmospheric pressure, yet little is known about the hydrogen-air mixture at sub-atmospheric pressures. In order to determine the hydrogen reaction limits in a vacuum, a number of experiments were performed and analyzed. The results were used to design a vacuum furnace system and processes with safeguards to protect against a severe hydrogen reaction.

Experimental Procedures

Tests were performed in a 9 in. high by 4.75 in. diameter steel test chamber with an aluminum lid equipped with four spring-loaded shoulder bolts to relieve the force of an explosion. The vessel was pumped down to a pressure of 0.1 torr (absolute pressure guage), and the chamber was backfilled with air to a desired pressure, after which it was backfilled with hydrogen to obtain the final absolute pressure and gas ratio for testing. Mixtures of hydrogen and air at ratios from 20:1 to 1:20 were used to determine the explosive/nonexplosive ranges in terms of pressure and ratio. The system was exposed to a spark or a glowing hot element to determine if combustion would occur. If a reaction occurred, pressure increased in the chamber, and if the increase was great enough, the spring-loaded lid popped up to release pressure (referred to as over-pressurization).

Gears ready for heat treating in a vacuum furnace.

Spark Plug Tests

Two experiments were performed using a 1/16 in. gap and 1/4 in. gap automobile spark plug, which were energized using a high voltage (5,000 V) spark transformer. With the 1/16 in. spark plug in 30% hydrogen, over-pressurized combustion occurred within the chamber at the lowest pressure (152 torr). As the ratio changes from this mixture, higher pressures are tolerated before over-pressurized combustion takes place. Additionally, if there was less than 10% or greater than 60% hydrogen in air, over-pressurization would not result (Fig. 1).

The same procedure was used for the 1/4 in. gap plug. The purpose of this test was to determine if the spark jumping a larger gap (higher energy spark) would alter the ignition points of the different ratios, since the spark would be higher power. There was no over-pressuring of the chamber below 10% hydrogen, but there was an increase up to 80% hydrogen (up from 60%) before no over-pressure was observed. A similarity between the two spark plug tests was the stoichiometric mixture (30% hydrogen and 70% air), the low point of the curve (Figs. 1 and 2), ignition at 175 torr.

Heated Wire Test

The heated wire test followed the same general procedure as the spark plug tests. The major difference was the use of a variable transformer whereby the voltage could be controlled, and, thus, allowing regulation

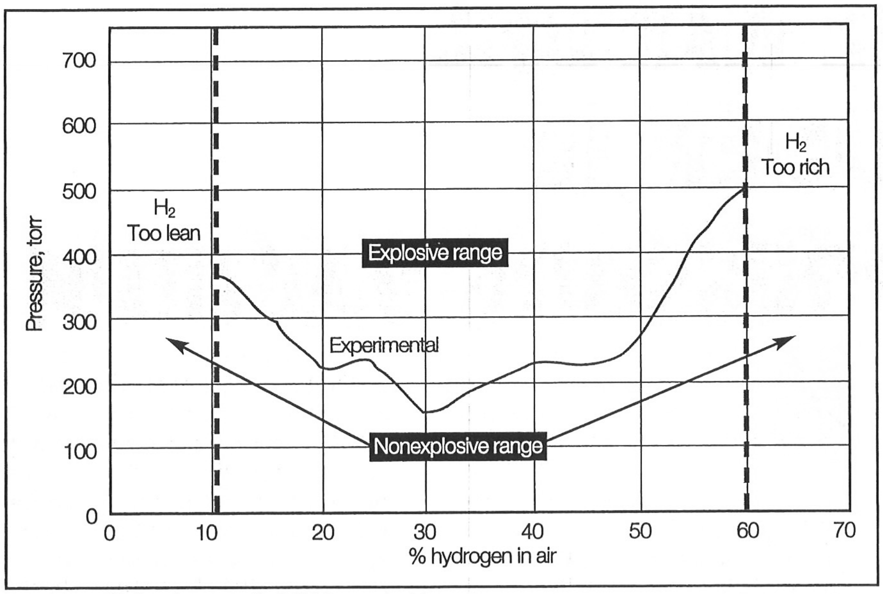

Figure 1. — High-voltage spark: 1/16 in. gap ignition range.

