

Finnish Recovery Boiler Committee

SKYREC STEERING COMMITTEE MEETING V

TIME March 24th, 2009 10.00 – 15.30

PLACE Pöyry House, Jaakonkatu 3, Vantaa

PARTICIPANTS

Steering group:

Lasse Koivisto	Andritz Oy, Varkaus
Hiroshi Matsuo	Sumitomo Metals, London, UK
Matti Tikka	UPM-Kymmene Oyj, Kymi, Chairman
Mika Paju	Oy Metsä-Botnia Ab, Joutseno
Timo Peltola	Sandvik, Helsinki
Keijo Salmenoja	Finnish Recovery Boiler Committee, Rauma
Kalle Salmi	Metso Power Oy, Tampere
Timo-Pekka Veijonen	Stora Enso Oyj, Pulp Competence Center Imatra

Group members without a right to vote:

Reijo Hukkanen	Stora Enso Oyj, Oulu
Esa Vakkilainen	LUT, Project coordinator, Lappeenranta
Outi Pisto	Finnish Recovery Boiler Committee, secretary

Marja Heinola	Andritz Oy, Kotka
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During the item 7.3.	Jouko Hildén	VTT, Espoo
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APPENDIXES

- I Project budget
- II Jouko Hildén, VTT: Organic amines and NOM in Steam Water Cycle

DISTRIBUTION

Steering committee and their substitutes
Durability Sub Committee
Board of the FRBC
OMP, MNN, EPT/Arkisto

1 ABSENCES

Martti Korkiakoski ja Sanna Siltala were not able to attend the meeting.

2 MEMO OF THE PREVIOUS MEETING

Hiroshi Matsuo noted that material HR11N chosen for the furnace material tests with diameter 63.5 mm is not immediately available but the tubes in the stock are of diameter 38 mm. Outi Pisto to take action with Boildec Oy.

The memo of the previous steering group meeting was accepted.

3 BUDGET

Sumitomo's attendance to the project increased the project budget with 105.000 € and is 805.000 €

Esa Vakkilainen went through the project budget and the ordered projects, see Appendix I.

4 SCHEDULE

The original schedule of the project is January 1, 2008 – June 30, 2010. Starting of the project was delayed because the decision of the project funding was received from Tekes in late April 2008.

It is possible to apply a one year extension to the project. The secretariat will prepare to apply for extension if needed.

5 FEES FOR 2009

Following time schedule for participation fees for SKYREC project was agreed in the Finnish Recovery Boiler Committee Board meeting 3/2008.

	2008	2009	2010
August	15.000 €	15.000 €	-
February	-	10.000 €	10.000 €
Sum	15.000 €	25.000 €	10.000 €

Sumitomo has accepted FRBC's proposal to attend the SKYREC project by accepting to pay 55.000 € of the preceding project SoTu II and the costs of SKYREC project (50.000 €). The sum 105.000 € is divided evenly to the years 2008 - 2010. Full 105.000 € has to be paid by Sumitomo before the detailed results of the SoTu II are given.

The first invoice (35.000 €) is sent and payment is received. The second invoice (35.000 €) will be sent in August 2009.

6 SUPERHEATER MATERIALS TO BE TESTED

6.1 Laboratory tests of superheater materials

The following superheater materials have been chosen to be tested in laboratory tests:

- 10CrMo9-10 (T22)
- T91
- Sanicro 28
- HR11N

Testing temperature is not yet decided.

6.2 Mill tests of superheater materials

	Andritz	Botnia	Metso	Sandvik	Sumitomo	S-E	UPM	Chosen materials
AISI 347	x		x	x		x	x	x
Overlay welded		x						
San 67				x		x	x	x
Alloy 28 (HR21, San 28)	x		x	x		x		x
TP310	x	x		x		x		x
HR11N	x				x	x		x
T91			x					
Super 625*	x	x	x		x		x	x
San 25		x						

* 50 Ni – 21.5 Cr – 17.5 Fe – 9 Mo

Reference material is needed.

7 ONGOING PROJECTS

7.1 WP3: Increase of steam pressure

7.1.1 TP3: Field tests of candidate furnace materials for high temperatures

The work has been ordered from Boildec Oy. The work covers 4 tests.

At the first phase the furnace material tests are conducted in one recovery boiler at Metsä-Botnia mill in Joutseno and 3 tests are conducted. Material testing temperature in all tests is 440 °C. Following materials have been chosen for the tests.

Table 7.1. Furnace test materials.

Test 1: April 2009	Test 2:	Test 3:
AISI 304L (reference material)	AISI 304L (reference material)	AISI 304L (reference material)
AISI 310S	Sandvik 67	Sumitomo
Sanicro 38	HR11N	Open
Sanicro 28	Welded 25 % Cr	Open

Sandvik has supplied the materials for the first test. The first test is going to be started in April 2009.

At the second phase additional tests could be done with 4 different materials at two different temperatures (lower temperature) if needed. Second phase has not been ordered yet. Ordering is actual when results from first phase are available.

7.1.2 TP2: Effect of the furnace heat load on the recovery boiler designing

Heat transfer properties of the recovery boiler char bed – cooling rate simulation is ordered from LUT and is ongoing. The work is to be done by the end of August 2009.

7.2 WP2: Increase of steam temperature

7.2.1 TM3: Corrosion chemistry with high steam values

Laboratory tests of superheater materials:

Laboratory tests of corrosion chemistry with high steam values in reducing conditions are ordered from Åbo Akademi and are ongoing. The work is to be done by the end of 2009.

The materials chosen are presented in section 6.1 above. Following salt compositions are chosen to be tested:

- pure sodium sulphate (Na_2SO_4)
- Na_2SO_4 + potassium sulphate (K_2SO_4) + slightly Cl
- Na_2SO_4 + more Cl
- Na_2SO_4 + potassium sulphate (K_2SO_4) + more Cl

Comments:

One sample could be exposed also to oxidising conditions after the reducing period.

7.3 WP1: New recovery boiler concepts in electricity production

7.3.1 S1: Broadening RB fuel flexibility

The laboratory combustion tests have been done at Åbo Akademi. The work will be completed by the next steering committee meeting in June 3rd.

The decision of the continuation is done after the first 9 tests are conducted and the results analyzed.

7.3.2 S3: Recovery boiler as a once-through boiler – concept study

The study is ordered from LUT and is ongoing. The work is to be done by the end of January 2010.

In order to be able to utilise the results of this subproject in superheater material tests, it was agreed in the steering committee meeting I/2009 that the tasks 1 and 2 will be ready in June 2009.

7.4 WP4: Quality of boiler water and steam

7.4.1 V0: Literature survey on degradation of organic compounds

Jouko Hildén, VTT presented the literature survey on degradation of organic compounds, Appendix II.

Hildén will make a proposal of the continuation of the project to the next Durability sub committee meeting on May 7th.

7.4.2 V3: Development of water treatment and quality control

A study of the effect of the water quality and boiler chemicals on the corrosion problems of the recovery boiler air preheaters is ordered from Teollisuuden Vesi Oy and is ongoing. Mill tests will be carried out at Laminating Papers mill, Kotka starting on week 14.

7.5 Intermediate reports on the ongoing subprojects

Secretary will ask subproject workers to send an intermediate report on the ongoing project to the secretariat two weeks before the steering committee meeting covering:

- what has been done so far in the project
- what is to be done in the next period.

