LABORATORY OF CHEMISTRY AND MATERIALS TECHNOLOGY

Coatings for exhaust heat recovery heat exchangers

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Energy Recovery and Power Generation from Waste Heat

25 February 2016

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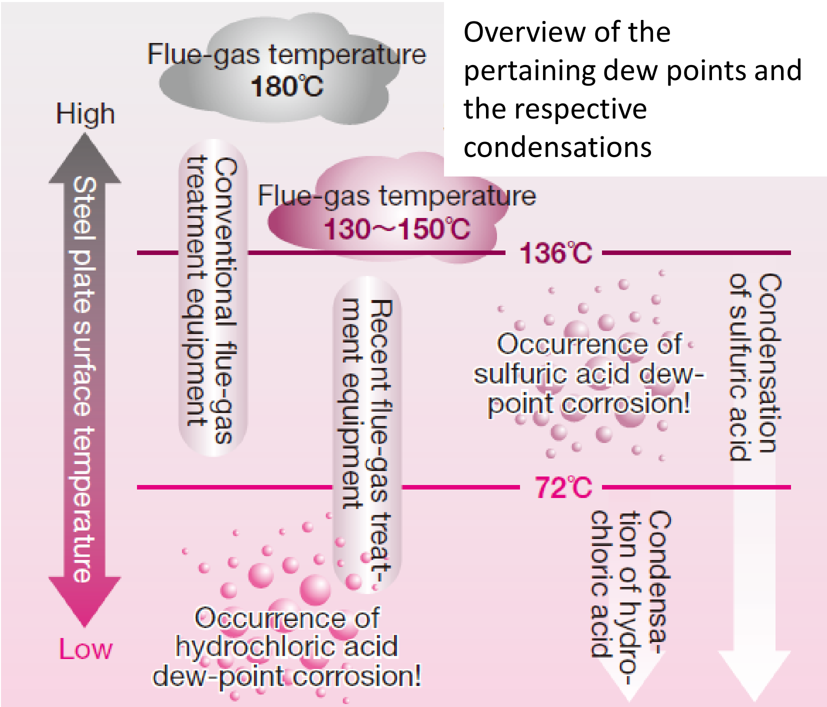
CSEF Centre for Sustainable Energy use in Food chains

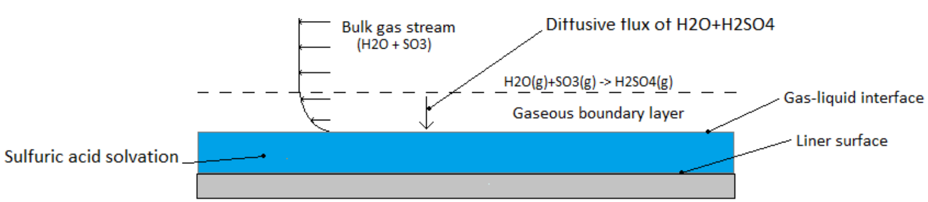
Brunel University London

I-ThERM

Understanding the problem



Overview of the pertaining dew points and the respective condensations



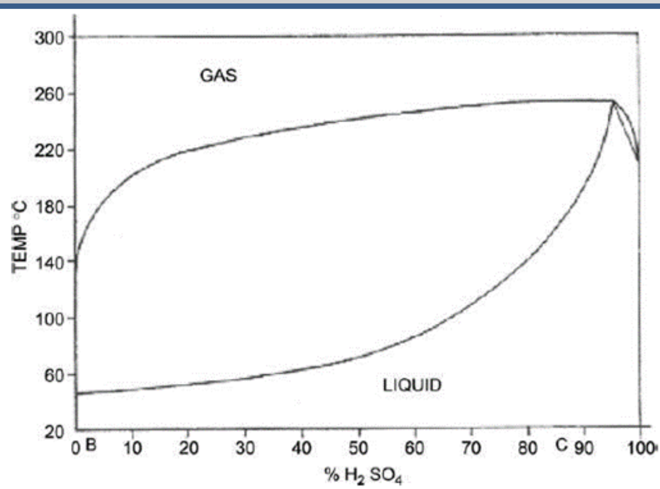
Below ca. 140 °C condensation of H_2SO_4
Below 100 °C condensation of H_2O
Below ca. 72 °C condensation of HCl

Actually this problem *condensates* the worst case scenario in Corrosion Science and Engineering:

