Cetamine® Technology

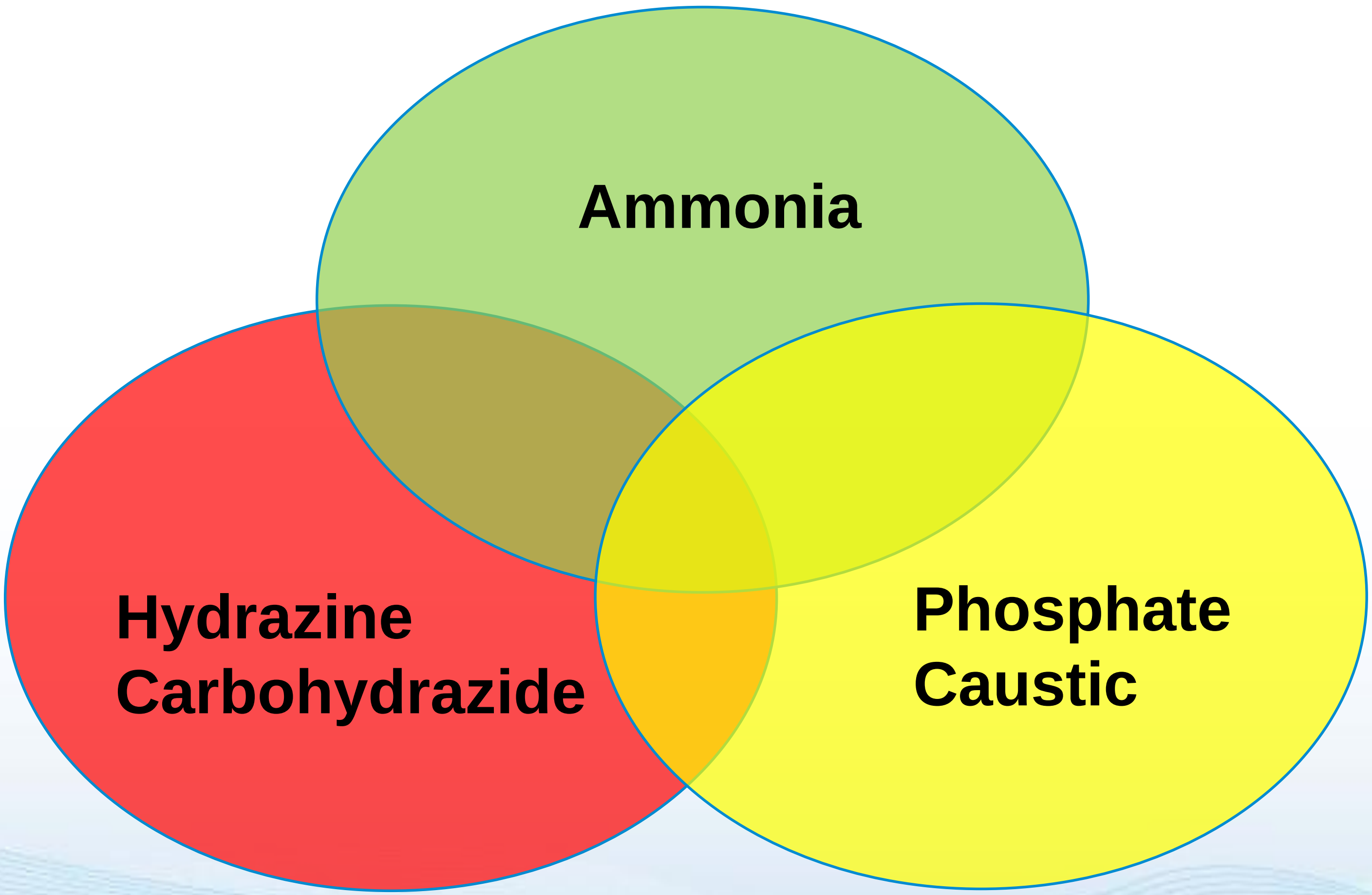
Jubail Corrosion & Materials Engineering Forum

April 2017

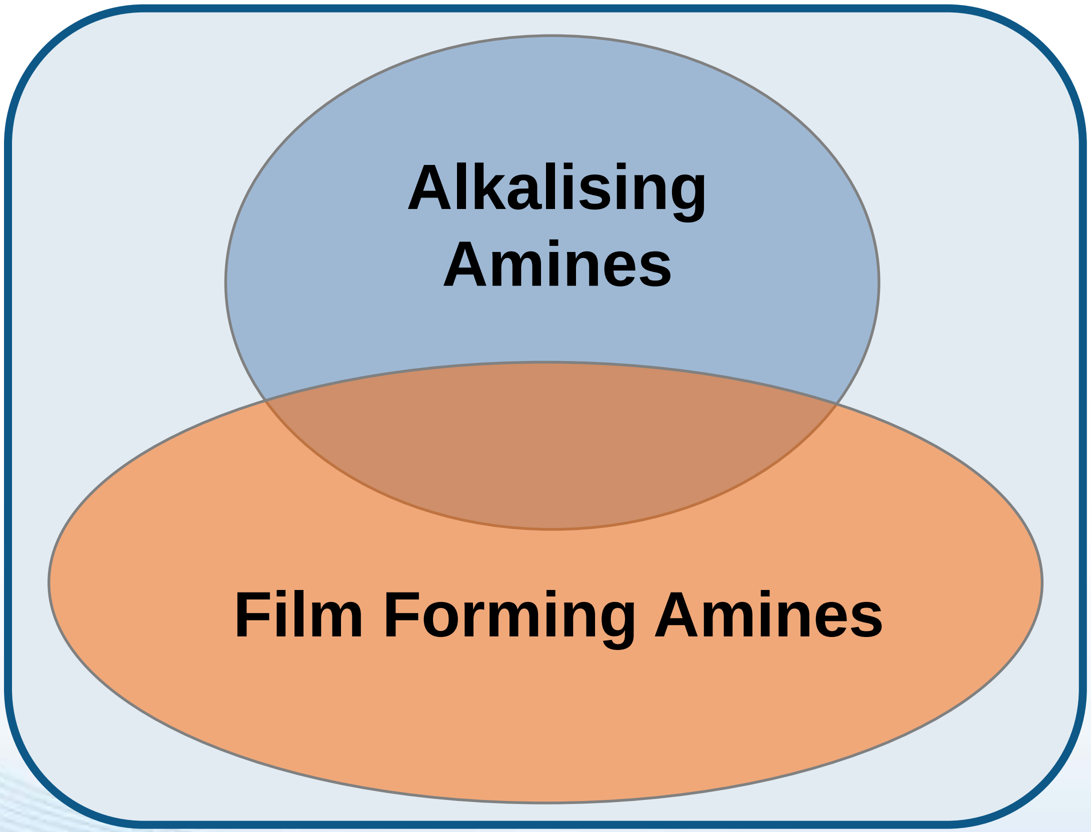
Presenter : Dave Johnson

BOILER WATER ADDITIVES

Taditional treatment concept



Cetamine® Technology



All-in-one product concept to treat the whole water steam cycle

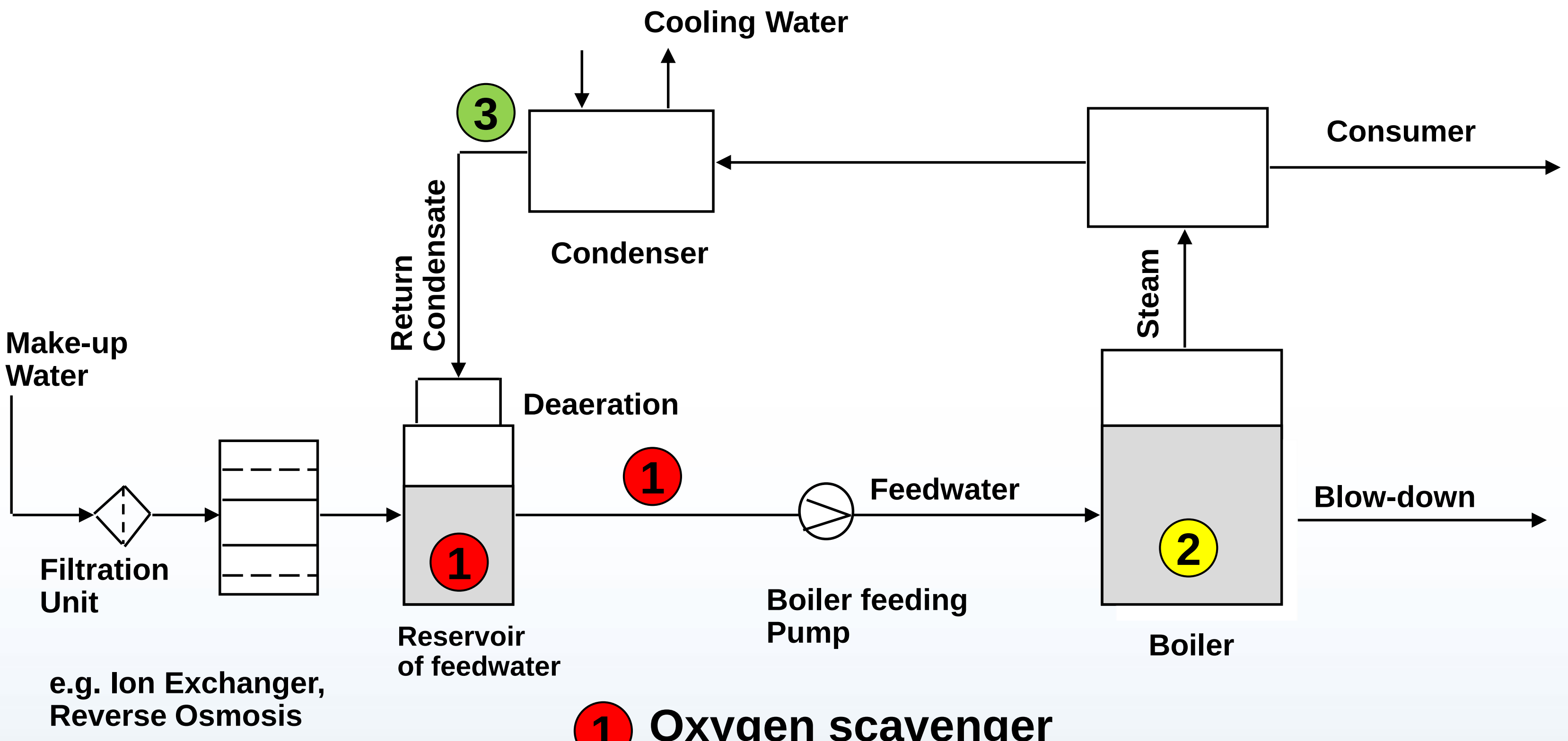
CETAMINE® TECHNOLOGY

Boiler Water Treatment with Film Forming Amines
Combination of three modes of action

- pH value adjustment in feedwater, boiler water and steam/condensate system by means of **Alkalizing Amines**
- Protection of the complete system due to film formation in feedwater tank, feedwater line, boiler water and steam/condensate system by means of **Film Forming Amines**
- Cleaning effect on metal surfaces with removal of existing deposits by means of **Film Forming Amines** and **Dispersants**

