THE FORMATION OF NON-CONDENSABLE GASES IN AMMONIA/ WATER ABSORPTION HEAT PUMPS MADE OF STAINLESS STEEL - LITERATURE REVIEW AND EXPERIMENTAL INVESTIGATION

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Abstract: Highly efficient ammonia/water absorption heat pumping (AHP) processes (e.g. the GAX-process) require a high desorption temperature level of e.g. 200°C and above. At these conditions the formation of non-condensable gases can take place, which can be dedicated to two chemical processes: corrosion of steel and thermal decomposition of ammonia.

Within a research project the possible use of stainless steel components at high temperature level has been investigated. Tests with an absorption/desorption test rig operating at temperatures up to 290°C as well as corrosion tests using autoclaves at temperatures up to 220°C have been performed. The produced non-condensable gas has been analysed using gas-phase chromatography in order to identify the responsible chemical process.

The results show a large initial corrosion rate which decreases with time. This may be explained by a passivation process of the steel surface. At all tests the carbon steel (ST37) autoclaves has shown significant lower corrosion rates compared to the stainless steel components. Regarding the thermal decomposition no dissociation products has been detected up to a temperature level of 290°C.

Key Words: absorption heat pump, non-condensable gases, corrosion, ammonia decomposition

1 INTRODUCTION

In recent years absorption heat pumps (AHP) for both cooling and heating applications attract increasing research interest, in particular in the small-capacity range. In order to increase the efficiency of natural gas driven ammonia/water absorption heat pumps advanced processes using high driving temperatures like multiple stage or the generator-absorber-heat-exchanger (GAX) process has been developed. One barrier which has been detected in particular at high temperature applications is the formation of non-condensable gases which influences the thermodynamic process negatively.

In general two main chemical mechanisms may cause the formation of non-condensable gases in ammonia/water absorption systems: corrosion of iron (Eq. 1) and the thermal dissociation of ammonia (Eq. 2). The products of these reactions are: solid magnetite and gaseous hydrogen in case of corrosion as well as gaseous nitrogen and hydrogen in the case of dissociation. In principle by analysing the composition of the non-condensable phase, the responsible chemical process can be determined. However, it shall be mentioned, that beside thermal decomposition the presence of nitrogen can also be caused by other chemical processes. McKelvy and Isaacs (1920) have described that if air is in the system the oxygen is used up for corrosion and mainly nitrogen and hydrogen can be detected in the gas samples. Furthermore it has been shown (Mansfeld and Sun 2003) that when sodium chromate ($NaCrO_2$) is used as corrosion inhibitor it can react with ammonia at high temperatures to form nitrogen and NaOH according to Eq. 3.

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2 \quad (1)$$

$$2NH_3 \rightarrow N_2 + 3H_2 \quad (2)$$

$$NH_3 + H_2O + Na_2CrO_4 \rightarrow 1/2N_2 + 2NaOH + Cr(OH)_3 \quad (3)$$

1.1 Corrosion of Steel

According to (1 even small corrosion rates lead to the formation of a considerable hydrogen amount, e.g. if a 0.01 mm thick layer of a 1 m² iron surface corrode uniformly to magnetite approx. 42 liter of gaseous hydrogen (at 1 bar and 20°C) are generated.

One problem of the investigation of corrosion phenomena regarding ammonia/water solution is that usually there are many variables like ammonia concentrations, temperature level, existing impurities, possible pre-treatment of the surface etc., which can greatly influence the corrosion rate. This is particular of interest, because even a very low corrosion rate must be avoided due to the formation of a considerable amount of non-condensable gases.