-Humidity
-H_2SO_4
-HCl
-High Temperature
-Gas flow i.e. increased transport phenomena
-Erosion

<u>Controlling the corrosion in such environment s rather ambitious…</u>

Understanding the problem



Phase diagram of sulphuric acid (Land, 1977) ($P_{H_2O}+P_{H_2SO_4} = 0.1$ atm)

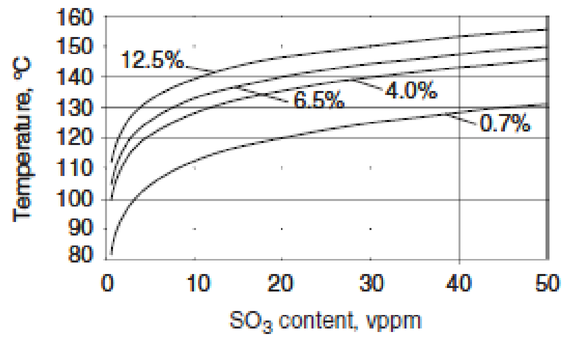


Fig. 1 Dew-point behavior of SO_3 at various water contents in the gas. Source: Ref 1

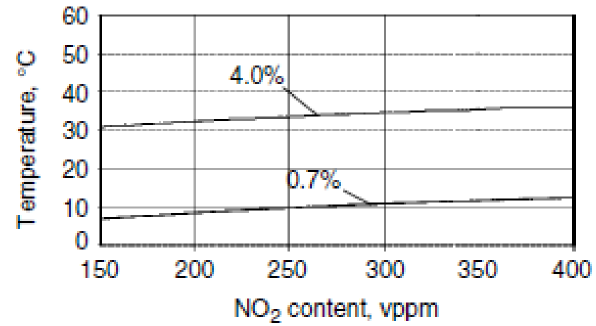


Fig. 3 Dew-point behavior of NO_2 at 0.7 and 4% water content in the gas. Source: Ref 3

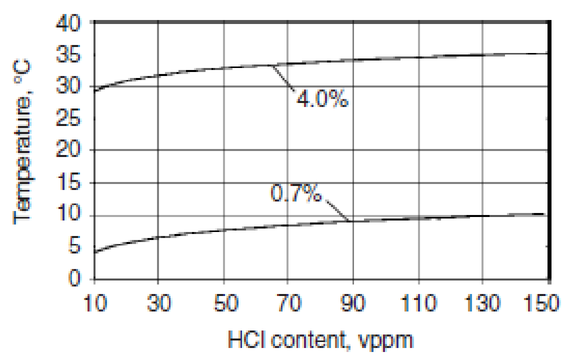


Fig. 2 Dew-point behavior of HCl at 0.4 and 7% water contents in the gas. Source: Ref 2

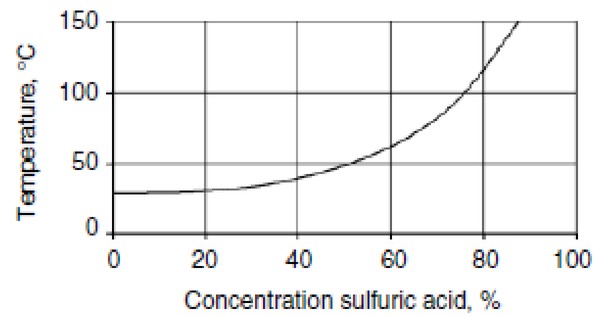


Fig. 4 Concentration of condensed sulfuric acid from an SO_3 gas containing 4% water

The concentration of the first condensates:

@120 °C → 75% H_2SO_4

@95 °C→67% H_2SO_4

Too concentrated!!!