8 PROJECTS UNDER CONSIDERATION

8.1 WP2: Increase of steam temperature

8.1.1 TM2: Corrosion chemistry with high steam values

Reijo Hukkanen will ask a proposal from VTT for the superheater material mill tests.

3 – 6 materials are able to be tested in VTT test probes. VTT is able to do mill tests earliest in August 2009. VTT probe diameter is 48.3 mm or 63 mm. Testing temperature will be discussed with VTT.

The tests could be carried out in MB Joutseno boiler.

Comments:

If the test probes are located to the side wall of the recovery boiler instead of front wall, the fastening has to stand the stress caused by sootblowing.



8.2 WP3: Increase of steam pressure

8.2.1 TP1: Ceramic structural materials

University of Oulu will send a new proposal on laboratory tests of the ceramic structural materials to Reijo Hukkanen on week 13.

8.3 WP4: Quality of boiler water and steam

Boildec's proposal Recommendation on water quality control in recovery boilers is received, decision postponed till fall.

9 OTHER ISSUES

The Swedish-Norwegian Recovery Boiler Committee's three-year study on state-of the art recovery boilers "Förutsättningar För Framtidens Sodapanna – 3FS" (The opportunities of future recovery boilers) has been finished and the final report on the project was distributed to the steering committee members on cd. The report can be also ordered from Värmeforsk (<http://www.varmeforsk.se>).

Secretary will scan the booklet "Recommendation for the protection of recovery boiler 1978" and send it to the steering committee members.

10 NEXT MEETINGS

The next meeting will be held on June 3rd at 10.00 a.m. Secretary will confirm the place.

The next meeting after that will be held on September 8th at 10.00 a.m at Metso Power Oy, Tampere.

APPENDIX I

Project budget

SKYREC

		Tender	2008	2009	2010	
WP1	New recovery boiler concepts in electricity production					Ordered
S1	Broadening RB fuel flexibility					Reservation
	- AA: Broadening RB fuel flexibility part 1	7 500.00 €		7 500.00 €		Proposal
	- AA: Broadening RB fuel flexibility	25 000.00 €		10 000.00 €	15 000.00 €	Not ordered
S2	Increase of recovery boiler electricity production					
S3	Recovery boiler as a once-through boiler - concept studies					
	- LTY: Recovery boiler as a once-through boiler - concept study	33 800.00 €			33 800.00 €	
	- TTK: Recovery boiler as a once-through boiler - concept study	100 000.00 €				
		66 300.00 €				
WP2	Increase of steam temperature					
TM1	Analysis and utilisation of the existing information					
	- TTK (reservation)	25 000.00 €				
TM2	New superheater materials, material selection					
TM3	Corrosion chemistry with high steam values					
	- AA: Laboratory tests of superheater materials	37 000.00 €		37 000.00 €		
	- AA: Mill tests of superheater materials - probe development	15 000.00 €				
	- AA: Mill tests of superheater materials	83 000.00 €				
	- VTT: Analysis of the test materials					
	- Saver: Mill tests of superheater materials	20 000.00 €				
TM4	Suitability of superheater materials with high steam values					
		145 000.00 €				
WP3	Increase of steam pressure					
TP0	Analysis and utilisation of the existing information					
	- FRBC's material recommendation (KTR)	25 000.00 €				
TP1	Ceramic structural materials					
	- OY: Ceramic structural materials, field tests	4 000.00 €				
	- OY: Ceramic structural materials, laboratory tests	16 877.00 €				
TP2	Effect of the furnace heat load on the recovery boiler designing					
	- LTY: Heat transfer properties of the recovery boiler char bed	14 800.00 €		14 800.00 €		
TP3	Field tests of candidate furnace materials for high temperatures					
	- Boildec: Field tests of furnace materials	98 000.00 €	19 600.00 €	74 480.00 €	19 600.00 €	
	- Boildec: Field tests of furnace materials (reservation)	50 000.00 €				
	- VTT: Analysis of the test materials	29 000.00 €		19 000.00 €	10 000.00 €	
		220 800.00 €				
WP4	Quality of boiler water and steam					
V0	Analysis and utilisation of the existing information					
	- VTT: Literature survey on degradation of organic compounds	17 700.00 €	5 310.00 €	12 390.00 €		
V1	Development of the testing method of chemicals					
	- VTT (reservation)	40 000.00 €				
V3	Testing of oxygen scavengers					
	- VTT (reservation)	50 000.00 €				
V2	Layer formation in autoclave tests					
	- VTT: Effect of water quality and different chemicals on magnetite layer	65 000.00 €				
V3	Development of water treatment and quality control					
	- Teollisuuden vesi Oy: Effect of the water quality and boiler chemicals o	94 350.00 €				
		59 200.00 €				
	- Teollisuuden vesi Oy: Effect of the water quality and boiler chemicals o	24 600.00 €		24 600.00 €		
	- Boildec Oy: Recommendation on water quality control in recovery boile	11 200.00 €			11 200.00 €	
		208 500.00 €				
WP5	Coordination and other					
K1	Coordinator	4 000.00 €			4 000.00 €	
K2	Secretary services					
K3	Meetings and communication	15 690.00 €	2 690.00 €	8 000.00 €	5 000.00 €	
K4	Translations	10 000.00 €			10 000.00 €	
In total		670 290.00 €	27 600.00 €	207 770.00 €	108 600.00 €	

APPENDIX II

Jouko Hildén, VTT: Organic amines and NOM in Steam Water Cycle

Organic Amines and Natural Organic Matter in Steam Water Cycle

Jouko Hildén

Materials for power engineering



Teknologiasta liiketoimintaa

Organic Amines

- **Background of the literary survey:**
 - Properties of organic alkalizing amines used in Finland:
 - Base strenght
 - Distribution between water and steam
 - Degradation in steam water cycle
 - Estimate effect on condensate quality based on above data and degradation products
 - Estimate effect of amines on air heater corrosion
 - Include preliminary estimate of failure cases by Andritz Oy ja Metso Power Oy
 - Brief review of the role of natural organic matter ingress

Organic Amines

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Organic Amines

- **Organic matter in water steam cycle:**
 - Organic matter may be present as
 - unwanted impurity
 - natural organic matter by make-up water or cooling water inleak
 - residual from plant erection or by maintenance procedures
 - functional additive
 - alkalizing amines
 - organic oxygen scavengers
 - dispersant and chelants to reduce boiler deposits
 - polyamines – film forming

Organic Amines

- **Why use alkalizing amines as functional additive – some most important reasons listed in literature**
 - Reduction of corrosion generation and corrosion product transport into the boiler
 - Improvement in the feedwater purity, which results in decreased blowdown losses
 - Faster startups (lower corrosion product transport during start up)
- Why are the abovementioned advantages expected to be achieved
 - Increased pH in the condensing steam – due the more favorable distribution behavior of amines in comparison to ammonia

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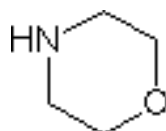
Organic Amines

- Alkalizing amines in Finland (Previous study 2007)

Alkaloiva amiini	Englannin kielinen nimi ja lyhenne	Kemikaaliseoksen kauppanimi
Sykloheksyyliamiini	Cyclohexylamine (CHA)	Boilex 510A ja Amercor 853s
2-aminometyylipropanoli	Aminoethylpropanol (AMP)	Boilex 510A ja Amercor 853s
Morfoliini	Morpholine (Morph)	KK-Amina 8026 ja Eliminox-Mor
Dietyyliaminoetanoli	Diethylaminoethanol (DEAE)	KK-Amina 8026
Etanoliamiinijohdannainen		KK-Amina 8026

Morpholine

Morpholine (Morph) is a weak base with molecular mass 87,12 g/mol and formula C₄H₉NO



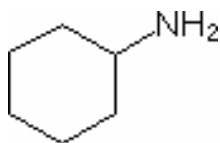
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Organic Amines

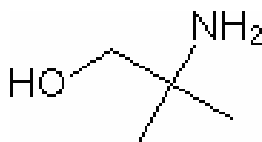
Cyclohexylamine

Cyclohexylamine (CHA) is a weak base with molecular mass 99,18 g/mol and formula $C_6H_{13}N$.