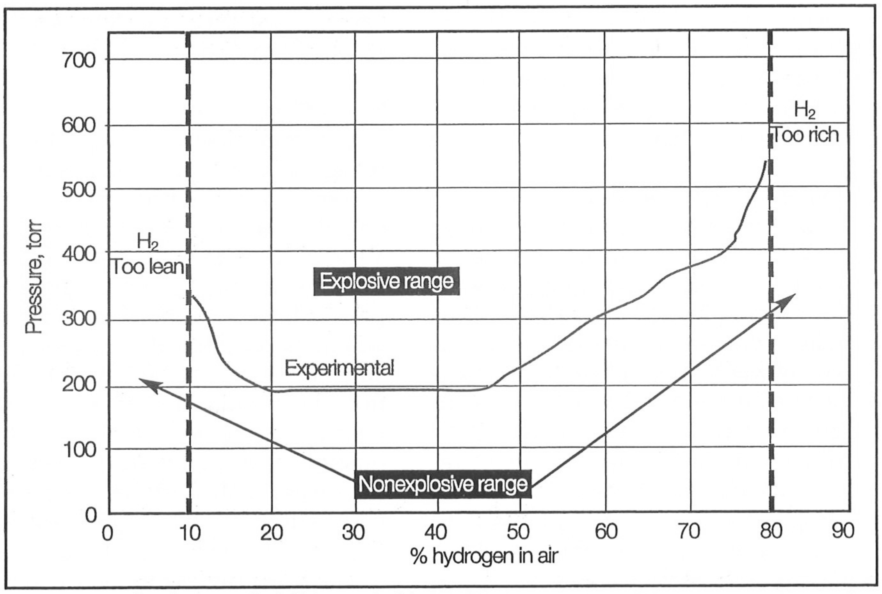

Figure 2. — High-voltage spark: 1/4 in. gap ignition range.

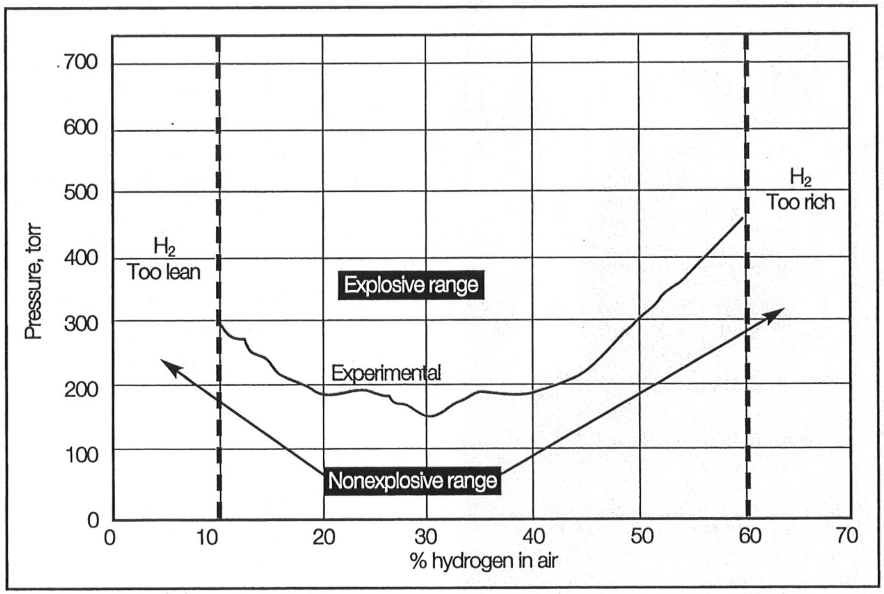

Figure 3. — Heated element wire ignition range.

of the temperature of the coil. This was done to simulate having hot material or heating elements as the ignition source within the furnace at atmospheric pressure. The general results relating pressure to hydrogen and air stoichiometry were very similar to the spark plug tests. The curve of the reaction points generally followed those of the previous tests. At the 30:70 ratio, ignition occurred at the lowest pressure (Fig. 3).

The importance of the heated wire test was the ability to monitor the additional variable of the temperature within the chamber. The temperature of the heated wire element was recorded for each reaction. Figure 4 shows temperature in relation to percent hydrogen in air at atmospheric pressure, and demonstrates that as the hydrogen percentage increased, the reaction occurred at a higher wire temperature.