PRODUCTS & DOSING POINTS

TRADITIONAL TREATMENT CONCEPT



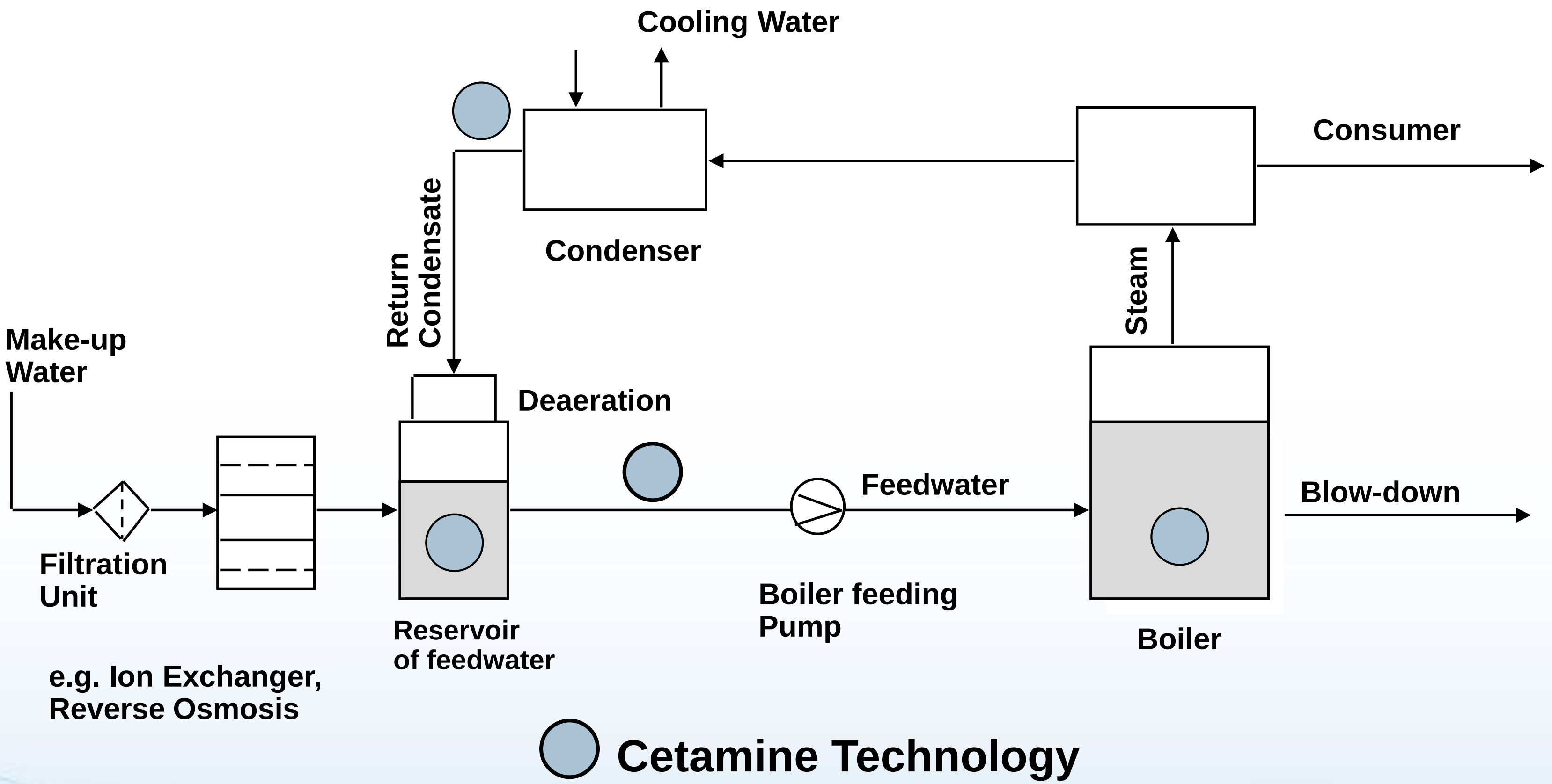
1 Oxygen scavenger

2 Internal treatment

3 Steam treatment

PRODUCTS & DOSING POINTS

CETAMINE® TECHNOLOGY



CETAMINE® FILMING AMINE (CFA)

$$R^1\text{-}[NH\text{-}R^2\text{-}]_n\text{-}NH_2$$

R^1 is an unbranched alkyl chain with 12 to 18 carbon atoms

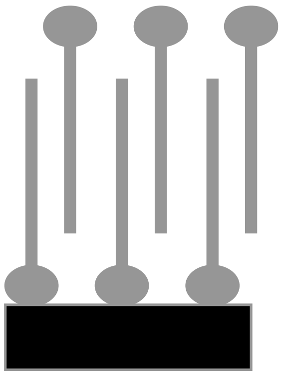
R^2 is a short-chain alkyl group with usually 1 to 4 carbon atoms

n is between 0 and 7

BENEFITS OF CETAMINE® TECHNOLOGY

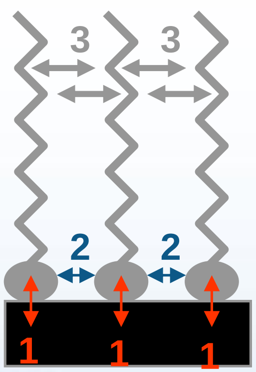
- Film formation on metal surfaces
- Magnetite layer stabilization
- Improved heat transfer
- Online cleaning effect
- Compatibility with online sensors
- Cetamine® Photometric Method
- Patent (EP 774017) on polymer containing Cetamine® products
- All Organic Product Concept
- Wet and dry lay-up of industrial systems
- Savings in energy and water

FILM FORMATION ON METAL SURFACES



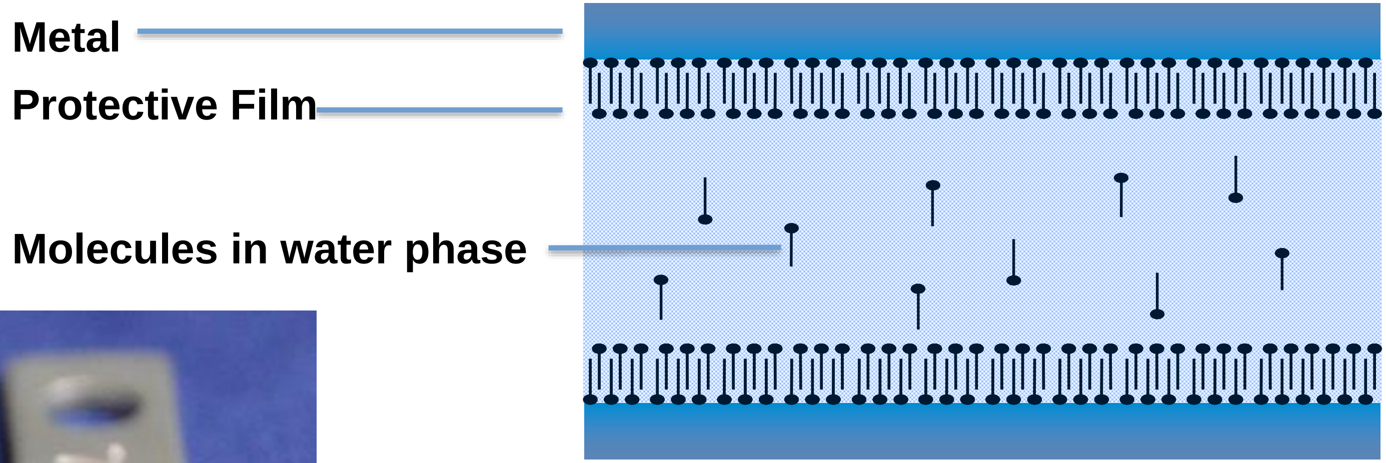
- Adsorption and Formation of a Protective Film on Metal Surfaces

- Hydrophobic Barrier between Water and Metal



1. Adsorption
2. Ion - ion
3. Hydrophobic bond

FILM FORMATION ON METAL SURFACES



FILM FORMATION ON METAL SURFACES

CORROSION PROTECTION UNDER ACIDIC CONDITIONS

VIDEO DELETED FOR FILE TRANSFER

Test Conditions

c(acetic acid)	= 2 ppm
pH	= 4.7
T	= 80 °C

untreated

Cetamine® pretreated

Fast motion of 40 minutes

MAGNETITE LAYER STABILIZATION

SHIKORR REACTION

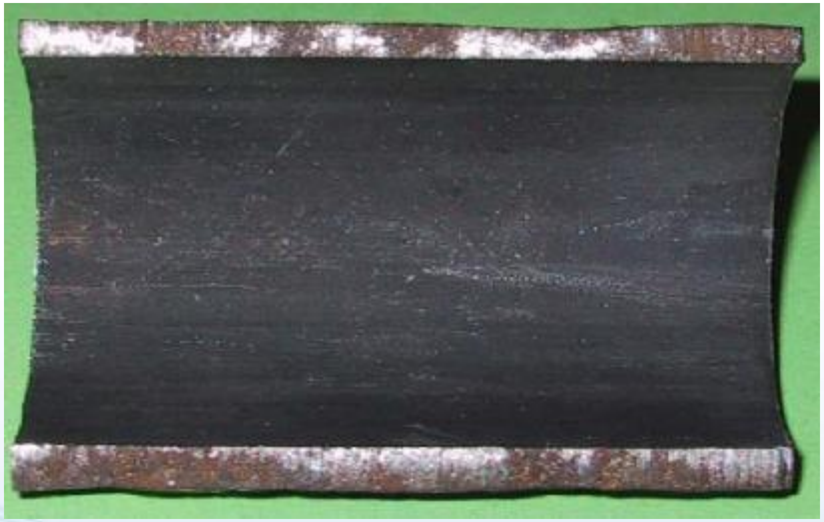
At high temperature the oxidizing effect of water enables magnetite production. The Shikorr reaction:

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

Dissolved Oxygen acts as Catalyst

Takes place at temperatures > 100 °C
Reaction is very fast at temperatures > 200 °C