2-amino-2-methyl-1-propanol

2-amino-2-methyl-1-propanol (AMP) is a weak base, but much stronger than ammonia or morpholine. Molecular mass is 89,14 g/mol and formula $C_4H_{11}NO$.



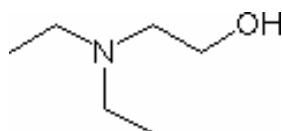
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Organic Amines

Diethylaminoethanol

Diethylaminoethanol (DEAE) or N,N-Diethylethanolamine is a weak base with molecular mass 117,19 g/mol and formula $C_6H_{15}NO$.



Ethanolamine

Ethanolamine (ETA) is a weak base, but much stronger than ammonia or morpholine. Molecular mass is 61,08 g/mol and formula C_2H_7NO .



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Organic Amines

- Volatility determines how amine distributes between water and steam
 - There is two notations generally used to describe volatility:

1. Relative Volatility = RV), described by formula:

$$RV = C_s/C_w$$

where C_s is concentration in steam and C_w is concentration in water

Note: Because only undissociated part of the amine is volatile the relative volatility is concentration dependent.

2. Distribution coefficient = K_d , described by formula:

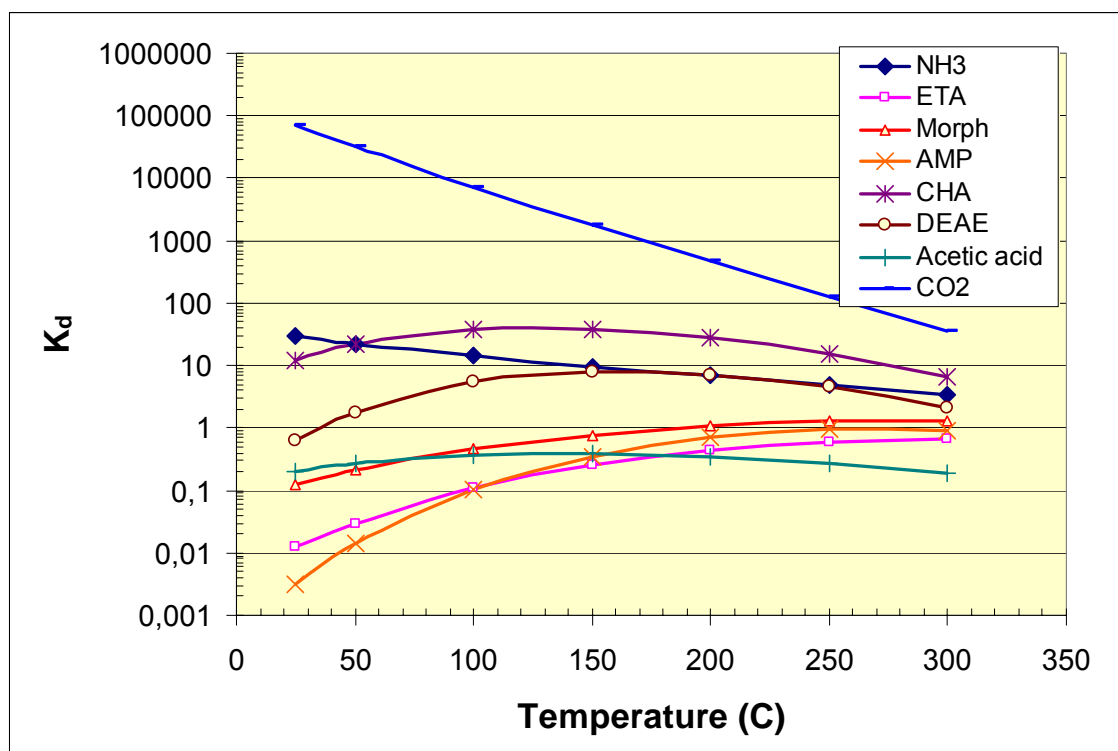
$$K_d = C_s/C'_w$$

where C'_w is concentration of undissociated part of the amine in water phase i.e. K_d is not concentration dependent



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Organic Amines

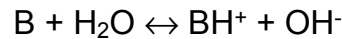


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Organic Amines

- Organic alkalizing amines are weak bases

- When dissolved in water amines partially ionize to form hydroxide ions (OH^-). The ionization reaction of weakly basic molecule B can be represented as:



- The base strength of the amine determines the ability of the amine to raise the pH of a water solution and is controlled by the unique ionization constant for that amine (K_b):

$$K_b = [\text{BH}^+][\text{OH}^-] / [\text{B}]$$

Amine with higher K_b will produce more OH^- ions per mole and will result in higher pH

- Since K_b is generally too small a number to express conveniently, ionization constants are often reported as $\text{p}K_b$ where

$$\text{p}K_b = -\log_{10} K_b$$

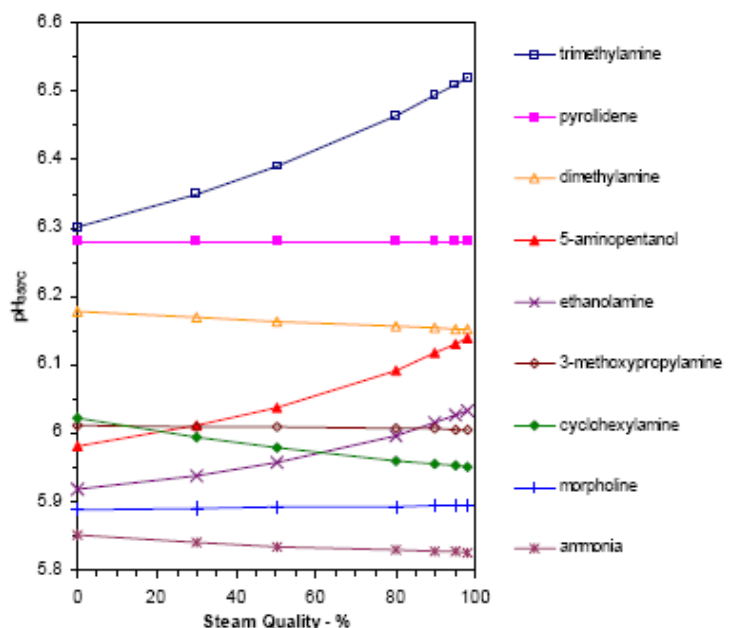
As a result, amine with lower $\text{p}K_b$ will have greater ionization and greater base strength

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Organic Amines

- "steam quality" 0% is pure water phase, and "steam quality" 100% is dry steam – (Note. Last values in picture are ~ 99%, i.e. wet steam water phase 1%)
- Concentration of chemicals used in calculation: 0,02 mmol/l (for ex. $\text{NH}_3 = 0,34$ ppm, morph = 1,74 ppm, CHA = 1,98 ppm)
- temperature 350 °C