Typically, the material of choice for NH_3/H_2O absorption heat pumps is carbon steel. In order to prevent corrosion in these systems usually corrosion inhibitors like sodium chromate (Na_2CrO_4) and/or sodium dichromate ($Na_2Cr_2O_7$) are used (McKelvy and Isaacs 1920). However, these chemical compounds are highly toxic and carcinogenic and the use within EU member states has been widely banned by 2002/95/EG (RoHS - Restriction of Hazardous Substances). Currently some exceptions to this regulation exist. One is the use of “hexavalent chromium as anti-corrosion of the carbon steel cooling system in absorption refrigerators”. However, it can be expected that this exception will expire in the near future (Gensch et al. 2009). In order to overcome the drawbacks of the conventional inhibitors using chromates alternative inhibiting substances and pre-treatment procedures for the system carbon steel and NH_3/H_2O have been suggested by several authors.

Agrawal and Hindin (1994) and Hindin (1995) from “Gas Research Institute” (GRI) have proposed to use silicon compounds which are soluble and stable in the ammonia and water solution (e.g. approx. 0.2 wt% of sodium silicate) as inhibitor. However, further investigations at GRI have shown that sodium silicate-inhibited directly gas fired chillers either have generated excessive amounts of non-condensable gas or they have developed excessive generator temperatures due to low solubility of the silicate in various regions of the chillers.

Downey (1996) from “Carrier Corp.” has proposed different silicates, molybdates or borates together with a hydroxide for ammonia/water systems. However, this is only mentioned in the patent but has not been claimed and no experimental results have been found.

Phillips and Whitlow (1998) have proposed strong bases such as sodium hydroxide, potassium hydroxide, caesium hydroxide or lithium hydroxide, preferably in combination with a buffer (like alkali-borate, -silicate, -molybdate or -acetate) to be used as corrosion inhibitors for aqueous ammonia systems. The presented test results show low hydrogen formation for the carbon steel test apparatus of less than 0.003 ml/day (at atmospheric pressure).

Erickson (2001) has proposed a process consisting of pre-treatment (pre-oxidizing) of the surface, the use of de-oxygenated and de-carbonated water as well as the use of inhibitors such as alkali metal base preferably with addition of one of alkali metal chromate, germanium dioxide, alkali molybdate or alkali thungstate.

Guerra (2002) from the company “Robur S.p.A” has suggested another inhibitor based on a strong base. The mixture consists of zinc borate, potassium hydroxide and potassium nitrate. From tests with commercial Robur chillers stable production rates of non-condensable gases of ca. 0.1 to 0.2 ml/hour are expected (after an initial operation period of ca. 100 days).

Hannon et al. (2000) and Mansfeld and Sun (2003) have proposed a dual protection method of pre-treating the carbon steel surface with a cerium oxide/hydroxide layer to prevent both corrosion of the metal and ammonia dissociation, and adding rare earth metal salts (preferably cerium nitrate) to the solution to act as a corrosion inhibitor. The presented experimental results show comparable to or better results than that of chromate inhibited systems even at high temperature levels between 205 and 245°C.

Even if there are several alternative inhibitors found in literature - to the knowledge of the authors - up to now only chromate based inhibitors are used in commercially available carbon steel ammonia/water heat pumps. At the first glance in the literature stainless steel is often treated as absolutely corrosion-resistant to ammonia/water and therefore it is recommended in many chemical stability brochures. In the above mentioned literature the main reason for using carbon steel instead of stainless steel is the lower material cost and better machinability (Agrawal und Hindin 1994, Phillips and Whithlow 1998).

At the second glance contradictory statements for stainless steel and ammonia/water can also be found in literature. Mansfeld and Sun (2003) state that corrosion problems can also be found where stainless steel and chrome-plated steel are used. At the Oak Ridge National Laboratory corrosion investigations with autoclaves have shown, that for ammonia/water (5% NH_3) at 180°C the corrosion rate was less than 0.002 mm/year for 304 stainless steel (Griess et al. 1985). The DECHEMA Corrosion Handbook (Behrens 1998, Kreysa and Schütze 2007) states that aqueous, diluted and concentrated ammonium hydroxide solutions attack austenitic CrNi- and CrNiMo-steels only slightly less than 0.05 mm/year at room temperature. At the boiling point (and/or at 100°C), however, the material losses increase to 0.5 mm/year. Above 100°C significant uniform surface corrosion can be expected. If the ammonia hydroxide solution contains additional substances, e.g. carbon dioxide or chloride, these steels often fail after a short period of use.

