

Hall 7A

CHILLVENTA

Chillventa Specialist Forums 2018 Chillventa Fachforen 2018

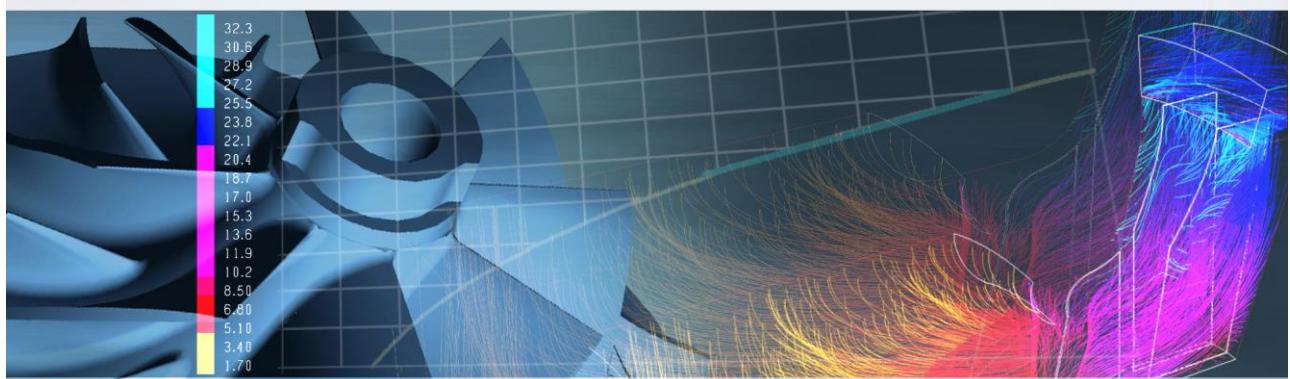
**CONNECTING
EXPERTS.**



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

1

ILK Dresden



Institut für Luft- und Kältetechnik Dresden gGmbH

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

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www.ilkdresden.de



► What is corrosion & 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 !

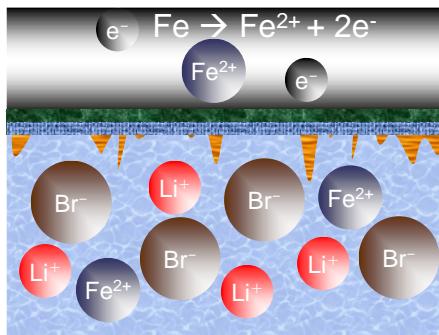
What is corrosion and what are Inhibitors ?



► 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

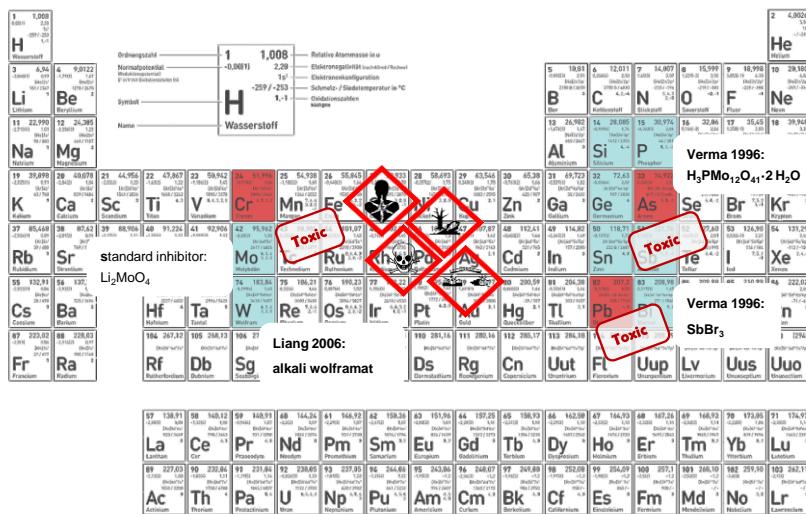


► Molybdates

- Advaguard 750® A/B



Research on Alternatives



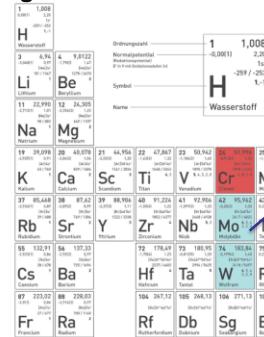
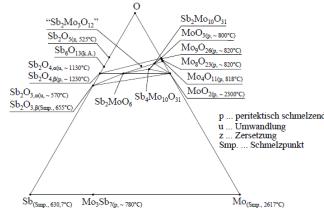
Research on Alternatives