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Organic Amines

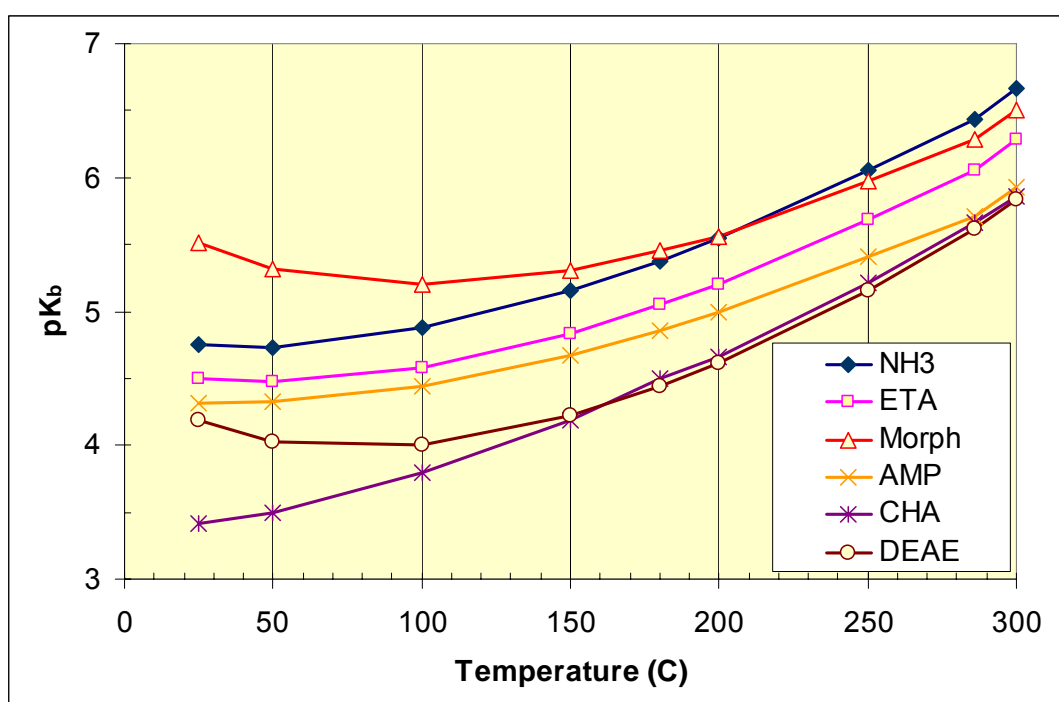
Calculated Values of Concentration Which Would Result in a pH of 6.2 at 270°C
(Balakrishnan, 2002)

Amine		Mol. Wt.	Concentration (mg/kg) for pH _{270°C} = 6.20	pH _{25°C}
Name	Symbol			
Ammonia	NH ₃	17.0	2.6	9.64
Ethanolamine	ETA	61.08	4.32	9.53
Morpholine	MOR	87.1	10.7	9.26
Dimethylamine	DMA	45.08	0.63	9.14
5-Aminopentanol	5AP	103.16	2.7	9.38
3-Methoxypropylamine	MPA	89.14	7.27	9.7
4-Aminobutanol	4AB	89.0	2.87	9.44
Pyrrolidine	PYR	71.1	0.97	9.13
Dodecylamine	DDA	185.4	5.64	9.46
Dipropylamine	DPA	101.2	1.76	9.24
Decylamine	DECA	157.3	4.75	9.46
Potassium Hydroxide	KOH	56.1	0.47	8.93



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Organic Amines



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Organic Amines

• Degradation of organic amines in steam water cycle:

- When introduced in the steam water cycle all organics also alkalizing amines are subject to hydrolysis and thermal degradation (decomposition and oxidation)
- An external supply of oxygen will accelerate oxidation process
- As a general rule volatile acidic degradation products are produced, such as acetic acid and carbon dioxide, but also other organic acids are found. The decomposition products result in lowering of pH
- Organic amines on the other hand produce, beside volatile acids, also ammonia. Both the remaining amine and ammonia dissociate into cations that will act to increase the pH

- Amine degradation kinetics can be measured and compared by deriving decomposition rate constants (k) by first order rate law:

$$d[A]/dt = -k[A]$$

- where [A] is amine concentration, t is time in seconds and k is rate constant (s⁻¹). Integrating we get first order rate law

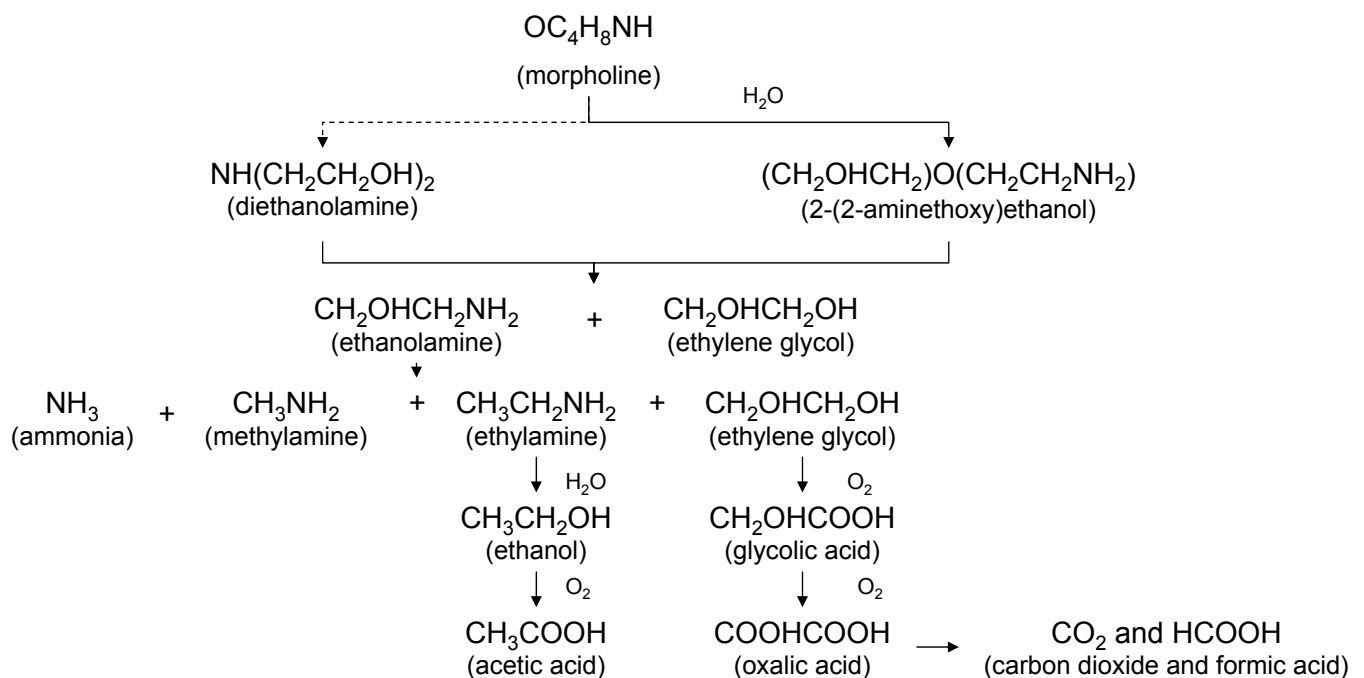
$$\ln C/C_0 = -kt \quad \text{or} \quad C = C_0 \cdot e^{-kt}$$

