# Use of film forming amines (FFA) in nuclear power plants for lay-up and power operation

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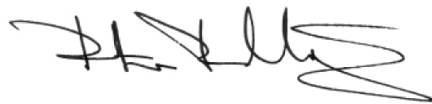
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# Contents

# 1      Introduction

This report presents a new corrosion inhibitor based on film forming amines (FFA). The film forming amines (FFA), which are often referred to as fatty amines or polyamines, are able to form a mono-molecular hydrophobic film or layer adsorbed on the metal surfaces, that constitutes a homogeneous protective barrier against corrosion by its water-repellent behaviour. FFA belongs to chemical substances of the class of oligo alkylamino fatty amines, the simplest representative being the well-known Octadecylamine (ODA). They show a high affinity to metal surfaces via the free electron pair of the amine functionality. The film established on the metal surface acts as a barrier for corrosive agents like oxygen and carbon dioxide (carbonic acid). According to lab and pilot plant studies, FFA based corrosion inhibitors provide a very high level of corrosion protection for carbon steels that are used in steam-water cycle of nuclear power plants (also in conventional auxiliary systems). Due to the volatility of the film forming amine, not only the steam generator (boiler) section but also the whole steam water cycle of the power plants, for example the condensate system, can be protected. The high affinity to surfaces can lead to a slow removal of surface deposits such as loose magnetite and impurities.

The Film forming amines are successfully used as water treatment additives since several decades. Especially in the field of industrial plants but also in steam water cycle of nuclear power plants of VVER type in Eastern Germany and Russia they have experienced positive treatment results. However, although steam water cycle including the steam generators of numerous VVER plants are operated since many years with FFA treatment, this technology was not applied in western nuclear power plants due to lack of knowledge and experience. Since several years, AREVA started to very successfully apply this treatment with a specific procedure in several PWR plants with the purpose to control the corrosion product transport into steam generators during the power operation and for long time lay-up of whole steam water cycle without using hydrazine. Even in a BWR plant this FFA treatment was applied in several parts of steam water cycle with success. The achieved results in several PWR, CANDU and BWR plants were excellent. Accordingly, based on the strong interest of the US nuclear industry, EPRI contracted AREVA to start with qualification program for US nuclear power plants.

This report summarizes the published information regarding the application of FFA in western NPPs as follows:

Chapter 2: Explains the motivation of the nuclear industry to apply FFA treatment;

Chapter 3: Summarizes the characteristics and behaviour of the FFAs and explains its mechanism;

Chapter 4: Described the requirements to be fulfilled for NPP applications with respect to impurity content, thermal stability, efficiency, and material compatibility;

Chapter 5: Describes the field application results and the gained experiences in PWR, HPWR and BWR plants;

Chapter 6: Describes the experience gained with FFA applications in component cooling systems (CCS) of the power plants;

Chapter 7: Gives a conclusive summary of the existing published information regarding the FFA treatment and gives recommendations for NPP plant engineers.

# 2 Background information

Steam generators (SG) of the pressurized water reactors (PWR) are the key components. Their reliability affects greatly the overall plant performance and availability. Worldwide experience showed that huge amount of PWR plants had in the past early 1970s up to 2000s serious corrosion and mechanical degradations in their SGs (see Figure 2-1) [EPRI, 2006]. These SG degradation problems often forced unscheduled and/or extended outages for preventive and corrective maintenance work, which were extremely costly in term of repair work, loss of power and personnel exposure. After implementing improvements regarding design, structural materials and water chemistry, PWR industry was successful in general to reduce these SG degradation problems significantly (see Figure 2-2) [EPRI, 2006]. However, there are still many PWR plants having SG thermal and corrosion degradation problems worldwide.
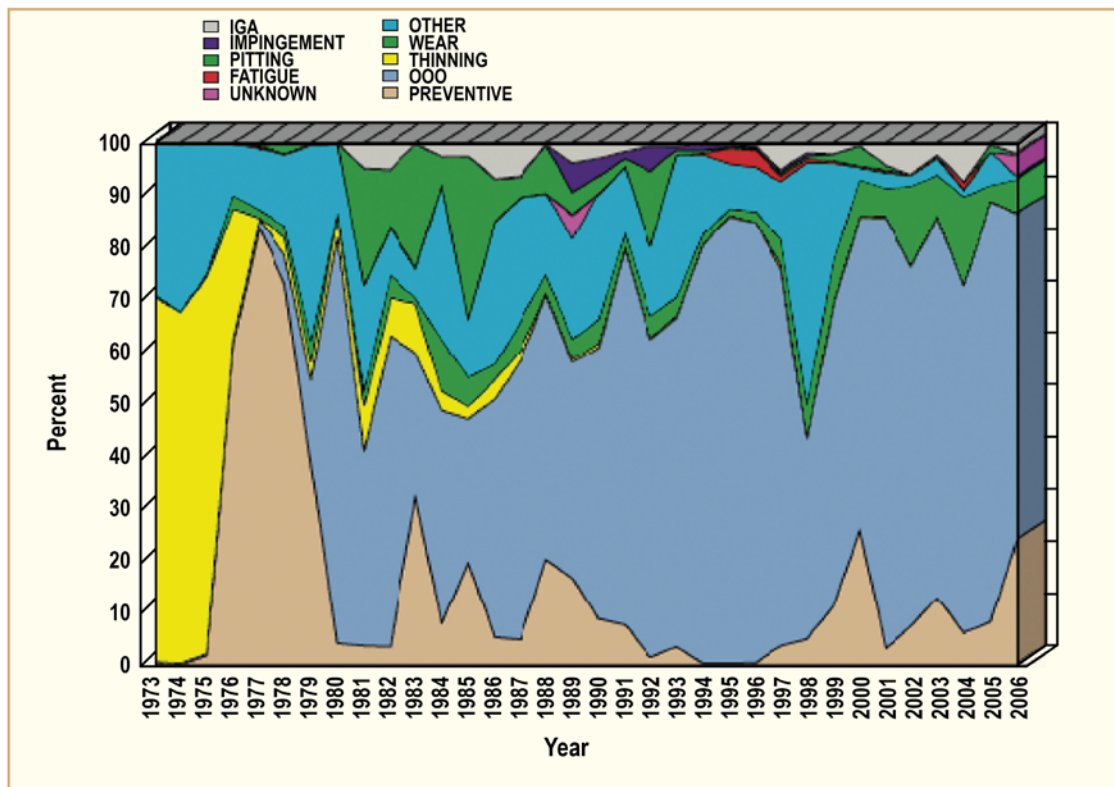


Figure 2-1:     Worldwide causes of SG tube degradation [EPRI, 2006].