Thick and porous, stable Magnetite layer
Acidic cleaning necessary if > 400 g/m²



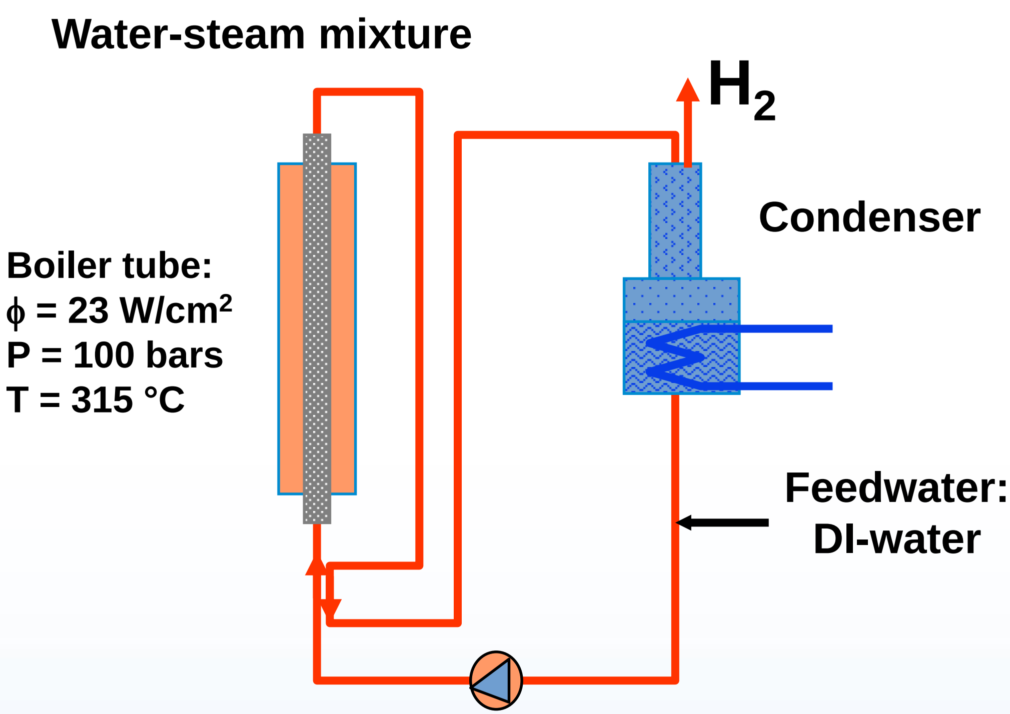
Magnetite Layer in Water-Tube Boiler

Cetamine prevents diffusion of oxygen towards the surface

Catalyzing effect is suppressed and the magnetite production is stabilized

MAGNETITE LAYER STABILIZATION

SHIKORR REACTION



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

<u>Schikorr Reaktion</u>

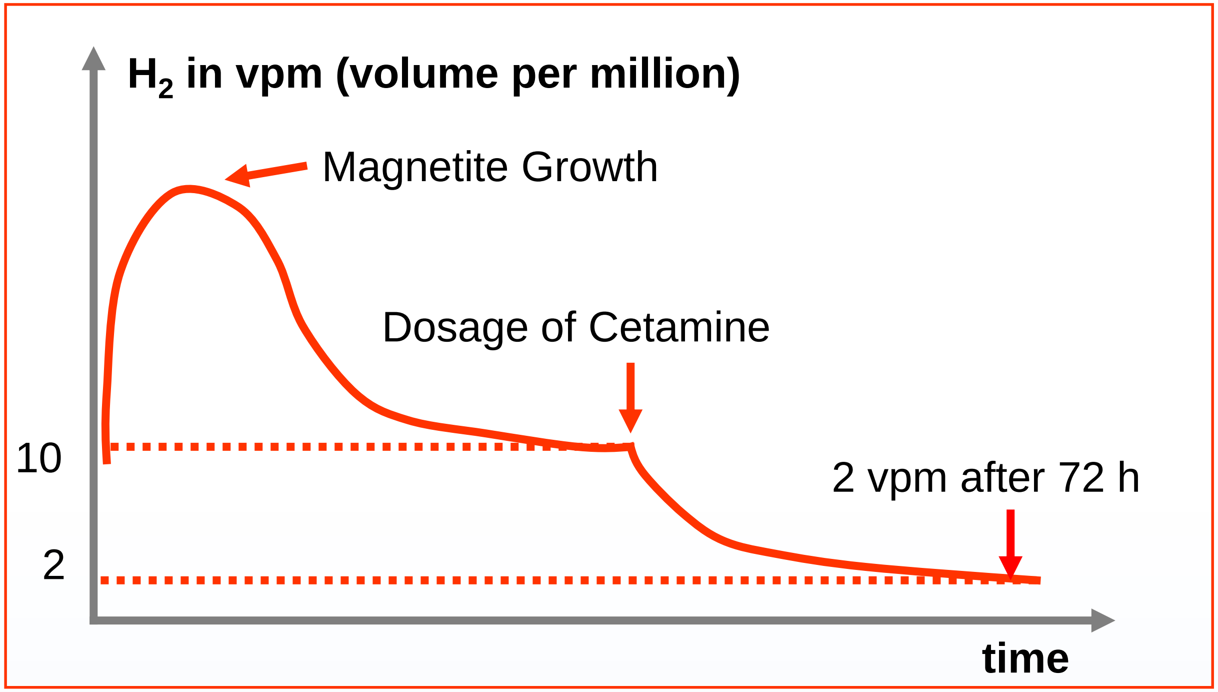
Magnetite Formation in Oxygen-Free Atmosphere

Determination of Hydrogen

Hydrogen Amount is Stoichiometrical Proportional to Magnetite Formation

MAGNETITE LAYER STABILIZATION

SHIKORR REACTION

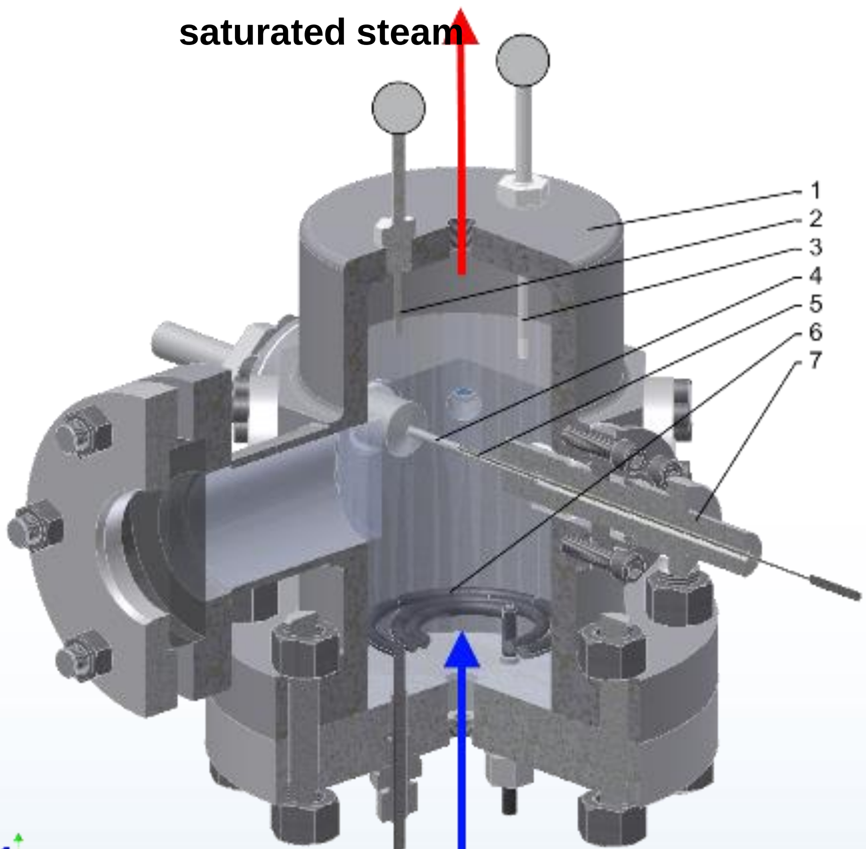


Increased Magnetite Growth without Treatment
After Addition of Cetamine Decreased Reaction Velocity

=> Leads to Thin, Compact & Homogeneous Magnetite Layers
=> Higher Heat Transfer and Less Corrosion Sensitive

MAGNETITE LAYER STABILIZATION

UNIVERSITY OF ROSTOCK, GERMANY



1. Pressure vessel
2. Sensor for steam temperature
3. Sensor for liquid temperature
4. Electrically heated steel tube
5. Sensor for inner tube temperature
6. Auxiliary heater
7. Current supply

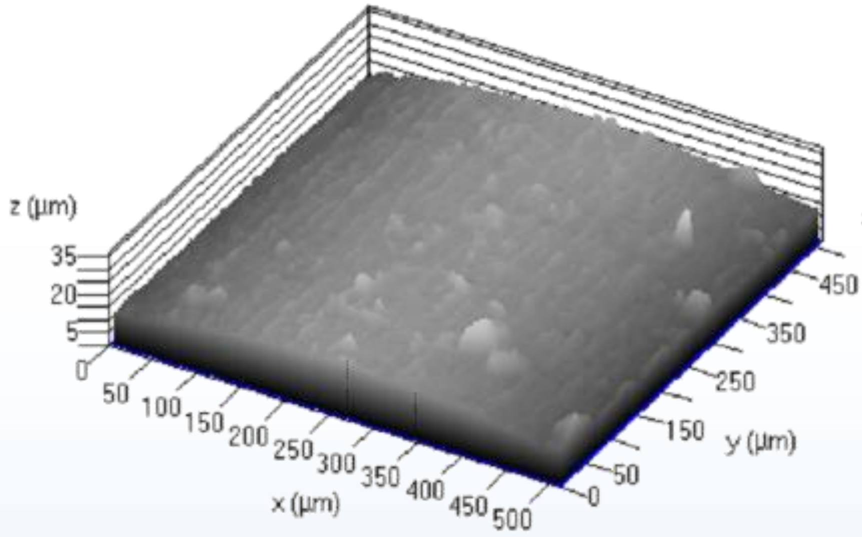
Shell boiler simulation at university of Rostock at „steady state“ conditions, p = 15 bar