Case Study: Reaction at 25% Hydrogen

In the tests of around 25 to 30% hydrogen in air, observed reactions did not make the lid pop up. For instance, at 25 to 30% hydrogen in air and a pressure of 150 torr, the chamber did not explode with enough force to pop up the lid; there was only a quick flash in the chamber. Although an explosion did not occur to over-pressurize the vessel, an internal reaction did, the pressures of which are shown in Fig. 5. This reaction, though contained and silent, is evidence that a reaction can occur in deeper vacuum and in richer and leaner hydrogen concentrations than evidenced by observation of overpressurization.

Final Test

Some vacuum furnaces used at Solar Atmospheres run using hydrogen in near vacuum conditions. If an air leak were to occur in the chamber during a hydrogen run, then a significant hydrogen-air reaction could occur. One way to prevent the air from accumulating in the chamber is to react the air at its potential point of entry. To do this, a high energy source is needed to initiate the reaction of hydrogen with the air. This scenario was modeled by putting different amounts of pure hydrogen in the chamber, and turning on the heating element set to a testing temperature. A valve was opened, allowing air to leak slowly into the chamber. The final step was to observe if there was burning at the inlet and determine how much hydrogen is needed to initialize the reaction.

Data from these tests show the air only reacted with the temperature of the element at or over 1200°F (650°C) and with a minimum pressure of approximately 225 torr of hydrogen. The air reacted at the exact point where the air entered the chamber; thus it is possible to prevent air from accumulating in a hydrogen atmosphere.

One way the air could leak in is in the event of a power failure where a valve does not close all the way. One safeguard is to have a generator that would turn on in the instance of a power failure. This generator would then turn on the strategically placed ignition/elements and heat up between 1200 and 1300°F (650 and 700°F). This would cause the air to react moderately if a leak were to occur. The heated elements will have to be placed a certain specific distance from the air leak to have any positive affect. More studies are necessary to find the distance between the air leak and the element wire where the air can still be controlled to react safely.

This scenario is very much like lighting a torch. If an igniter is placed close to the torch to ignite, the ignition will be immediate, with little reaction. If the igniter is further away from the torch, the ignition will be delayed and more violent. The reason this occurs is that the gas of the torch has time to accumulate before it reaches the ignition source. The same principle is occurring by the air reacting at the inlet. If the hydrogen can be ignited with the air at the point of entry of the air, then the reaction will not be as violent, but instead a semi-controlled reaction. If the air were allowed to accumulate then the reaction will be much stronger and ignite more forcefully.

Diluting Gas

Hydrogen alone will easily burn if vented out of a pipe into open air and ignited with an energy source. After performing tests with different mixtures of hydrogen and an inert diluting gas (nitrogen or argon), Solar concluded that extremely lean hydrogen mixtures (<5%) will not burn in open air if diluted with an inert gas; lean mixtures (5 to 25% hydrogen) will burn, but will not support a flame once the energy source is taken away; and mixtures of 25 to100% hydrogen in inert gas will burn and sustain a flame once the energy source is taken away.

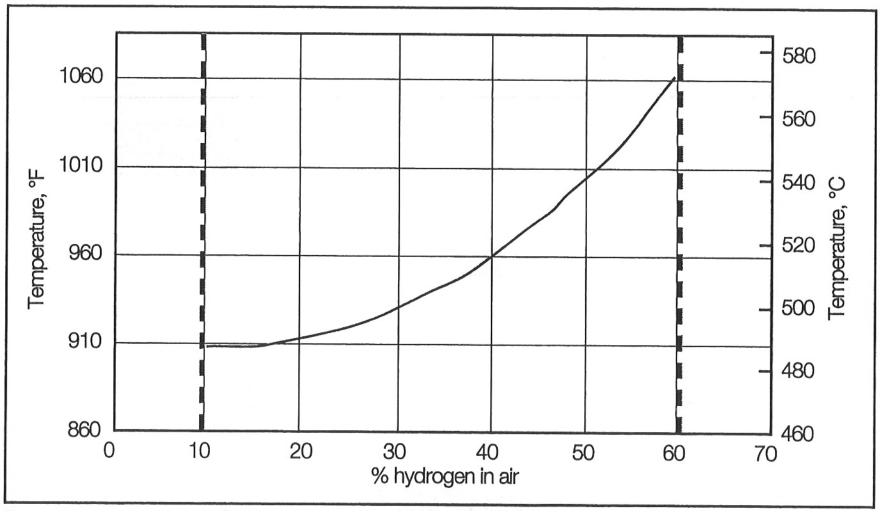

Figure 4. — Temperature of ignition points in relation to percent hydrogen in air.