# 3 Properties of Film Forming Amines

## 3.1 Hydrophobic film formation with FFAs

The most effective FFAs are the aliphatic amines (known also as fatty amines) with 10 to 18 carbon atoms in the chain. As chemical substance they belong to the oligo-alkyl-amino fatty amine family. The general formula of the FFA can be written as $R1-[NH-R2-]_n-NH_2$, where n is an integer between 0 and 7, R1 is an un-branched alkyl chain with 12 to 18 carbon atoms and R2 is a short alkyl chain with 1 to 4 carbon atoms [Betova et al., 2014 and Jack et al., 2015]. FFAs can have mono- or polyamine groups. The amine is the hydrophilic head and the hydrocarbon alkyl chain is the hydrophobic tail of the FFAs. The free electron pair of the amine nitrogen atom has a strong affinity for metals; therefore, FFAs bonds to metal surfaces by adsorption of these amine groups through their free electron pair, whereas an ionic interaction between the amino groups and van der Waals forces between the alkyl chain exist as illustrated in Figure 3-1. In case of FFAs with monoamine (n=0) this amine bonds to surface with its hydrocarbon chain sticking out forming a hydrophobic film, while a FFA with polyamine attaches to surface at more than one location and their hydrocarbon hydrophobic chain is oriented somewhat parallel to the metal surface (see Figure 3-2) [Jack et al., 2015]. Octadecylamine (ODA) has the simplest FFA structure with monoamine group. It has the molecular formula of $C_{18}H_{39}N$ or $CH_3-(CH_2)_{17}-NH_2$.



Figure 3-1:     Adsorption of amines on a structural material surface in high-temperature water [Betova et al., 2014]



Figure 3-2:     Schematic representations of FFA films: monoamine (left), polyamine (right) [Jack et al., 2015]

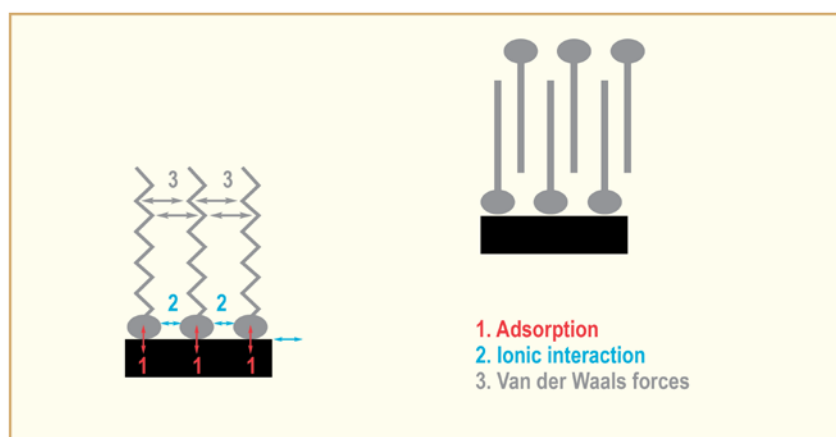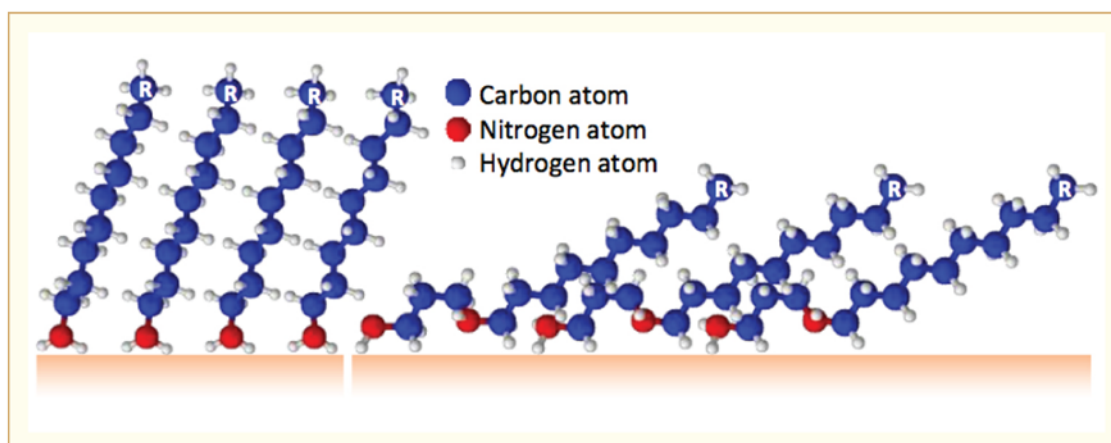The hydrophobic film produced by FFA application is proposed to be monolayer in thickness and its effectiveness does not increase with further continued treatment beyond that what was required to maintain the monolayer coverage on the system surfaces. [Betova et al., 2014]. This film forms on the metal surfaces a barrier against water and all corrosive substances; therefore, it protects the metal surfaces from corrosive attacks. Once it is formed, its protective behaviour remains for a long time periods, even it is no more injected [Jäppinen et al., 2016]. The forming of hydrophobic FFA film depends on the metal surface area, the temperature, pH value of the medium, time duration, and the excess of the FFA in the water phase [Choi et al., 2016 and Betova et al., 2014]. Therefore, it is not possible to have a correlation between the injected and on surfaces adsorbed amount of the FFA. Only a portion of the injected FFA remains as emulsion soluble in the water. These free soluble FFA builds so-called micelle, which is dispersed in a liquid colloid that forms an aggregate with hydrophilic head regions in contact with surrounding water sequestering the hydrophobic single-tail regions in the micelle centre (see Figure 3-3). Only the free FFA in water, i.e. micelle, can be analytically determined, but not the FFA bonded to the metal surfaces. FFA can usually be detected quantitatively at concentrations as low as 0.5 ppm.
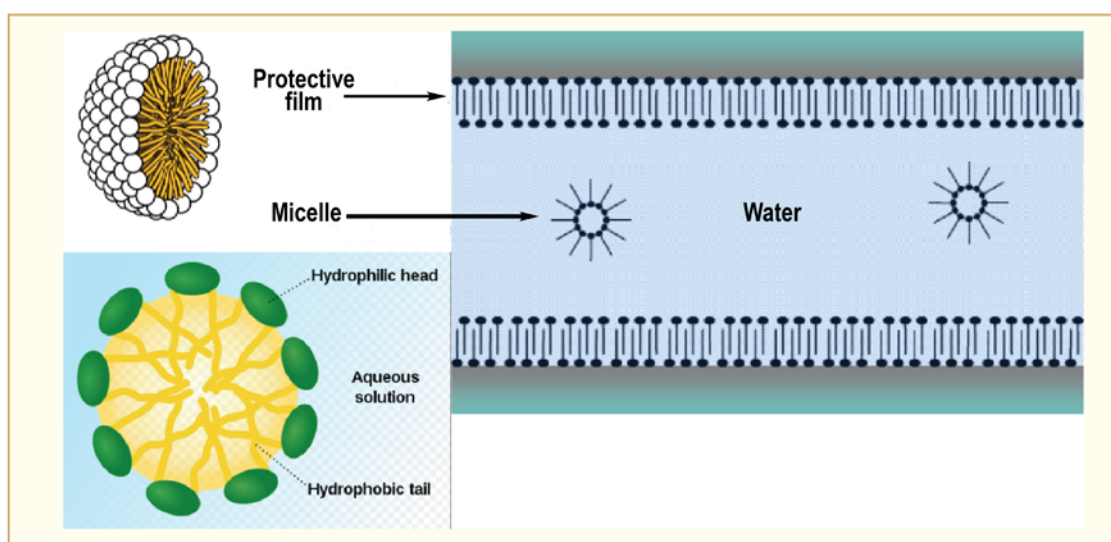