MAGNETITE LAYER STABILIZATION

UNIVERSITY OF ROSTOCK, GERMANY

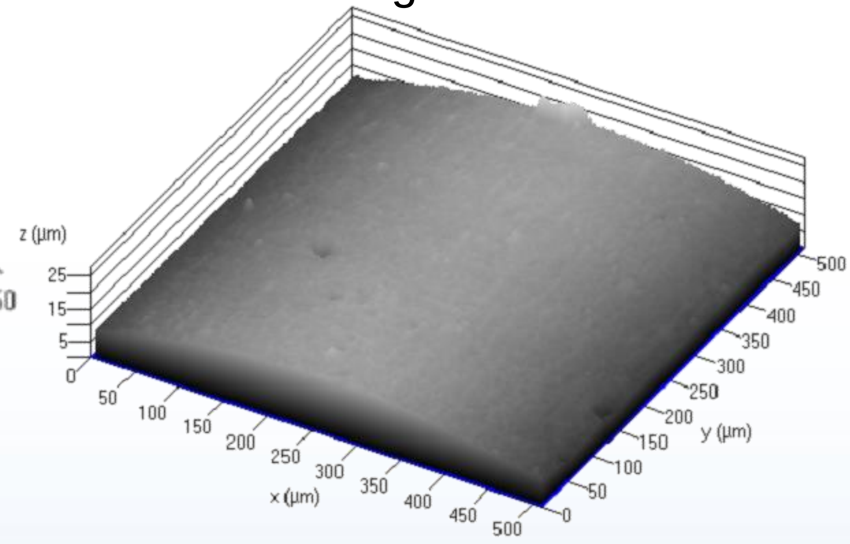
Traditional Treatment

- high micro roughness
- inhomogeneous surface



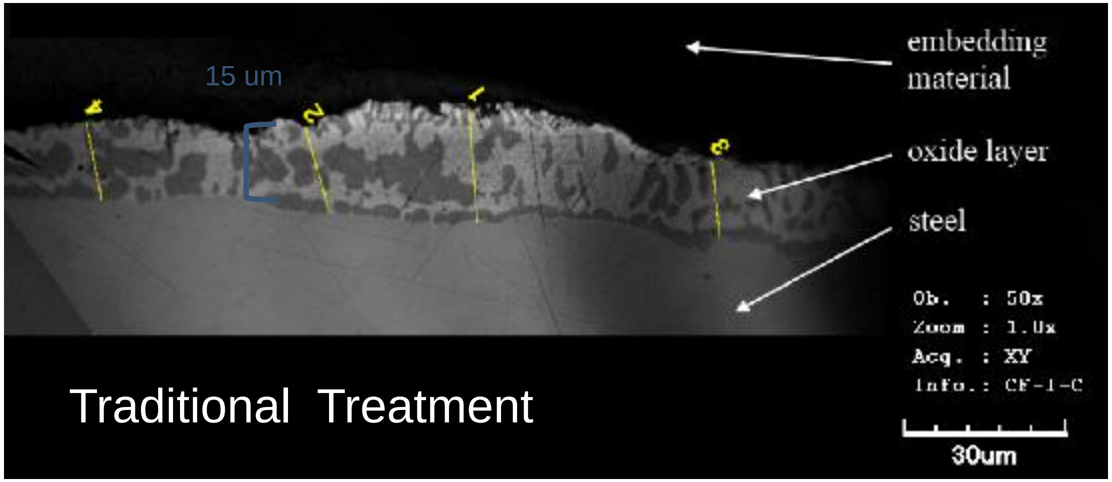
Cetamine® Treatment

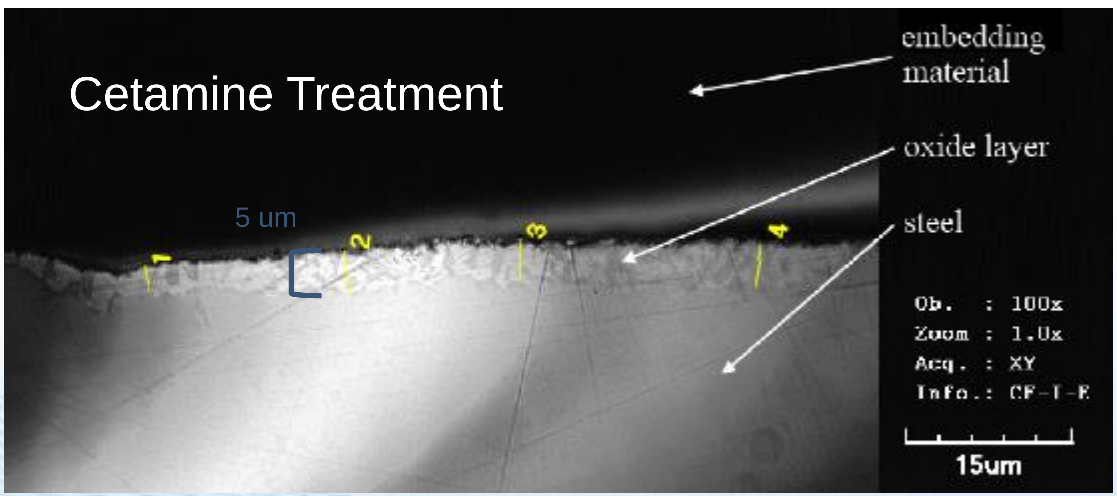
- low micro roughness
- homogeneous surface



MAGNETITE LAYER STABILIZATION

UNIVERSITY OF ROSTOCK, GERMANY





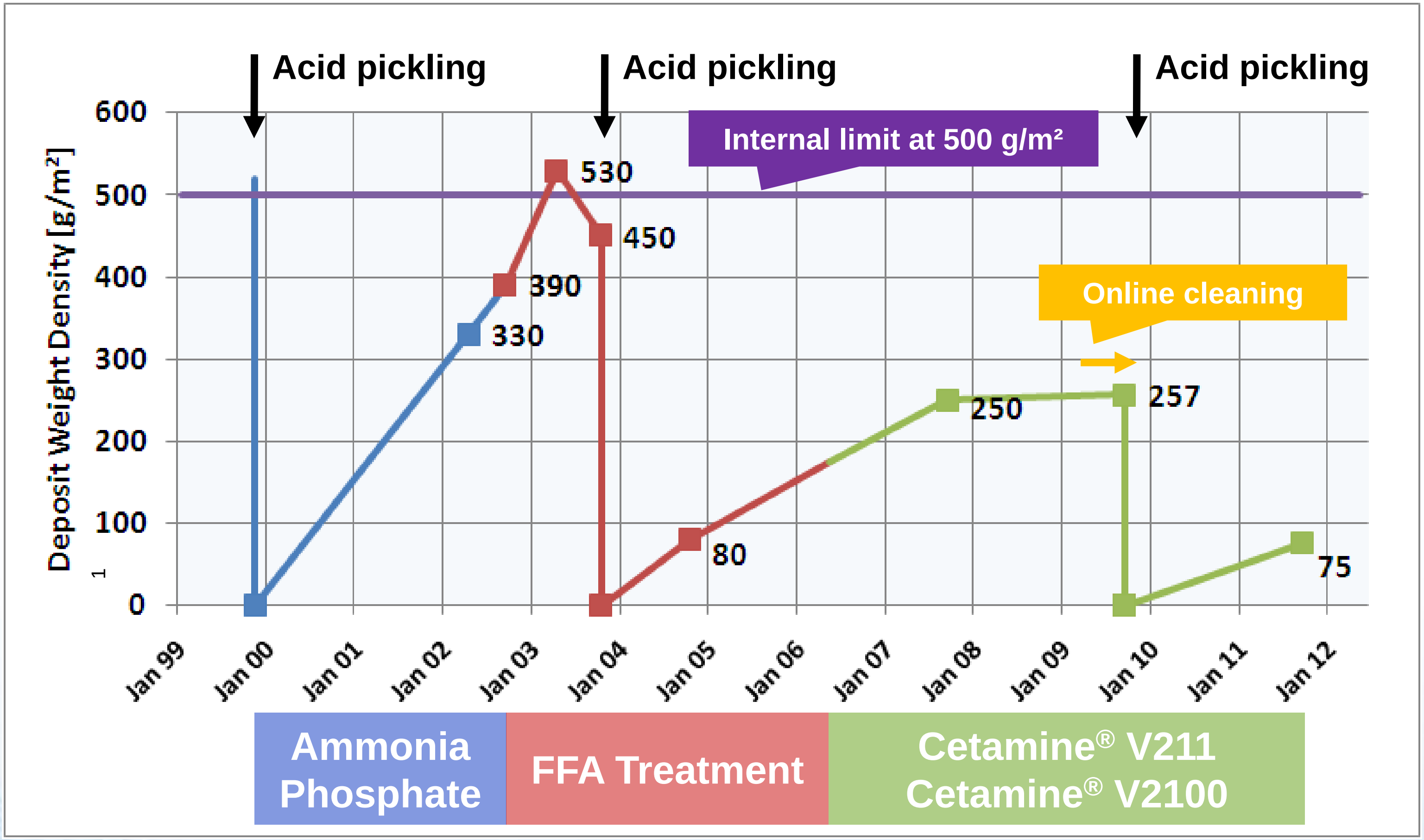
Cross Section
Examination
of Tube Surfaces

(Different Scale)

MAGNETITE LAYER STABILIZATION

PAPER INDUSTRY

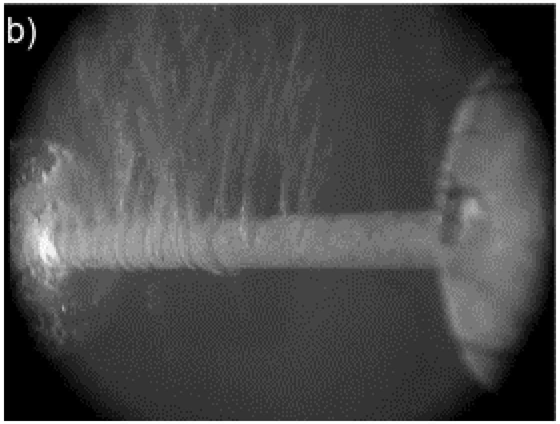
Iron Oxide Layer Development in 90 bars Water-Tube Boiler, Paper Industry



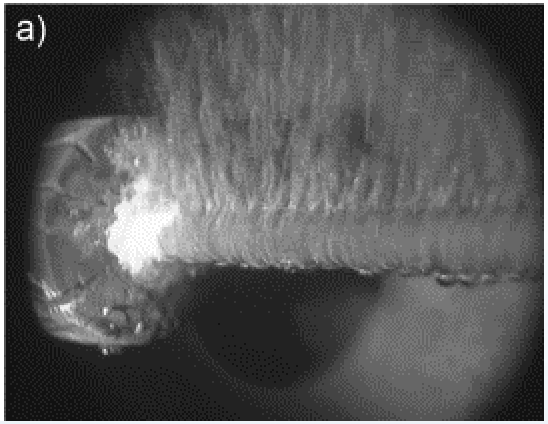
[1] According to ASTM 3483-05 Standard Test Methods for Accumulated Deposition in Steam Generator Tubes

IMPROVEMENT OF HEAT TRANSFER

UNIVERSITY OF ROSTOCK, GERMANY



Traditional Treatment



Cetamine® Treatment

Impact Of Cetamine® on Metallic Surfaces

Pictures of test tubes during test phase (with oxide layer)

- **Larger number of bubbles on the surface with Cetamine® treatment**
- **Increased bubble frequency**

Improvement of heat transfer

Shell boiler simulation at university of Rostock at „steady state“ conditions, p = 15 bar

