MATERIALS CONSIDERATIONS IN HYDROGEN PRODUCTION

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ABSTRACT

Correct selection and application of materials is essential to ensure safety and economy in production, transportation and storage of hydrogen. There are several sources of materials challenges related to hydrogen. Established component producers may have limited experience in this specific field. Process developments may involve new process conditions with new demands on the materials. Further, new materials will be added to the engineering toolbox to be used. The behavior of these materials for hydrogen service may need additional documentation. Finally, focus on hydrogen susceptibility and hydrogen damages alone may take away awareness of other subjects as trace elements, by-products and change in raw materials, which may be of as high importance for safety and quality. This overview of challenges and recommendations is made with emphasis on water electrolysis.

INTRODUCTION

Production, handling and storage of hydrogen have been done in the industry for years. However, process developments and new applications, for instance in transportation, put new challenges to selection of materials.

Hydro has long experience with hydrogen from water electrolysis and ammonia steam reforming. In addition Hydro has a long history in manufacturing of electrolysers. Hydrogen is also a by-product from chlorine production. This production is the source of hydrogen for a recently built hydrogen filling station in Norway. In a long industrial history relative few incidents are related to the effect of hydrogen gas on materials. Most hydrogen incidents in Hydro are related to high temperature hydrogen, but the nasty experiences are not related to material damages, but to leaks of hydrogen and hydrogen out of control. In 1997 a CO_2 transfer line exploded in a length of 850 meters due to insufficient nitrogen purging during a plant shut down, see figure 1. No injuries at all were experienced. In 1985 an ammonia plant experienced a hydrogen leak in a high temperature area with the result of a fire. Incidents related to water electrolysis are not caused by hydrogen as a gas, but other environments or process conditions.

Figure 1: CO_2 line after hydrogen explosion

The safety aspects of hydrogen are naturally related to the properties of hydrogen: ignition limits, the diffusion rates, the leak rates and the interaction of hydrogen with materials. With respect to degradation of materials and interaction with materials it is important to be aware of the influence of any trace elements that are present, intended or not.

It is essential to build on established knowledge for hydrogen without forgetting the possible problems or challenges that may be experienced in introduction of new materials, design and changing of external environment or process conditions.

MATERIALS

General hydrogen and metallic materials evaluations are covered by several guidelines. At low temperatures, hydrogen embrittlement (HE) is the degradation mechanism. The embrittlement effect is described to occur in the temperature range from -100 to +100°C, reaching a maximum around room temperature. The yield strength of the materials is reported to be unchanged, but when entering the yield area, the material shows a brittle fracture. Guidelines for handling of hydrogen at low temperatures are “Hydrogen Transportation Pipelines” by EIGA [1] and “Safety Standard for Hydrogen and Hydrogen Systems” by NASA [2]. At higher temperatures, above 200°C, hydrogen attack (HA) is the degradation mechanism for unalloyed and low alloyed steels. This is described in “Steels for Hydrogen Service at Elevated Temperatures” by API [3].

The basics from the documents on steels for ambient temperature are the strength limits for unalloyed and low-alloyed steels. High strength steels may be used by allowing lower utility rate with respect to stress levels. For stainless steels with a low level of nickel, there is a risk of metal structure transformation which increases the hydrogen susceptibility. Nickel alloys, on the other hand, should be avoided in hydrogen gas service.

The importance of trace elements is shown through the observation that small amounts of oxygen in the hydrogen will eliminate the hydrogen embrittlement [4].

Motivated by the need for ultra high strength and low weight, carbon fibre reinforced plastics are introduced for storage of hydrogen. Testing and qualification are based on natural gas requirements. For these types of materials, a clear focus on production control is needed as changes in fabrication conditions may be detrimental to quality.

To our knowledge there are no effects on plastics or elastomers from gaseous hydrogen used within the advised temperature limits. Rapid gas decompression may be detrimental to this group of materials.

