IEA HPP Annex 34 - Nationaler Beitrag Task C

"Thermische Zersetzung und Korrosion in NH_3/H_2O Absorptionswärmepumpen"

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Nationaler Beitrag [1)]

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  - *a) Korrosion*
  - *b) Zersetzung*
- Versuchsanlagen
  - *a) Thermosiphonteststand*
  - *b) Autoklaven*
  - *c) Probennahme*
- Experimentelle Ergebnisse
- Zusammenfassung

Bsp. für Beiträge aus anderen Ländern

[1)] Moser H., Zotter G., Kotenko O., Rieberer R. (2011): "The Formation of Non-Condensable Gases in Ammonia/Water Absorption Heat Pumps Made of Stainless Steel – Literature Review and Experimental Investigation", Int. Conf. of Ammonia Refrigeration Technology, Ohrid, Macedonia.

Motivation / Einordnung in Annex 34

Annex 34
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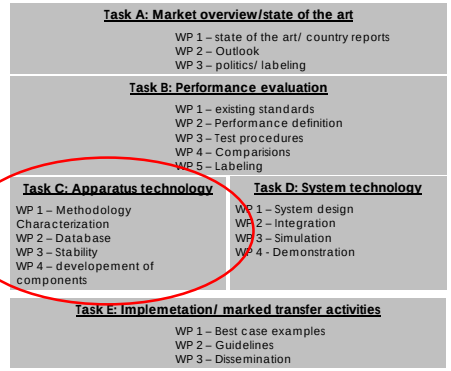
Task C: Apparatus technology

Der Task C befasste sich mit der Komponentenentwicklung für thermisch angetriebene Wärmepumpen mit Fokus auf z.B.: Alterung, thermische Stabilität, Korrosion, Inertgasbildung, Lärm usw.



THE FORMATION OF NON-CONDENSABLE GASES IN AMMONIA / WATER ABSORPTION HEAT PUMPS MADE OF STAINLESS STEEL

Fundamentals and Literature Review

- Corrosion
- Dissociation – Thermal Decomposition of NH_3

Fundamentals

High performance NH_3/H_2O absorption heat pump processes are limited by the generator temperature because of two chemical processes:

1. Corrosion of steel

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$

2. Thermal dissociation of ammonia

$$2NH_3 \rightarrow N_2 + 3H_2$$

Corrosion Rate

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$

Conversion factor: ca. 20,8 g_{Fe} / g_{H2}
ca. 1,87 g_{Fe} / l_{H2} (@ 1 bar, 20°C)

Example:

Surface Fe	Corrosion Fe	H2_Production (@ 1bar, 20°C)
m²	mm	l
1	0.001	4
1	0.01	42
1	0.1	422

Even small corrosion rates lead to considerable H_2-production rates!

Literature Review - Corrosion of Carbon Steel

Carbon steel and corrosion inhibitors are commonly used for NH_3/H_2O AHP

Corrosion inhibitors are sodium chromate and/or sodium dichromate.

These substances will probably be phased out in near future because of there toxic and carcinogenic nature.

Alternative inhibitors are currently under development e.g.:

- Silicon compounds
- Strong bases
- Pretreatment of the surface

Literature Review - Corrosion of Stainless Steel

Partly inconstant predictions found in literature for aqueous ammonia solution and Stainless Steel (SS)

Chemical stability brochures:

- *SS is often treated as "absolutely resistant"*

Dechema Corrosion Hand Book (2007)

- *minor attacked at room temperature (corrosion rate < 0.05 mm/year)*
- *@ boiling point and/or 100°C (corrosion rate ca. 0.5 mm/year)*
- *> 100°C significant uniform surface corrosion*

ORNL (1995):

- Stainless steel 304 < 0.002 mm/year (for 5% NH_3 @ 180°C)

No research on inhibitors with stainless steel has been found in Lit.

Literature Review - Dissociation

Contradictory information on dissociation in AHP have been found in literature e.g.:

McKelvy & Isaacs (1920):

- Hydrogen comes from corrosion process
- Nitrogen comes from air when oxygen is removed due to corrosion
- Temperatures in common AHP are too low for dissociation

Guerra (2002):

- Dissociation take place when in certain situations the temperature exceeds 300 – 350°C

Broesby-Olsen (1996):

- Catalytic dissociation of NH_3 with Nickel as catalyst at temperatures as low as 110-120°C.

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Experimental Setup

- Thermosiphon Test Rig
- Autoclaves
- Sampling and Measurement Method

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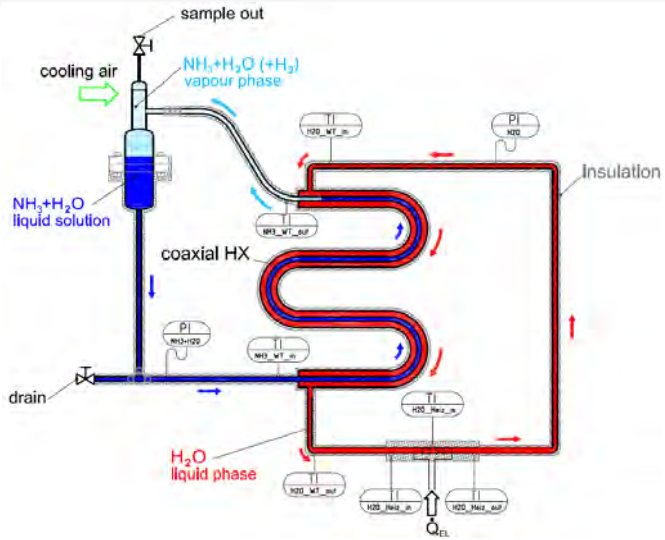
Thermosiphon Test Rig:



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Thermosiphon Test Rig:

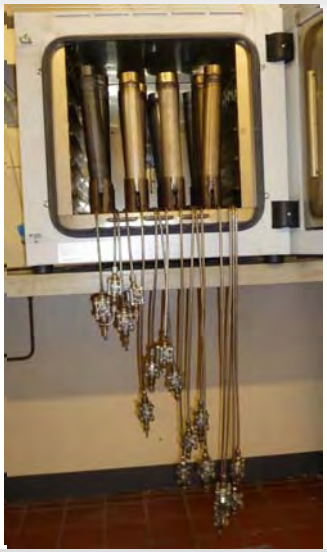
Autoclaves for Corrosion Tests

16 Test Probes have been constructed

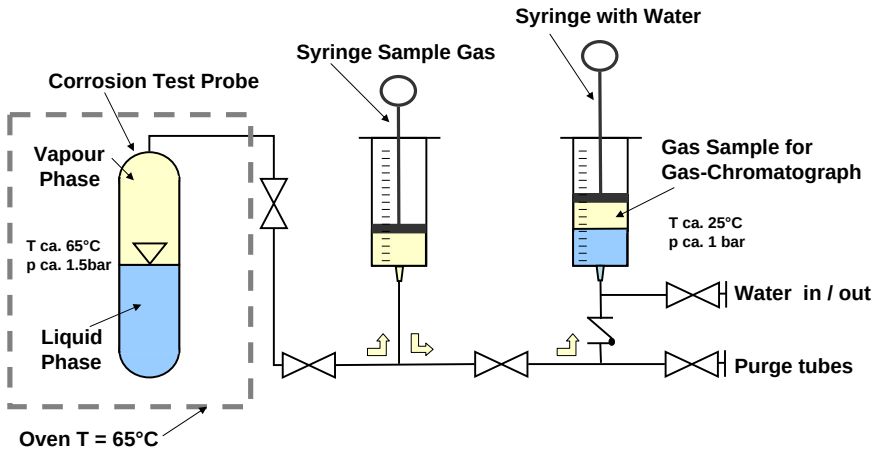
- 4 pcs. of St 37
- 4 pcs. of 1.4307
- 4 pcs. of 1.4404
- 4 pcs. of 1.4571

For stainless steel probes welding has been performed:

- without any precaution
- with forming gas only
- with acid cleaning only
- with forming gas and acid cleaning



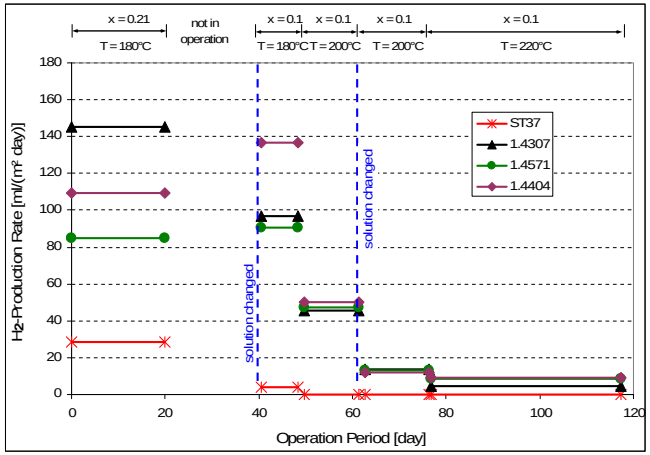
Gas Sampling and Measurement



Experimental Results

- Autoclaves
- Thermosiphon Test Rig

Results with Autoclaves

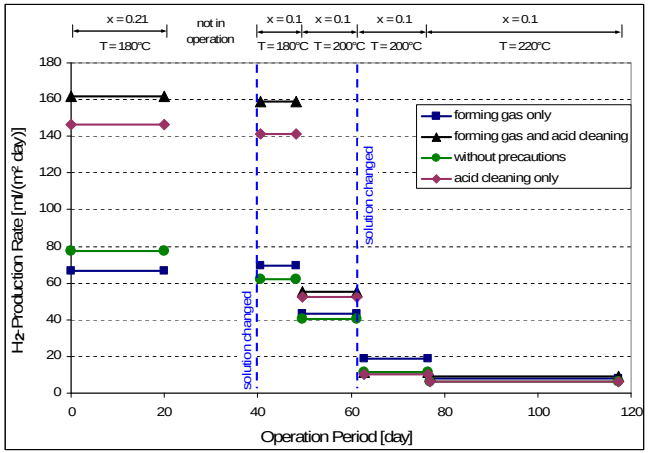


Average values for 4 probes

X… [kg_{NH3} / $kg_{Solution}$]

