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Behaviour of Two Products Containing Film Forming Amines (FFA) in the Secondary Circuit Physico-Chemical Conditions of the Pressurized Water Reactor (PWR)



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International Conference on Film Forming Substances

INDUSTRIAL CONTEXT

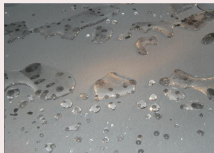
- Lay-up of the secondary circuit of nuclear power plants (PWR)
- Secondary circuit chemistry: **CHALLENGES**
 - *Health-environment: decrease the use of hydrazine*
 - *Safety: blockage and fouling limited*
 - *Cost: lay up implementation and follow up simplified*
 - ...

EXPECTED EFFECTS OF FFA

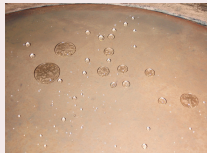
Protection against corrosion of all the secondary circuit
(steam and liquid parts) during lay-up



Ramminger et al. 2012



Wagner et al. 2014



Anghel et al. 2014

- ⇒ Formation of a **protective and hydrophobic** film
- ⇒ Heat transfer performance seems to be improved

FFA INJECTION

- short duration / **intermediate duration** / continuous
- during normal operations, before lay up
- in the feedwater before the steam generator

OBJECTIVES OF THIS STUDY

- Study of the behaviour of 2 products containing FFA

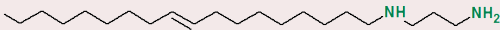
1- Odacon[®] (Reicon)

Main FFA: $C_{18}H_{37}NH_2$ (ODA)



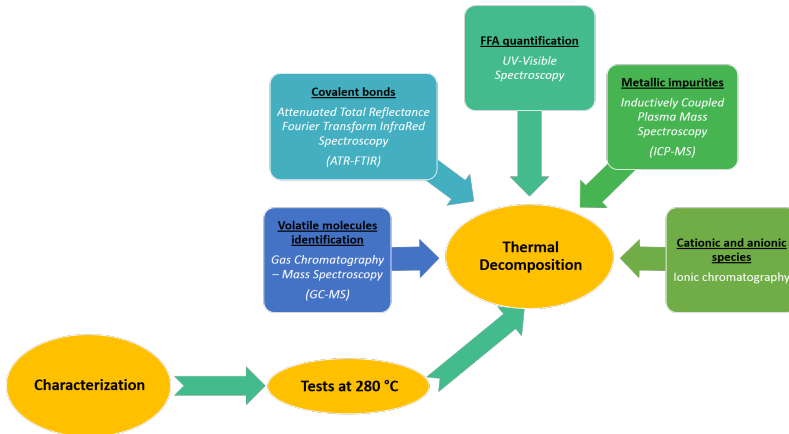
2- Cetamine[®] (Kurita)

Main FFA: $C_{18}H_{35}NHC_3H_6NH_2$ (OLDA)



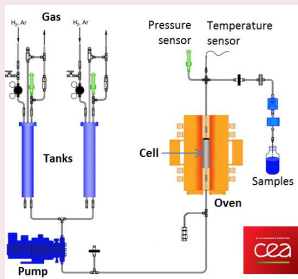
- ⇒ Evaluate the stability of the FFAs
- ⇒ Identify the decomposition products

SAME METHODOLOGY FOR ODACON[®] AND CETAMINE[®]



EXPERIMENTAL TEST DEVICE

- Specific device (GROZIE):
 - One-pass circulation system \Leftrightarrow the solution is constantly renewed
($t_{residence} = \rho(T)V_{cell} / Q_L$)
 - Or no circulation
- Designed to work in a one phase flow
 $25 < T(^{\circ}\text{C}) < 360$ and $0.1 < P(\text{MPa}) < 20$



EXPERIMENTAL CONDITIONS ~ PHYSICO-CHEMICAL CONDITIONS OF THE SECONDARY CIRCUIT

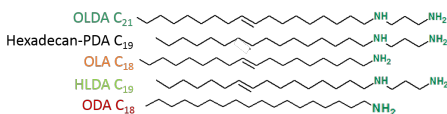
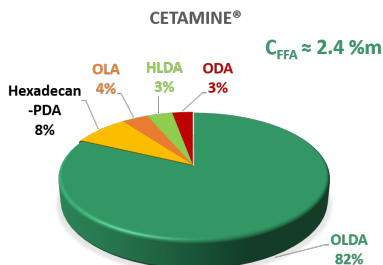
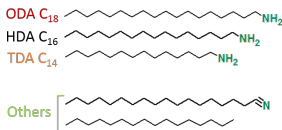
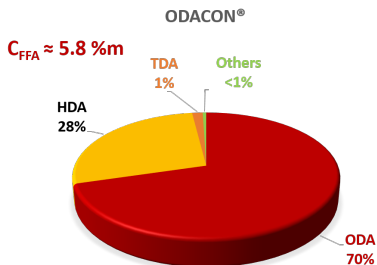
| Product | Duration | C _{FFA} | T | P | pH | C _{ETA} |
|-----------|----------|---------------------|---------|--------------------|-----------|---------------------|
| - | - | mg.kg ⁻¹ | °C | 10 ⁶ Pa | at 25 °C | mg.kg ⁻¹ |
| Odacon® | 20 min | 32 | 280 ± 1 | 10 ± 0.2 | 9.8 ± 0.1 | 3.5 |
| | 1 week | 38 | | | | 3.5 |
| Cetamine® | 20 min | 109 | 280 ± 1 | 10 ± 0.2 | 9.8 ± 0.1 | - |
| | 1 week | 104 | | | | - |