W. Cox et al, Components Susceptible to Dew-Point Corrosion© 2006 ASM International. ASM Handbook, Volume 13C, Corrosion: Environments and Industries (#05145G)

Understanding the problem

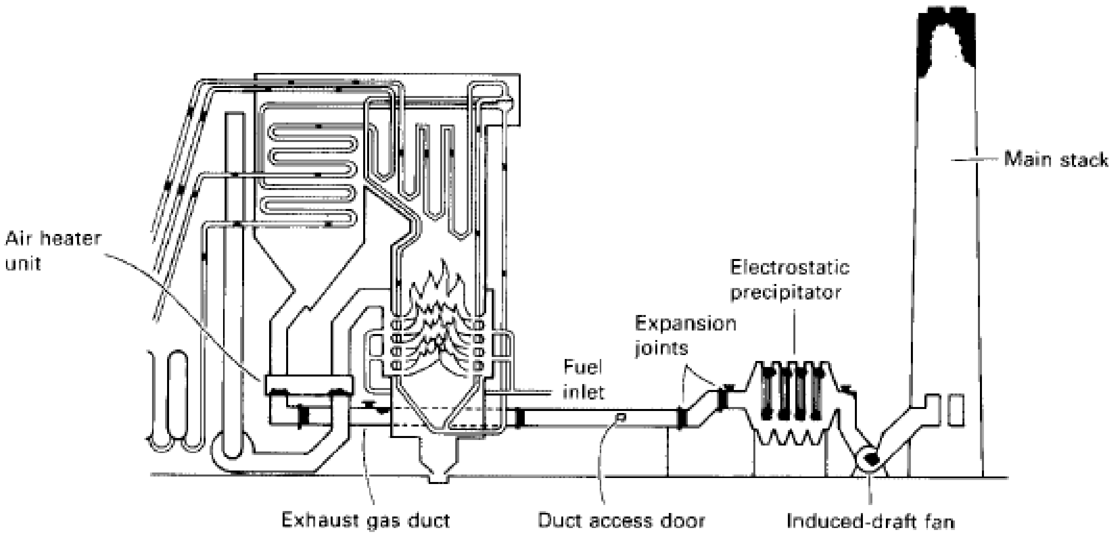


Fig. 5 Fossil-fired power generation boiler showing areas susceptible to dew-point corrosion (black areas)

Table 1 Polymers used in condensing heat-recovery systems

Type	Maximum temperature °C	Maximum temperature °F	Cost ratio
Polypropylene (PP)	80(a)	175(a)	1
Polyvinylidene fluoride (PVDF)	150(b)	300(b)	25
Perfluoralkoxy copolymer (PFA)	240	465	55
Polyetherketone based (PEEK)	300–330	570–625	95

(a) At 2 to 3 atm. (b) At 5 to 6 atm

It is difficult to give blanket advice on lessening dew-point corrosion problems because much depends on the precise plant configuration and service environment. However, general comments on **materials** selection, plant **operation**, use of neutralizing **additives**, **maintenance**, good housekeeping, and lagging (**insulation**) are offered in the sections that follow.

W. Cox et al, Components Susceptible to Dew-Point Corrosion© 2006 ASM International. ASM Handbook, Volume 13C, Corrosion: Environments and Industries (#05145G)

Ways to prevent corrosion_In general

- **Materials selection**
  Alloy selection
- **Design**
  Novel design approaches to minimize corrosion,
- **Control of Ambient**
  Temperature, pH, humidity, chemical concentrations
- **Coatings**
  Metallic, non-metallic, liners, new approaches
- **Inhibitors**
  Organic and non-organic inhibitors
- **Cathodic Protection**
  Impressed current, sacrificial anode
- **Anodic protection**

Typical examples of some cases will be presented and commented hereafter

Material Selection

Excellent Review may be found in:
The corrosion Resistance of Ni-containing alloys in Sulfuric acid and related compounds, 1983

- **Commercial available alloys claim improved resistance**
- From Thyssem Krupp
- S-TEN from Nippon Steel
- SX Sulfuric Acid Acid Steel from Edmeston
- etc

TABLE XCII
Plant Corrosion Tests in Wet Chlorine Gas and Sulfuric Acid Saturated with Chlorine