IMPROVEMENT OF HEAT TRANSFER

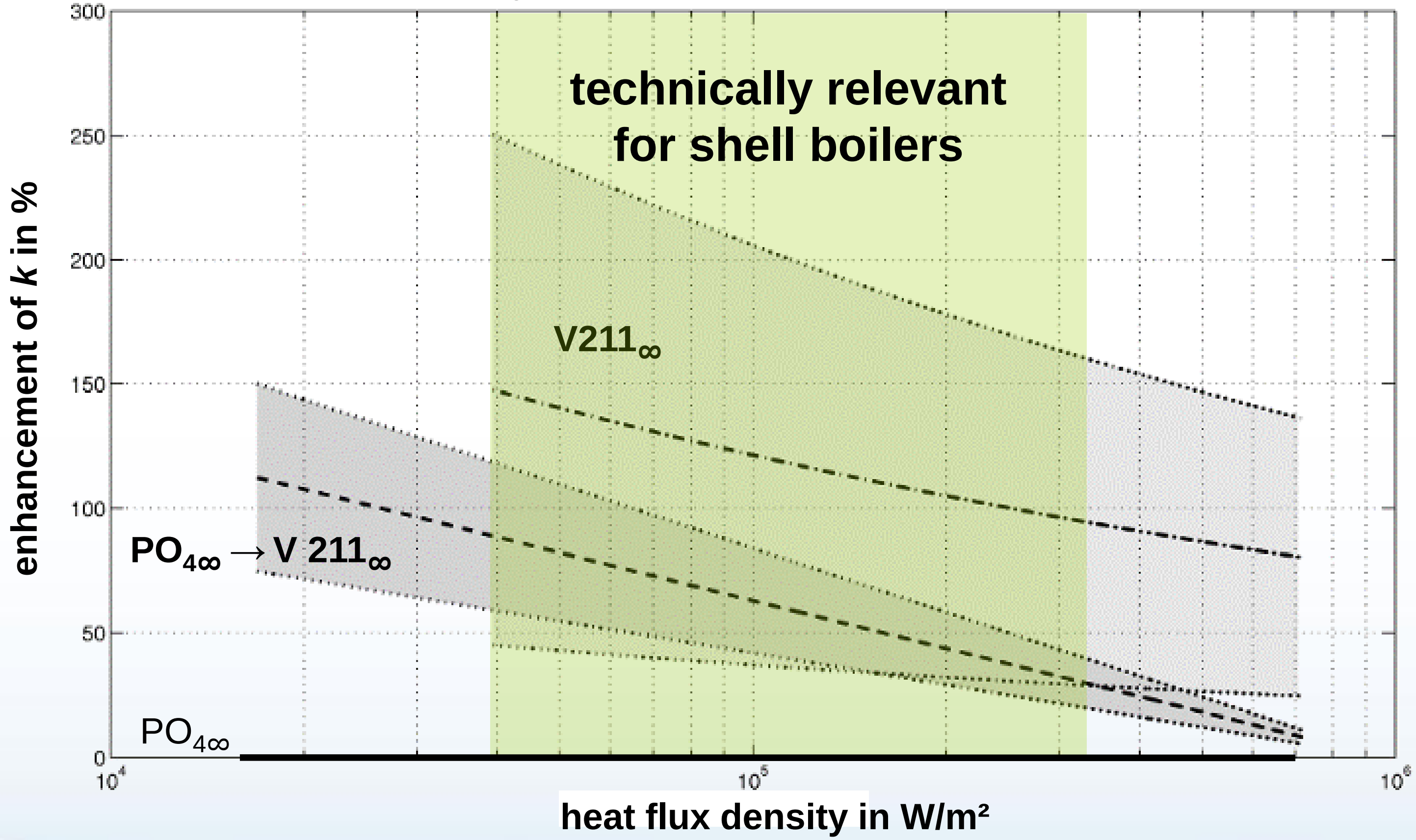
UNIVERSITY OF ROSTOCK, GERMANY

VIDEO DELETED FOR FILE
TRANSFER

IMPROVEMENT OF HEAT TRANSFER

UNIVERSITY OF ROSTOCK, GERMANY

(Net) improvement of the heat transmission coefficient k at steady state, p_s = 15 bar compared to Na_3PO_4 treatment (0 % correspondingly)



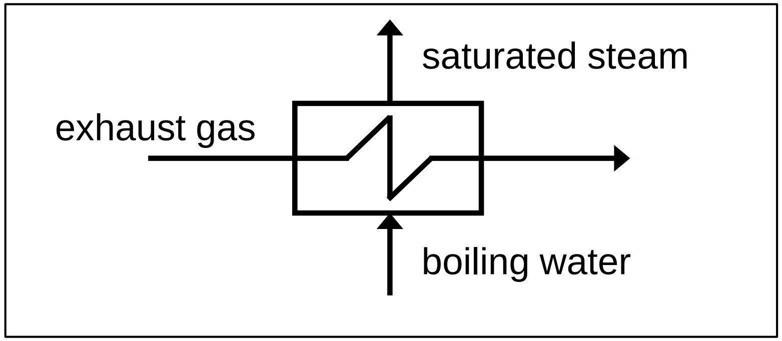
Shell boiler simulation at university of Rostock at „steady state“ conditions, p = 15 bar

CALCULATED ENERGY SAVINGS

UNIVERSITY OF ROSTOCK, GERMANY

Fuel	Natural Gas
Rated output:	30 MW
Max. efficiency:	91 %
Water pressure:	15 bar
Water temperature:	198.3 °C

Shell boiler (fire tube boiler)

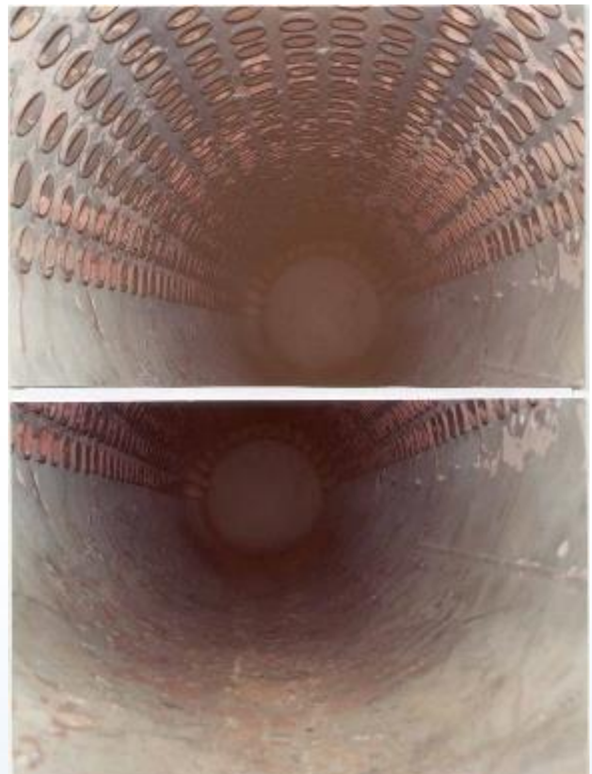


	Operating point 1 (20% load capacity)		Operating point 2 (100% load capacity)	
Treatment	Traditional	Cetamine®	Traditional	Cetamine®
Exhaust gas Input Temperature	~ 541°C	~ 541°C	~ 724°C	~ 723°C
Exhaust gas Outlet temperature	~ 364°C	~ 363°C	~ 251°C	~ 249°C
Degree of efficiency	51.5%	52.0%	89.9%	90.2%
Relative gain	0.5%		0.3%	
Annual savings	12.500€		38.000€	

ONLINE CLEANING EFFECT

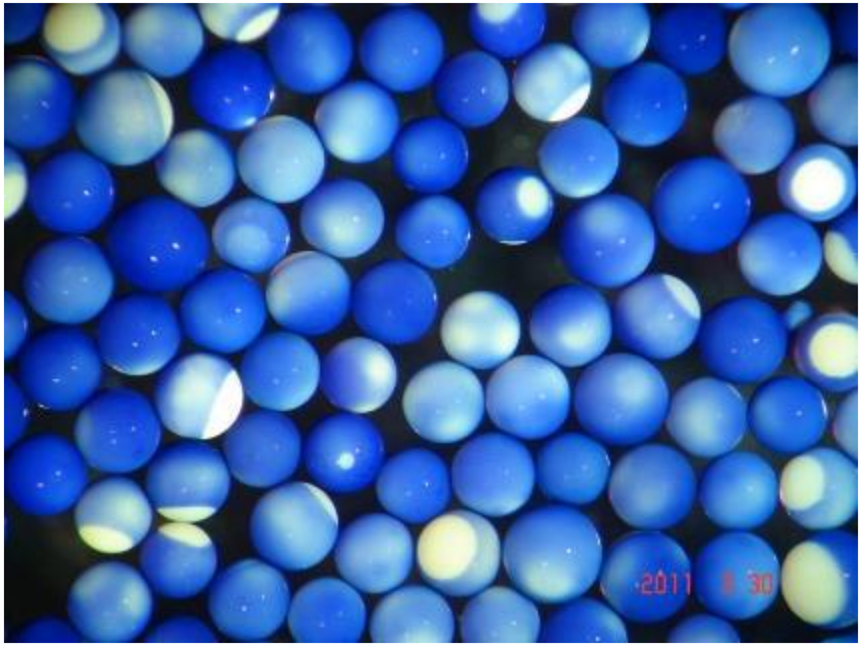
Removal of Existing Scale / Dispersing of Scale Forming Salts

Before
Cetamine® Treatment



After some months with
Cetamine® Treatment

COMPATIBILITY WITH CONDENSATE POLISHING UNIT



- Microscopic photos of strong acidic cationic resin before (left) and after colouring test (right) indicates excellent appearance after 8 years
- Full recovery after standard regeneration, No loss of exchange capacity
- Decreased regeneration frequency due to decreased iron return in condensate

See : VGB Powertech 8/2014 – The Influence of Film Forming Amines on the Exchange Behaviour of Condensate Polishing Resins
J Savelkoul, F Oesterholt, R van Lier, W Hater

COMPATIBILITY WITH ONLINE SENSORS

Compatibility of Cetamine with SWAN Online-Sensors			
	Cetamine®	FFA product 2	FFA product 3
Conductivity	☺	X	X
pH	☺	YES	X
Sodium	☺	YES	YES
Oxygen	☺	YES	YES

Cetamine® products are compatible with relevant online-sensors used under these test conditions

Full study was published by SWAN Analytical Instruments in *PowerPlant Chemistry 2012, 14(9) "Impact of Film-Forming Amines on the Reliability of Online Analytical Instruments"*

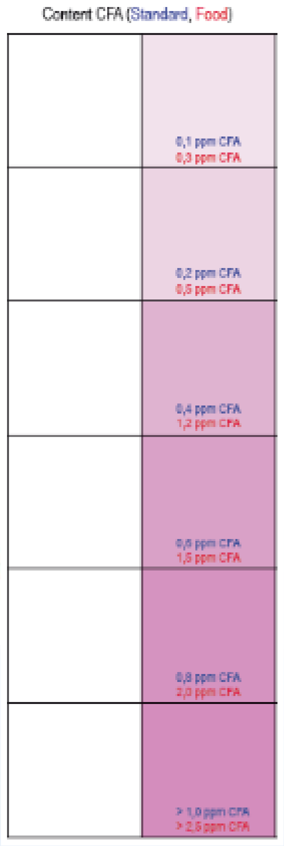
CETAMINE® ANALYSIS

CUSTOMIZED SOLUTIONS

Cetamine® Photometric Method

Cetamine® Monitor

Cetamine® Test Kit



26

WET AND DRY LAY-UP

- Long lasting film stability under wet and dry conditions
- Preservation of industrial systems
- No need of dry air or nitrogen
- Less Fe and more stable pH values
- Faster restarts after shut-down period
- Highly flexible treatment concept tolerating flexible system operation
- Saving time and money

See : Dry Lay-up of Steam Generators with Film Forming Amines : Studies and Field Experience
W. Hater, A. de Bache, T. Petrick – PPChem 2014 16(5)

COMPATIBILITY WITH PREVIOUS TREATMENT

Cetamine products are compatible with:

- Phosphate based products
- Caustic based products
- Dispersants
- Hydrazine / Carbohydrazide
- DEHA
- Tannines
- Molybdate (closed systems)

Cetamine products are NOT compatible with:

- Sulfites stop the **Sulfite** based treatment a couple of hours before the transition
- VITON seals – exchange to EDPM or equivalent