Figure 3-3:        Soluble (micelle) and attached form of filming amines, [Betova et al., 2014]

It is believed that the use of FFA with multiple amine groups might be more beneficial with respect to efficacy because it provides for a given FFA concentration more coverage of the surface and could provide stronger bonding of hydrophobic film to metal surface [Choi et al., 2016].

For producing hydrophobic films the plant system surfaces it is not necessary to have bare metal surfaces. Also in the operating PWR plants FFA can be applied to build protective hydrophobic films. It is also reported that magnetite layers on carbon steel surfaces even favour the formation of hydrophobic films. The homogeneity of the film depends on the thickness and porosity of the magnetite layer. The thicker the magnetite layer and more porose it is, longer is the application duration with higher FFA concentration to fill and cover the porose gab surfaces of the magnetite layer [Delaunay et al., 2016].

Film forming by FFA application is also influenced by pH value of the medium. For Octadecylamine (ODA) it is experienced that the optimum pH value of the medium is between 8.0 and 8.5. During the application the condensate pH value is controlled in this range. If the pH values are outside of this range, the hydrophobic film usually strips off and can cause deposits in the steam traps and condensate lines [Betova et al., 2014].

Due to strong surface affinity of the FFAs they can gradually replace and remove the loosely attached substances like particulate iron oxides, copper and/or ionic impurities from the surfaces. A possible way of interaction of the FFAs with the hydroxyl-iron oxides under complex formation on the surface is shown in Figure 3-4. The release of such loosely attached particulate iron oxides and ionic

impurities was observed during FFA injection in the plants, which can be illustrated as a sketch in Figure 3-5.
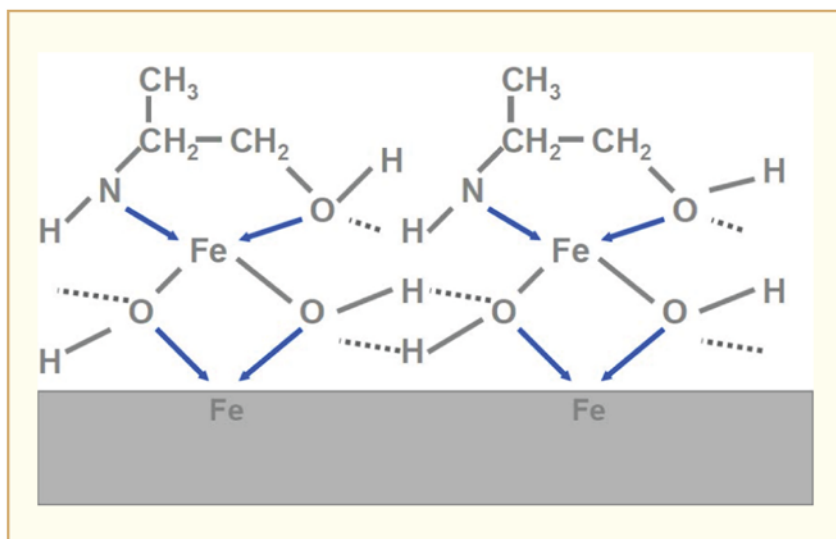


