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Hydrogen Generation Makes Switching from Dissociated Ammonia Attractive

Abstract:

For decades, industrial gas providers have tried to develop a compelling reason for metal thermal processing shops to switch from the dominant dissociated ammonia atmosphere technology to hydrogen/nitrogen blended gas “synthetic” atmospheres. Two problems interfered with this business approach – ammonia for dissociation was generally very cheap, and the alternatives that the industrial gas companies proposed did not solve all of the issues faced by the thermal processors.

The offerings of the industrial gas providers failed to displace dissociated ammonia in most installations because the cost of the atmosphere was high as compared with dissociated ammonia, and the solution proposed by the industrial gas providers simply replaced one highly hazardous gas delivery and storage problem – ammonia – with another – hydrogen. Users and their local Authorities Having Jurisdiction did not find the tradeoff attractive to swap ammonia storage for hydrogen storage.

Onsite hydrogen generation technology makes it possible to replace delivered, stored hazardous ammonia with “zero-inventory” onsite generated hydrogen and stored or generated nitrogen. This approach eliminates the hazardous material objection to ammonia replacement for thermal processors, and makes it much more interesting to consider replacement of DA with hydrogen/nitrogen. While economic issues remain, a look at total costs of operation makes hydrogen/nitrogen generation a viable, and growing solution for thermal processors.

Presentation will review several successful customers that transitioned from DA to hydrogen generation and nitrogen deliverer and storage or generation. Presentation will consider costs, compliance and process results.

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Draft paper:

History of ammonia and hydrogen furnace atmospheres in the US

Pure ammonia gas, NH3, can be dissociated into a blend of 75% hydrogen and 25% nitrogen for use as a protective annealing and brazing atmosphere for metal thermal processing. According to Dan Herring in volume II of his landmark Atmosphere Heat Treatment book, dissociated ammonia has been used as a heat treating atmosphere since the 1930's. Per Herring, dissociated ammonia was introduced as an economical alternative to pure hydrogen atmospheres, which at the time were extremely expensive. At that time, pure hydrogen was produced in relatively few refinery and chemical sites, and was expensive to buy and expensive to distribute in the considerable quantities needed for metal thermal processing. The high cost of delivered hydrogen at the time was driven by a relatively tight supply, and very high cost distribution. Pure hydrogen was just becoming widely produced in the oil refining industry, and had to be compressed and distributed as a highly pressurized gas at 2000 psig or higher – very inefficient when a high pressure hydrogen steel cylinder held just over 1 pound of hydrogen, but weighed nearly 200 lbs. Hence a 40,000 pound truckload of cylinders contained only a little over 200 pounds of hydrogen, or 40,000 scf.

Since commercialization of the Haber-Bosch production process in the early 20th century, ammonia has become one of the most widely produced and distributed inorganic industrial chemicals because of its popularity as an agricultural fertilizer and industrial refrigerant. Because of its wide use for farming and refrigeration, ammonia is unique among hazardous chemicals for the breadth of storage and use sites. As compared to using compressed pure hydrogen gas in inefficient heavy steel cylinders, mid-century thermal processors chose increasingly to buy their hydrogen-containing atmosphere in the form of pressurized liquid ammonia – NH3. NH3 was much less expensive to transport, because it was stored at 250 psig instead of 2000+ psig, hence the ratio of cargo to container weight was much more attractive. Ammonia was also widely available in the US, both through widespread local ammonia distribution for agriculture and refrigeration, and because it was transported by rail in pressurized liquid bulk railcars, enabling relatively low cost distribution.

Ammonia is easily dissociated (split) into pure hydrogen and pure nitrogen in the ratio of 75% H2, 25% N2 using a low-cost nickel-based catalyst in a heated retort. Dissociated ammonia made it possible to get the benefits of hydrogen in a molecule form that was attractively priced, widely understood, and was distributed broadly at low cost. Ammonia processors introduced special grades of anhydrous ammonia, called metallurgical grade, which were low in oil and especially dry in order to meet the unique needs of thermal processors.

