

HYDROGEN SUPPLY METHODS FOR HEAT TREATING OPERATIONS

Many manufacturing processes today rely on hydrogen as an important protective and reducing atmosphere, especially in the production of stainless steel alloys. The method of gas delivery should be carefully evaluated to optimize production efficiency and to minimize manufacturing costs.

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Hydrogen has been used in both pure form and in gas mixtures for many years in thermal and metallurgical processes such as sintering, brazing, annealing, powder coating, metal injection molding and welding operations as a protective and reducing atmosphere, especially in the production of stainless steel alloys. Today, metallurgical and process engineers have a wider range of choices in how they obtain hydrogen. While hydrogen is the most abundant element in the universe, because it is mixed with other elements in nature, it must be manufactured, stored, and supplied to meet the purity, pressure, and volume requirements of specific industries and applications. According to the U.S. Department of Energy (DOE; www.doe.gov) and National Hydrogen Association (NHA; www.hydrogenus.com), the U.S. hydrogen industry currently produces 9-million tons of hydrogen per year (enough to power 20-30 million cars or 5-8 million homes) for use in chemicals production, petroleum refining, metals treating and electrical applications.

As demand increases, improvements in hydrogen production technology are offering new, cost-effective and environmentally sound options for metal producers. In weighing these options, metallurgists and heat treaters must consider the location of their facilities; hydrogen-use patterns; current average hydrogen consumption and estimated future needs; and storage, siting, regulatory, and maintenance issues. It also is necessary to take into account the level of hydrogen purity required for a specific process.

methane reformation, dissociation of ammonia (HN_3), and electrolysis.

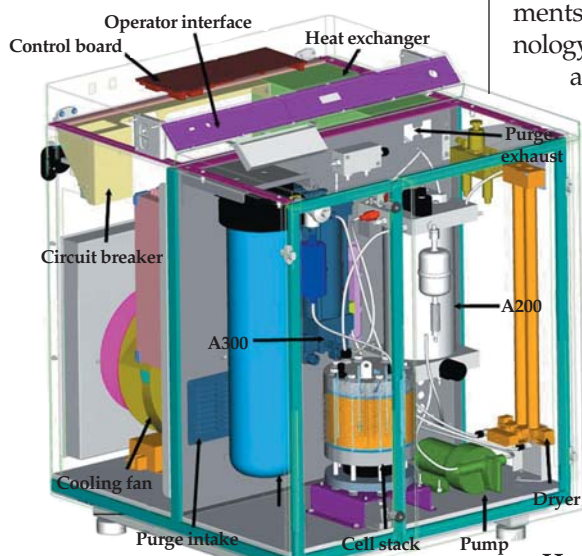
Steam methane reformation. More than 95% of the hydrogen produced today in the U.S. comes from steam reforming natural gas according to DOE. The process involves heating natural gas to a temperature of approximately 850°C (1560°F) over a nickel catalyst bed, yielding a mixture of carbon monoxide (CO) and water (H_2O). The mixture is then cooled and catalyzed with steam to yield pure hydrogen and CO_2 .

The advantages of reforming fossil fuels for hydrogen are that reforming systems use existing fuel transportation and pipeline infrastructures, are less expensive than other hydrogen production methods, and reduce the need to transport and store hydrogen. The disadvantages of reforming fossil fuels for hydrogen are that reforming systems are complex, large and expensive; use nonrenewable feed stocks; and generate air pollution through combustion. Most significant for metallurgical operations that require a high level of hydrogen purity is that reforming methods can leave carbon monoxide and source fuel in the reformed hydrogen.

Dissociation of ammonia (DA). Hydrogen can be produced by dissociating ammonia at a temperature of about 980°C (1800°F) with the aid of a catalyst. This results in a gas mixture consisting of 75% hydrogen and 25% nitrogen. The mixture is often used as a protective atmosphere for applications such as brazing or bright annealing.

DA makes inexpensive hydrogen in a gas mixture. However, the hydrogen produced by DA is impure because it contains nitrogen and water. Also, ammonia is a highly regulated, poisonous, flammable, and noxious gas.

