ICRN 33

IAPWS Certified Research Need – ICRN

Film Forming Substances in Water/Steam Cycles (Fossil, Nuclear, Industrial, and Geothermal Plants)

The IAPWS Power Cycle Chemistry Working Group is aware of increasing use in the boiler and steam industry of film forming substances (FFS) that are utilized as corrosion inhibitors within the water/steam cycle. However, there are a significant number of scientific unknowns related to the use of these compounds, their modes of operation in relation to corrosion inhibiting, and other properties such as influences on steam generating and steam condensing processes, physical properties, and application benefits.

When applied correctly, the use of FFS can have benefits for reducing corrosion in water/steam cycles, particularly improving wet and dry conservation during shutdown/layup. Equally, misapplication of FFS can result in poorly performing applications where additional corrosion protection is not provided, the risk of plant damage/failure occurring is increased due to corrosion, and the applications are uneconomic in nature.

This ICRN is intended to stimulate research to provide additional technical data and understanding to provide responses to the Research Needs list provided in this document.

Although encouraging work in this area, IAPWS is not able under its statutes to provide financial support. The IAPWS contacts can provide any further development information and will liaise between research groups.

Issued by the
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Background

Film forming substances (FFS) are organic corrosion-inhibiting molecules, comprised of carbon and hydrogen together with nitrogen and/or oxygen, that have been applied in water and steam cycles since the 1970s to minimize both online and offline corrosion of iron and copper materials.

IAPWS has developed two Technical Guidance Documents (TGDs) to assist the operator of plants with guidance related to the application and use of film forming substances:

- **IAPWS TGD8-16(2019)**
  IAPWS Technical Guidance Document: Application of Film Forming Substances in Fossil, Combined Cycle, and Biomass Power Plants
  October 2019 Revision
- https://www.iapws.org/techguide/FFS.html

- **IAPWS TGD11-19**
  IAPWS Technical Guidance Document: Application of Film Forming Substances in Industrial Steam Generators
  October 2019
- https://www.iapws.org/techguide/FFS-Industrial.html

Since 2017, IAPWS has also hosted 7 international conferences on film forming substances.

FFS are applied at concentrations, as active molecules, in the µg/L concentration range in water and steam cycles due to their ability to reduce online and offline corrosion of ferrous and copper materials that are oxide coated. FFS applied in water and steam cycles are required to have a volatility in steam similar to that of ammonia and sufficient thermal stability up to supercritical pressures (~ 250 bar) and steam temperatures exceeding 600 °C, so that the residence time of the compounds in the cycles is sufficient to provide corrosion protection.

IAPWS recognizes that film forming substances (FFS) have been cited in the literature as both chemical substances with specific offline hydrophobic film forming properties and commercial products containing these chemical substances. In the past all film forming substances were sometimes misleadingly referred to as film forming amines even when they were non-amine-based. This has led to much confusion and misunderstanding in the literature so IAPWS has standardized the following terminology.

- Film Forming Substances (FFS): Film Forming Substances describe defined chemicals with film forming properties. They adsorb onto the water/steam surfaces of a plant. FFS could be amine-based or non-amine-based.

- Film forming amines (FFA): defined group of organic substances with specific functional groups. Because the chemical definition covers a wide range of amine molecules, the TGDs list three substances, which have been the subject of intensive research, and where significant application experience is available. The FFA listed in the TGDs are the following three chemicals that are defined with a unique numerical identifier assigned by Chemical Abstracts Service (CAS):

Octadecylamine	(ODA)	CAS-no.: 124-30-1
Oleylamine	(OLA)	CAS-no.: 112-90-3
Oleyl Propylenediamine	(OLDA)	CAS-no.: 7173-62-8

- Film forming amine products (FFAP): Commercially available products which contain a FFA as the active FFS. They can also contain further substances such as alkalizing amines, emulsifiers, reducing agents, and dispersants (e.g., polycarboxylates). The operator will need to ask the supplier of the commercial product whether the FFA is included in the listing above and the composition.

