New Corrosion Inhibitors and on-site Service Possibility for LiBr-Absorption Chillers

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What is corrosion and what are inhibitors?

- Solutions state of the art
  - Research on alternatives
    - New approach and linking to works from other scientific fields
  - Tests
    - Laboratory tests
    - Field tests + results
- Proof of the protective effect
  - Evaluation of laboratory tests
- New on-site service possibility
- Conclusion and outlook

What is corrosion and what are Inhibitors?

- Conditions in the machines
  - Lithium bromide solution with 54% salt by mass
  - Rough vacuum
    - Negative relative pressure
    - Leakage causes air infiltration
  - Several different metal materials
    - Formation of local elements
  - Temperatures up to 200 °C (triple effect)
    - Acceleration of chemical reactions

CORROSION!
Solutions state of the art

Effects of chemical inhibitors (example Iron)

1. Avoiding of inhomogeneous magnetite layer
2. Formation of stable single-phase protective layers
3. Formation of stable multi-phase protective layers

Inhibitors (examples)
- Chromates
  - Used before 2000
  - restricted
- Nitrates
  - Formation of NH₃
- Molybdates
  - Advaguard 750® A/B

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S.Feja; Nürnberg Messe, New Corrosion Inhibitors and on-site Service Possibility for LiBr-Absorption Chillers, 17.10.2018

Research on Alternatives

Liang 2006:
alkali wolframat

Vorma 1996:
H₃PMo₁₂O₄₁·2H₂O

Vorma 1996:
SbBr₅

http://www.wolfenthal.de/drucken
Advaguard® 750 A/B
- composition protected by patent
- Used primarily in York machines
  → Only few problems known
- ILK, others: No experience!

Verma 1996:
A: H₃PMo₁₂O₄₁·2H₂O
B: SbBr₃

Tests of the new inhibitors

- Laboratory test
  - Artificial aging over 10 days
  - Metals (Cu, S 235, 1.4404)
    + Silver solder
    + CuP - solder

- Temperature
  - Before project: up to 120 °C
  - NEW: 140 °C (Single Effect Chiller ~ 90 °C max.)
    → 32x acceleration of reactions
    → 1 year in 10 days, but

  Brandt tested in 2004: 200 °C; 2.8 bar
  - for Triple Effect ARM

ILK tested at 250 °C NH₃/Water in high-pressure autoclaves last year

Proof of the protective effect

- Evaluation of laboratory tests with CIP I
  - Artificial aging over 10 days

- Metal content in solution with ICP / OES

- Mass loss on metal strips
Evaluation of laboratory tests with CIP I
- REM/EDX + Cross-section preparation of copper samples removed with CIP I

Material copper
- Protective layer mainly of antimony

Material silver solder
- 45 % Silver, 27 % copper, 26 % zinc, ...

May be: first REM/EDX pictures of protective layers for copper in LiBr

Proof of the protective effect

Sb₂MoO₆ + Sb₄Mo₁₀O₃₁ + Sb₂Mo₁₀O₃ = CIP I

Tests of the new inhibitors

Field tests with partners:
- CIP I

Machine 1
- May 2016
  - 925 ppm copper found
  - Inhibitor added
- July 2017
  - 12 ppm copper
  - Where now?

Machine 2
- May 2016
  - 120 ppm copper
  - Inhibitor added
- December 2016
  - 2 ppm copper
  - Where now?

Sb₂MoO₆ + Sb₄Mo₁₀O₃₁ + Sb₂Mo₁₀O₃ = CIP I

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www.likdresden.de
WHY?

- Absorption machines have to be checked once a year
- Solution analysis have to be done in external laboratory

Expensive, time consuming

Development

- Ready to use sets for analysis
- Step by step instructions
- Maintenance instructions

Content

- Density and concentration of LiBr in absorption solution and refrigerant
- pH-value and Lithium Hydroxide concentration
- Dissolved Copper and Iron
- Inhibitors:
  - Molybdate
  - Chromate
  - Antimony based inhibitors

Analysis protocol and Maintenance instructions
Conclusion and outlook

- Development of two corrosion inhibitor packages
  - CIP I based on Antimony-Molybdenum-mixed oxides
  - CIP II Molybdenumtrioxid + „x“
- Protection effect proofed especially for copper & solders
  - Electrochemical tests
  - Laboratory tests (REM/EDX)
  - Field tests in real applications
- CIP I is registered as patent
- On site service for absorption chillers