Generally it can be concluded from the literature review, that for carbon steel corrosion inhibitors are needed. Alternatives to chromate inhibitors are currently under development. The use of stainless steel for high temperature ammonia/water heat pumps is questionable at present and no information regarding corrosion inhibitors for this system have been found.

1.2 Dissociation of Ammonia

As discussed above the second chemical mechanism beside corrosion of steel which can be responsible for the formation of non-condensable gases is dissociation of ammonia according to Eq. 2.

Regarding this phenomenon only a few contrary literature sources have been found for the prevailing thermodynamic conditions in AHP. Broesby-Olsen (1996) discusses catalytically augmented dissociation of ammonia with nickel as catalyst at temperatures as low as 110-120°C. Seidel (1996) investigated the dissociation of NH_3/H_2O solutions in a stainless steel autoclave at temperatures above 200°C. He concluded that the formation of the non-condensable gases by means of the dissociation and corrosion is almost equal and should not be an obstacle for the construction of a triple-effect-machine. Guerra (2002) discusses the splitting of ammonia molecules when in certain situations, which can be brief and transient, extremely high temperatures exceeding 300-350°C are attained in the circuit. Generally from the literature review no clear information acc. the thermal dissociation of ammonia/water at different temperature levels has been found.

2 EXPERIMENTAL SETUP

Initially the aim of the project discussed in this paper was to investigate thermal decomposition of ammonia under typical conditions occurring in high temperature AHP made of stainless steel and to determine the temperature limits for trouble-free operation. Therefore a test rig comprising of a thermosiphon cycle has been constructed. The first test results turned out, that the initial assumption, that for stainless steel components corrosion plays a minor role compared to dissociation, was wrong and thus autoclaves for corrosion tests have been constructed.

2.1 Thermosiphon Test Rig

In order to investigate thermal dissociation of ammonia a test rig has been designed and constructed in such a way that preferably realistic conditions for an AHP can be simulated. For the test rig common stainless steel components (1.4301, 1.4404 and 1.4571) has been used, in order to heat ammonia/water solution up to 300°C and withstand pressures up to 120 bar.

In Figure 1 a schematic drawing of the test rig is shown. The generator - which consists of a co-axial tube-in-tube heat exchanger - is heated by a secondary water loop, which itself is electrically heated. Both circuits, the secondary water loop and the ammonia water solution are circulated by means of a thermosiphon, where the electrically heated water circuit and the generator work as a bubble pump. This approach allows to easily control and measure the temperature level of the driving heat for the generator and at the same time avoids local over-heating (which likely occurs in an electrically heated generator). The partly evaporated ammonia/water solution rises up and flows into an air-cooled condenser/absorber section. This includes a vessel where test probes can be inserted. The vapour-phase coming from the generator is then absorbed by the solution and is fed back to the generator, completing the working cycle. At the top of the condenser there is a connector through which the gas sample for the analysis can be extracted.

For the experiments the electrical heater has been controlled with respect to a certain temperature level of the heating water. In the test rig the ammonia/water solution circulates and the absorption and desorption process takes place under similar conditions as in a typical AHP. After a certain operation period a gas sample was withdrawn and analyzed.