  Examples of alkalizing amines are listed below. They are defined with a unique numerical identifier assigned by CAS:

2-Aminoethanol (Monoethanolamine)	CAS-no.:	141-43-5
Cyclohexylamine	CAS-no.:	108-91-8
2-Amino-2-methylpropanol	CAS-no.:	124-68-5
2-Diethylaminoethanol	CAS-no.:	100-37-8
Morpholine	CAS-no.:	110-91-8
3-Methoxypropylamine (MOPA)	CAS-no.:	5332-73-0

- Film Forming Products (FFP): This term was introduced in the original IAPWS TGD8-16 to summarize all commercially available products in this class which do not contain film forming amines (FFA). The exact chemistries of these FFP are normally proprietary and can cover a wide range of molecules but the ones commonly commercially available are known to be carboxylate or dicarboxylate-based molecules in the approximate C7-13 range.

- Some known examples of these molecules and their unique numerical identifier assigned by Chemical Abstracts Service (CAS) are as follows. Note this list is not exhaustive.

*N*1,*N*9-Diethylnonanediamide	CAS-no.:	93476-02-9
Nonanedioic (azelaic) acid	CAS-no.:	123-99-9
Diammonium azelate	CAS-no.:	63075-84-3
Dodecanedioic acid (DDDA)	CAS-no.:	693-23-2
Heptanoic acid	CAS-no.:	111-14-8
Nonanoic acid	CAS-no.:	112-05-0
Undecanoic acid	CAS-no.:	112-37-8
cis-4-decendionic acid	CAS-no.:	72879-22-2
Sorbitol fatty acid ester	CAS-no.:	72869-62-6
Ethylene bis-stearamide	CAS-no.:	110-30-5

- There is a significant information gap in relation to the physical properties of all these molecules, their interactions and behaviors in water/steam cycles, and their mode of operation to list but a few areas of interest that this ICRN hopes to resolve.

List of Problems that have Emerged from Application of FFS

The original FFS TGDs included a Section 8 delineating the activities that should be undertaken before application of an FFS. Most of the problems that have been experienced worldwide and reported at the IAPWS FFS conferences relate to organizations not following the “Section 8

Guidance". The main ones relate to acquiring knowledge on the typical levels of corrosion product transport and identification of levels of internal deposits on heat transfer surfaces.

A partial listing of the main problems areas includes:

- Increasing levels of internal deposits on heat transfer surfaces in fossil boilers and HRSG HP evaporators
- Under-deposit corrosion associated with the internal levels of deposits
- Gunk deposits on internal drum surfaces and on steam turbine components
- Ineffective corrosion control.

Research Needed

Due to the major knowledge gaps associated with FFS, the following areas of specific research needs are listed.

Specific key research needs identified include:

1. Effects of film forming substances on the growth rate of iron, copper, and chromium oxides in water and steam systems. Fundamentals of actual mechanism(s) of corrosion protection and how exactly iron and copper feedwater corrosion products are reduced. Information from this will allow assessment of transitioning between different FFA and FFP and the identification of risks and possible interactions with other products in the water/steam cycle including dispersants in nuclear cycles.

2. Mechanism related to increased iron oxide deposits on heat transfer surfaces under FFS dosing (FFA and FFP). Iron oxide transport and dispersion mechanisms and iron oxide deposition under FFS conditions including potential FFS influenced boiler/HRSG tube failure mechanisms.

3. Film formation, kinetics, structure, diffusion, and porosity on water- and steam-touched oxide surfaces. Information is available for ODA and OLDA but is needed for OLA and importantly for any FFP. Researchers would likely need to have direct discussions with current FFP suppliers re the exact chemical composition of their products and the active components in them to assist with determining these properties.

4. Uncertainty of stability limits and decomposition products. Information is available for ODA and OLDA but is needed for OLA and any FFP.

5. Uncertainty of adsorption onto oxide surfaces as a function of film forming substances. Information is available for ODA and OLDA but is needed for OLA and any FFP.

6. Measurement of surface tension is needed. Initial measurements have been conducted for ODA but are needed for the other FFA and any FFP. This will enable IAPWS and operators to assess whether steam turbine performance is increased on application of an FFS.

7. Improved standard analysis methods for FFS products – both for grab sample/off-line and on-line/continuous analysis.

The practical outcome(s) of this ICRN would be the development of additional technical information that assists with providing a basis for more selective, effective (corrosion inhibiting), lower risk, better monitored, application of FFS in steam generating plants. This will lead to amendment of the current IAPWS TGDs and prevention of continuing failure/damage following misapplications of FFS.

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