► New Approach and linking to works from other scientific fields

► Advaguard® 750 A/B

- composition protected by patent
- Used primarily in York machines
- Only few problems known
- ILK, others: No experience!



Verma 1996:

- A: $H_2PMo_2O_4 \cdot 2H_2O$
B: $SbBr_3$



Darstellung und Charakterisierung ternärer Molybdate in den Systemen M - Mo - O (M = Sn, Pb, Sb); Dissertation; S. Feja – Dresden 2004

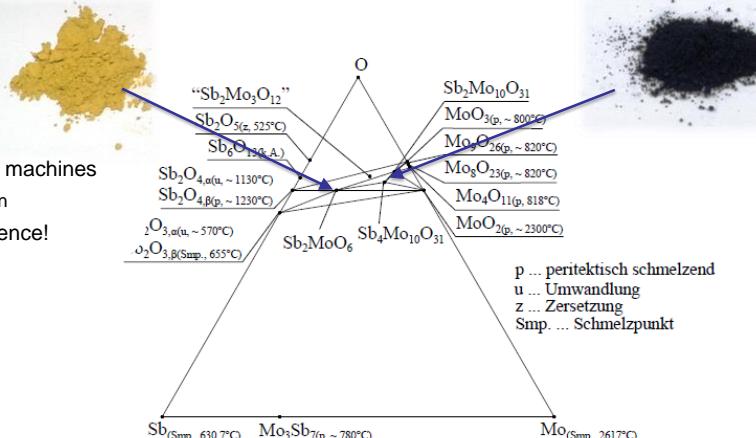
Research on Alternatives



► New Approach and linking to works from other scientific fields

► Advaguard® 750 A/

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Tests of the new inhibitors



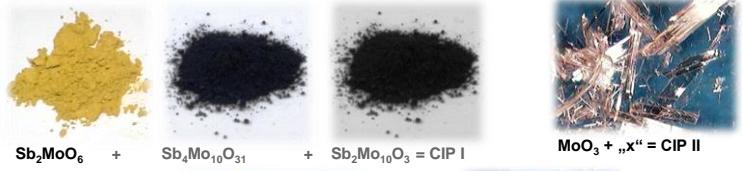
► Laboratory test

► Artificial aging over 10 days

► Metals (Cu, S 235, 1.4404)

