it's all about innovation

DANISH TECHNOLOGICAL INSTITUTE

Fouling release coatings for steam condenser in thermal power plants

S. Holberg, R. Losada
Danish Technological Institute, Denmark

Outline

- EU-project "MATChING"
- State-of-the-art/background
- First experimental results

MATChING Project

MATerial TeChnologies for performance Improvement of cooling systems in power plants

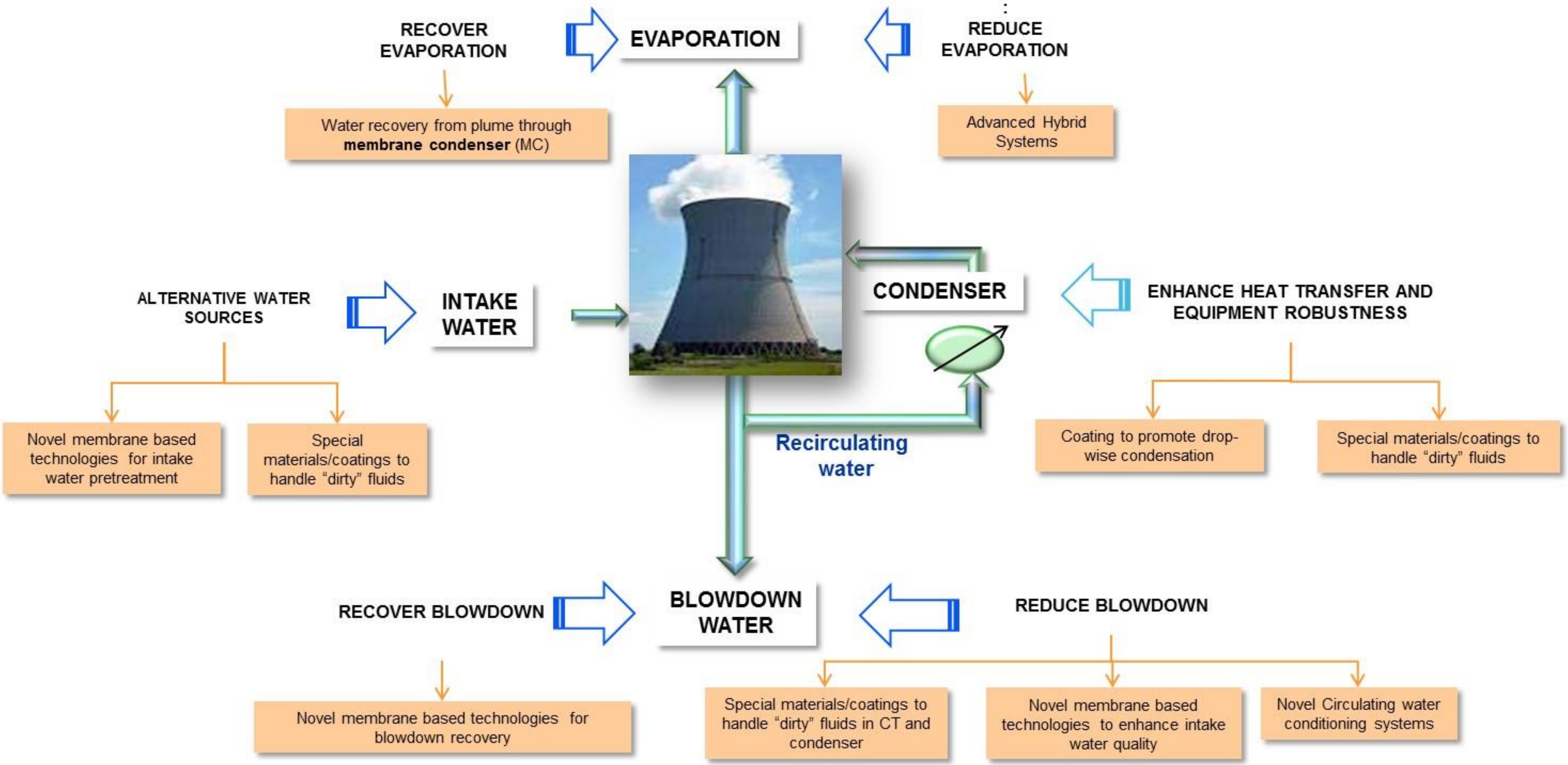
DANISH TECHNOLOGICAL INSTITUTE

Partners from 6 EU Countries: 4 from Italy, 4 from Belgium, 3 from Spain, 3 from the Netherlans and 1 from Denmark