Figure 3-4:     Surface complex formation between an amine and a hydro-oxidized iron surface, [Betova et al., 2014]
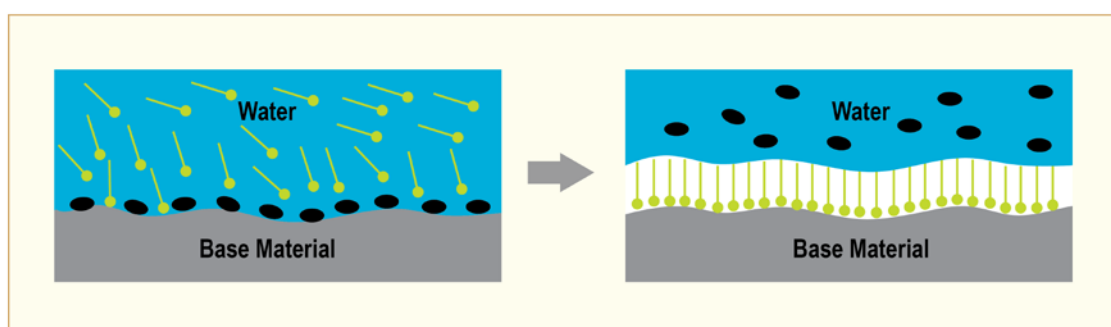


Figure 3-5:     A simplified scheme of the action of film-forming amines (yellow) on the release of impurities from surfaces (black), [Betova et al., 2014]

FFA increases the zeta potential of both magnetite and steam generator tubes (e.g. Alloy 800) and maintains it at positive values in the whole operating pH range. Thus FFA could also provide an electrostatic repulsive force in analogy to the polymeric dispersants [Betova et al., 2014].

The field experience revealed also a beneficial effect of FFA application on heat transfer coefficient on boiling surfaces. It has been experienced that FFA application form smooth hydrophobic surfaces, which increases the heat transfer coefficient by introducing additional nucleation sites. Usually when the number of nucleation sites is limited, steam bubbles grow and combine with nearby bubbles forming steam gas pockets along the heated surfaces. This steam film blankets the heated surface and prevents the water from reaching the heated wall, which results in decrease of heat transfer efficiency. The hydrophobic film on the heated surface forces the steam bubbles to release from the wall faster before they grow and thus prevents steam from blanketing the heated wall. This phenomenon has been also demonstrated in laboratory measurements and recorded by videos. These video records revealed much more vigorous boiling when hydrophobic film was formed by FFA [Topp, 2010] and [Betova et al., 2014]. Increased bubble formation also leads to a lower heat flux density needed for nucleation occur [Choi et al., 2016].

## 3.2 Physical and chemical properties of the FFA Octadecylamine (ODA)

In this section the properties of the FFA is explained mainly based on the Octadecylamine (ODA), because the most published information exists from ODA as most used FFA in the industry and the only one applied in VVER and PWR plants.

Octadecylamine with the chemical formal $CH_3-(CH_2)_{17}-NH_2$, is a long chain aliphatic mono-amine with a molar mass of 269 g/mol; and has a melting point of 54-55°c and boiling point of 349°C. At ambient temperatures ODA is paraffinic type white colour solid mater. ODA is non-toxic except it may cause light mucosal irritation. Further physical and chemical properties of ODA are summarized in the following sections in more detail.

### 3.2.1 Thermal properties of ODA

The thermal decomposition (better defined as conversion) of ODA to secondary and tertiary aliphatic amines starts at 80°C and accelerates with increasing temperature according to the chemical reactions [Bäßler, 1997] and [Ramminger et al., 2012]:

Equation 3-1: $\qquad$ $2\ R-NH_2 \rightarrow R_2-NH + NH_3$

Equation 3-2: $\qquad$ $3\ R-NH_2 \rightarrow R_3-N + 2\ NH_3$

Equation 3-3: $\qquad$ $R-NH_2 + R-NH \rightarrow R_3-N + NH_3$

Equation 3-4: $\qquad$ $R-NH_2 \rightarrow R'-CH=CH2 + NH_3$

Magnetite accelerates these thermalized reactions catalytically. According to investigations this thermolysis at 250°C results after 1800 hours in 35-40% ODA, 30% Di-ODA and 10-15% Tri-ODA. The result of this ODA thermal decomposition doesn't mean that the hydrophobic film built loses it protective hydrophobic behaviour. The secondary and tertiary aliphatic amines, Di-ODA and Tri-ODA have stronger dipole moment and accordingly they are stronger bonded to the metal surfaces providing stronger hydrophobic protection. This thermolysis behaviour of ODA indicates that the hydrophobic films on the secondary side systems formed by ODA treatment might have different chemical composition depending on the system operating temperatures.

According to [Bäßler, 1997] above 450°C ODA decomposes thermally completely to $NH_3$, $H_2$, $CO_2$ and $CH_4$, without producing any harmful organic substances such as low molecular organic acids. However, according to [Betova et al., 2014] ODA would form satisfactory protective film also in the range of 350-560°c with the best quality film at 480°C! Obviously, although there exist no consistently information regarding the decomposition temperature of ODA, it must be at temperatures far above the operating temperatures of the PWR secondary side systems!

### 3.2.2 Solubility of ODA

The solubility of ODA is an important property, which determines the application conditions. ODA has low solubility in water at ambient temperatures (about 1 mg/kg) that increases with increasing temperature as shown in Figure 3-6 and Figure 3-7. In Figure 3-7, the interception of the curves of the "saturation concentration" and of the "turbidity points" gives the **Krafft point** of the colloidal solution (also known as Krafft temperature; named after German chemist Friedrich Krafft). The Krafft point is the minimum temperature above, which the FFA (ODA) solubility escalates by forming micelle. The so-called **micelle** is a dispersion of ODA, which is formed as colloidal aggregates in a liquid with hydrophilic head regions in contact with surrounding water sequestering the hydrophobic single-tail regions in the micelle centre. Below the Krafft point the micelle cannot be formed; the ODA remains as undissolved crystals in the water. The Krafft point is actually a point of phase change, at which ODA can exist simultaneously as crystalline, micelle and monomer. The critical micelle concentration (**CMC**) is defined as the concentration of ODA above which micelles form and all additional ODA added to the solvent forms micelles.