2.2 Autoclaves

Because the first tests with the thermosiphon test rig turned out that considerable corrosion take place a second test facility consisting of an oven and 16 gas tight vessels (autoclave) have been build up (Figure 2). Four different kinds of steel (ST37, 1.4307, 1.4404 and 1.4571) each for four vessels has been used. All 16 vessels were equipped with a ball valve on one side and the 12 stainless steels vessels had different welding treatment: no acid cleaning and no forming gas; only forming gas (N_2); only acid cleaning (with Antox 71 E Plus, Chemetal); acid cleaning and forming gas (N_2). The vessels made of carbon steel (ST37) were thought as a reference, and they were not treated by acid cleaning nor forming gas during welding.

As it is shown in Figure 2 only the vessels are situated inside the oven, the ball valves are outside. All of the 16 vessels have been pressure and leak tested, evacuated and filled with ammonia/water solution. Then they were put into an oven, heated up and remained in this condition for several days. In order to detect the possible occurrence of small leaks during operation the mass of autoclaves have been exactly measured with a balance before and after the test period. Furthermore the valves are turned to bottom, in order to establish a liquid barrier between gas phase and valves.

It should be mentioned, that the results obtained in autoclaves often do not match observations done on real life absorption heat pumps, as discussed by Guerra (2002). However, the results from autoclave testing can serve as an approximate evaluation of the corrosion of different materials, welding treatment and possible inhibitors.

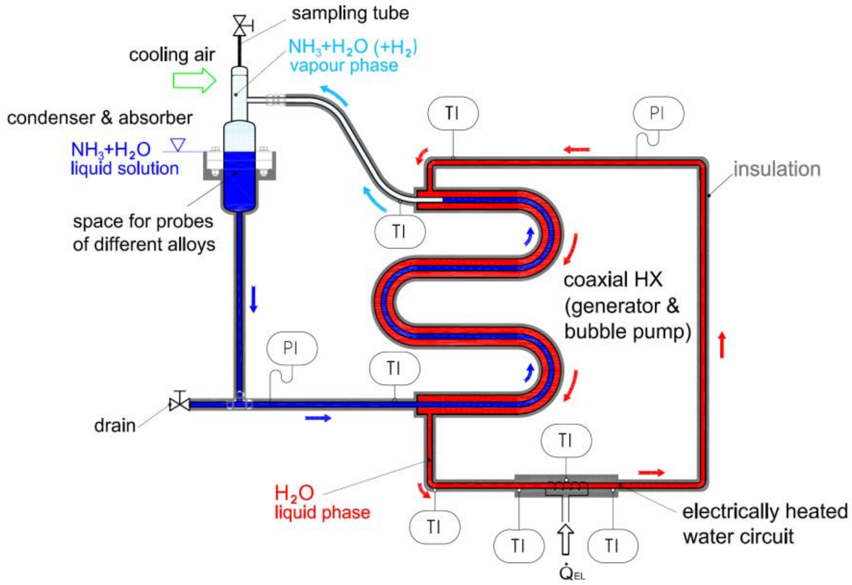

Figure 1: Schematic drawing of the thermosiphon cycle test rig with indicated instrumentation

Figure 2: Photo of the autoclaves in the oven

2.3 Sampling and Measurement Procedure

In order to determine corrosion and thermal decomposition the quantification of the products N_2 and H_2 is necessary. Therefore a gas chromatography setup (GC) has been used and calibrated for the molecules of NH_3, H_2, N_2 and O_2.

As shown in Figure 3 two syringes have been used for gas sampling, one syringe is empty and the second one is filled with approx. 20 ml of water. Before gas sampling the oven (or test rig) is heated up to a certain temperature level in order to achieve a pressure level slightly above atmospheric pressure and all tubes are purged with pure ammonia. By operating the valves the initially empty syringe is filled automatically with sampling gas and serves as a gas volume meter. By pushing down the plunger of the first syringe the gas is passed through a non-return valve to the second syringe where the ammonia is absorbed in the water and the plunger is lifted only due to the non-condensable components. This procedure has been repeated until the plunger of the second syringe was not moving anymore when sample gas was introduced. This means that all non-condensable gases have been withdrawn from the autoclave or thermosiphon test rig respectively. The gas phase of the second syringe has then been analysed using gas-chromatography to determine the components and assign it to the responsible chemical process, i.e. corrosion or thermal decomposition.