As ammonia availability increased through the 20th century, dissociated ammonia use grew to the point that DA had become the primary atmosphere for annealing, brazing and sintering of ferrous and non-ferrous metals. For decades since, dissociated ammonia has served as a low-cost, flexible atmosphere for annealing and brazing of materials that can be processed in hydrogen and nitrogen containing atmospheres. DA has also been popularized for use in sintering green parts made of carbon steel powdered metal into fully dense products.

During the second half of the 20th century, the availability of pure hydrogen became more widespread as additional refineries were built for crude oil processing and gasoline production, and hydrogen production for refining became standard. Hydrogen is a central reactant in the refining process, and most refineries were hydrogen-short, requiring that additional hydrogen be produced through on-site hydrogen production to complete the refining process. Thus, over decades, geographically dispersed hydrogen production arose, making hydrogen more widely available within many industrial areas for trucking in compressed form. During this period, the business model of the on-site hydrogen plant also became accepted, whereby an industrial gas company such as BOC (now Linde), Union Carbide (now Praxair) or Air Products would build a hydrogen plant at the refinery , sell the refinery all the hydrogen contracted for on a take-or-pay basis and reserve some production for merchant (trucked) sales. This was the beginning of the widespread availability of merchant (shipped) gaseous cylinder and later tube trailer hydrogen.

In the latter half of the 20th century, the US space program facilitated the introduction of liquid hydrogen, originally developed for fueling space vehicles. Liquid hydrogen plants purify and liquefy impure hydrogen gas (often purchased as an impure byproduct stream from chloralkali plants and in pure form from refineries) into a denser cryogenic liquid form of pure hydrogen. While the extremely frigid liquid hydrogen requires special materials of construction for tanks and trailers, the introduction of liquid hydrogen as a commercial product enabled much lower-cost transportation than inefficient pressurized gas distribution. The improvement in shipping economics is driven by improved load to tare weight – a tube trailer of hydrogen weighing 40,000 lbs might contain 120,000 scf, while a liquid hydrogen trailer weighing 40,000 lbs will contain over 10 times the volume at 1.35MM scf.

Once the North American industrial gas industry achieved widespread liquid hydrogen availability through multiple plants partly subsidized by the needs of the space program, the industry began to hunt for customers for the pure hydrogen now much more widely and economically available.

For several decades, industrial gas providers have tried to develop a compelling reason for metal thermal processing shops to switch from the historically dominant dissociated ammonia “generated” atmosphere technology to hydrogen/nitrogen blended gas “synthetic” atmospheres. Two problems interfered with this business approach – ammonia for dissociation was generally very cheap, and the alternatives that the industrial gas companies proposed did not solve all of the issues faced by the thermal processors.

Ammonia in the community

The widespread use and storage of ammonia in farming, industrial and community facilities (including refrigerated warehouses, ice rinks and heat treat facilities) came with it relatively frequent leaks and subsequent community response incidents, including injuries and death. Even today, there are multiple reports of ammonia leaks occurring every week across North America. Anhydrous ammonia is toxic, seriously irritating and corrosive to mucous membranes, flammable, and has a powerful odor that can cause panic if even a tiny quantity leaks. Such leaks and the related incidents were at one time thought to be part of a successful industrial society, but today's communities are much less the accepting of the safety and nuisance issues related to ammonia storage. Additionally, many of the facilities that employ ammonia, which used to be adjacent to open fields and farmland, have become islanded among homes, stores, and community buildings, so the reaction to an ammonia release is immediate and often frenzied.

In recent years, an additional issue has arisen to cast ammonia delivery and storage in yet another negative spotlight – the use of ammonia as a precursor to illicit methylamphetamine drugs of abuse. That alternative, illicit ammonia use creates the issue of damage and resulting leaks created by sabotage and theft of stored ammonia – adding to the multiple community relations issues of ammonia storage.