# 4 Specification for FFA appropriate for use in PWRs

Since several decades FFAs are used in many commercial fossil fired power plants as inhibitor for carbon steel corrosion by forming hydrophobic films. Although the exact chemical formulations used are often proprietary to the chemical vendors, some commonly used FFA chemicals are given in the following [Betova et al., 2014]:

- **Octadecylamine {ODA)**; this product is the most used FFA and was applied many times in VVER plants and also recently several times at PWR plants, once at HPWR plant and once at a BWR plant. It has the chemical formula of $CH_3(CH_2)_{17}NH_2$;

- **Stearyl dipropylene triamine**; This amine has the molecular formula of $C_{24}H_{33}N_3$;

- **Hexadecylamine**; This amine, also called 1-aminohexadecane, cetylamine or HAD, has the chemical formula of $C_{16}H_{35}N$;

- **Tetradecylamine**; This amine, also called 1-aminotetradecane or myristylamine, has the chemical formula of $CH_3(CH_2)_{12}CH_2-NH_2$;

- **Oleylamine**; The chemical formula of this amine is $CH_3(CH_2)_7CH=CH(CH_2)_7CH_2NH_2$;

- **N-oleyl-1,3-diaminopropane (OPD)**; This amine has the molecular formula of $C_{21}H_{44}N_2$;

Among all these FFA products ODA is the only one product that is applied in many times in VVER plants and recently in PWR, BWR and HPWR plants. The qualification of this product was performed by Eastern German research organizations together with Russian organization for the VVER plants; and recently by AREVA GmbH for PWR, BWR and HPWR plants. Further, it is nontoxic and environmentally friendly. However, there have historically been some concerns regarding the use of excess ODA concentration that may result in gelatinous sticky deposits [Drexler et al., 2011] that had to be removed manually. Therefore, the ODA treatment supplier should have the experience to apply it properly.

Recently EPRI has developed a qualification matrix with recommendations given for the development of specifications that can be used by PWR and HPWR plant utilities to identify an appropriate FFA chemical for use in their power plant [Choi et al., 2016]. The utility can make his decision based on the comparison of the available FFA test results provided by the FFA supplier with the recommended qualification matrix specifications, which is summarized in the following sections:

## 4.1 Purity requirements

Based on the assumption that FFAs will be applied continuously during the power operation similar to the general pH control agents, EPRI recommendation for the FFA impurity limits is 0.5 mg/kg for sodium, chloride, sulphate, fluoride, iron, copper and lead [Choi et al., 2016]; similar to the impurity limits given for the ETA. However, FFA (ODA) application for PWR and HPWR plants is designed in different way: ODA injection is applied only for 2-3 weeks at the end of the fuel cycle before shutting-down the plant for annual outage for lay-up purposes. Therefore, for such a short time period much less stringent impurity limits can be accepted for such FFA applications. Because, the total ingress and accumulation of the impurities in the steam generators is actually of concern rather than the short term impurity concentration in the feedwater.

## 4.2 Stability requirements (High and low temperature)

High temperature stability for the organic chemicals used in secondary side of PWR plants is an important issue; because, by their thermal decomposition organic acids as break-down products are produced, which are increasing the conductivity of condensate, feedwater and steam and therefore making the impurity monitoring difficult. The recommendation of EPRI is to select a FFA, which has sufficiently thermal stability so that it doesn't contribute too much to cation conductivity. This recommendation is fulfilled by ODA perfectly (for detailed information please see Section 3.2.1). Even though mono-ODA, as it is injected, starts to decompose above 80°C; it produces hereby di- and tri-

ODA, which also form stable hydrophobic films on the structural material surfaces and have very high thermal stability. No other organic acids are built, which can contribute to conductivity increase. The complete thermal decomposition of ODA, di- and tri-ODA is reported to be above 450°C (or even at higher temperatures), which is no more relevant for the PWR plants.

Also for storage purposes for FFAs, EPRI recommends a low-temperature stability for concentrated FFA products of at least shelf life of two years. However, for short time dilute FFA injections of two to three weeks as ODA is applied in PWR plants, it doesn't make any sense for long term storage of this product at plants. It is recommended to use dilute emulsion of ODA, with commercial name ODACON®, for the applications.

# 4.3      Efficacy Requirements

FFAs are expected to build a hydrophobic film on the surfaces of the structural materials, which repels the water from the metal surfaces and thus avoiding the material corrosion. Therefore, the efficacy of the applied FFA can be demonstrated either by its water rejection or by corrosion inhibition behaviour. According to EPRI recommendation at least one of these tests should be included in FFA specification:

## 4.3.1      Visual inspections by water droplet test

This is the simplest way to confirm the efficacy of the formed hydrophobic film on the structural material surfaces. The water that is poured on the surface is repelled as droplets, indicates the hydrophobic behaviour of the surface (see Figure 4-1).



Figure 4-1:      Condenser (left) and feed water pump steam turbine (right), [Ramminger et al., 2012]

## 4.3.2      Contact angle measurement:

In this test, a drop of water is placed on the with FFA treated metal surface. The angle formed between the drop wall and the surface is due to interfacial tension between the surface and the air, between the water and the air, and between the water and the surface. The higher the angle, the more hydrophobic is the surface (see Figure 4-2).