THE CETAMINE® PRODUCTS

CETAMINE V, F vs. CETAMINE G

Steam Generators		
Cetamine® V210	Cetamine® G810	Softened water (good quality)
Cetamine® V211	Cetamine® G811	Demin water, power plants
Cetamine® V2100	Cetamine® G820	Demin water, online cleaning
Cetamine® V2000	Cetamine® G840	Softened water (poor quality)
Closed Heating / Cooling		
Cetamine® F3100	Cetamine® G900	Systems containing copper / brass
Specific Products		
Cetamine® V217	Cetamine® G817	Food Industry: FDA § 173.310
	Cetamine® G815	DRY LAY-UP
Cetamine® V212	Cetamine® G830	WET LAY-UP

CFA Cetamine Filming Amine
AA Alkalizing Amine
Ox.Sc. Oxygen Scavenger

THE CETAMINE® PRODUCTS

EXAMPLES

Steam Generators		
Cetamine® G810	CFA + AA	Softened water (good quality)
Cetamine® G811	CFA + AA	Demin water, power plants
Cetamine® G820	CFA + AA + Polymer	Demin water, online cleaning
Cetamine® G840	CFA + AA + Polymer	Softened water (poor quality)
Closed Heating / Cooling		
Cetamine® G900	CFA + AA + Polymer	Systems containing copper / brass
Specific Products		
Cetamine® G817	CFA + AA	Food Industry: FDA § 173.310
Cetamine® G815	CFA + AA	DRY LAY-UP
Cetamine® G830	CFA + AA + Ox.Sc.	WET LAY-UP

CFA Cetamine Filming Amine
AA Alkalizing Amine
Ox.Sc. Oxygen Scavenger

Hydrazin- and Cyclohexylamine- free

CETAMINE® PATENT

The dispersant containing products Cetamine® V2000, V2100 and F3100 are protected by the European Patent EP 774017

The same is true for Cetamine® G820, G840 & G900 as these products contain:

- The same CFA
- The same dispersant

Cetamine® G820, Cetamine® G840, Cetamine® G900 are protected by the European Patent EP 774017

CETAMINE® TECHNOLOGY – TYPICAL APPLICATIONS

Over 1.000 applications

in Steam Boilers & Closed loops

CETAMINE® TECHNOLOGY – TYPICAL APPLICATIONS

Type of industry	Operational pressure [bar / psi]	Steam capacity [T/h / lbs/h]
CHP plant	113 / 1600	250 / 551 000
TLE (petrochemical)	125 / 1800	350 / 772 000
Power plant	145 / 2100	670 / 1 477 000
Petrochemical	210 / 3050	170 / 375 000
Steel Mill	70 / 1015	340 / 750 000
Power plant	135 / 1950	660 / 1 455 000
Gas purification	30 / 440	400 / 882 000
Paper mill	90 / 1300	120 / 265 000

CREATING VALUE TO CUSTOMERS

A refinery saves 170 000 € annually with Cetamine® Program

CREATING VALUE TO CUSTOMERS

A steel mill saves 200 000€ in closed circuit treatment with Cetamine® technology

CREATING VALUE TO CUSTOMERS

A Chemical Group saves 74 000 € annually with Cetamine® Program in each site

CREATING VALUE TO CUSTOMERS

A Pharmaceutical Industry saves more than 40 000 € annually with Cetamine® Program

CREATING VALUE TO CUSTOMERS

A paper mill reduces by 50% its water consumption with Cetamine®

Selectect references of Cetamine® Technology applications in power plants and industrial power plants

Country	Market	Application	P [bar]	Product	Turbine Manufacturer
Belgium	Sugar mill	Boiler water	20	Cetamine V217 K	
Monaco	Waste incineration	Boiler water	30	Cetamine V232	Blohm-Voos
France	Waste incineration	Boiler water	30	Cetamine V227	12 MW condensation turbine
Czech Republic	Waste incineration	Boiler water	40	Cetamine V2100	Siemens
Germany	Biomass power plant	Boiler water	40	Cetamine V211	M+M Turbinentechnik
Germany	Waste incineration	Boiler water	40	Cetamine V211	Ansolta
Germany	Power plant	Boiler water	40	Cetamine V2100	
Iberica	Zinc Production	Boiler water	40	Cetamine V211	KKK
Iberica	Fertilizers production	Boiler water	40	Cetamine V211	1 Siemens + 1 AEG
Germany	Waste incineration	Boiler water	42	Cetamine V211	MAN Turbo AG
Italy	Refinery	Boiler Water	42	Cetamine V211	
Germany	Textile industry	Boiler water	45	Cetamine V211	BBC
Germany	Waste incineration	Boiler water	60	Cetamine V211	Siemens
Iberica	Automotive	Boiler water	60	Cetamine V211	Siemens
Germany	Paper industry	Boiler water	69	Cetamine V211	Siemens
France	Waste incineration	Boiler water	70	Cetamine V277	
Israel	Paper industry	Boiler water	90	Cetamine V211	Siemens
Germany	Power Plant	Boiler water	98	Cetamine V211	ABB
Germany	Power plant	Boiler water	98	Cetamine V211	
UK	Power plant	Boiler water	120	Cetamine V219	
Saudi Arabia	Power plant	Boiler water	120	Cetamine V211	
Netherlands	Petrochemistry	Boiler water	125	Cetamine V215	
Poland	Power plant	Boiler water	140	Cetamine V211	
Ukraine	Power plant	Boiler water	145	Cetamine V210-35	
Belgium	Power plant	Boiler water	180	Cetamine V101	
Germany	Power Plant	Boiler water	190	Cetamine G810	
Germany	Petrochemistry	Boiler water	200	Cetamine V211	
Germany	Power plant	Closed system		Cetamine F3100	

KEY POINTS

- Complete plant protection
- Suitable concepts for all types of industry
- Long lasting film, forgiving treatment
- Low human toxicity
- Organic treatment program, high cycles possible
- Easy to apply and to control
- Very clean appearance of plant, e.g. turbine blades
- Improvement of heat transmission coefficient
- Cost efficient
- Lot‘s of experiences also in High Pressure Systems

Experience with Cetamine in a high pressure steam system of a Naphtha Cracker

André de Bache

Basic principles of high pressure boiler-water treatment (I)

Aims of successful boiler-water treatment

- Adequate pH in feed-water, boiler water and steam-condensate system
- Avoid precipitation of scale-forming salts and iron oxides
- Elimination of dissolved oxygen by means of thermal deaerator and oxygen scavengers
- Neutralization of CO_2
- Passivation of surfaces and magnetite layer stabilization
- Minimize risk of carry-over

Cetamine in a high pressure steam system of a Naphtha Cracker

Petrochemical Industry, Netherlands

Naphtha Cracker

Full Paper : 3-Years Experience with Polyamines in High Pressure Steam System of a Naptha Cracker

R. van Lier, G. Janssen, J. Savelkoul

Published in PPChem 2008 (3)

System characteristics (I)

Customer:	Netherlands
Industry:	Petrochemical Industry, Naphtha Cracker
Production:	Ethylene and propylene by steam cracking
Boiler-system:	Heat Recovery Steam Generators (HRSG) Transfer Line Exchangers (TLE)
Fuel:	Methane (from the process) and natural gas
Pressure:	125 bar
Steam temperature:	520 °C (superheated)
Steam production:	350 to 450 t/h + 100 t/h imported steam
Condensate return:	100 % (ca. 50 % via CPU)
Make-up water:	DI water, 15 to 80 t/h
Feedwater:	Thermally deaerated at T = 125 °C
Turbines:	Back pressure/condensation turbines and back pressure turbines

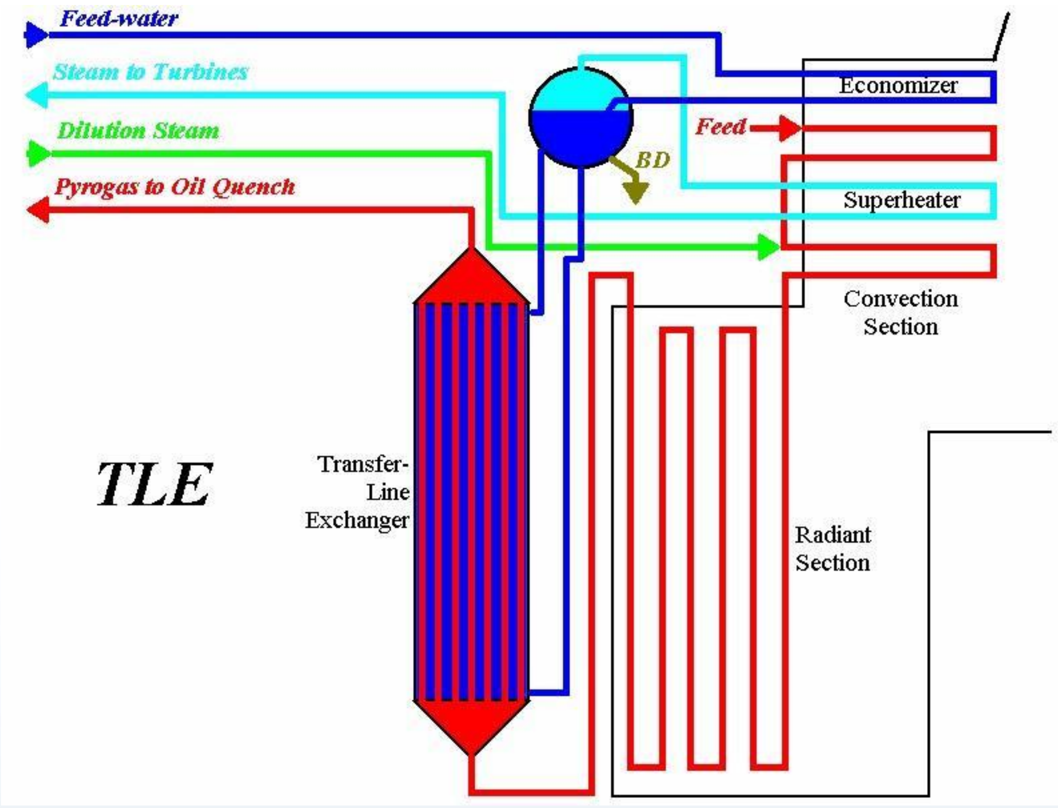
System characteristics (II)

Condensate Polishing Unit (CPU)

- Turbine condensates pumped back directly to deaerator (ca. 50 %)
- Condensates of steam in preboilers and tracing lines pass CPU
- Potentially contaminated with hydrocarbons and inorganic salts
- Small flow of blow-downs also pass CPU