The thermal processing industry embraced the use of first gaseous and later liquid nitrogen as a blanketing, inerting and diluent substance alongside dissociated ammonia, but the industrial gas industry had to work much harder to popularize the sale of hydrogen to replace dissociated ammonia in thermal processing. While there were many process advantages to custom-blending atmospheres of pure, dry hydrogen and pure, dry nitrogen versus the 75% hydrogen or lower pure or diluted DA atmospheres, the process advantages did not outweigh the economic disadvantages of higher cost of the two pure gases, storage equipment and blender required.

Interestingly, in many US jurisdictions it would not be possible to open a new thermal processing facility using dissociated ammonia atmospheres – the local Authority Having Jurisdiction (AHJ) – Fire Marshal or similar - would not permit the installation of a new ammonia tank. Ammonia is classified as a Highly Hazardous Material under Federal law, and is governed under EPA Responsible Management Planning requirements and OSHA Process Safety Management. The thermal processors now using dissociated ammonia are doing so because they are grandfathered in, but the actual use of DA is shrinking over time because new users are often choosing other options in preference to storing ammonia.

Ultimately, the hydrogen offering of the industrial gas providers often failed to displace dissociated ammonia because the cost of the resulting atmosphere was high as compared with dissociated ammonia, and the solution proposed by the industrial gas providers simply replaced one highly hazardous gas delivery and storage problem – ammonia – with another – hydrogen. Users and their local Authorities Having Jurisdiction did not find the tradeoff attractive to swap ammonia storage for hydrogen storage.

Onsite hydrogen enters the picture

While the large-scale production of hydrogen using hydrocarbon reforming for refineries had long ago become routine, small-scale production of hydrogen for industrial applications did not appear economically attractive in the US until late in the 20th century. Over the past two decades, several technologies and multiple providers have emerged to offer on-site hydrogen generation – the ability to generate relatively small quantities of hydrogen, at a customer's site, as the customer demands, with very limited or zero storage of hydrogen inventory. Different generation technologies offered different combinations of strengths – capital cost, operating cost, space utilization, permitting ease, load-following, hydrogen purity, ease of operation, hydrogen pressure, maintenance, and reliability. As of 2017, PEM water electrolysis has emerged as the primary hydrogen generation technology alternative to delivered hydrogen for thermal processing users smaller than a steel mill or plate glass facility. For small and medium-sized thermal processors using hydrogen-based atmospheres, PEM water electrolysis combines relatively low capital cost, outstanding space utilization, permitting ease, load-following, hydrogen purity, ease of operation, hydrogen pressure, and reliability. The only shortfall of PEM water electrolysis as compared with alternatives is operating cost, where electricity-driven electrolysis is costlier than making hydrogen from natural gas.

PEM water electrolysis onsite hydrogen generation technology makes it possible to replace delivered, stored hazardous ammonia with "zero-inventory" onsite hydrogen generation and stored or generated nitrogen. This approach eliminates the hazardous material objection to ammonia replacement for thermal processors, and makes it much more interesting to consider replacement of DA with hydrogen/nitrogen. While economic challenges remain, a look at total costs of operation makes hydrogen/nitrogen generation a viable, and growing, atmosphere solution for thermal processors.

Customer interest and results

Over the last five years, Proton OnSite has assisted five diverse customers to directly replace their ammonia dissociators with hydrogen/nitrogen blending for furnace atmospheres, and is working with several others. The driving force in every case was to get rid of ammonia delivery and storage. These customers included two merchant heat treaters, a manufacturer annealing strip products, a manufacturer of wire employing strand furnaces, and a manufacturer of industrial equipment with an in-house heat treating operation. In several other cases, Proton supplied hydrogen generation to manufacturers who had previously shifted from DA to delivered compressed gas hydrogen as a short-term solution, but now were ready to optimize their hydrogen supply approach.

Proton has seen strong preference by heat treating prospective customers using DA to get away from storing ammonia. The hassles and risks of ammonia storage, the challenges of dissociator maintenance, the rising prices and impactful quality issues with metallurgical grade ammonia deliveries are all making DA less attractive. More ominously, the results of a potential ammonia release, including the disastrous publicity and resulting fines and compliance costs, are all driving people away from accepting ammonia storage. Ironically, of the many ammonia releases every year, the agricultural and refrigeration users are responsible for the vast majority, and the thermal processing industry is responsible for only a small fraction. Nonetheless, the frequency of releases by others, and impactful results of a release mean that heavy regulation apply and significant penalties result from releases by any ammonia system owner.