# 5 Field application and experience with FFAs

FFA applications offer significant benefits for the corrosion product control in the PWR secondary side for protecting the steam generator performance over the current techniques of pH control agents. This is because, they are not significant expensive and don't require complicated operating procedures, and they are flexible to changes in annual outage duration. The application of ODA in several PWR plants has demonstrated that forming a hydrophobic film on structural material surfaces in the secondary side systems has inhibited the corrosion of the structural materials. Use of this alternative lay-up procedure resulted in reduced corrosion product transfer into steam generators during start-up operations. In the following sub-sections the experience gained by ODA applications will be summarized.

## 5.1 PWR plants

### 5.1.1 Almaraz NPP Units

#### 5.1.1.1 Background information for FFA application

Almaraz NPP is a Westinghouse designed three loop PWR plant with two units each has 1000 MWe. The start of the commercial operation was in 1983 and 1984 for Unit 1 and Unit 2, respectively. The original steam generators (OSG) of both units were designed by corrosion sensitive Alloy MA 600. Due to SG tube corrosion problems (ODSCC: Secondary Side Stress Corrosion Cracking), in both units the OSGs had to be replaced, which was performed in 1996 and 1997 in unit 1 and unit 2, respectively [Arias et al., 2016]. The Siemens-KWU designed replacement steam generators (RSG) with Alloy NG800 tubing material were designed to produce 10% more power. This could be realized by installing more SG tubes with narrow gaps between the tubes. The power uprate of 10% could be realized after replacement of the HP turbines (Siemens-Westinghouse designed) in 2010 and 2011 for unit 1 and unit 2, respectively. The consequence of designing more tubes with extremely narrow gaps had consequence of difficult corrosion product removal from the top of tube sheet (TTS) by tube sheet lancing (TSL) cleaning during annual outages. Due to not completely cleaning of the tube sheet, the deposits on the TTS increased and got harden with operating years, beneath which also impurities were concentrated. These hard deposits on the TTS started to squeeze the tubes causing TTS denting (see Figure 5-1). First denting indications have been observed in 2006 at unit 1. This was followed by ODSCC indications measured by ECT technique in 2008 caused by concentrated impurities and tensile stresses produced by the denting [Arias et al., 2014]. Soon in the following years the same phenomena were experienced in unit 2.
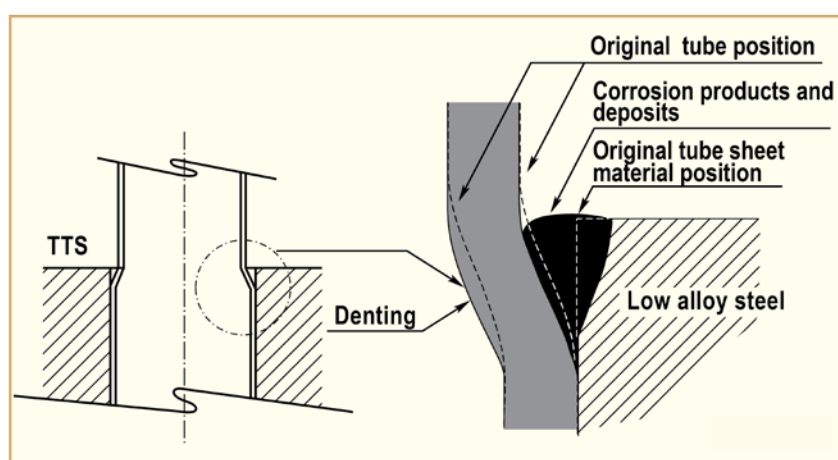


Figure 5-1:    Schematic view of denting at the TTS crevices [Staehle & Gorman, 2001]

As counter measure it was decided to remove the TTS deposits by chemical cleaning followed by TSL and by reducing the feedwater iron transport into steam generators by modifying the secondary side chemistry. For this purpose small amount of ETA was injected in addition to the applied H-AVT chemistry (hydrazine ammonia chemistry with high pH values). ETA addition was necessary, because of the high ammonia sink (about 8%) [Arias et al., 2014] in the condenser evacuation system due to extremely high suction efficiency of the condenser air removal pumps, which resulted in insufficient pH values to counteract the FAC in the two phase flow steam systems that was the main contributor to feedwater iron concentration. In addition to this chemistry modification it was also decided to apply FFA as complementary measure for the existing secondary side chemistry to further reduce the feedwater iron transport into steam generators as well as serving as feasible alternative strategy for the used common lay-up procedures in the subsequent annual outages. After successful completion of the qualification program that consists of determining the compatibility of the FFA application with the plant secondary side materials, applied chemistry and resins, this FFA application using ODA injection was introduced by AREVA GmbH as first time for the PWR plants. The first trial FFA application was performed in 2011 at unit 1. Due to extremely favourable results with respect to

- Protection of the structural materials during the outage,

- Reducing the feedwater iron concentration and

- Removal of the impurities beneath the steam generator deposits

it was decided to use this FFA procedure further as standard complementary measure to already applied water chemistry in both units [Ramminger et al., 2012]. Mine while, between 2011 and 2016, almost every year eight successful FFA applications were performed by AREVA GmbH in both Almaraz units as follows:

- Unit 1:

    o First FFA application in 2011 (end of cycle 21),

    o First refreshment application in 2012 (EOC 22),

    o Second refreshment application in 2014 (EOC 24) and

    o Third refreshment application in 2015 (EOC 25)

- Unit 2:

    o First FFA application in 2012 (end of cycle 20),

    o First refreshment application in 2013 (EOC 21),

    o Second refreshment application in 2015 (EOC 23) and

    o Third refreshment application in 2016 (EOC 24)

In the following sections the application conditions and the achieved results are explained.

## 5.1.1.2 Application of FFA in Almaraz units

Applications at Almaraz unit took about three weeks by injecting ODA in the Feedwater/Condensate system several times at plant power operation at the end of the cycle before shutting down the plant to annual outage [Ramminger et al., 2012]. The chemistry control of the application and the decision for the termination of the ODA injection is performed according to AREVA GmbH's criteria. For this purpose, the following chemistry parameters are monitored [Arias et al., 2016]:

- By Grab sampling:

    o Anions: Fluoride, Chloride, Sulphate, Acetate, Formate, in SG Blow-down and in Feedwater;

    o Cation: Sodium in SG Blow-down and Feedwater;

    o FFA concentration: ODA in Feedwater, SG Blow-down, Main Steam, Heater drains and Main Condensate.