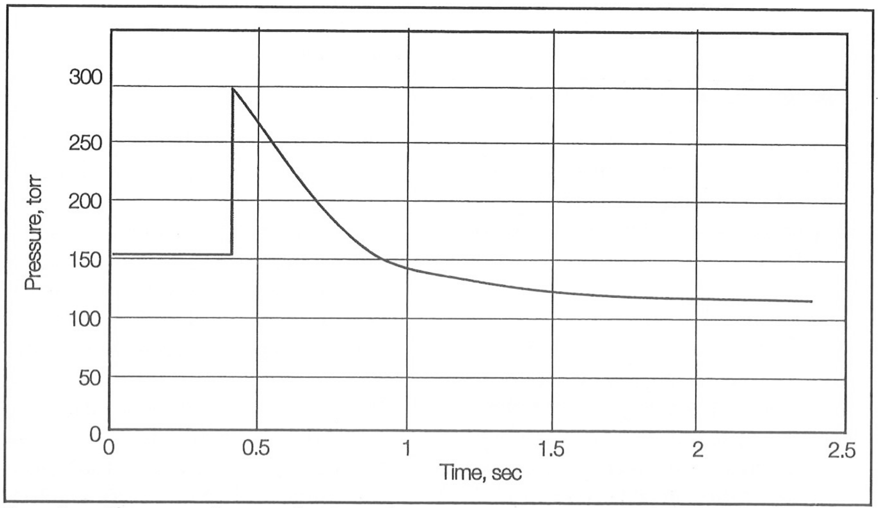

Figure 5. — The pressure increase of an internal reaction over time at 25 to 30% hydrogen.

Overall, argon showed slightly better flame suppression than nitrogen.

Conclusion

The difference in reaction points for the different methods of ignition (for all three test conditions) is shown in Fig. 6. The 1/4 in. gap spark had the highest energy, and, therefore, ignited the mixture to the point of over-pressurizing the vessel in a wider range of ratios than the other ignition methods. The heated element wire and the 1/16 in. gap spark had relatively the same ignition points. One area where the three tests were comparable was at the point of stoichiometric mixture. At this point the reaction has a high probability of ignition. As the mixture varies from that point, the air-hydrogen mixture would have a less likely chance of igniting.

More tests are scheduled in this area. A second reaction chamber, roughly four times the volume of the current vessel, has already been built. The objective is to model an actual vacuum furnace and conduct more of the same

It is very important to maintain a vigorous, well-documented maintenance plan to ensure safe vacuum furnace operation.

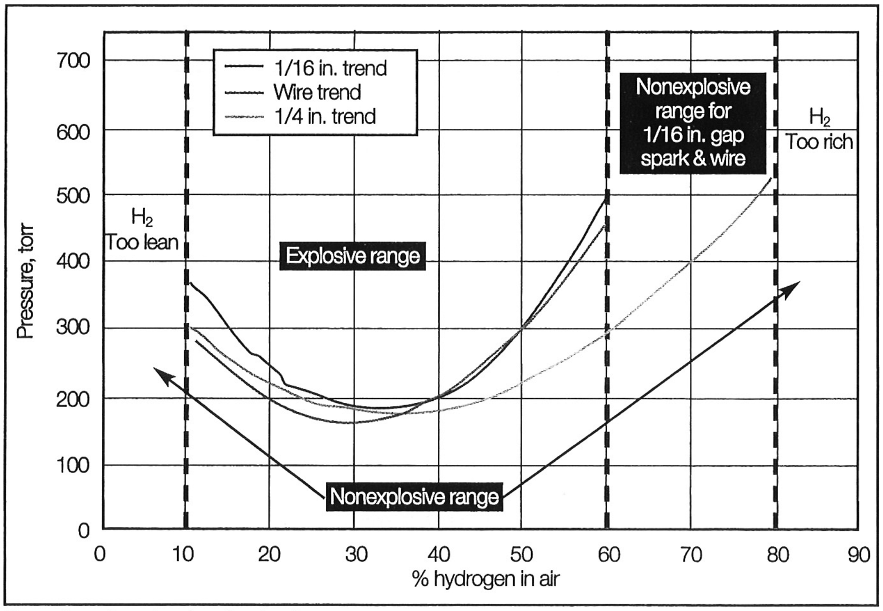

Figure 6. — Reaction data for the three tests.

tests. This would improve concepts on how to design a vacuum furnace that would have safeguards incorporated to prevent a devastating hydrogen-air reaction.