Every one of Proton's customers who chose to replace dissociated ammonia with hydrogen/nitrogen blended atmospheres did so to get rid of stored ammonia. Their major concern in making the change was to make sure that their process results remained the same or improved. From an economic basis, they wanted to make sure that they understood their anticipated costs, and that those costs would be competitive. All understood that they would be installing new equipment to replace existing, depreciated systems, so there would be capital costs to assume.

Expectations and results

Replacing DA with blended atmospheres consisting of generated hydrogen and delivered, stored or generated nitrogen creates processing options for thermal processors and requires several choices. Some of the questions that arise:

- Will I replace my fixed DA blend (75% hydrogen/25% nitrogen) with an identical or different fixed gas blend, or do I wish to have blend flexibility ?
- Is it advantageous to distribute a DA-like gas throughout the facility to minimize operator retraining requirements ?
- If there are multiple furnaces in a facility, does the operator wish to have flexibility to provide different blends to each furnace ?
- Is there any need or benefit to being able to provide 100% hydrogen to any furnace(s) ?
- Does the existing DA gas internal facility piping meet the national Fuel Gas code ?

Because the pure generated hydrogen and the delivered or generated nitrogen are both drier than generated DA gas, Proton customers have demonstrated across multiple facilities and operations that a leaner blend (less hydrogen) will generally deliver equivalent results in terms of annealing and brazing. The reduction in furnace atmosphere water content enables more effective surface cleanup, even with lower hydrogen content in the furnace atmosphere gas. As compared with undiluted DA (75% H2, 25% N2), Proton customers have seen blends as lean as 35% hydrogen in balance (65%) vaporized liquid nitrogen yield equivalent and acceptable results. Because nitrogen is a fraction of the cost of hydrogen, a leaner blend is more economical. This means that thermal processors might be able to plan for smaller hydrogen generation capacity and correspondingly larger nitrogen capacity than a strict molecule conversion from DA might otherwise indicate. Because nitrogen generation or delivery/storage equipment and the nitrogen gas itself, whether generated or delivered, are less expensive than hydrogen, the leaner the blend, the more attractive the overall economics.

Where it is practical to do so, Proton is now suggesting that potential DA to hydrogen/nitrogen atmosphere prospective customers embark on a short test period using two or more different cylinder blends of various hydrogen percentages to bracket the acceptable hydrogen blend range for their furnaces and products. If a leaner blend proves successful, then a lower hydrogen generation capacity will suffice, and smaller, less expensive hydrogen generation equipment can be chosen - reducing first cost, operating and maintenance costs, and the space required for hydrogen generation. Every Proton DA conversion customer to date has been able to utilize more dilute blends than the 75/25 blend they used with undiluted DA.

Once the process of thinking about a DA replacement has begun, then thermal processors often would like to consider attaining additional atmosphere flexibility, even beyond a single, leaner facility blend. While this is an opportune time to consider such enhancements, it is important to maintain a focus of needs versus wants, as the costs associated with additional flexibility can drive up the cost of the project. Proton works hard with customers to differentiate between DA replacement, atmosphere enhancement, process flexibility and capacity expansion to understand and control capital and operating cost drivers. It is important to maintain a clear-eyed approach to needs versus wants.

Certain customers put great value on the ability to access 100% hydrogen atmosphere, since they were limited to 75% hydrogen in 25% nitrogen with DA. Proton assists these customers, who often wish to process metals subject to nitriding if nitrogen is present, to plan carefully for hydrogen generation capacity versus furnace total atmosphere requirements, and including the possibility of furnace sequencing. It is important to avoid having to oversize their hydrogen generator to enable a processing approach that they may rarely require. In specific cases, Proton has supplied customers with low pressure hydrogen surge storage capacity to enable a smaller hydrogen generator to demonstrate higher effective capacity for batch 100% hydrogen applications.