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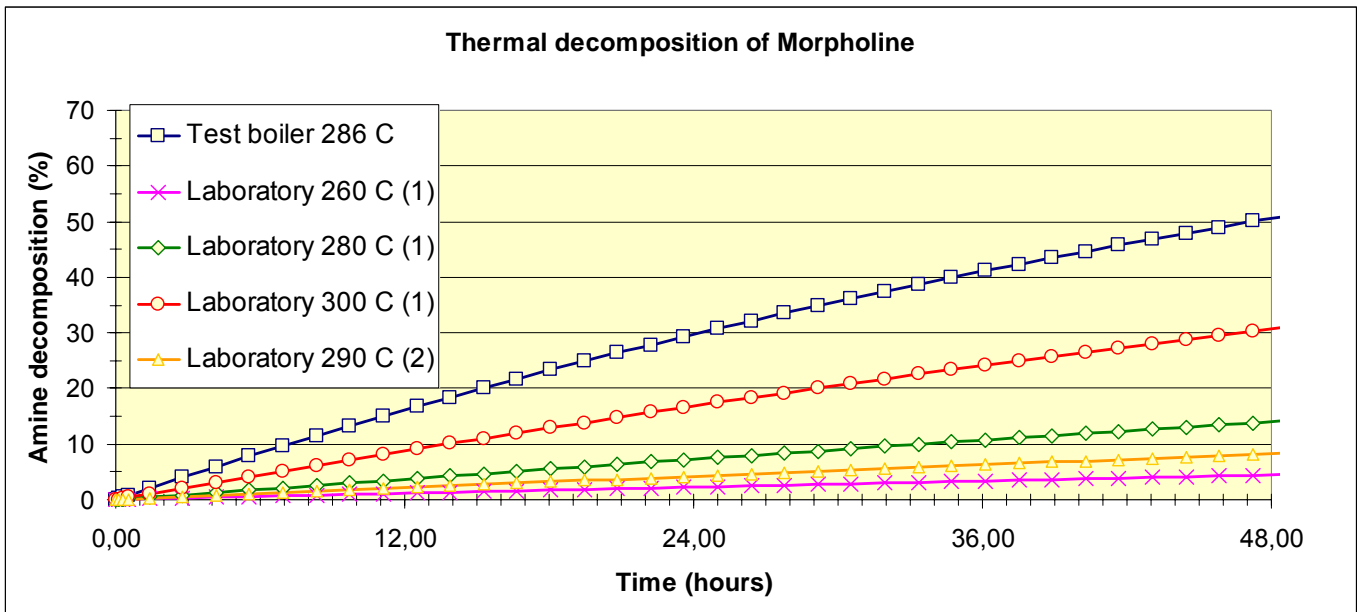


Organic Amines

• Break down of morpholine (Gilbert & Lamarre 1989)



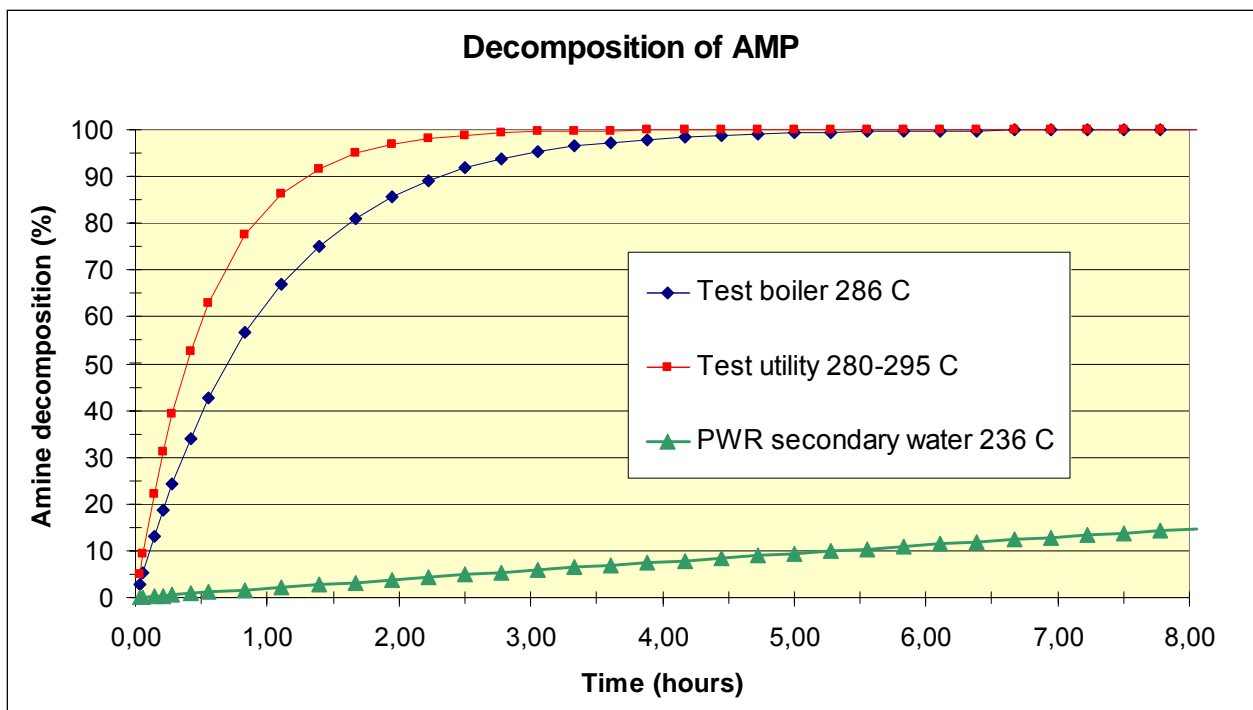
Organic Amines



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Organic Amines



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Organic Amines

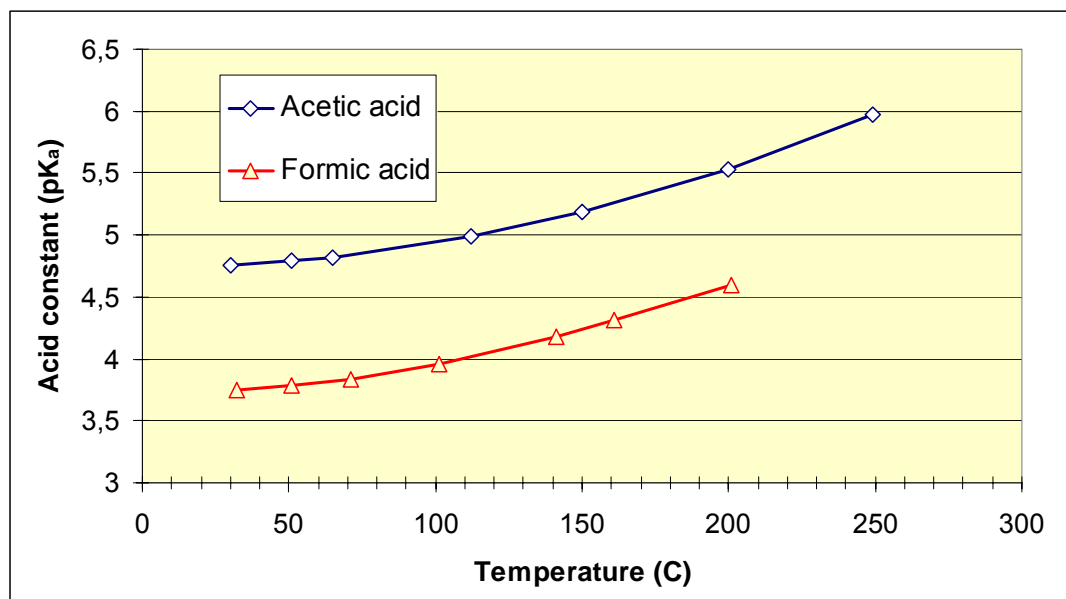
- Decomposition products of amines in test boiler feed water heater (FWH) . Temperature increase in FWH 140 – 280 °C