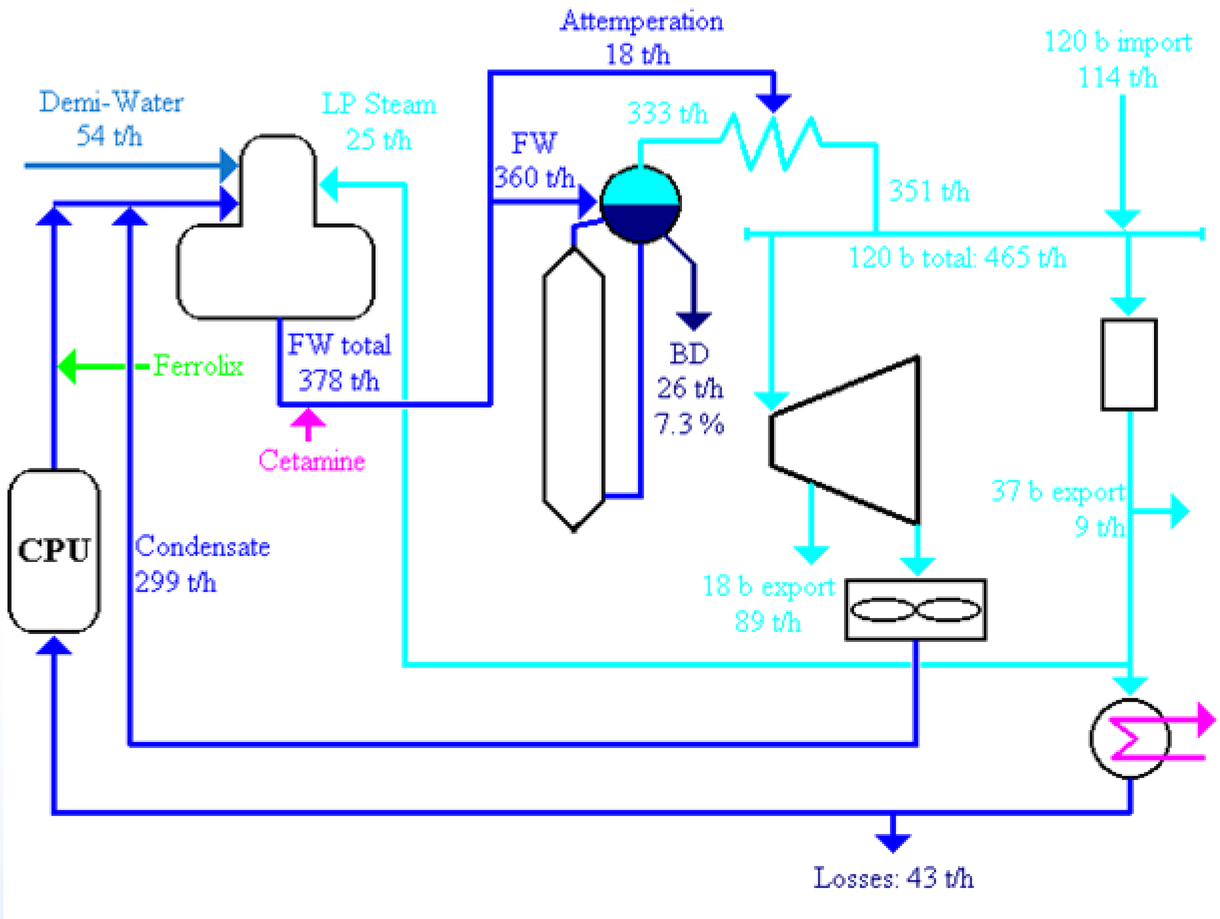
- Two trains of standard carbon filter
- Cationic exchanger
- Mixed bed polisher configuration

System characteristics (III)



- 12 cracking furnaces
- Each furnace has its own HP steam system
- One drum serves either 2 or 3 TLEs
- HP steam is superheated by hot flue gas
- Temperature of superheated steam is controlled at 520 °C by feedwater attemperation
- Superheated steam is expanded over turbines
- Turbines drive cracked gas compressor and C2 and C3 compressor

System characteristics (III)



System characteristics (IV)

- Very high heat flux transfer line exchangers
- Sensitive to fouling and corrosion

- Minimalistic design (no mud drums or large headers, little instrumentation)

- Multiple individual steam systems with centralized water treatment
- Only blowdown rate to adjust boiler water quality

- Variable steam rates during the process

- No preventive chemical cleaning

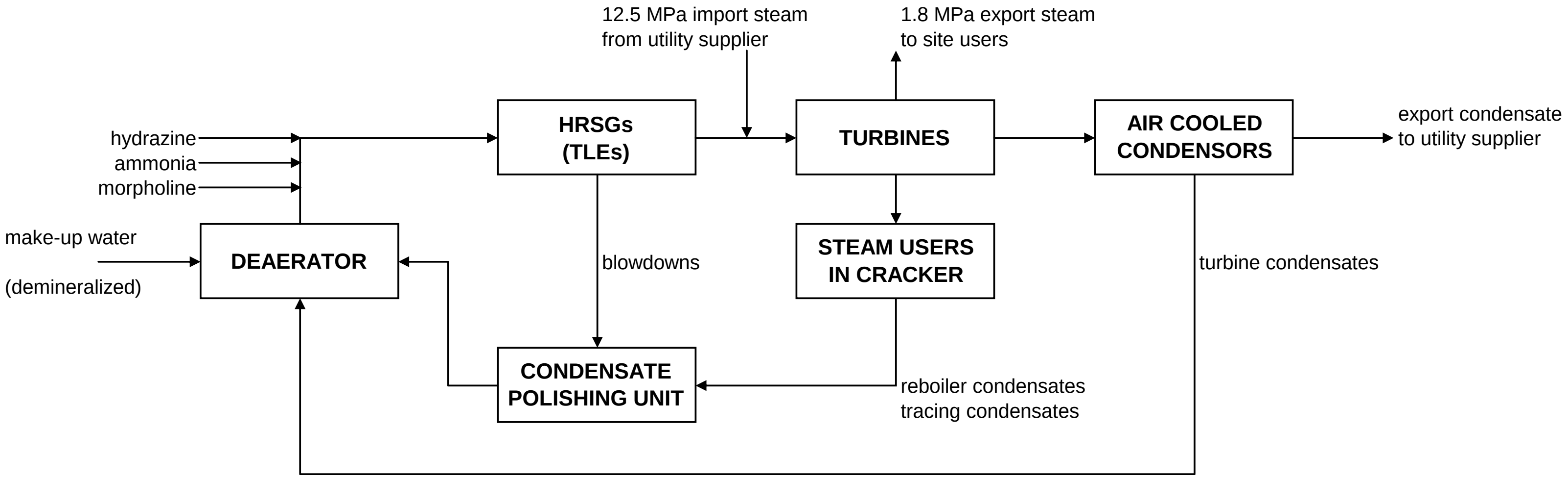
System characteristics (V)

Transfer Line Exchanger (TLE)

- Cooling of cracked gas from 800 – 850 °C to ca. 500 °C
- Local heat fluxes of several hundreds of kW/m²
- Highest heat flux zone coincides with physical low-point
- Deposits will accumulate there with conventional water/steam treatment

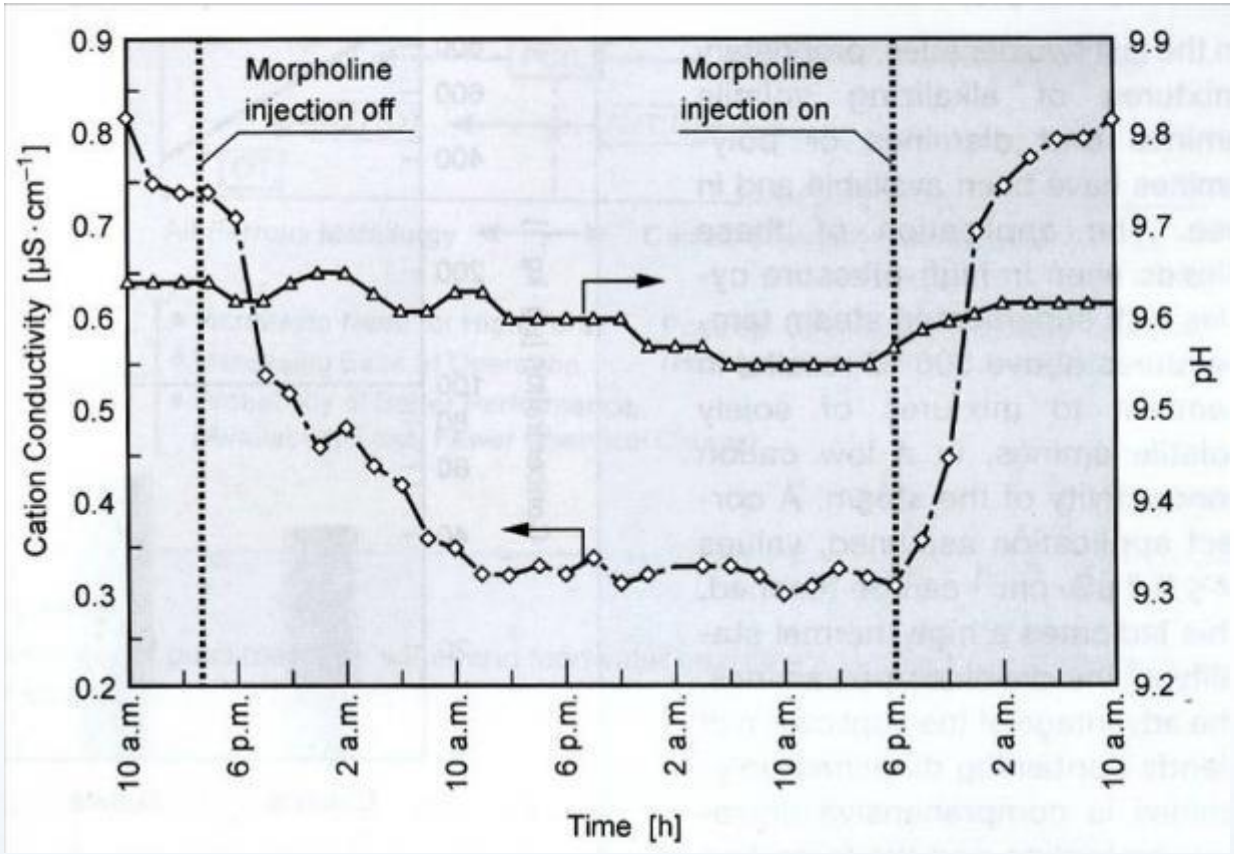
Example of boiler tube failier

History of water treatment (I)



- Treatment program caused flow-accelerated corrosion (FAC) in pre-boiler and condensate systems and first condensate corrosion (FCC) in condensate lines due to morpholine degradation
- Transport of iron (oxides) and fouling of thermally highly loaded heat transfer surfaces (TLEs)
- Boiler tube failures