Alloy	Corrosion Rate																	
	Test 1		Test 2		Test 3		Test 4		Test 5		Test 6		Test 7		Test 8		Test 9	
	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy
HASTELLOY alloy C	0.01	0.4	0.003	0.1	nil[a]	nil[a]	nil	nil	nil	nil	0.02	0.8	0.02[b]	0.9[b]	0.15[c]	6[c]	0.13[d]	5[d]
HASTELLOY alloy C—as welded	0.01	0.2	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
HASTELLOY alloy C—welded and annealed	0.03	1.1	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Type 316 stainless steel	0.003	0.1	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Carpenter alloy 20Cb	0.08	3.1	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
MONEL alloy 400	>2.72[e]	>107[e]	–	–	–	–	>2.03[e]	>80[e]	–	–	–	–	–	–	–	–	–	–
Carbon Steel	>1.32[e]	>52[e]	–	–	–	–	–	–	–	–	–	–	–	–	–	–		–
Titanium	0.05[c]	1.9[c]	>0.99[e]	>39[e]	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil
Zirconium	–	–	–	–	0.51	20	>2.03[e]	>80[e]	0.51	20	>2.29[e]	>90[e]	>1.09[e]	>43[e]	1.27[f]	50[f]	>0.76[e]	>30[e]
CHLORIMET alloy 3	–	–	–	–	0.01[b]	0.5[b]	0.01	0.4	0.02	0.6	0.28	11	0.23[b]	9[b]	0.51[f]	20[f]	1.37[d]	54[d]

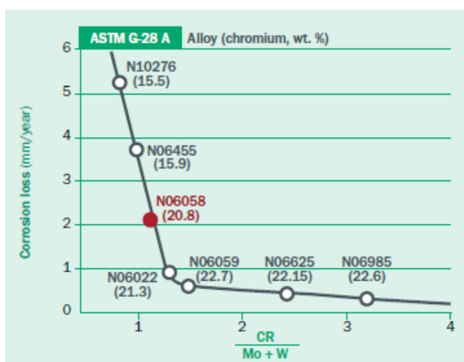
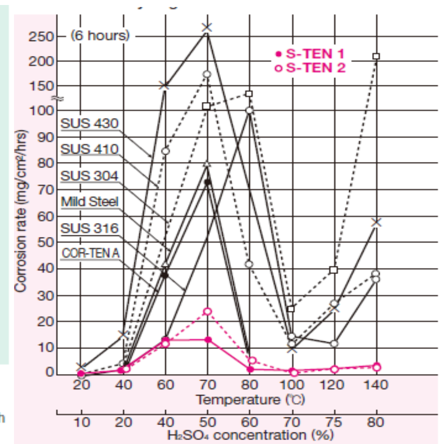
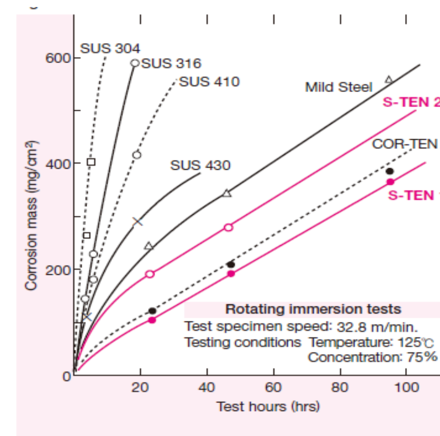


Figure 1 Corrosion loss of nickel-chromium-molybdenum alloys in boiling 50 % H2SO4 with 42 g/l $Fe_2(SO_4)_3$ x 9 H_2O in accordance with ASTM G-28 A as a function of their ratio of chromium to molybdenum plus tungsten, from [3] with addition of a corrosion rate obtained on a sample of alloy UNS N06058.





Inhibitors

Sulfuric Acid Dew Point

Neutralizing additives, usually calcium or magnesium oxide/ hydroxide, tend to have an ad hoc usage, especially in oil-fired situations. Their benefit in preventing acid smuts is proven, but their ability to reduce corrosion rates consistently is less certain..

$MgO+SO_3 \rightarrow MgSO_4$

Questionable performance

Paul A. Schmidtchen, High Activity Magnesia Use for SCR Related SO3 Problems

Reese et al. 1965 J. T. Reese, J. Jonakin and V. Z. Caracristi. "Prevention of Residual Oil Combustion Problems by Use of Low Excess Air and Magnesium Additive" Transactions of the ASME, Journal of Engineering for Power, pp 229-236, April 1965.

Levy and Merryman, 1965 A. Levy and E. L. Merryman. "SO3 Formation in H2S Flames." Transactions of the ASME, Journal of Engineering for Power, 87 Series A, pp 116-123, January 1965.

Direct injection of ammonia has been employed to reduce flue gas acidity, but the resultant formation of sticky bisulfite deposits can lead to severe fouling

Nitric Acid Dew Point.

No additives are available to prevent nitrate Stress Cracking Corrosion.