More information: www.matching-project.eu

MATChING: Combining technologies

DANISH TECHNOLOGICAL INSTITUTE

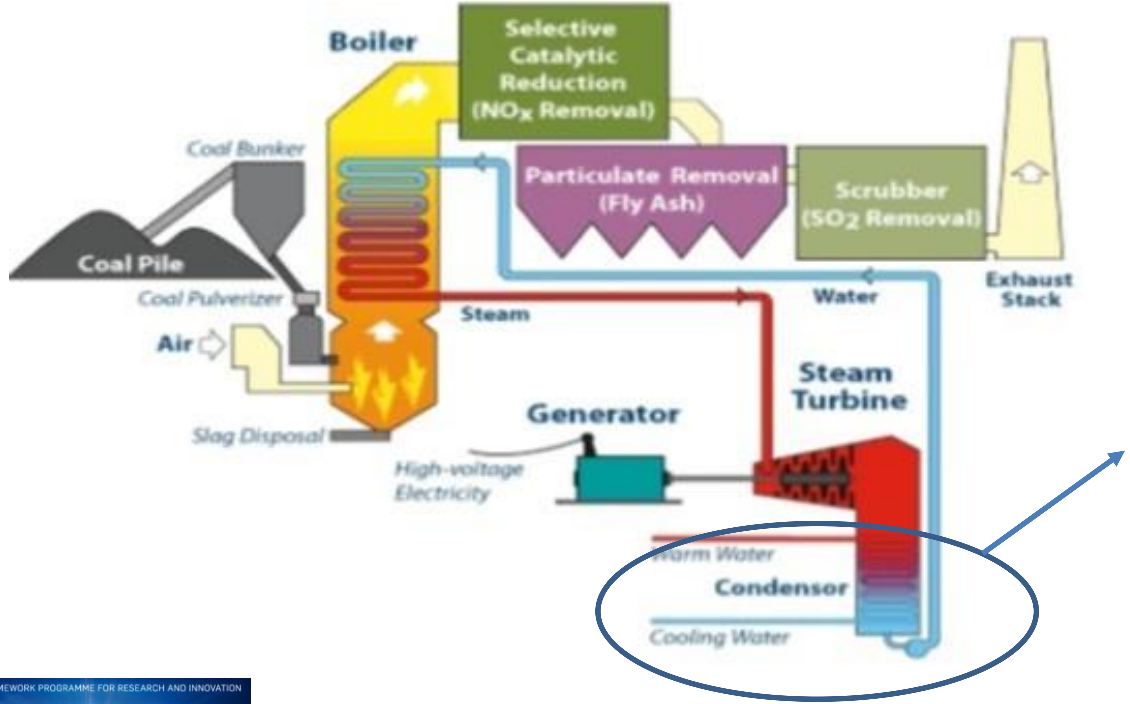


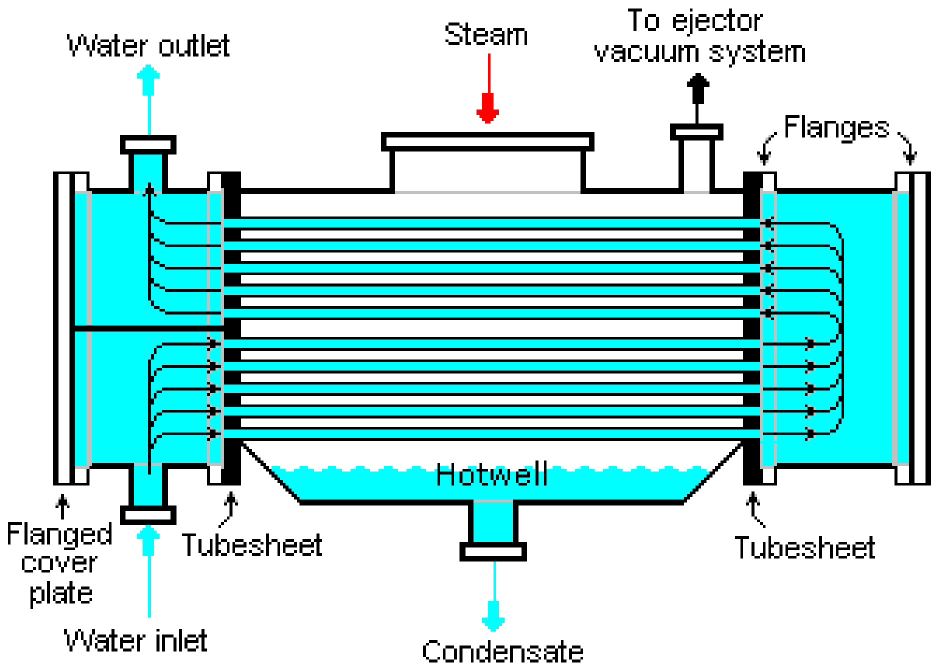
More information: www.matching-project.eu

"As Pontes"
Spanish coal-fired, fresh-water cooled power plant

A coated condenser will be run in a test loop

DANISH TECHNOLOGICAL INSTITUTE





Coatings for bio-fouling mitigation

DANISH TECHNOLOGICAL INSTITUTE

State-of-the-art:

Commercial coatings for ship hulls work well

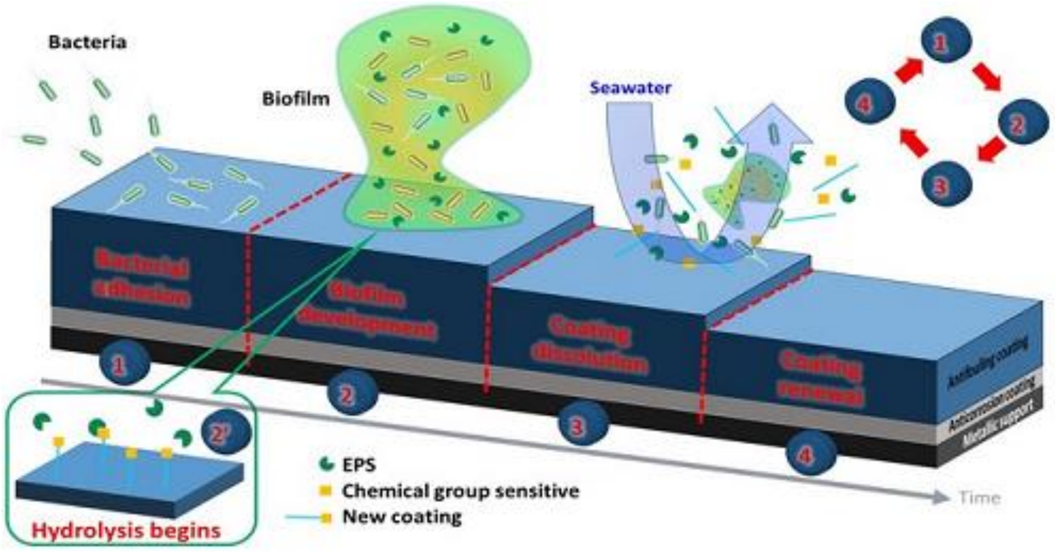
DANISH TECHNOLOGICAL INSTITUTE

Coatings for bio-fouling mitigation

"Antifouling coatings"

Release biocide to kill micro-organisms.

"*Self-polishing coatings*" Most antifouling coatings are self-polishing coatings. They undergo a controlled "degradation" in water to provide fresh surface with fresh biocide



"Fouling release coatings"

Do not prevent settlement of bio-fouling, but reduce fouling adhesion. Flow removes attached organisms.

- *Free of biocides*
- *Non-sacrificial, not self-polishing*

→ Therefore chosen for MATChING

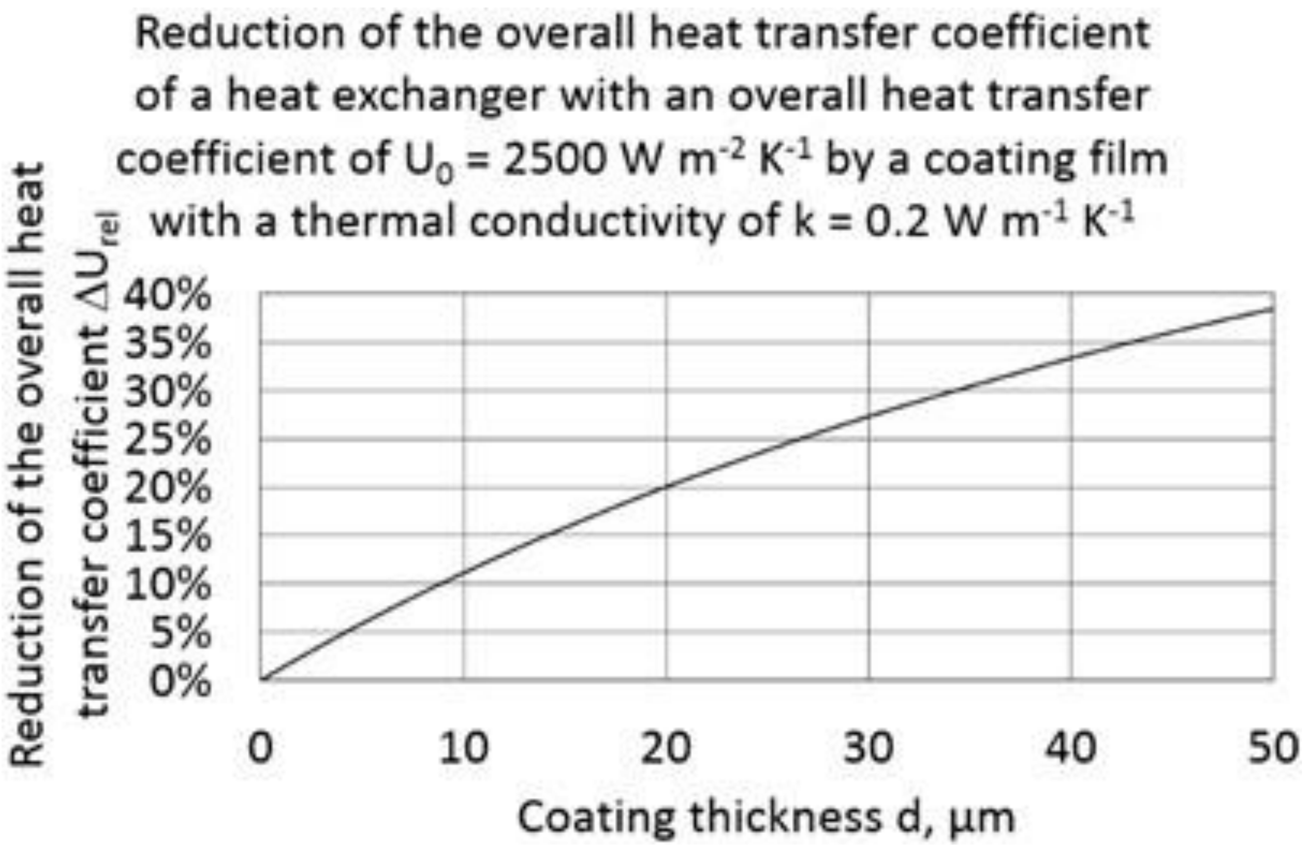
- *Require flow to provide a drag force*