EXTERNAL ENVIRONMENT

To ensure safety in handling of hydrogen, the materials selection must allow for the external environment in addition to the influence of hydrogen. Coastal areas and industrial areas may represent an outer environment detrimental to the materials. Chlorides combined with humidity and sun may lead to stress corrosion cracking of stainless steel where wet-dry conditions are experienced. It may therefore be necessary to paint stainless steel or to build proper shelter to the metal surfaces. Buried pipelines and storage tanks may also require special considerations dependent of soil conditions.

VALUE OF DATABASES FOR INCIDENTS

API RP 941 covers hydrogen at high temperatures and a basic figure is the Nelson diagram. The diagram is a synthesis of years of experience. It describes the suitability of different materials with temperature and partial pressure of hydrogen as parameters. This diagram demonstrates the benefit of reporting and registration of damages.

Databases exist for hydrogen incidents both in US and in EU, it is however not always easy to get to the root cause of the incident. There may be several reasons for this. It may be difficult to reveal the root cause of the incident, or there may be several interacting factors that lead to the final incident. Other reasons may be that it is embarrassing and negative for the company brand to reveal all elements in an investigation. There may also be elements of proprietary information not to be revealed.

From the database of HyFLEETCUTE, none of the incidents can be identified to have the hydrogen-material selection root cause. Leakage of hydrogen, however is reported a number of times. Hydrogen out of control is as mentioned in the introduction critical to safety, and leakages are related to compressors, valves, filling nozzle or filling hose.

Hydrogen may be a tracer gas for leak testing because the molecule is so small that it will find all practical sources of leak. This is also the reason why hydrogen will escape more easily than other gases, and the reason why the tolerances and material selections need more attention than for other gases. The diffusion coefficient is 4 times that for methane.

Both feasibility projects and the databases for hydrogen incidents reveal that leak of hydrogen is a major problem. A lot of observations are related to compressors, valves, flanges, connections and hoses. This may be a design problem or a manufacturing problem more often than it is a materials selection problem.

WATER ELECTROLYSERS

Hydro has been in the electrolyser business for years. Potassium hydroxide is the electrolyte in the process. Both carbon steel and stainless steel have been used for years for the different process parameters. The process development has introduced higher pressures to the equipment. It is experienced that the earlier durable materials are not usable for the new process conditions [5]. The temperature and concentration limits for the use of stainless steels in caustic at atmospheric pressure are well established. Increased pressure will affect the environment by increased oxygen content in the caustic, which again is critical for the corrosion resistance to stainless steel, see figure 2. On the lye/hydrogen side of the process, there are no problems.

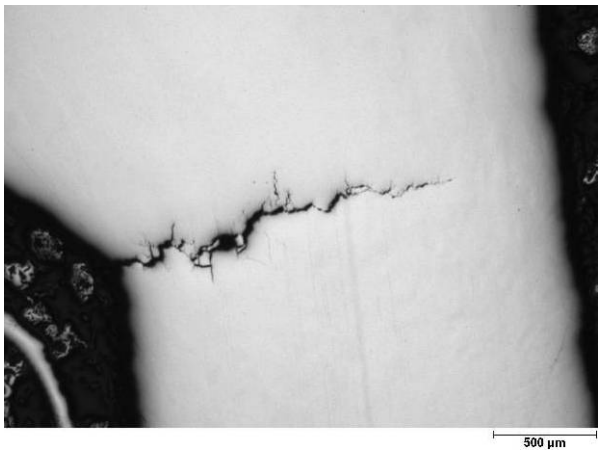

Figure 2. Stress corrosion cracking of stainless steel in potassium hydroxide, water electrolyser

High pressure oxygen gas also requires special attention with respect to materials selection. The ignition temperature in oxygen for different metals varies significantly. Here it is also important to have focus on plastic materials in gaskets and demisters [6].

SUM-UP

Hydros materials experience in hydrogen production may be summarized in the following bullet points:

- Build on existing knowledge when designing and selecting materials for hydrogen service.
- Variations in process conditions may have large consequences upon materials selection.
- Data bases are important tools in materials selection, but the organizing of these bases is crucial to obtain the highest value.
- Most incidents in the hydrogen business are not directly related to hydrogen compatibility of materials.
- External environment or variation of process conditions may give unexpected degradation of materials.
- There should be focus on trace elements in production, transportation and storage of hydrogen.

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