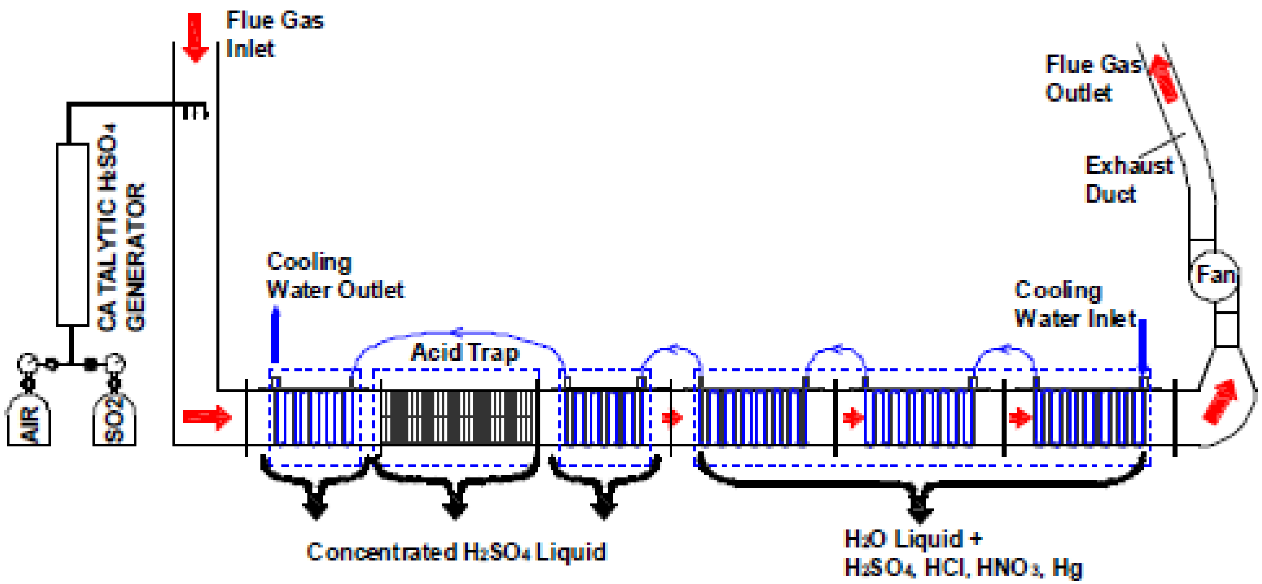
W. Cox et al, Components Susceptible to Dew-Point Corrosion© 2006 ASM International. ASM Handbook, Volume 13C, Corrosion: Environments and Industries (#05145G)

"Acid Traps"

A section of inlet duct filled with closely spaced vertical flat plates aligned parallel to the flow direction.

-Acid traps reduced the vapor phase acid concentrations entering the heat exchangers just downstream of the traps by 10.2 to 13.7 % for T>Dew point

-Acid trap reduced the sulfuric acid flux on the heat exchanger positioned just downstream of the trap by 33 to 42 %. T<Dew Point



2011-levy-(energy RESEARCH CENTER)-Recovery of water from boiler flue gas using condensing heat exchangers

Coatings_Overview

- For concrete stack lining, an expensive **fluoroelastomer** has given outstanding protection against acid dew-point attack,
  - but the material is permeable to moisture and hence is unsuitable for use on a carbon steel substrate.
- Less expensive **modified coal tar epoxy** has performed well in some applications
  - but good quality surface preparation is critical.
- **Glass flake polyester** coatings can be satisfactory provided that the substrate cannot flex, especially during cold weather, because such coatings can be very brittle at low temperatures.
  - but exhibits low thermal conductivity
- An **isocyanate-cured epoxy** material has also been successful in less troublesome plant conditions.
  - but exhibits low thermal conductivity
- For air heater elements, **double-dipped enamel coatings** are likely to be most effective
  - but add significantly to the capital cost.
- **Arc sprayed aluminum, chromia, and alumina** materials,
  - but arc sprayed aluminum has been reported to be generally satisfactory for high-temperature gas turbine stack applications. However, in these stacks, severe thermal conditions can lead to exfoliation and acidic rust flaking.