Both anti-fouling and fouling release coatings are usually applied with high film thickness, e.g. 200 µm

Effect of coating thickness

DANISH TECHNOLOGICAL INSTITUTE

Heat exchangers require coating thickness far below 200 µm for good thermal conductivity



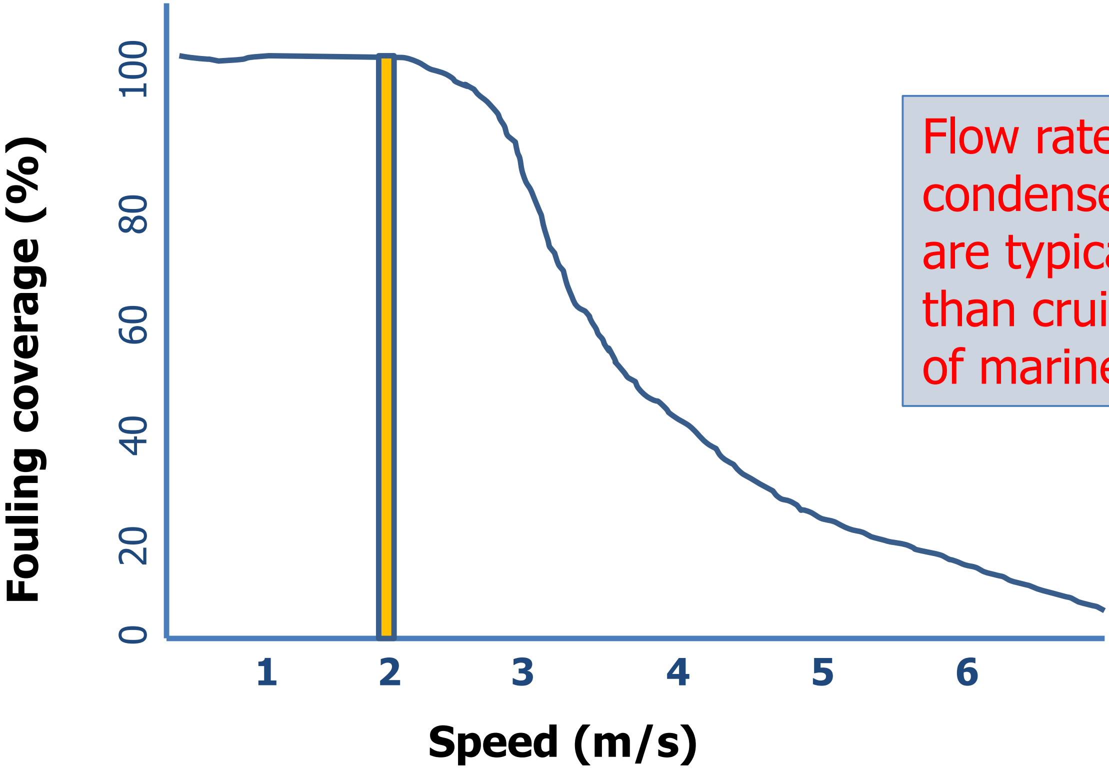
Overall heat transfer coefficient
$U_0 = 2500\ W\ m^{-2}\ K^{-1}$

Typical value for steam condensers in power plants

DANISH TECHNOLOGICAL INSTITUTE

Effect of flow/drag force

Fouling-release coatings are today widely applied on merchant ships and ferries.
To be effective they require a drag that is typically reached at 6 knots (~ 3.1 m/s)



Flow rates in surface condensers (2 m/s) are typically lower than cruising speeds of marine vessels

DANISH TECHNOLOGICAL INSTITUTE

Fouling release coatings in MATChING

Fouling release coatings →

Requirements
- Thickness <20 microns (minimal heat transfer impact)
- Possible to apply ID of condenser tubes
- Efficient at 2m/s flow rate

Laboratory Activities

Synthesis

1-Development of new coatings
2-Modification of commercial systems

General characterization

Thickness, Applicability etc

Specific Characterization

Fouling adhesion and durability tests

Industrial Prevalidation(ENDESA)
Litoral plant (Almeria, South Spain)
Fouling release performance. Raceaway reactor (sea water), 64 days.