Recommendations

After performing these tests with hydrogen and air mixtures at vacuum-level pressures, we posit the following as safety precautions when using hydrogen in a vacuum chamber. In addition, operating in accordance to NFPA 86 section 12.3 and 12.4 is recommended.

Furnace Design

Communication with the manufacturer of the furnace is imperative to ensure the pertinent recommendations below will be installed on the vacuum furnace.

- Use intrinsically safe equipment (*designed to be incapable of releasing electrical or thermal energy that would ignite a hazardous atmospheric mixture*) and redundant safety control designs (*redundancy is the repetition of critical components to increase the reliability of the system*) when using hydrogen. Such systems help to minimize operator mistakes such as venting, door opening, air releasing, and backup safeties in the event of a hardware failure.
- Use an oxygen probe to detect an air leak in the vacuum system, with O_2 sensor limit set to 10 to 15 ppm.
- Use an inert diluting gas to lower the flammability limit of gas exiting from the chamber and/or vacuum pump exhaust, if burning at gas exit is not applicable.
- Use hydrogen-compatible check valves in any hydrogen gas system, whether on the supply or exhaust side of the furnace.
- The relief valve and/or chamber release valve must be vented outdoors via hard pipe on an upward angle to ensure no trapped hydrogen gas. One can even connect an inert gas line to this venting line for purging capabilities to ensure no trapped gas.
- Add a manual safety shutoff valve to hydrogen supply line that is easily accessible and prominently labeled for quick manual supply shutoff by the operator.
- All hydrogen supply lines must be hydrogen-compatible and rigid (*no plastics*).
- Before addition of hydrogen is enabled, use a safety interlock that will not allow addition of hydrogen to the furnace until the furnace has been evacuated to below 50 microns of mercury.
- Hydrogen supply lines must be equipped with a high and low pressure switch to prevent operation above or below specified pressure ranges in the system.
- Components that use hydrogen must be designed and approved for hydrogen use.
- Vacuum pumps on all furnaces should have "run monitors" installed and interlocked to ensure that the pump itself (not just the pump motor) is operating.
- If not connected to an inert gas line, the gas ballast valves on all vacuum pumps should be plugged to prevent accidental introduction of air into the pump while hydrogen is being used.
- Change all vacuum line air-release valves to normally open style. Pipe those valves to an argon supply equipped with a low pressure regulator (with pressure gauge) set no higher than 1 psig.
- Remove any sight glasses from the furnace.
- Provide five times the volume of inert gas, preferably argon, equipped at all times to purge the furnace of hydrogen in an emergency or power failure situation.

Vacuum Thermal Processing

The following precautions cannot be made by the furnace manufacturer and must be addressed by the user during processing.

- Leak rate must be 15 microns of mercury per hour or less on the furnace prior to any processing with hydrogen.
- Operate below half the LEL (lower explosive limit) of hydrogen (therefore 2% or 15 torr) if the cycle allows for it.
- Before opening door, pump down to less than 100 microns of mercury and backfill with inert gas. It is recommended to perform this operation one additional time to flush out any hydrogen gas trapped in the pumping exhaust system.
- Have the operator wipe the furnace door O-ring every time prior to door closure.
- Always have an operator nearby when operating with a hydrogen atmosphere.

Preventative Maintenance

It is very important to maintain a vigorous, well-documented maintenance plan for the vacuum furnace. In addition to normal preventative maintenance, it is recommended to perform the following additional maintenance precautions.

- Ensure there are no leaks in any gas supply lines by bubble-checking all fittings routinely.
- Replace O-rings if they appear to be flat.
- Take solenoid valves apart and clean the surfaces and components.
- To avoid pump failure, perform oil changes monthly on pumps and maintain good condition of belts and various grease fittings. **HTP**

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