Coatings_State of the Art

Evaluation of Surface Coatings on Heat Exchangers

David J. Kukulka
State University of New York College at Buffalo
1300 Elmwood Avenue
Buffalo, New York 14222 USA

Paul Leising
Cameron Compression
3101 Broadway
Buffalo, NY 14225 USA

Type	Uncoated	Uncoated Cleaned and Rerun	Teflon Based Coating	Electro - Coating	Epoxy Based Coating	Heresite Coating
Large PHE	X	X	X			
Small PHE	X	X		X	X	
Brazed PHE	X					X

Performance decrease

- Uncoated: ca. 56.5%
- Coated: 47% (on average)
- Increase of performance after cleaning

Corrosion/Fouling performance

- Corrosion was eliminated (?) in all coated plates

Kukulka, D. J., & Leising, P. (2009). Evaluation of surface coating on Heat Exchangers. *Chemical Engineering Transactions*, *18*, 339-344.

Coatings_State of the Art

PERGAMON

Electrochimica Acta 47 (2002) 2969–2979

ELECTROCHIMICA Acta

www.elsevier.com/locate/electacta

Corrosion resistance of ternary Ni–P based alloys in sulfuric acid solutions

Guojin Lu, Giovanni Zangari *

Available online at www.sciencedirect.com

SCIENCE DIRECT

ELSEVIER

Surface & Coatings Technology 200 (2005) 2510–2514

SURFACE & COATINGS TECHNOLOGY

www.elsevier.com/locate/surfcoat

Electroless Ni–Cu–P–PTFE composite coatings and their anticorrosion properties

Q. Zhao *, Y. Liu

ELSEVIER

Surface and Coatings Technology 155 (2002) 270–284

SURFACE & COATINGS TECHNOLOGY

www.elsevier.com/locate/surfcoat

Graded Ni–P–PTFE coatings and their potential applications

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[c]School of Chemical Engineering, Dalian University of Technology, Dalian 116012, PR China

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

ELSEVIER

Corrosion behavior of electroless deposited Ni–Cu–P coating in flue gas condensate

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[a] Department of Materials Science and Chemical Engineering, Dalian University of Technology, 158 Zhongshan Road, Dalian 116012, China

[b] Urban Construction Department, Beijing Institute of Civil Engineering and Architecture, Beijing 100044, China

Electroless Ni-P-Cu-PTFE deposition and corrosion performance

Table 1
Compositions and operating conditions of electroless Ni–P–PTFE and Ni–Cu–P–PTFE

Compositions (g/l)	Ni–P–PTFE	Ni–Cu–P–PTFE
$NiSO_4 \cdot 6H_2O$	25	50
$CuSO_4 \cdot 5H_2O$		1
$Na_3C_6H_5O_7 \cdot 2H_2O$	18	60
$NaH_2PO_2 \cdot H_2O$	30	25
$CH_3 \cdot COONa$	18	
$(CH_2)CS$	1 ppm	
NH_4CH_3COO		40
PTFE (60 wt.%)	10 ml/l	4–18 ml/l
$C_{20}H_{20}F_{23}N_2O_4I$ (FC-4)	0.4	0–0.6
pH	4.8	7–9.5
T (°C)	88	70–88

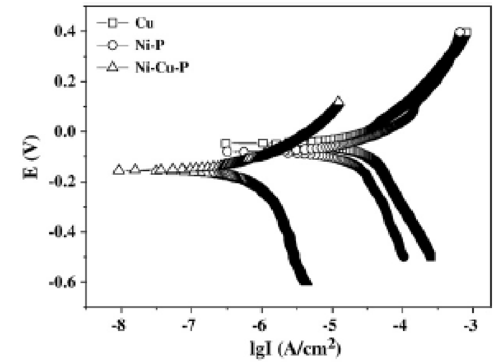
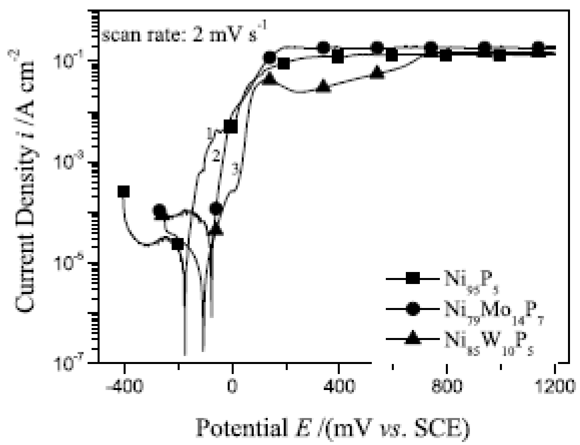