- Plant on-line monitoring:

    o In Main Condensate: pH, Cation Conductivity, Oxygen, Sodium and Degased Conductivity;

    o In Heater Drains: pH and Cation Conductivity;

    o In Feedwater: pH, Cation Conductivity and Oxygen;

    o In SG Blow-down: pH and Cation Conductivity;

    o In Main Steam: pH, Cation Conductivity, Specific Conductivity and degased Conductivity.

During the FFA application no thermal decomposition products in the systems with up to 280°C operating temperatures were detected by conductivity measurements. Examples for unit 1 and unit 2 applications are given in Figure 5-2 and Figure 5-3, respectively. Both examples with low conductivity values measured in Main Steam and Main Condensate indicating absence of organic acids that usually produced by thermal decomposition of organic amines.

With aid of the chemistry monitoring the FFA application process can be applied without violating the plant specific specified Action Levels of the Water Chemistry Guidelines. An example is given in Figure 5-4. The criteria to terminate the FFA application are [Ramminger et al., 2012]:

- Violation of the Action Level 1 (AL1) values for Chloride and/or Sulphate;

- ODA concentration reached the equilibrium value at all sampling points

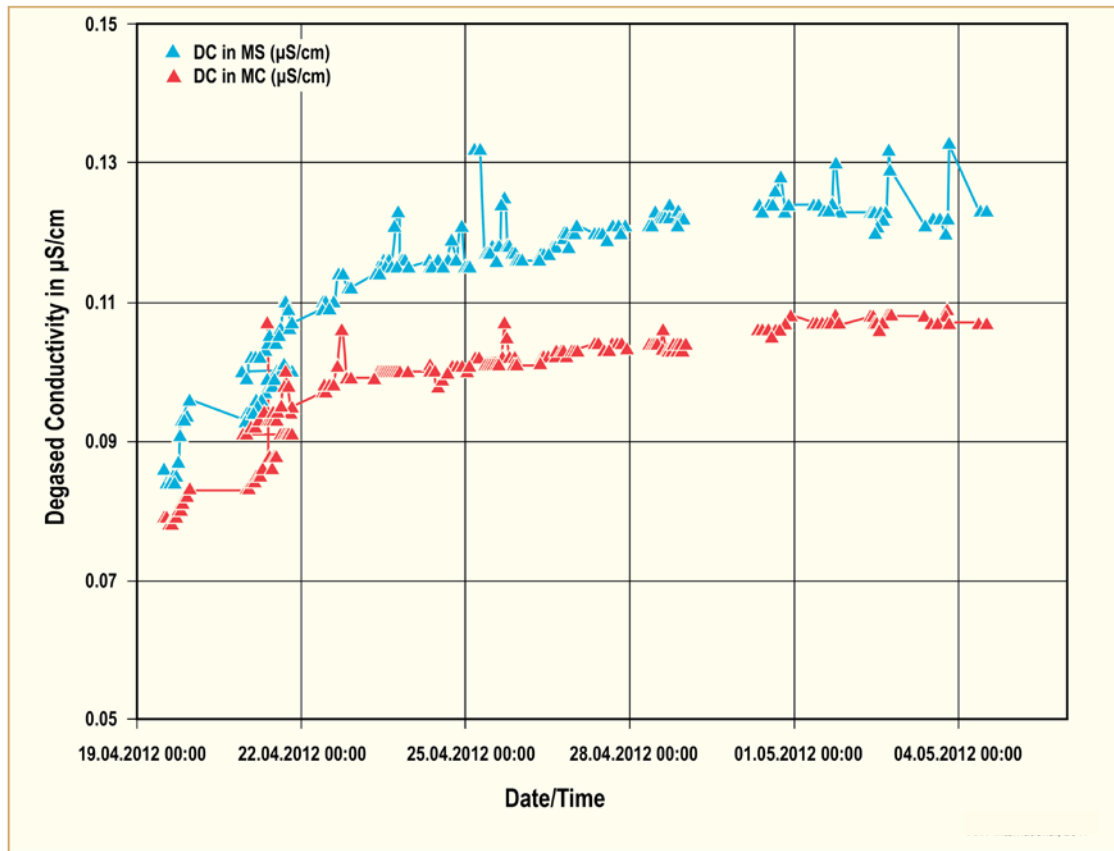Figure 5-2:    Degased Conductivity in Main Steam and in main Condensate during the FFA Application at Almaraz unit 1, [Ramminger, 2015]

A repetition of the FFA application (refreshment application) in the secondary side of a PWR plant is required in case of:

- Iron concentration in FW starts to increase and/or SEP

- The heat transfer efficiency of the SGs starts to decrease due to increased tube deposits.

# 6 Use of FFAs in component cooling systems

## 6.1 Background information

The corrosion inhibition of the structural materials in Component Cooling Systems (CCS) of the power plants can be a quite challenging issue. Because, these systems are usually designed with mixed structural materials; mainly with carbon steel pipe works having copper or stainless steel cooler/heat exchanger tubes. The demineralized water in the CCS systems needs from time to time to be make-up by oxygen containing make-up water due to leakage losses. Oxygen ingress through make-up water injections causes corrosion of the carbon steels. Therefore, in early times chromate was used as corrosion inhibitor in CCS, which is no more allowed due to its classification as toxic mater. Therefore, as of presence the corrosion inhibition of the CCS is usually provided by other inorganic inhibitors such as hydrazine, molybdate, and nitrite. However, all these inorganic corrosion inhibitors have disadvantages as follows:

- Hydrazine use is getting more and more restrictions due to its classification as carcinogenic substance.
- Nitrite is also toxic and has significant drawbacks such as the susceptibility to microbiological degradation; however, due to economic reasons still used.
- Molybdate needs to be applied at high concentrations to provide adequate corrosion inhibition. As heavy metal, release of molybdate containing water may have restrictions

Therefore, several organizations have considered the FFA application as an alternative corrosion inhibition treatment for the CCS. The results of the investigation studies for feasible FFA application in CCS performed in a pilot test plant and also several field application results are well explained in the publication of [Foret et al., 2013]. In the following sections the information given in this publication is summarized.