Amine	Ammonia (ppb)		Acetate (ppb)		Formate (ppb)	
	Amine only	Amine plus O ₂	Amine only	Amine plus O ₂	Amine only	Amine plus O ₂
NH ₃	---	---	20	9	16	16
DAE	71	54	5	10	4	6
ETA	-3	58	17	20	14	122
Morph	2	11	8	13	5	19
AMP	79	72	4	11	3	34
MPA	4	17	9	7	8	29
3HQ	5	34	10	15	10	120

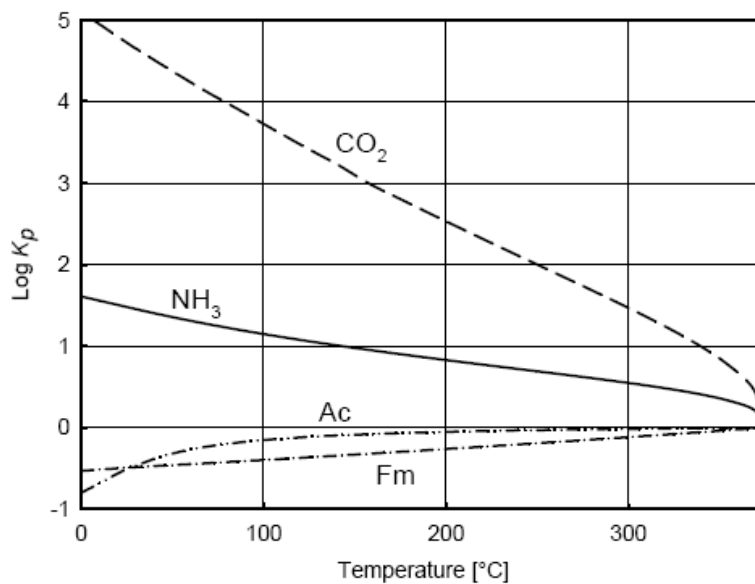
- AMP and DAE hydrolyze -> NH₃
- Oxygen increase ammonia formation with other amines also
- Deoxygenated conditions no remarkable acetate and formate production
- Oxygen increases formate production by ETA and 3HQ

Organic Amines

Organic acids



Organic Amines



Volatility of acetic and formic is quite stable over temperature range 100 – 350 °C and is a little less than water. Volatility of carbon dioxide is dependent on temperature and rises 5-log on cooling over the temperature range

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Organic Amines

• Natural Organic Matter – NOM

- NOM can enter water-steam cycle mainly by make up water.
 - Recovery boilers usually have high demand for make up water compared to utility boilers.
 - This calls for care to be taken to eliminate organic matter in water treatment.
- Amount of organic matter can be measured by TOC (total organic carbon) analyzers (down to ppb-level)
- TOC has (especially NOM) many forms and often associated with inorganic ions (chloride, sulfate etc.). Individual substances of NOM not feasible fractionated and identified.
- LC-OCD method to separate organic matter to seven different groups according to size

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Organic Amines

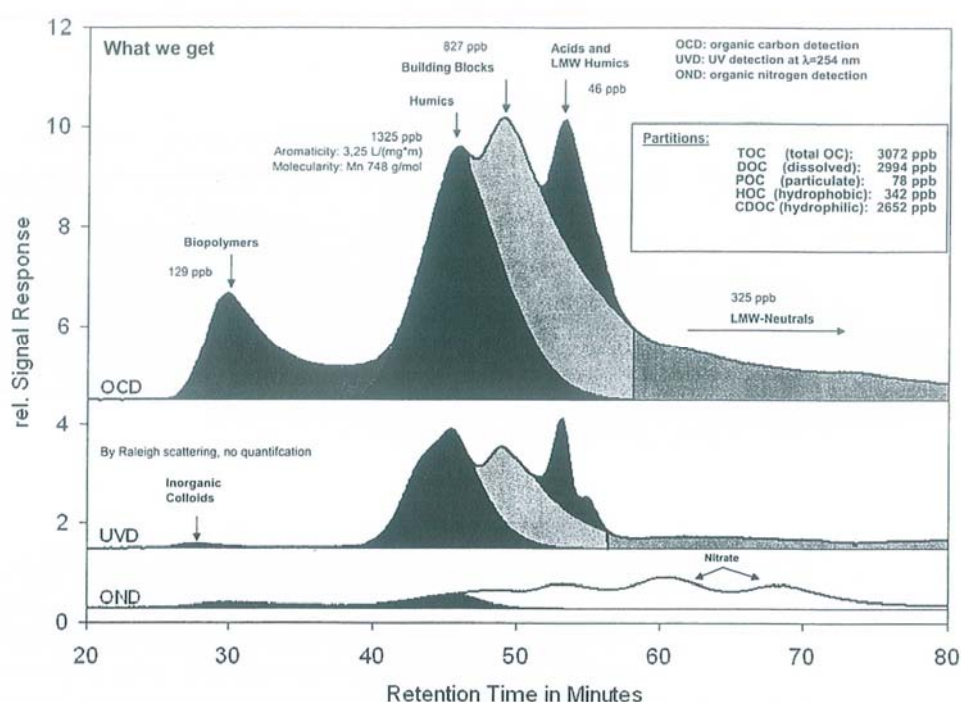
Liquid Chromatography – Organic Carbon Detection (LC – OCD)

- Particulate matter (size greater than 0,45 μm)
- Hydrophobics (HOC)
- Hydrophilic (CDOC), with sub division
 - a) Polysaccharides/Proteins/Biopolymers
 - b) Humics (including aromaticity and molecularity)
 - c) Building Blocks (hydrolysed breakdown products of humics)
 - d) Low-molecular weight neutrals and amphiphilics
 - e) Low-molecular weight organic acids



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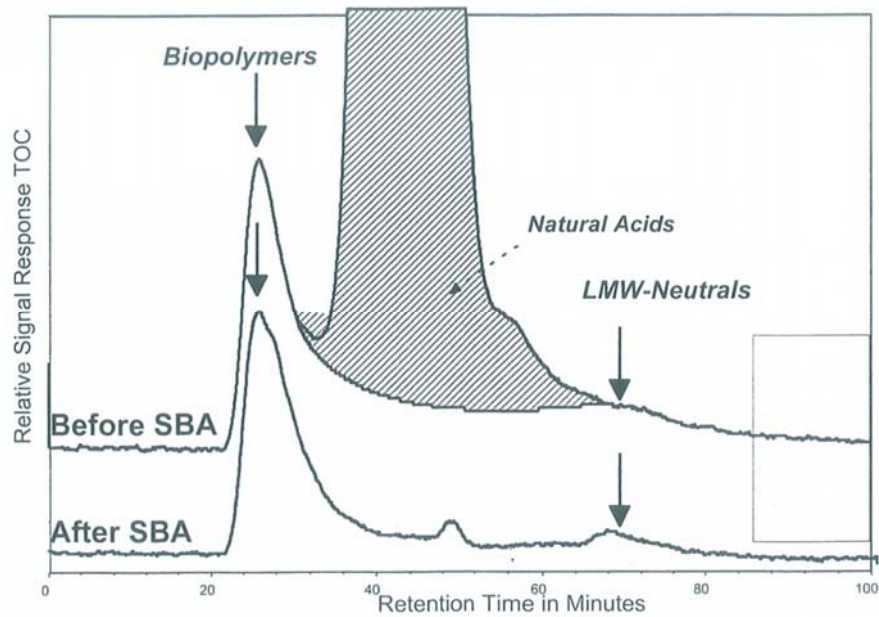
Organic Amines