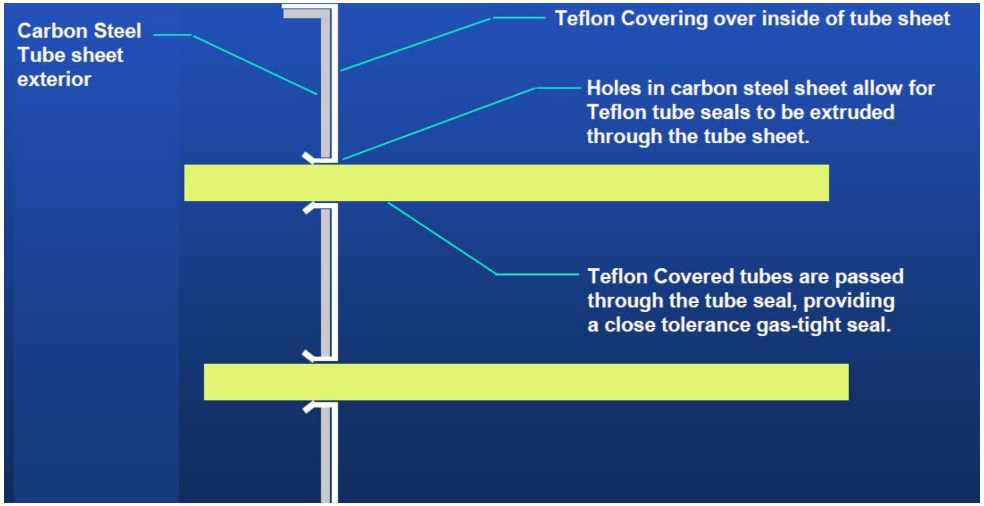
Fig. 1. Polarization curves of samples in flue gas condensate at temperature of 60 °C



- Addition of W to Ni/P alloys can slightly improve their corrosion resistance.
- On the contrary, addition of Mo has little or no obvious beneficial effect on alloy corrosion characteristics

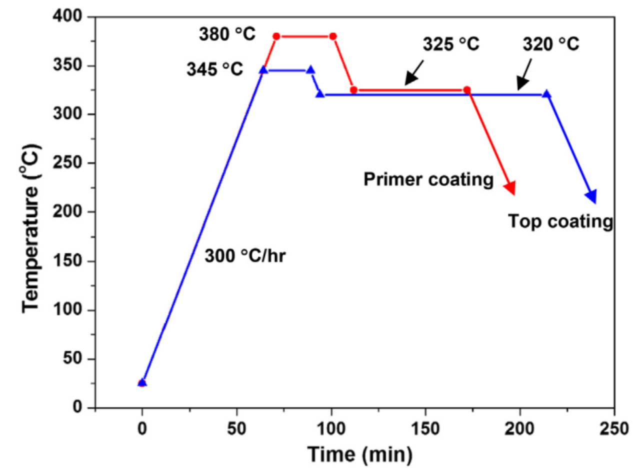
Coatings_State of the Art

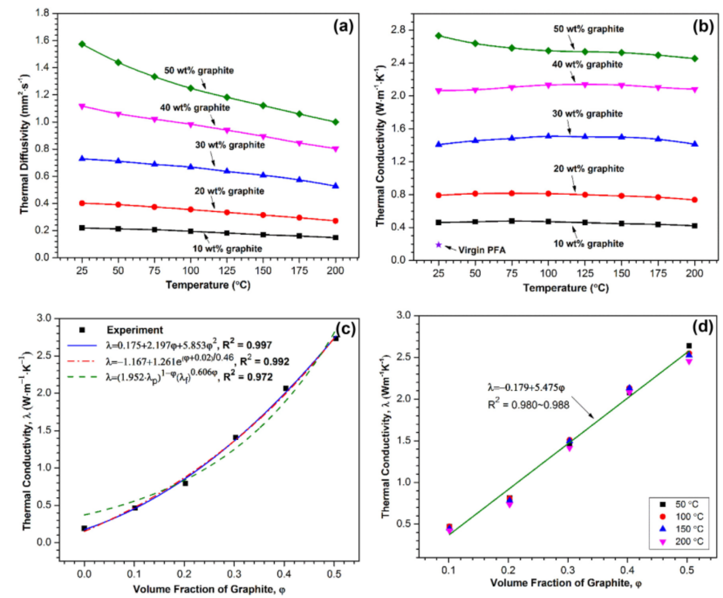
- **Teflon covered pipes (commercially available product, USA)**
  - CHX, 15 mil (<400um) Teflon covering