Industrial Validation(EdF)
Pericles facility (Chatou, France). The facility consists of four mirror image pilot cooling systems that are able to operate independently.

Demonstration(ENDESA)
As Pontes power plant (NW of Spain). Condenser pilot

DANISH TECHNOLOGICAL INSTITUTE

Coating development

References

- 316 stainless steel
- Commercial epoxy coatings
- Commercial fouling release coating for ship hulls (based on silicone rubber + hydrophilic additive)

Development

	Surface energy is not specifically low	Low surface energy
”soft”	**Silicone rubber with hydrophilic additive**	**Silicone rubber**
”hard”	**Sol-gel coatings** (inorganic-organic hybrid coatings)	**Sol-gel coatings with silicone additive** Have been highly effective against crude-oil fouling, but bio-fouling is different ☺

All coatings are applied by standard methods (spraying/dipping)

DANISH TECHNOLOGICAL INSTITUTE

Coating development

Thin coatings (minimal impact on heat transference)

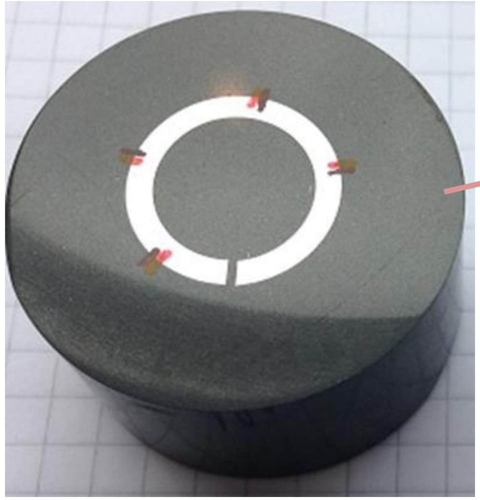
Surface	Thickness (μm)	Modulus	Surface tension (mN/m)
AISI 316L	-	-	53
"SiRu1"	22±3	Soft	18.6
"SiRu1-thin"	7±3	Soft	18.6
"SiRu2"	13±3	Soft	Similar to SiRu1
"SolGel1"	4±1	Hard	21.1
"SolGel2"	4±1	Hard	31.2

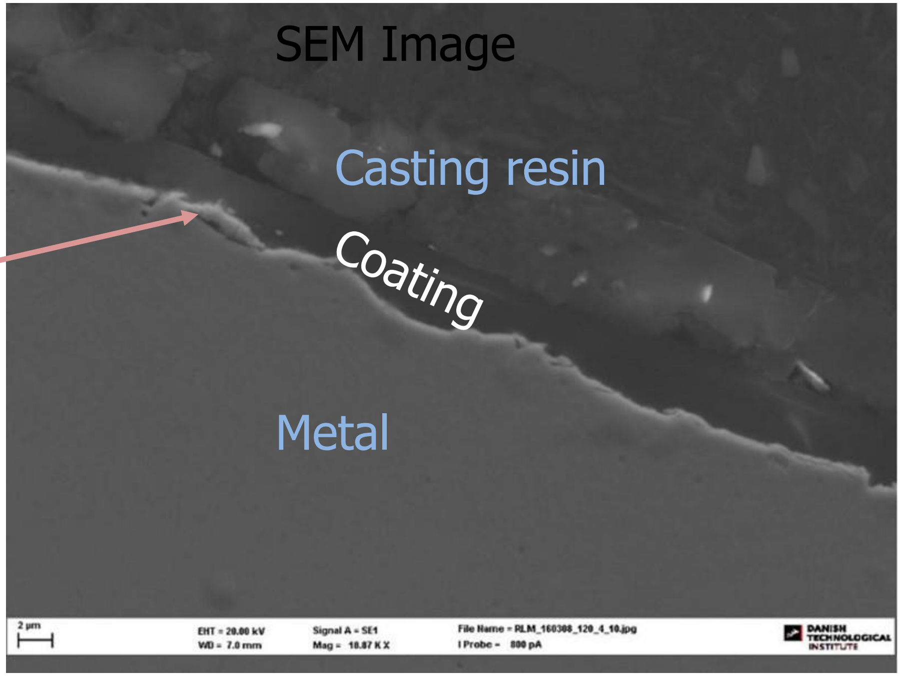
SiRu: silicone rubber coatings developed at DTI, Polymer chain length SiRu2>>>SiRu1
SolGel: organic-inorganic hybrid coatings prepared by sol-gel processing at DTI. SolGel1 contains a low S.E additive missing in SolGel2.