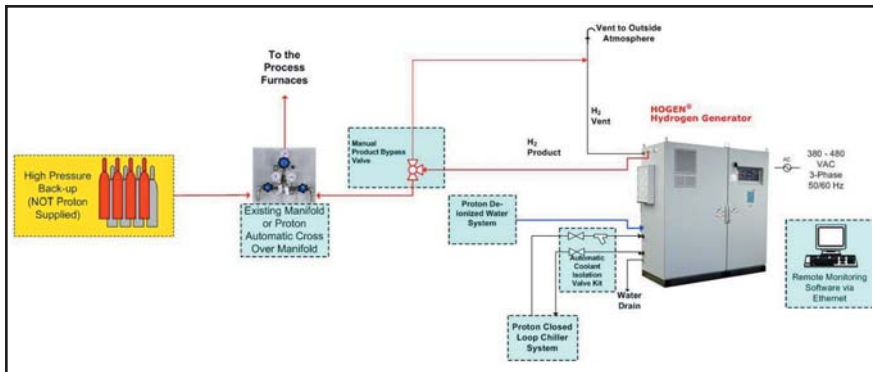
Electrolysis is a process in which electricity is used to decompose water into



Three-dimensional view of Hogen hydrogen generator system

Hydrogen Production Methods

Commercially available hydrogen production methods include steam



Schematic of Hogen on-site hydrogen gas generator system at Chand Eisenmann Metallurgical, Caribou, Maine.

its elemental components hydrogen and oxygen. The separation occurs within either a liquid (e.g., alkaline) or solid (polymer) electrolyte. Polymer electrolytes are used in proton exchange membrane (PEM) electrolysis, which was applied during the first U.S. space missions and evolved through the use of electrolyzers developed to produce oxygen in submarines.

Because it does not use a caustic alkaline electrolyte, PEM electrolysis offers advantages of simplicity of operation and maintenance and the purity of the hydrogen gas generated. PEM electrolysis is capable of producing hydrogen flow rates ranging from 300 cm³/min to 228 scf/hr. PEM electrolyzers can operate over a wide range of electrical capacities and take advantage of peak generation periods.

Hydrogen Delivery

Heat treaters requiring pure hydrogen atmospheres have traditionally relied on hydrogen deliveries in compressed (generally 2,400 psi) or cryogenic liquid form (-253°C, or -420°F) and stored in cylinders or tube trailers, which are typically left on the manufacturing site. The distribution range for high-pressure cylinders and tube trailers is typically 100 to 200 miles (160 to 320 km) from the hydrogen production facility. For longer distances of up to 1,000 miles (1,600 km), hydrogen is usually transported as a liquid in super-insulated cryogenic over-the-road tankers, railcars, or barges, and then vaporized for use at the customer's site.

While delivered hydrogen is often very pure, and arrives in a convenient-to-use stored form, it also has disadvantages. Delivered hydrogen can be expensive for remotely located cus-

tomers, and the site's productivity can be affected when access and security requirements impede delivery or when staff is diverted from their jobs to load or unloading cylinders. In addition, the occupational safety regulations of many municipalities now prohibit industrial sites to store large quantities of flammable gas.

Delivered Versus On-Site Hydrogen Considerations

Hydrogen generators can serve even very large heat treating operations by using one or more units. With a current per-generator maximum flow rate of 228 scf/hour (166,000 scf/month), on-site hydrogen generators are generally used by U.S. companies that use less than 500,000 scf/month. Outside the U.S., where the availability of delivered hydrogen may be more limited, four or more Proton Hogen H gas generators can meet needs exceeding 500,000 scf/month.

Many heat treaters are adopting the PEM electrolysis technology available commercially through advanced on-site systems. Current PEM hydrogen generator technology creates high-purity hydrogen at high pressure (up to 218 psig, or 15 barg), eliminating the need for compression.

The latest hydrogen generators can provide hydrogen having equivalent or greater purity than that of delivered hydrogen from a system that holds no gas inventory and that requires no deliveries. This is accomplished at a cost often equal to or less than delivered hydrogen or generated DA gas.

Hydrogen generators provide a particularly attractive solution for captive or commercial heat treating operations that process stainless steel components, operate 24/7, and have furnaces requiring a low-to-medium hydrogen flow rate, and that are located in areas where hydrogen delivery and storage is difficult or prohibited.

Case Study

The impracticality of long-haul hydrogen delivery routes and site logistics motivated a heat treating facility in northern Maine to seek alternative ways to obtain hydrogen. In 2003, Chand Eisenmann Metallurgical's Caribou, Maine, production facility relied on ten deliveries per month of hydrogen gas cylinders to supply the plant's four sintering furnaces.

According to company president Mark Eisenmann, at full capacity, one



Chand Eisenmann Metallurgical's Hogen on-site hydrogen gas generator system installation.

furnace alone required the transport, storage, and hook-up of 25 hydrogen cylinders per day (80,000 ft³/month) to supply the 100% hydrogen atmosphere required for its process. Hydrogen purity and consistent supply are critical in the furnaces to sinterbond (diffusion bond) porous parts to the assembly hardware of stainless steel microfilters the company manufactures for its process-filtration customers. Sinterbonding offers a significantly stronger part than using an interference fit alone, ensuring that the porous component will not be easily removed, and it provides corrosion resistance.