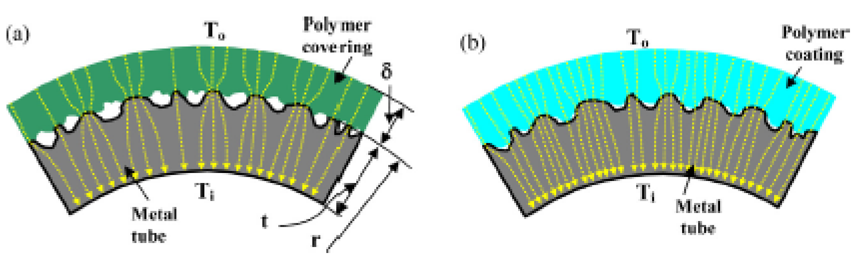


Fluoropolymers for condensing Heat Exchangers

- post-blending graphite particles into perfluoroalkoxy (PFA) powder
- Curing @380oC
- Improved scratch resistance
- Improved thermal diffusivity







He, Y., Walsh, D., & Shi, C. (2015). Fluoropolymer composite coating for condensing heat exchangers: Characterization of the mechanical, tribological and thermal properties. *Applied Thermal Engineering*, *91*, 387-398.

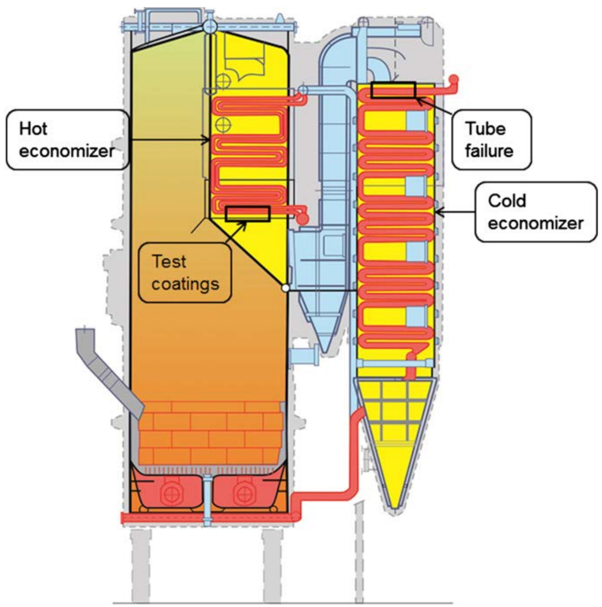
Coatings_State of the Art

HVOF for biomass-fired fluidised bed boiler

- Fe–27Cr–11Ni–4Mo and Fe–19Cr–9W–7Nb–4Mo

- exposed to biomass boiler conditions for two years
- Improved scratch resistance

- The low alloyed boiler tubes had suffered severely with a corrosion rate as high as 2 mm/year
- Dense thermal spray coatings offered excellent protection during the exposure



Oksa, M., Varis, T., & Ruusuvuori, K. (2014). Performance testing of iron based thermally sprayed HVOF coatings in a biomass-fired fluidised bed boiler. *Surface and Coatings Technology*, *251*, 191-200.

Conclusions from the State of the Art

- There is no coating with satisfactory performance at such harsh environments
- Open issues on materials and coatings performance
- Very limited open access results and publications
- In most cases there is a trade-off that must be balanced, i.e. heat transfer coefficient and thermal conductivity vs. corrosion protection
  - Coating thickness increase:
    - (+) Increased corrosion protection
    - (-) Decreased heat transfer coefficient
    - (-) Decreased thermal conductivity
- Is there any solution that may treat them both simultaneously?

New approaches

This is the our main role within I-ThERM

Develop coatings exhibiting

- Increased heat transfer coefficient
- Improved corrosion protection, through easy removal of the condensates from the surface

_Thank you

Thank you for your time

Energy Recovery and Power Generation from Waste Heat

25 February 2016

Brunel University London, Uxbridge, Middlesex, UB8 3PH

Financial support from H2020, i-ThERM project Contract 680599 is acknowledged