DANISH TECHNOLOGICAL INSTITUTE

Application

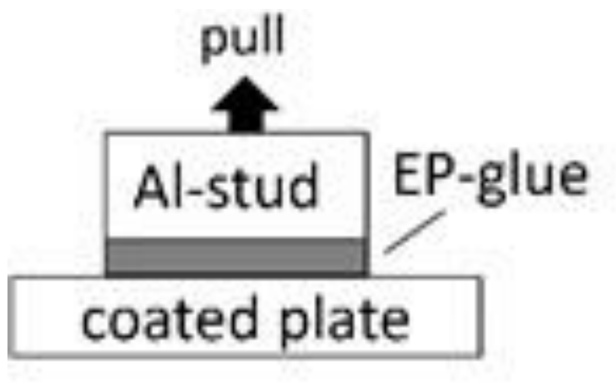
Successful applications of a 4 μm thick coating on the ID of Ø:18 mm tubes, 1 m long





Pseudo-barnacle adhesion

Pseudo barnacle test* (inspired by ASTM 2011 barnacle adhesion)
Barnacles: Particularly severe form of marine fouling due to the strong adhesion
The removal of epoxy studs glued to the surfaces results in adhesion forces similar to those of real living barnacles.



Pseudo barnacle test

According to Kendall´s theory** (adhesion of hard objects)

$$F_{pull\text{-}off} \propto w_a^{1/2} K^{1/2} d^{-1/2}$$

Wa: Work of adhesion,
depends on surface tension
K: Depends on modulus
d: Film thickness

Low interfacial tension, soft material, high film thickness → low adhesion

*Stein et al. Structure property relationships of silicone biofouling release coatings: Effect of silicone network architecture on pseudo-barnacle attachment strengths. Biofouling, vol.19 (2003)
**Kendall K. The adhesion surface energy of elastic solids. Journal of Physics D: Applied Physics, vol.4 (1971)

DANISH TECHNOLOGICAL INSTITUTE

Pseudo barnacle adhesion

Surface	Thickness (µm)	Pseudo barnacle adhesion
AISI 316L	-	>10 MPa
Epoxy	18±3	3.9±0.9
SiRu1	22±3	0.33±0.06
SiRu1-thin	7±3	0.33±0.04
SiRu2	13±3	0.66±0.10
SolGel1	4±1	0.22±0.09
SolGel2	4±1	0.50±0.11

Results do not follow Kendall´s theory with respect to thickness and modulus

- Kendall: Silicone rubber (softer, thicker) should be best
- Results: Steel and epoxy are poor, but SolGel (harder, thinner) is as good

Possible further explanations

- Low surface roughness
- **Interfacial slippage concept***
  Mobile polymer chains in the interphase reduce adhesion
  Silicone rubber or the silicone additive in SolGel1 may provide such effect

→ Both silicone rubber and sol-gel coatings outperform bare steel and epoxy coating

*Golovin, K et al, Design durable icephobic surfaces. Science Advances, vol. 2 (2016)
Beemer, D.L et al. Durable gels with ultra-low adhesion to ice. Journal of Materials Chemistry A, vol. 4 (2016)

DANISH TECHNOLOGICAL INSTITUTE

Durability (repeated removal)

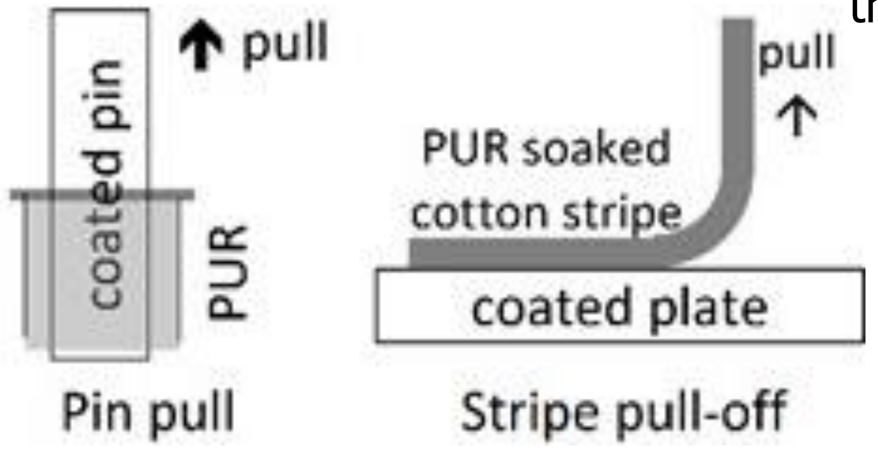
Pseudo barnacle test: Usually freshly coated sample

Experience from other tests
- Initially low adhesion is not sufficient
- Mode of removal plays an important role

Pin pull test
A coated pin is mold in PU-resin and pulled along the pin's axis

Stripe pull off
A cotton stripe is impregnated with PU resin and glued to coated plates.