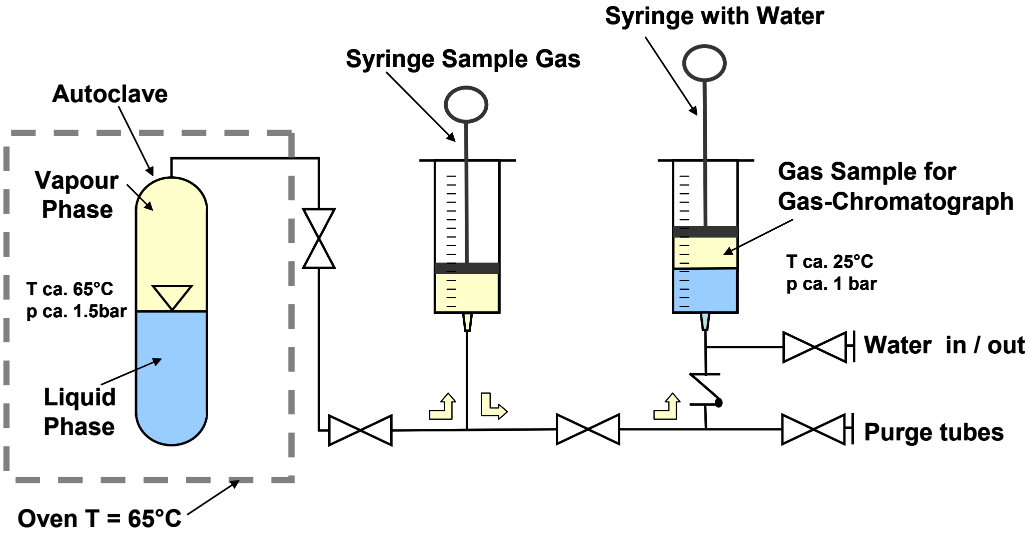

Figure 3: Schematic drawing of the experimental setup for gas sampling

Note: The amount of water in the second syringe has been limited to 20 ml in order to accomplish both, absorb a major amount of ammonia and limit the possible effect of dissolving a part of the non-condensable components of the sample gas in the water.

3 RESULTS AND DISCUSSION

The analysis of all samples from the autoclaves and the thermosiphon test rig showed only very moderate amounts of nitrogen and oxygen. Since the percentage of nitrogen to oxygen in the samples was similar to the air composition, it has been concluded, that a small amount of air was within the sample and that the whole amount of hydrogen can be attributed to corrosion. This means, that no thermal decomposition not even at temperatures up to 290°C has been detected.

Because corrosion of the inner surface is the assumed origin of non-condensable gases the hydrogen production rate has been related to the inner surface area of the thermosiphon test rig (0.18 m²) and the autoclaves (ca. 0.038 m²), in order to obtain comparable results for the corrosion rate. The volume has been measured at room temperature and ambient pressure.

Figure 4 shows the hydrogen production rates of the four different autoclave materials ST37, 1.4307, 1.4404 and 1.4571 (mean value of four autoclaves with different welding precautions) over the operation period. The temperatures and ammonia concentration (x in $kg_{NH3}/kg_{solution}$) of the solution filled into the autoclaves are given in the upper section of Figure 4. The stainless steel autoclaves show similar hydrogen production rates to each other, but compared to the ST37 autoclaves these rates are much higher. E.g. within the initial operation period of 20 days in the 1.4307 autoclaves ca. 145 $ml_{H2}/(m^2\ day)$ and in the ST37 autoclaves ca. 28 $ml_{H2}/(m^2\ day)$ have been generated. Furthermore a sharp decrease of the hydrogen production rate with increasing operation period can be seen, which might be explained with the initial formation of a protective layer (passivation) within the autoclaves.