Capital and Operating costs

Among the customers converted by Proton from DA to generated hydrogen and blended hydrogen/nitrogen atmospheres, the average hydrogen generator cost has been about $250k, with a range from under $100k for a small hydrogen generator serving two 6" belt furnaces up to over $450k for a system to replace multiple dissociators serving over a dozen strand furnaces with multiple tubes in each. Electrical cost, which is the main consumable cost, averages under $1.50 per operating hour per 100 scf of hydrogen produced. Unlike a dissociator, a Proton hydrogen generator can load follow, so electrical costs go down at partial use rate. The hydrogen generator can also be shut down nights and weekends to save additional power if hydrogen is not needed to keep furnace belts clean.

While electrolysis hydrogen generation uses a considerable amount of electricity to split water to liberate hydrogen, the equipment itself is highly efficient, especially as compared with electrically-heated ammonia dissociators. Two electrical efficiency challenges with dissociators are that:

- Their electrical consumption does not vary meaningfully with variations in atmosphere requirements, so at any flow rate less than full production, the electrical requirements to heat the retort are wasting power
- Because dissociators operate at high heat, and are negatively affected by on-off cycles, the normal procedure is to leave the dissociator hot all of the time, using electricity even when no ammonia is being dissociated

In contrast, proton exchange membrane hydrogen generators are fully load-following, and the electrical use is exactly proportional to the hydrogen use rate, plus the units can be turned off at night, on weekends, or whenever atmospheres are not going to be used for several hours. Shutdown is immediate, and actual startup time before hydrogen is available is less than 10 minutes from a cold start.

Equipment planning and sizing

Once the equipment is ordered, installed, and commissioned, the time comes to cut over from the old DA atmospheres to the new blended atmospheres. Most Proton customers to date have chosen to start the process by duplicating their previous atmospheres to start, and then gradually leaning down the gas blend over time while monitoring process results to ensure that product quality remains as desired. This approach is cautious, but non-optimized. Proton is now encouraging customers to embrace blended gas cylinder testing in advance if practical, to better understand and more precisely size their hydrogen and nitrogen generators.

By understanding, and planning specifically for the required hydrogen generation capacity needed, and blending range required, capital costs can be minimized. Also, because furnaces require a specified minimum atmosphere flow rate to maintain a safe and process-friendly oxygen-free internal environment, it is critical that reductions in hydrogen requirement and capacity be balanced with capacity additions to the (less expensive) nitrogen supply. Hence nitrogen capacity – whether LIN tank size, or vaporizer capacity, or nitrogen generation capacity - will need to be reviewed as well.

It is important to understand that switching from DA to hydrogen/nitrogen will mean that a means of supplying hydrogen must be provided (generation, in this case), and that nitrogen will be required as well. Interestingly, many of the thermal processors currently using DA that speak with Proton have little or no nitrogen capacity in place, meaning that they are already out of compliance with NFPA 86, the Furnace standard. In the case of one large-scale customer, we needed to be aware that their use of nitrogen from their existing LIN delivered nitrogen system would go up by at least 25% of the amount of DA gas that they were using, but in fact, the nitrogen use rate rose closer to 50% of the DA rate formerly used since a more dilute blend satisfied their atmosphere results. Because nitrogen costs far less than even the operating costs for hydrogen generation, replacing hydrogen with nitrogen to the greatest degree possible will save money.

Ideally, if a few test runs using pre-blended cylinders can be accomplished up-front, both hydrogen use rate and nitrogen use rate for H_2/N_2 blends can be approximated in advance, to make sure that all systems are appropriately sized and capital investment can be optimized.

Conclusions

To date, Proton has assisted five customers to date to replace their stored ammonia and dissociated ammonia atmospheres with blended hydrogen/nitrogen. These customers have benefitted in the following ways:

- Relief from the risk of ammonia catastrophe
- Improved atmosphere quality to improve product quality
- Increased atmosphere flexibility to broaden processing flexibility
- Ease of cutover from old atmosphere process to new
- Minimal impact on organization or procedures