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Organic Amines

- Ion exchange removing organic matter

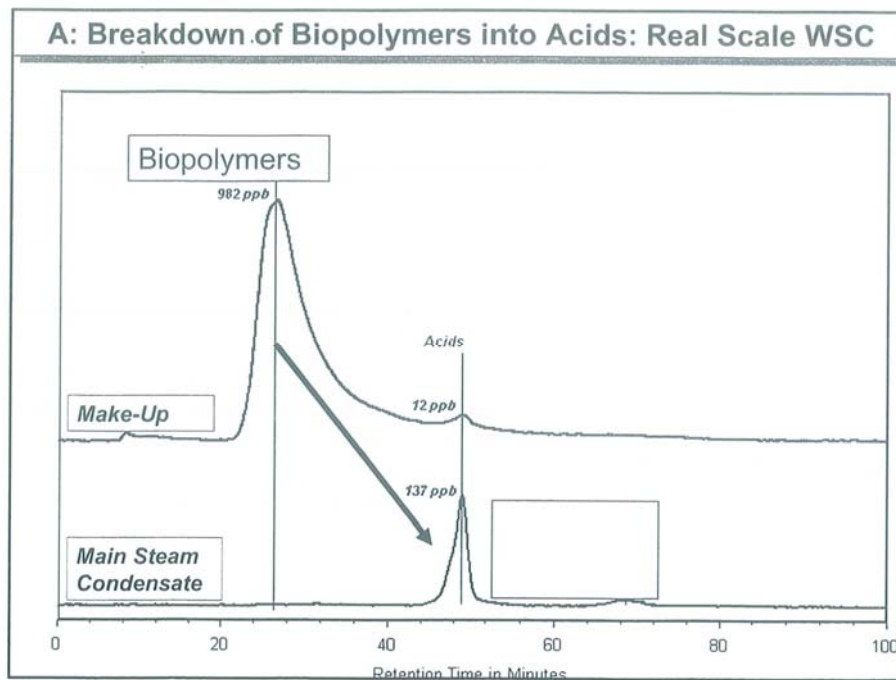


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Organic Amines

- Degradation of natural organic matter in steam-water cycle



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Organic Amines

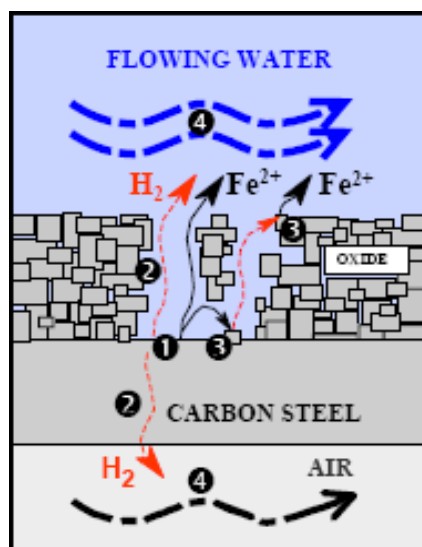
- **Effect of organic matter on materials of construction:**
 - Organic matter in the form of NOM or alkalizing amines, polyamines or organic oxygen scavengers is not harmful for materials of construction.
 - Greatest effect of organic matter is caused by its break-down products – low molecular mass organic acids (LMMOA), carbon dioxide and inorganic acids (formed as a result of inorganic ions bound to organic structure)
 - Above mentioned cause changes in pH, especially condensate pH on varying steam quality.
 - Most pronounced corrosion mechanism enhanced by organic matter, by affecting pH is concluded to be Flow Accelerated Corrosion (FAC)

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Organic Amines

- FAC occurs in water and water-steam mixtures (single-phase FAC and two-phase FAC) .
- FAC does not occur in dry steam.



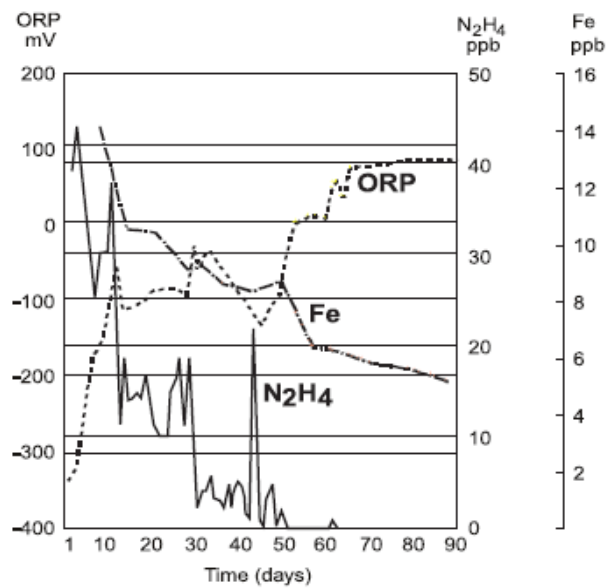
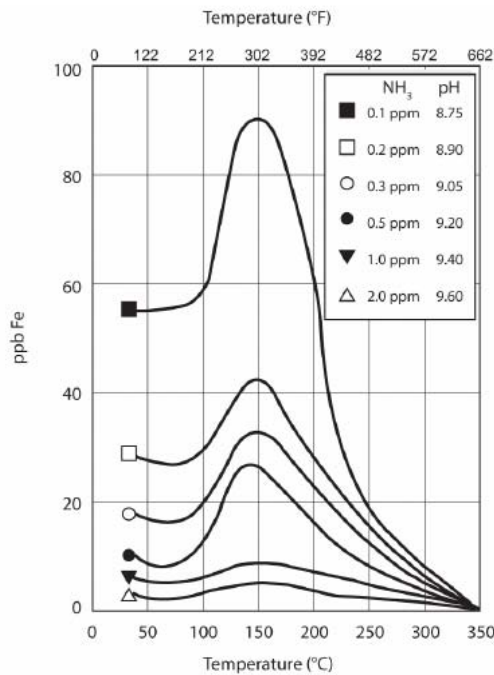
1. Steel oxidation at metal/oxide interface:
 - soluble ferrous ions: $\text{Fe} + 2\text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{OH}^- + \text{H}_2$
 - and magnetite: $3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2$
 it is assumed that one-half of the total amount of oxidized iron is converted into magnetite at the metal-oxide interface
2. diffusion of:
 - iron soluble species through the oxide layer porosities from the metal surface to the main water flow,
 - hydrogen produced at the metal-oxide interface into water via the oxide porosities (or through the steel),
3. dissolution-reduction of magnetite at the oxide/water interface:

$$\frac{1}{3}\text{Fe}_3\text{O}_4 + (2-b)\text{H}^+ + \frac{1}{3}\text{H}_2 \rightarrow \text{Fe}(\text{OH})^{(2-b)+} + (\frac{4}{3} - b)\text{H}_2\text{O}$$
4. diffusion of soluble iron species in flowing water from the oxide-water interface and hydrogen transfer in air by convection.