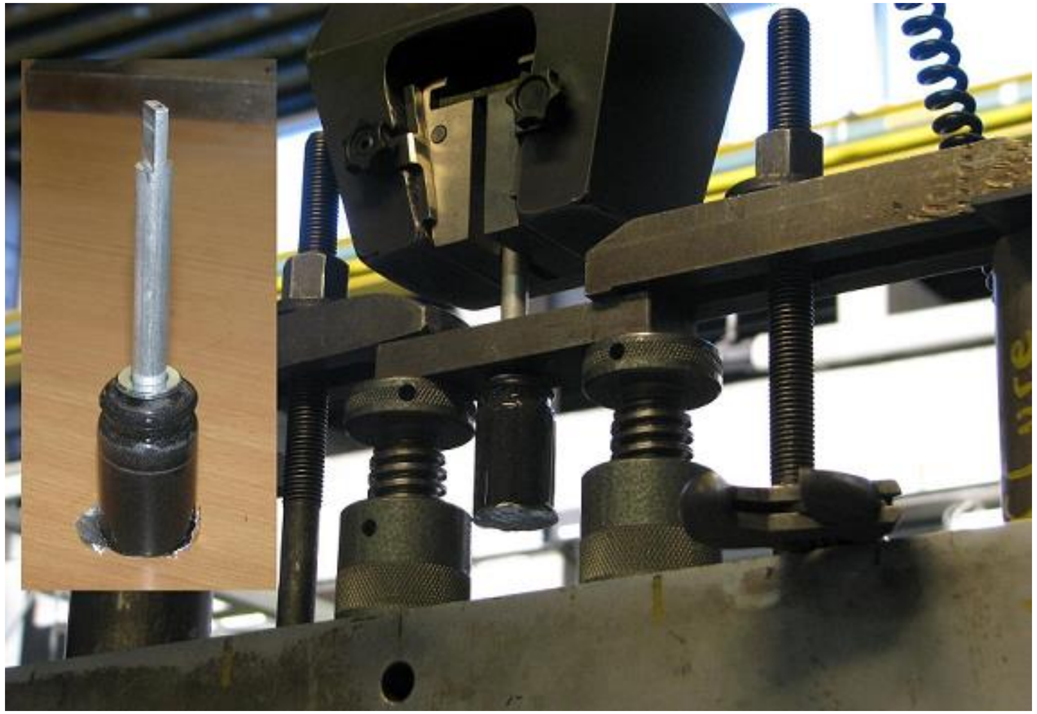
The stripe is pulled off perpendicular to the surface, measuring maximum force



DANISH TECHNOLOGICAL INSTITUTE

Durability (repeated removal)

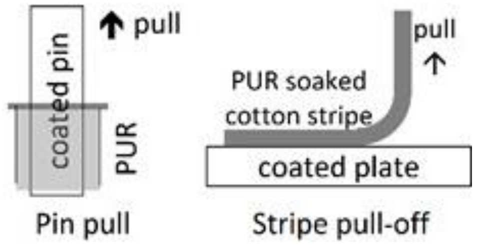
Pin Pull test



Stripe pull off

DANISH TECHNOLOGICAL INSTITUTE

Durability (repeated removal)



Pin Pull test

Surface	Max Pressure 1st pin pull in MPa	Max Pressure 7th pin pull in MPa
SiRu1	1.5±0.0	2.3±0.1
SolGel1	0.95±0.0	4.4±0.1

Stripe pull off

Surface	Max tension 1st stripe pull-off in N/m	Max tension 11th stripe pull-off in N/m
SiRu1	16±10	37±17
SolGel1	90±27	1000±30

Initial (1st test):
SolGel1 and SiRu1 similar in pin pull, but SiRu1 shows lower adhesion in stripe pull-off.

Repeated (7th/11th test):
The repellent properties of SolGel1 degrade faster than those of SiRu1 (silicone rubber)