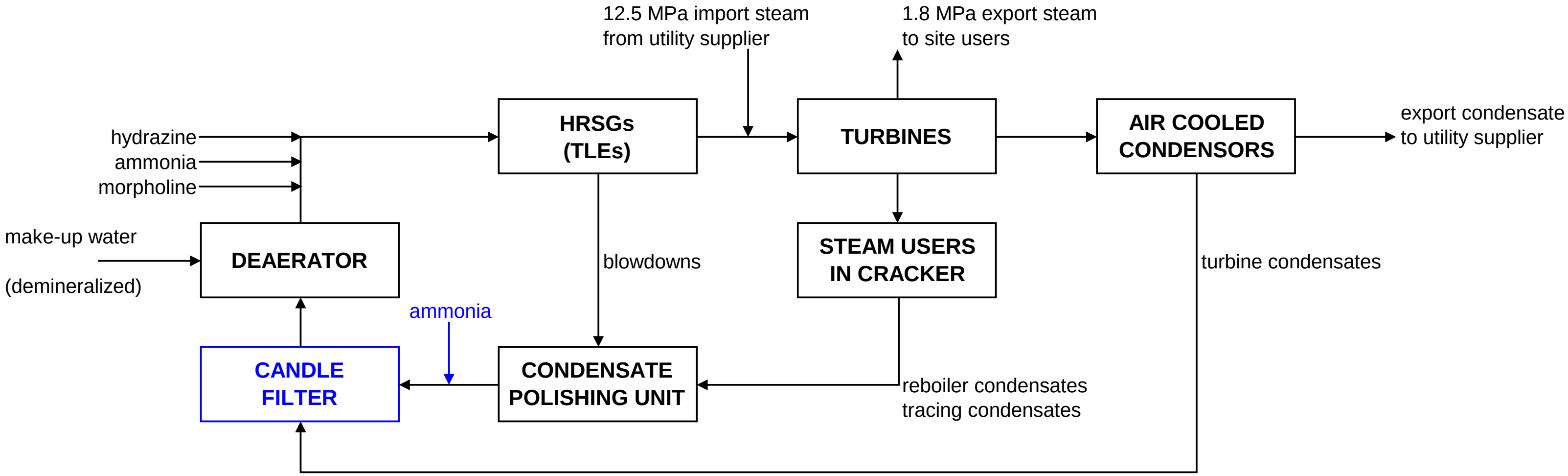
History of water treatment (II)



Source: J. Savelkoul, P. Janssen and H. Verhoef, "Monitoring of First Condensate Corrosion (FCC) in Industrial Steam Systems", PowerPlant Chemistry 2001, 3(6), 326-330.

Experience with Cetamine in a high pressure steam system of a naphtha cracker

History of water treatment (III)

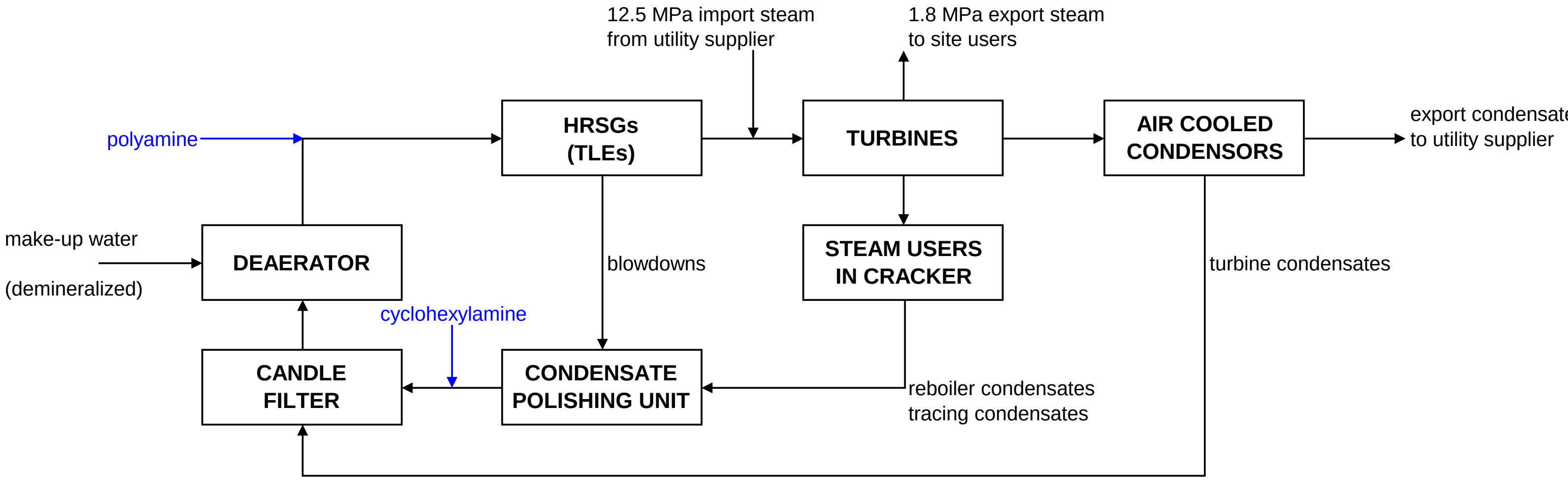


- Alkalization of condensate line from CPU to deaerator to minimize FAC
- Installation of cartridge filter to remove suspended iron oxides
- Increasing of ammonia concentration in feedwater from 0.2 ppm to 1 ppm to neutralize acidic morpholine degradation products and limit FCC

History of water treatment (IV)

- Despite modifications difficulties with corrosion persisted
- Root cause was thermally instability of morpholine
- Many investigations and literature studies led to treatment program based on products with neutralizing and film forming amines in 2005

History of water treatment (V)



- Improved steam quality (acid conductivity)
- Water and energy savings due to blow-down reduction
- Time between regenerations of cationic exchangers in CPU has more than doubled
- Metal surfaces in TLEs and drums show thin, uniform magnetite layer
- Turbine blades were exceptionally clean and free of corrosion damage

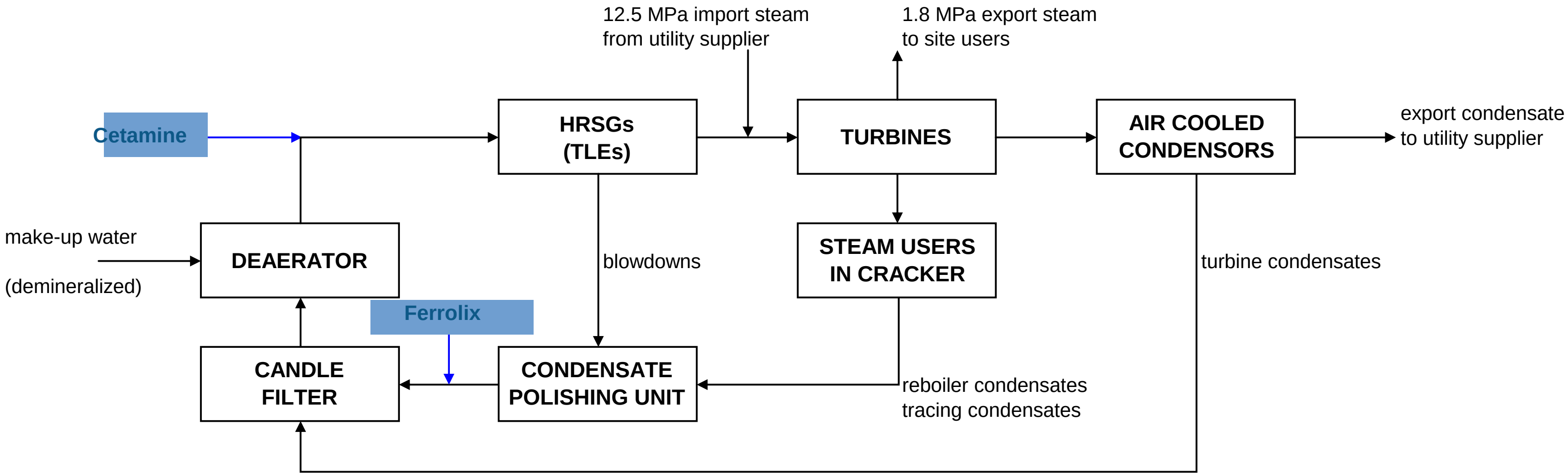
History of water treatment (VI)

Negative experience of the treatment

- Sticky deposits in pre-boiler and condensate system
- Cationic exchanger resin lumping in CPU
- Shortcomings of analytical methods for FFA
- Higher than expected FFA residuals

Changeover from former supplier to Cetamine from Kurita (BKG Water Solutions)

Water treatment with Cetamine (I)



Objectives

- Provide our internal analytical method to detect residual of FFA
- Keep the right dosage and avoid sticky deposits in the system
- Maintain the same level of blow-down
- Maintain the system parameters according to the customers and our experience

Water treatment with Cetamine (II)

Treatment details

- Cetamine (FFA/AA): ca. 20 g/m^3 of make-up water
  injection after deaerator

- Ferrolix (CHA): ca. 11 g/t of condensate
  injection after CPU

KURITA
efficiency for industry

Water parameters (I)

control limits	feedwater	boiler (TLEs)	turbine condensate
pH	9.0 – 9.5	8.5 – 9.5	8.5 – 9.5
total iron [ppb]	< 100	< 100	< 100
silica [ppb]	< 20	< 250	< 20
conductivity [µS/cm]	1 -15	< 10	5 - 15
acid conductivity [µS/cm]	< 0.2	---	---
FFA [ppm]	0.2 – 0.3	0.2 – 0.3	0.2 – 0.3

Water parameters (II)

feedwater	control limits	2009 average
pH	9.0 – 9.5	9.3
total iron [ppb]	< 100	45
Silica [ppb]	< 20	7
conductivity [µS/cm]	1 -15	7.3
acid conductivity [µS/cm]	< 0.2	0.4
FFA [ppm]	0.2 – 0.3	0.2

Water parameters (II)

boiler water (TLEs)	control limits	2009 average
pH	8.5 – 9.5	9.2
total iron [ppb]	< 100	44
Silica [ppb]	< 250	48
conductivity [µS/cm]	< 10	7.2
acid conductivity [µS/cm]	---	---
FFA [ppm]	0.2 – 0.3	0.25

Water parameters (II)

turbine condensate	control limits	2009 average
pH	8.5 – 9.5	9.15
total iron [ppb]	< 100	44
Silica [ppb]	< 20	9
conductivity [µS/cm]	5 - 15	8.0
acid conductivity [µS/cm]	---	---
FFA [ppm]	0.2 – 0.3	0.2

Conclusion

- Steam quality has greatly improved [PPChem 2008 (3)]
- Important water and energy savings have been realized due to blow-down reduction [PPChem 2008 (3)]
- Time between regenerations of cation exchangers in CPU has more than doubled [PPChem 2008 (3)]
- Inspections have shown TLEs and drums effectively protected against corrosion by a thin, uniform, adherent magnetite layer [PPChem 2008 (3)]
- Turbines were exceptionally clean and free of corrosion [PPChem 2008 (3)]

- The customers control parameters were met
- Reliable Kurita analytical method makes sure not to overdose FFA
- No Risk of sticky deposits
- Customer is satisfied with our treatment program and services todate

CONTACT SLIDE

Dave Johnson
Technical and Marketing Manager KME

Kurita Middle East FZE
PO box 263958
Office 1010, Floor 10,
Jafza One, Jebel Ali Free Zone,
Dubai, United Arab Emirates

Phone + 33 (0)6 62 26 98 97
Email dave.johnson@kurita.eu
Web www.kurita.eu

THANK YOU FOR YOUR ATTENTION

Learn more by visiting

www.kurita.eu