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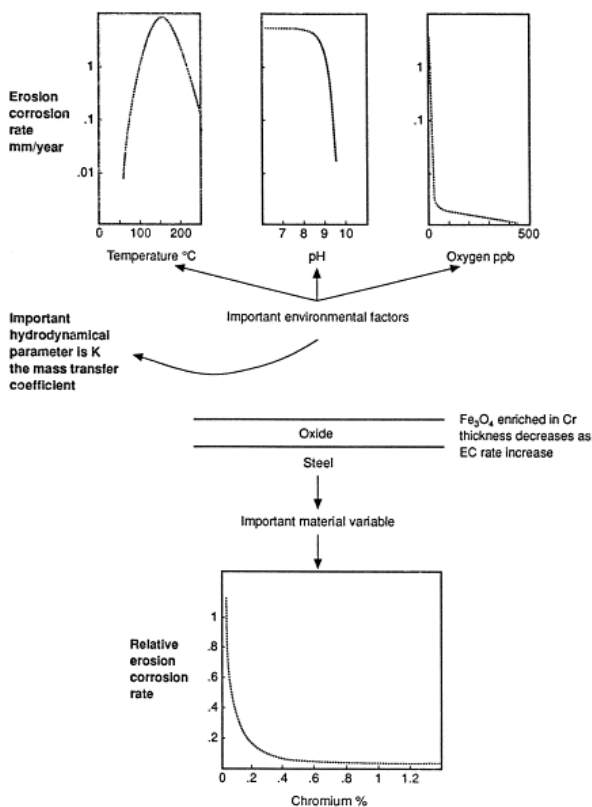
Organic Amines



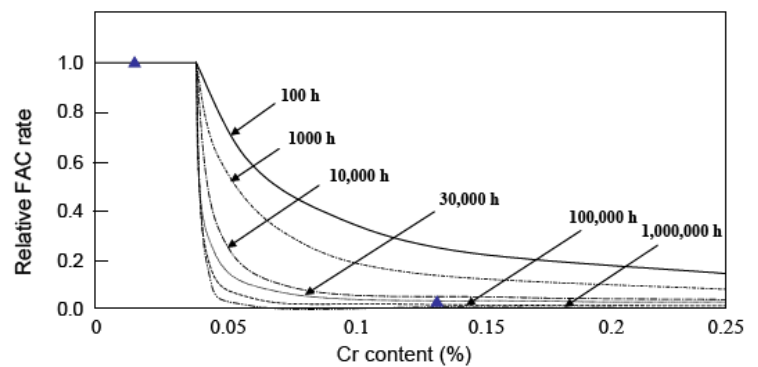
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Organic Amines



Schematic effects of important variables on flow assisted corrosion of carbon steel in water (Poulson, B. Wear, 233-235 (1999). 497-504)



"Bouchacourt" model for chrome content and exposure time effect on relative FAC rate with carbon steels.

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Organic Amines

• Conclusions

- Many alkalizing amines have favourable distribution coefficient compared to ammonia
- Amines degrade thermally producing volatile acids, but amine provides cations for counterbalance
- NOM degrade partly thermally and form volatile acids, but provide no cations for counterbalance.
- NOM can also cause ingress of inorganic anions – chlorine -> hydrochloric acid formation
- All organic increase cation conductivity in the cycle (may mask ingress of contaminants from other sources)
- Amines can affect condensate polishers
- Organic treatment chemicals not generally included in Water Conditioning Guidelines
 - VGB and EPRI Perspective: Organics not needed

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Organic Amines

• Conclusions

- Limit values for organics difficult to set
 - No conclusive evidence that breakdown products of TOC are harmful to materials of construction
 - Type of TOC must be taken into account
 - Type of cycle chemistry has an impact of breakdown of TOC
- However VGB R450 L (2004) states dissolved organic carbon (DOC) content in make-up water should not exceed 0.2 ppm. It is recommended to strive for less than 0.1 mg/l. (the knowledge of the type of organics is very important and not the sum parameter DOC). Even the lowest value might be too high in special cases, depending on the nature of organic matter and make-up water demand.
 - > High make-up rates require a minimization of the DOC content

Summary: Limits shall be determined plant specific

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Organic Amines

• Conclusions

- By literature survey and air heater corrosion cases it is estimated that the failures are caused by two-phase FAC.
 - Failures occur on temperature range 140 – 180 °C
 - Failures occur on two-phase zone
 - Failures occur on areas where equipment geometry promotes turbulent flow
 - Environment and failure mode are similar compared to air cooled condensers and low pressure feed water heaters in fossil boilers

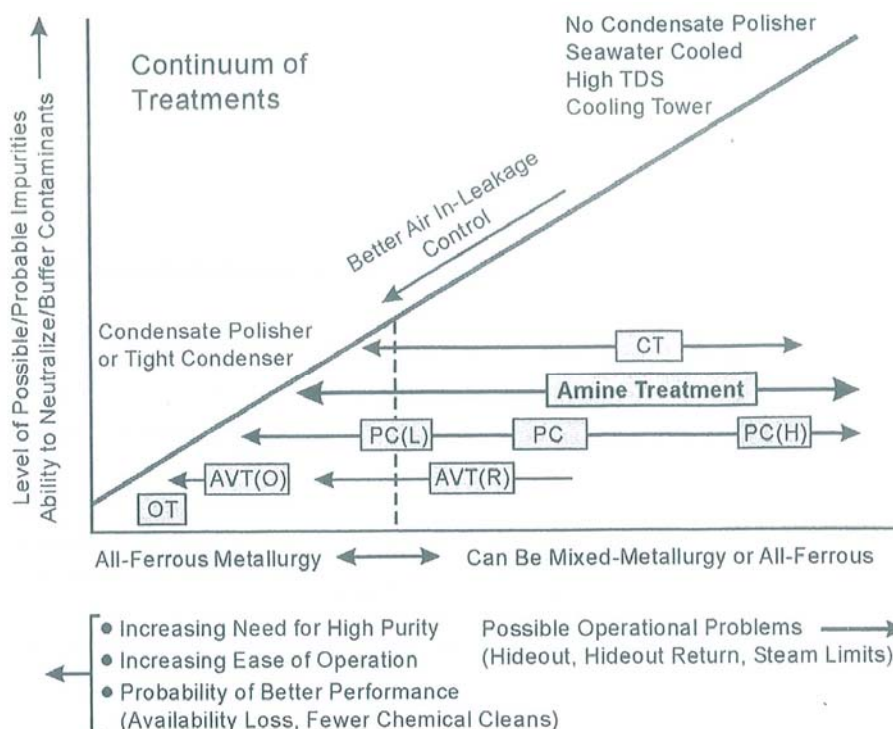
• Prevention of FAC

- For air cooled condensers the current approach is to operate with higher pH in the range of 9.6 to 9.8 or even above.
- Dimensioning or structural means to reduce turbulence
- Use of chromium alloyed construction materials (minimum 1,25 % recommended) – If two phase FAC exists chromium alloyed steel is probably most cost effective solution in utility boilers and HRSG's [48] – (this will of course just address FAC locally and not the root cause of the problem)
- Local pH adjustment for ex. Feeding amine to air heater steam line.



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Organic Amines



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