SolGel1 has silicone solely in the surface, as compared to bulk silicone rubber

DANISH TECHNOLOGICAL INSTITUTE

First validation in an algae plant

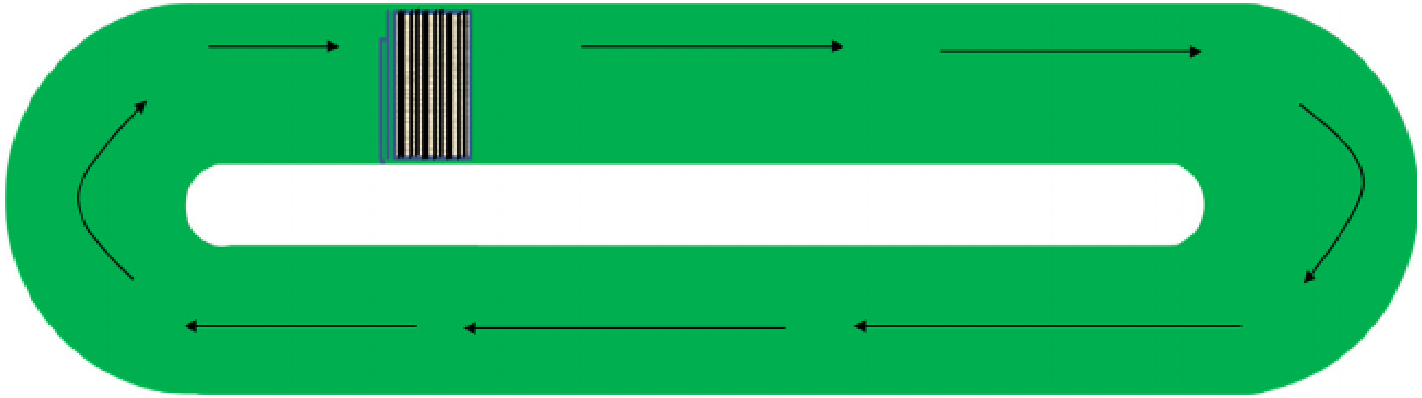
Litoral, Southern Spain

DANISH TECHNOLOGICAL INSTITUTE

First validation in an algae plant

Raceway reactor in a green house
Sea water, T=15-27°C, V=10m^3, continuous flow 2 m/s
Nannochloropsis gaditana (seawater microalgae), c=0.9 g/l

Steel coupons (SAF 2205) were coated and immersed into the reactor



DANISH TECHNOLOGICAL INSTITUTE

First validation in an algae plant

- 64 days exposure
- Fouling mass analysis:
  - Drying and weighing (analytic balance)
  - Complete fouling removal with water
  - Drying and weighing again to calculate the fouling mass Δm

D02
SolGel coating

D14
Silicone rubber coating
Commercial

D10
Organic coating
Commercial

Surface	Sample no.	Δm after fouling removal in g	Coating thickness
Sol-gel coatings *(organic inorganic hybrid coatings)*			
SolGel1 (silicone additive → repellent surface)	D01	**0,05**	~5 µm
SolGel2 (same as SolGel1, but without silicone)	D02	**0,04**	~5 µm
SolGel3 (with silicone additive)	D03	**0,22**	~3 µm
SolGel4 (with silicone additive)	D05 D06	**0,09** **0,07**	~7 µm
SolGel5 (same as SolGel4, but without silicone)	D07 D08	**0,15** **0,04**	~7 µm
Silicone rubber based materials			
SiRu1	D11	**0,57**	~50 µm
SiRu3 (different cross-linker as SiRu3)	D09	**0,85**	~50 µm
SiRu4 (with hydrophilic additive)	D12	**0,23**	~50 µm
Commercial fouling release, silicone ship hull paint (contains hydrophilic additive)	D14 D13 D15 D16	**0,04** **0,14** **0,11** **0,11**	~100 µm
Organic coating			
Commercial epoxy ship hull paint	D10	**0,43**	~100 µm

Best: Stainless steel
Good: Sol-Gel and commercial fouling release (No effect of silicone additive in Sol-Gel)
Bad: Epoxy and silicone rubber without hydrophilic additive

Conclusions from first validation

DANISH TECHNOLOGICAL INSTITUTE

Need for more real-life tests with sample repetition.
Laboratory tests without real-life validation do not seem meaningful.

Test shows snap-shot after 64 d. Fouling growth easier on top of existing fouling.
Longer exposure needed to better analyze coating differences.

→ Significance is limited. But what can we learn anyway?

- Novel, thin, fouling-release coatings performed as good or better than commercial coatings, no visual evidence of coating degradation
- A flow rate of 2 m/s is most likely insuffient for fouling release action
  → Use higher flow rates (often not desired)
  → Improve fouling-release coatings
  → Alternative (new project?): Develop biocidal anti-fouling coatings / Adapt commercial anti-fouling coatings to low thickness and higher temperatures (faster biocide release)
- Contrast between pseudo barnacle test and algae plant results, esp. with respect to surface energy and interfacial slippage

DANISH
TECHNOLOGICAL
INSTITUTE

The authors like to thank the European Union for funding through the H2020 project MATChING, grant agreement 686031

www.matching-project.eu

Thank You!

THE FRAMEWORK PROGRAMME FOR RESEARCH AND INNOVATION
HORIZON 2020

MATChING
MATERIALS & TECHNOLOGIES FOR PERFORMANCE IMPROVEMENT OF COOLING SYSTEMS IN POWER PLANTS