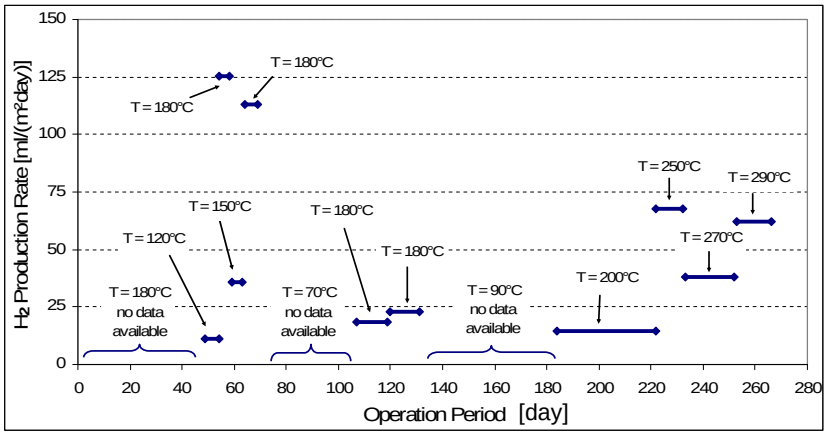
m^2… inner surface of probes

Results with Autoclaves



Average values of the 3 SS probes with different precaution

Results with Thermosiphon Test Rig



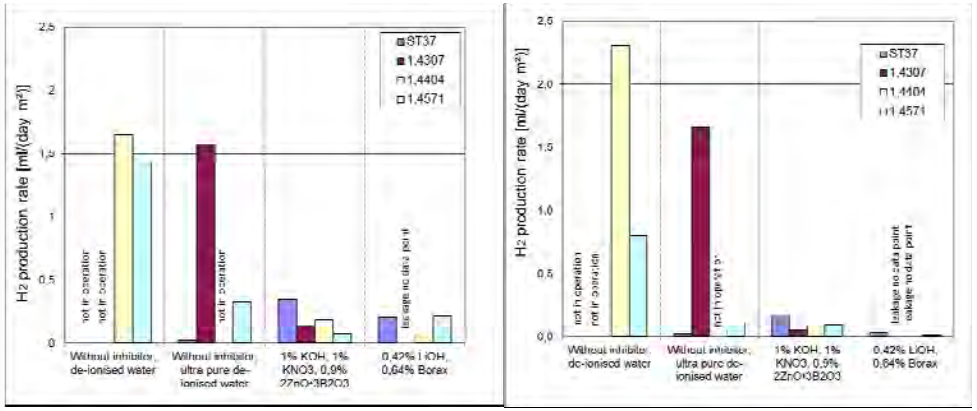
Tests with autoclaves using inhibitors

Final test with autoclaves with and without inhibitors were carried out in order to:

- observe possible thermal decomposition of ammonia at a temperature of 300°C **√ no decomposition detected!**
- investigate possible influence of the water quality on the corrosion and
- influence of inhibitors on the inert gas formation

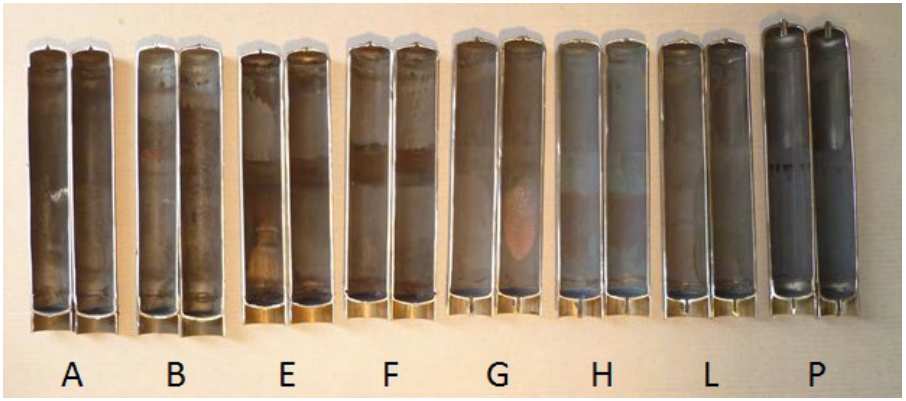
Tests with autoclaves using inhibitors

(x = 10%; t = 220°C)



22.12.2010 – 27.01.2011 10.02.2011 – 12.04.2011

Probes after Tests



All probes show thin corrosion layer – no significant difference between probes
According to calculation (based on measured amount of H_2): ca. 0.001 mm

Summary NH_3/H_2O Dissociation & Corrosion

- No thermal dissociation of ammonia has been detected up to temperatures of < 300°C
- A large initial hydrogen production rate which decreases with time has been observed
- Mild carbon steel (ST37) has shown significantly lower hydrogen production rates compared to stainless steel
- Further work is necessary in order to investigate possible precautions
- Inhibitors reduces production of inert gases slightly
- A follow up project should be initiated

Danksagung

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Danke für Ihre Aufmerksamkeit