+ Silver solder

+ CuP - solder



$\text{Mo}_3 + \text{"x"} = \text{CIP II}$

► 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

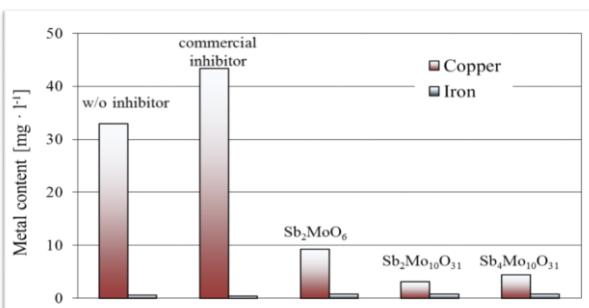


► Evaluation of laboratory tests with CIP I

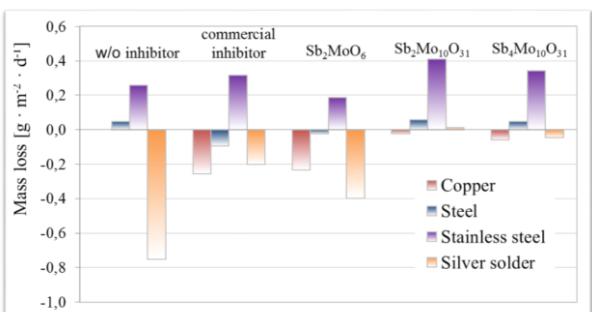
► Artificial aging over 10 days



► Metal content in solution with ICP / OES



► Mass loss on metal strips

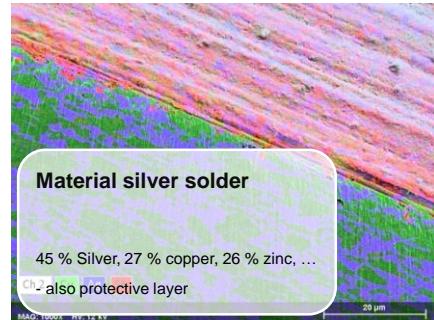
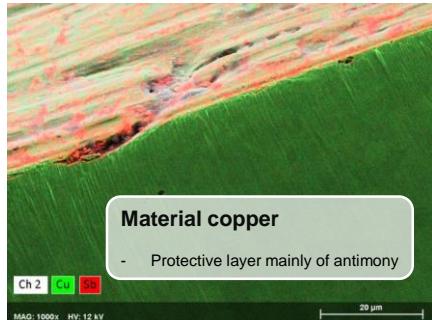


Proof of the protective effect



► Evaluation of laboratory tests with CIP I

- REM/EDX + Cross-section preparation of copper samples removed with CIP I



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

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?

fallen out →
← and/or deposited



ON-Site Service



► 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



ON-Site Service



► 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

Analyse des Absorptionsmittels - Lösungsmittellösung / Kühlerflüssigkeit			
Wärmespeisung	9	2. Wagung	3. Wagung
Masse des Leerküfers		9	Durchschnitt
Masse des vollen Küfers	1. Wagung	9	
Küfers	g/cm³		
Dichte	%		
Konzentration			Bemerkung
pH Wert und Alkalinität			
pH Wert mit Papier	Tropfen	Bodenreduktor	mg/l
Alkalinität		2. Test	
Inhibitoren			
Antimon	1. Test	Bemerkung	
Molybdate		Sollkonzentration	mg/l
Metalls		Bemerkung	
Kupfer			
Eisen			
Analyse des Küfersmittels	9	2. Wagung	3. Wagung
Dichtemessung		9	
Masse des Leerküfers	1. Wagung	9	
Masse des vollen Küfers	g/cm³		
Dichte	%		
Konzentration			Bemerkung
Figur 1: Beispieldokument für die Zustandsüberwachung einer Absorptionsanlage			

Durchführung		
- Füllen Sie 2,5 ml pure Absorptionslösung mit einer Pipette in das Reagenzglas.		
- Gießen Sie 1 ml Eisengelbe mit 1 M HCl zur Absorptionslösung.		
- Eine Rose-Purpurfarbung zeigt Kupfer an.		
Vergleichen Sie die Färbung der Lösung mit der Farbtabelle für den Kupfertestweis.		
Tabelle 3: Handlungsempfehlung bei Kupferhalten im Küfersmittel		
Klar	1 < mg/l	Handlungsempfehlung
Leicht Rosa	2-20 mg/l	Keine Handlung notwendig
		Beginnen Korrosionstest
Schwach Purpur	20-50 mg/l	Keine Handlung notwendig
Purpur	50-100 mg/l	Beginnen Korrosionstest
Stark Purpur	> 100 mg/l	Kupferwerte durch Kontrollen lassen. Wenn möglich Zugabe eines Kupfersalzes. Start Korrosion am Kupfersalzen. Analyse am ILK-Korrosionstest.

Conclusion and outlook



Gefördert durch:



aufgrund eines Beschlusses
des Deutschen Bundestages

- ▶ Development of two corrosion inhibitor packages
 - ▶ CIP I based on Antimony-Molybdenum-mixed oxides
 - ▶ CIP II Molybdenumtrixoid + „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



Vielen Dank für's Zuhören

Fragen ?

CHILLVENTA
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Visit us in hall 5
at stand 5-123

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