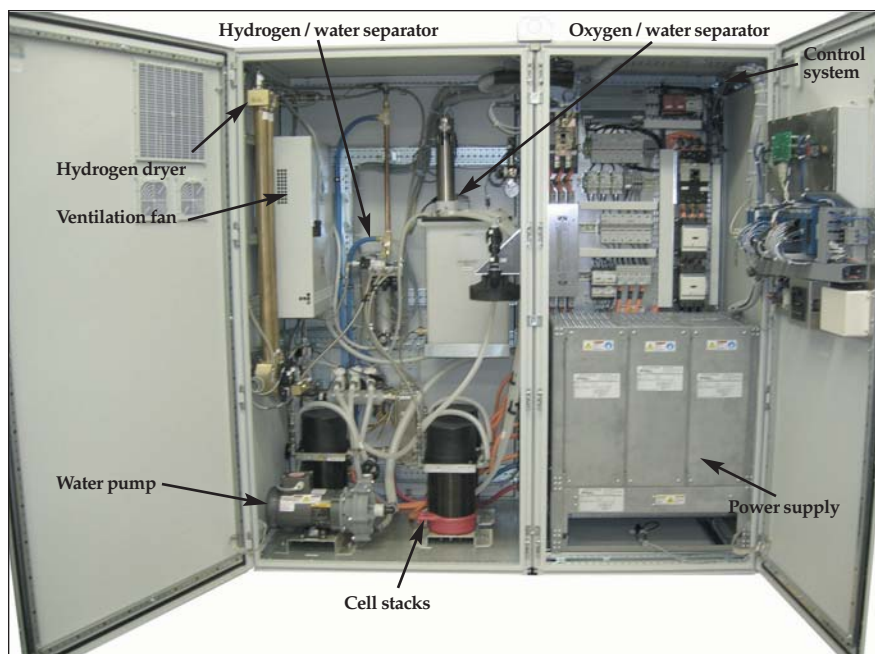
Within two years, the plant's sintering atmosphere requirements increased to 120,000 ft³/month, motivating the company to evaluate alternative technologies that could offer a more reliable, lower cost hydrogen supply. Hydrogen deliveries were complicated because there was no direct distribution route from the gas supplier, which manufactures hydrogen in Canada and ships it in bulk to New Jersey before its transfer to a hub in southern Maine and its subsequent transport more than 350 miles north to Caribou.

As a result, the delivery of hydrogen cylinders to Caribou added more than \$2,000 per month to manufacturing costs, higher than delivery fees to more centrally located urban heat treating and sintering facilities.

Eisenmann looked at liquid hydrogen as an alternative source, and found that although liquid hydrogen costs were 20% lower than hydrogen gas costs, delivery challenges, reliability, and site preparation presented similar problems as with delivered hydrogen cylinder gas supply. For example, to accommodate liquid hydrogen, the company would have to create a special area for a liquid storage tank and a separate docking pad for delivery.

In January 2004, the company began testing on-site hydrogen generation technology. During an 18-month period, the company installed and operated two Proton Hogen S40 hydrogen generators, which supplied a combined 80 scf/hour to one of the plant's furnaces.

During this period, Chand Eisenmann documented increased produc-



Components of installed Hogen hydrogen gas generator system.

tivity of furnace operators at the facility due to the elimination of time and energy spent in changing and moving cylinders. In addition, furnace use increased, processing improved, and overtime cost associated with workers having to report to work to check the plant's cylinder supply during extended holiday or plant shutdowns was reduced.


Additional on-site capacity was required to meet the needs of all four furnaces within the plant. In July 2005, Proton exchanged the company's two Hogen S40 systems for a new Hogen H 6m hydrogen generator, which offers up to 228 scf/hour of 99.9995% pure hydrogen gas.

According to Eisenmann, while the company originally expected to break even on its capital investment in five years, the Hogen H 6m system already paid for itself in savings on the facility's hydrogen delivery costs. Because the generator system operates at up to 218 psig pressure and automatically adjusts to furnace hydrogen demand (100 ft³/hour when idling and 150 ft³/hour when the furnace doors are open), the generator offers all the advantages of other high-pressure hydrogen sources. No operators are required to open, close, and change out cylinders, so a significant labor savings is realized.

Installation Logistics

Site preparation, installation time, and cost to hook up the hydrogen gen-

erator was minimal, requiring only simple electrical and plumbing connections. A water chiller purchased with the system to maintain a constant water temperature for proper cooling of the proton exchange membrane cell stacks within the generator has required minimal maintenance.

According to Eisenmann, the hydrogen generator provided the company with excellent protection from hydrogen price increases associated with fuel price surcharges, which are commonly assessed for delivery of liquid hydrogen, compressed gas tube trailers, and cylinders. 

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