Figure 5 shows the evaluation of the same set of experimental data. Here the hydrogen production rates are shown for the different welding treatment methods (mean values of three stainless steel autoclave materials). It is clearly visible that those autoclaves which underwent acid cleaning produce substantially more hydrogen then those which were not acid cleaned, at the initial period of testing. After approx. 50 days the difference in the hydrogen production rate is negligible, no matter if there was any welding treatment or not.

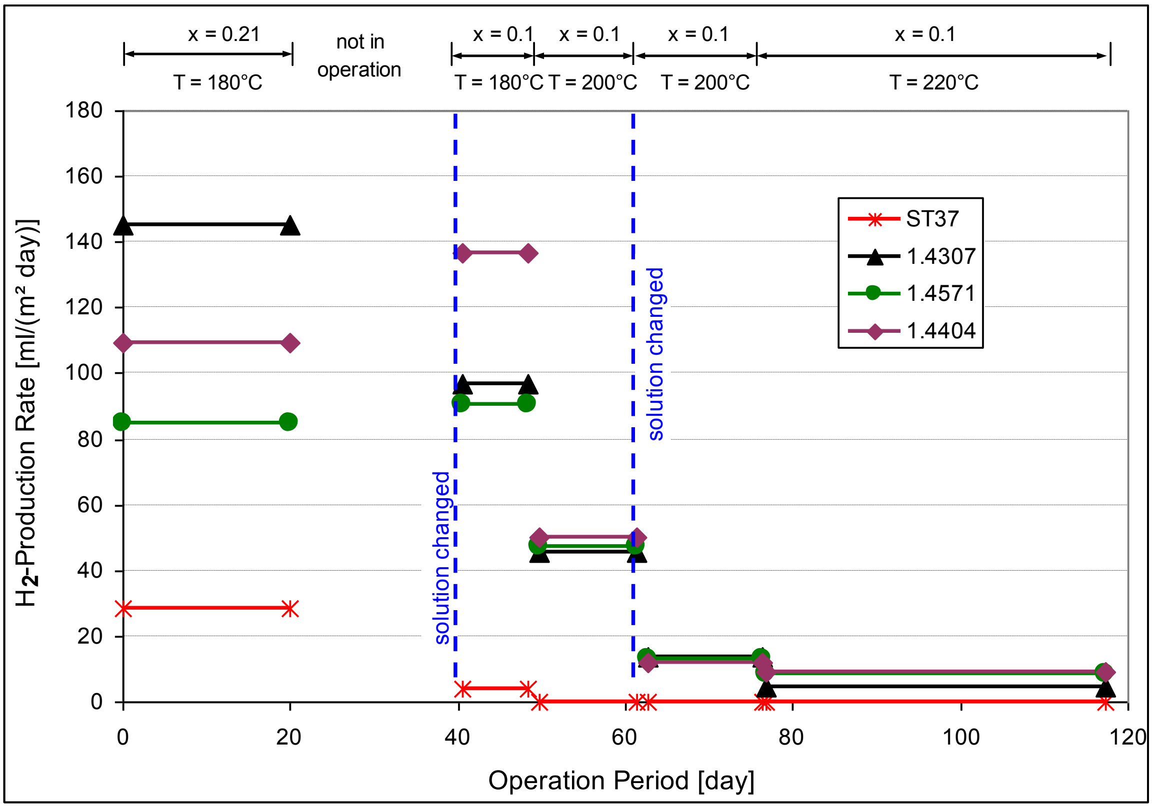

Figure 4: Mean value of the hydrogen production rates for different autoclave material (ST37, 1.4307, 1.4404 and 1.4571)