- pH is adjusted at 25 °C with diluted ammonia

MEASURED PARAMETERS

- T, P
- C_{FFA} by UV-visible spectroscopy

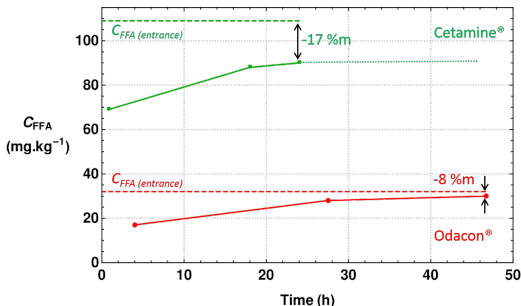
Characterization of the 2 FFA mixtures



→ No detection of metallic and ionic impurities in the 2 products
except traces of Na in the Odacon®

THERMAL STABILITY OF THE STUDIED FFAs (1/2)

- After 20 min of residence time at 280 °C



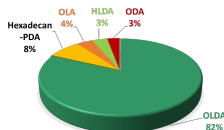
$\Delta C_{FFA} = -8 \%m \Leftrightarrow 2 \text{ mg.kg}^{-1}$ adsorbed on the cell surface
 \Rightarrow no thermal decomposition of FFA in Odacon®

$\Delta C_{FFA} = -17 \%m + 3 \text{ mg.kg}^{-1}$ adsorbed on the cell surface
 $\Rightarrow 14 \%m$ of FFA seems to be decomposed

BUT

- For the Cetamine[®]

With the UV-visible spectroscopy analysis method:
Measured absorbance \approx OLDA absorbance



\Rightarrow 7 %m of FFA were thermally degraded (not detected by the analyses)

OR

$\Rightarrow \Delta C_{FFA} \approx 0$ (14 %m of FFA not detected by the analyses)
but OLDA was decomposed in other FFAs

THERMAL STABILITY OF THE STUDIED FFAs (2/2)

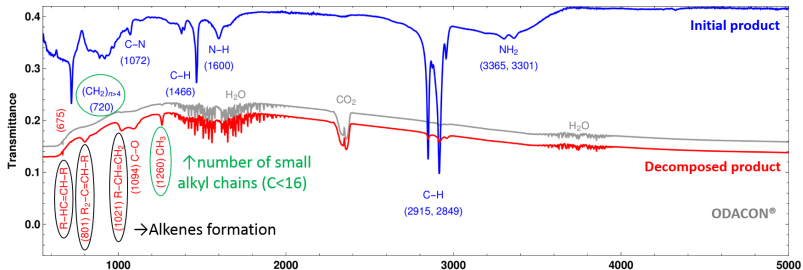
- After **1 week** of residence time at 280 °C
 - $\Rightarrow \Delta C_{FFA} = -76$ %m for the test with Odacon[®]
 - $\Rightarrow \Delta C_{OLDA} = -84$ %m for the test with Cetamine[®]

FFA IDENTIFICATION IN THE THERMALLY DEGRADED SOLUTION

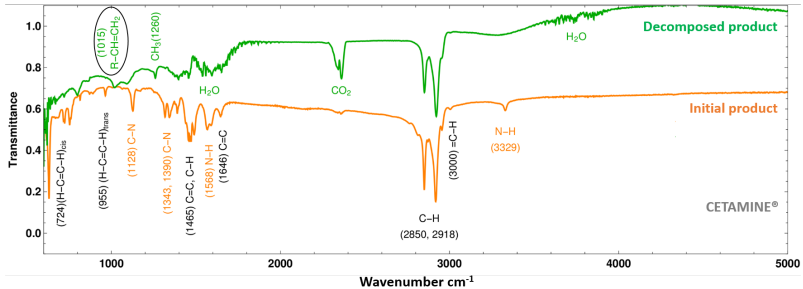
Analytical method: Gas Chromatography Mass Spectroscopy (GC-MS)

- Odacon[®]
 - Detection of ODA and HDA (∈ initial product)
 - Disappearance of TDA
- Cetamine[®]
 - Disappearance of the main FFA: OLDA
 - ↑ of OLA and ODA proportions
 - Formation of HDA

⇒ Consistent with the decomposition of OLDA in FFAs with shorter alkyl chains.



→Alkenes formation



IONIC SPECIES

Analytical method: Ionic chromatography

After **1 week** of residence time at 280 °C

- **Formation of ammonia NH_4^+** for both products
 \Rightarrow Consistent with the detection of alkenes R-CH=CH_2
with ATR-FTIR spectroscopy analysis



- **Formation of carboxylates, mainly acetate CH_3COO^-** only for Cetamine[®]

CONCLUSIONS

- For 20 min residence time in the physico-chemical conditions of the secondary circuit
 - ⇒ **No decomposition** of the Odacon[®]
 - ⇒ **Very little decomposition** of the Cetamine[®]
- **Significative decomposition** for 1 week residence time
 - ⇒ the products mainly formed are FFAs *which does not respond with the quantification protocol of FFAs*
 - ⇒ formation of NH_4^+ and alkenes R-CH=CH_2

PERSPECTIVES

- Determination of the **distribution coefficient** of the 2 products at steam generator temperature *i.e.* 275 °C



Thank you for your attention

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