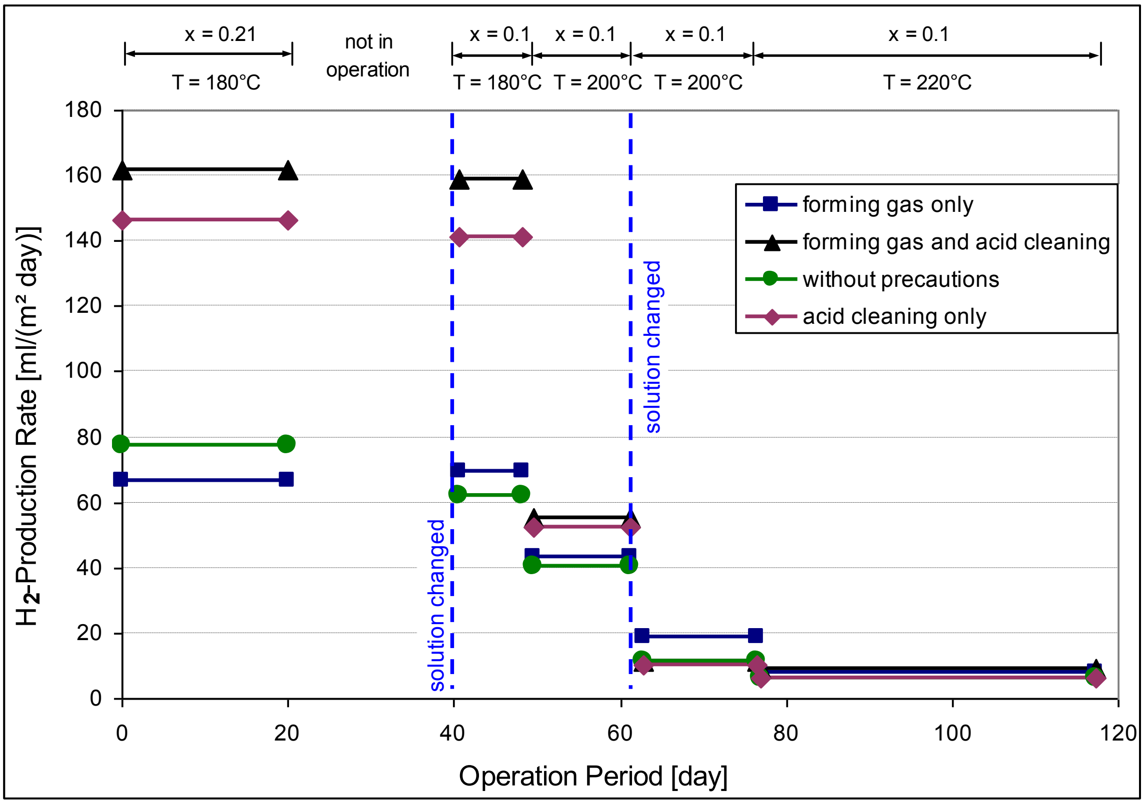

Figure 5: Mean values of the hydrogen production rates for different welding treatment methods

Note: In order to recheck the experimental setup in two ST37 vessels a certain amount of hydrogen has been added to the ammonia/water solution. After one week of operation at 200°C and 25 bar the amount of hydrogen have been measured and the results complied with the previously inserted amount in a range of +/- 9%. Thus it has been concluded that the experimental setup is appropriate for the quantitative evaluation of the hydrogen production rates.

Figure 6 shows the results obtained with the thermosiphon test rig. The initial ammonia concentration of the solution was ca. 20%. Due to the sampling process the ammonia concentration has been decreased to approx. 7% within the total operation period. The first test which was carried out at 180°C for about 7 weeks could not be evaluated with enough precision due to gas sampling problems and therefore this measurement value is missing in Figure 6. After this operation period test runs at 120, 150 and 180°C have been done. Those at lower temperatures show lower hydrogen production rates than at 180°C. This indicates that in the initial phase of operation (ca. 70 days) the temperature (between 120 and 180°C) influences the corrosion rates. After further 38 days operation at ca. 70°C two tests at 180°C have been conducted. The results show much lower hydrogen production rates compared to previous results at 180°C. Compared to the results observed with the autoclaves a similar decrease of the hydrogen production rate with time has been observed at 180°C. After further 53 days of operation at ca. 90°C the temperature level has been increased to 200, 250, 270 and 290°C. For these temperature levels a moderate increased hydrogen production rate has been observed.

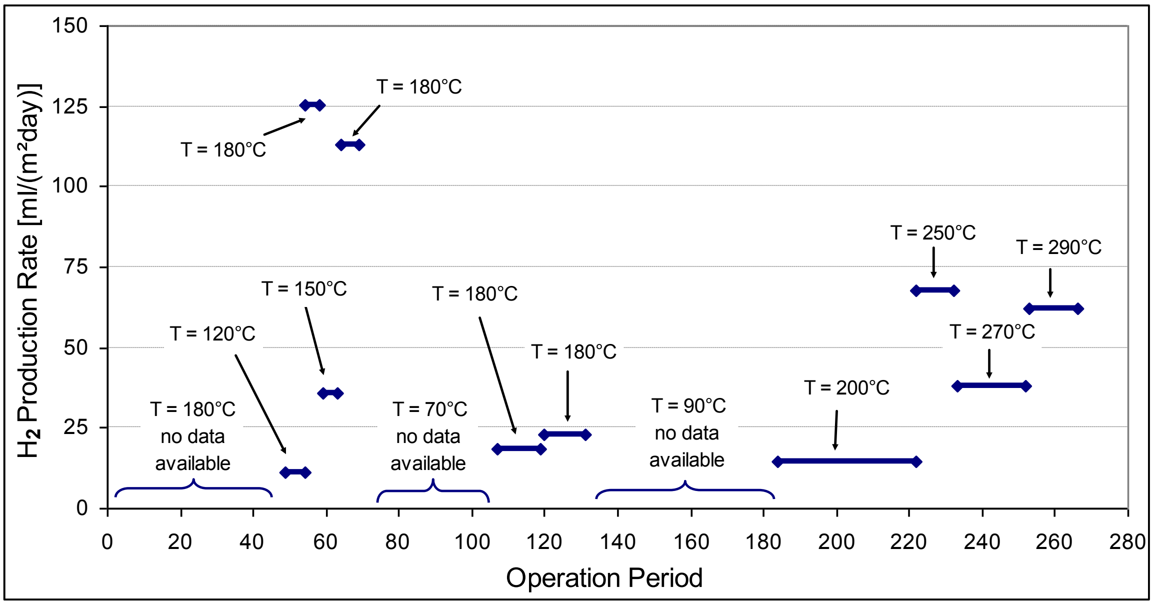

Figure 6: Hydrogen production rates measured at the thermosiphon test rig

4 CONCLUSION

The formation of non-condensable gases in AHP has a negative effect to the process or even may lead to system malfunction. From a literature review two possible reasons have been evaluated, corrosion and thermal dissociation. However, the gathered information is not totally consistent and information regarding the system stainless steel and ammonia/water is very limited. Within this work two test facilities, a stainless steel thermosiphon cycle and 16 autoclaves (12 made of stainless steel and 4 carbon steel) have been investigated with ammonia/water at different temperatures.

Following main findings can be summarized:

- No thermal decomposition of ammonia has been detected up to temperatures of 290°C.
- Mild carbon steel (ST37) has shown significantly lower hydrogen production rates compared to stainless steel.
- A large initial hydrogen production rate which decreases with time has been observed.

From the results obtained up to now it can be concluded that in contradiction to the expectations carbon steel might be the material of choice instead of stainless steel for ammonia/water absorption heat pumps. If and how corrosion can be reduced for stainless steel components by means of pre-treatment or inhibitors has not been investigated up to now. In order to investigate this phenomenon in detail further tests are planned.

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