## 6.2 CCS pilot plant studies

The results of two different test series are presented in the publication [Foret et al., 2013]. The first test was performed at 40°C, where in demineralized water the corrosion inhibitor effect of nitrite, molybdate and FFA was investigated for carbon steel and copper material. The second test was focussing on the comparison of molybdate and FFA as corrosion inhibitor on a multi-metal system consists of carbon steel, brass and aluminium at an elevated temperature of 75°C. For both test series oxygen containing demineralized water was used and the duration of both tests was about two weeks.

The results of the first test at 40°C with respect to corrosion rates and the development of iron concentration in cooling water are given in Figure 6-1 and Figure 6-2, respectively.
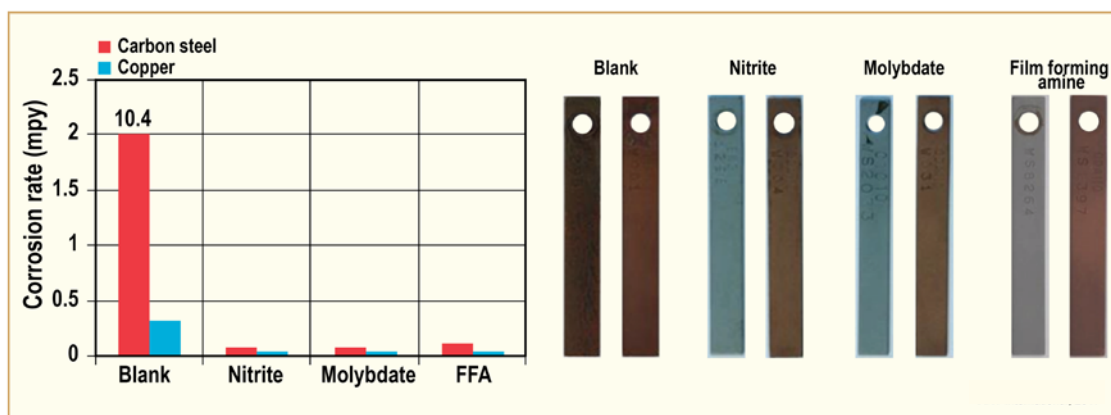


Figure 6-1: Left figure: Corrosion rates for different corrosion inhibitors at 40 °C Right Figure: corrosion coupons before pickling treated with different corrosion inhibitors (left coupon: carbon steel, right coupon: copper), [Foret et al., 2013]
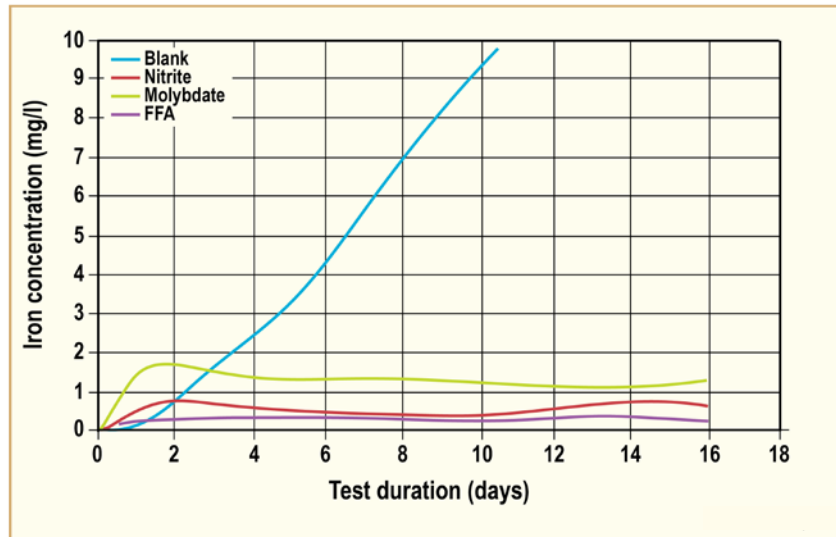
Figure 6-2:     Development of iron concentration in cooling water of a pilot closed cooling systems treated with different corrosion inhibitors at 40°C, [Foret et al., 2013]

The results of the second test are given in Figure 6-3. These test results confirm the FFA application for CCS as an excellent alternative corrosion inhibitor. Especially for aluminium FFA seems to be a better corrosion inhibitor.

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# Nomenclature

$K_d$:          Dissociation constant

MPa:          Mega Pascal pressure unit

µS/cm:          Conductivity unit

ppb:          Parts per billion concentration unit

ppm:          Parts per million concentration unit

# List of Abbreviations

| | | | | |
|---|---|---|---|---|
| AAS: | Atom adsorption spectroscopy | | MB: | Mixed bed resins |
| AL: | Action level | | MC: | Main condensate |
| AVT: | All volatile treatment | | MMS: | Mitigation monitoring system |
| FFA: | Film forming amine | | MS: | Main steam |
| BWR: | Boiling water reactor | | NG: | Nuclear grade |
| CANDU: | CANada Deuterium Uranium (Heavy water PWR designed by AECL) | | NPP: | Nuclear power plant |
| | | | ODA: | Octadecylamine |
| CC: | Cation conductivity | | ODACON | Name of the commercial ODA product |
| CCS: | Component cooling system | | | |
| CMC: | Critical micelle concentration | | ODSCC: | Outer diameter stress corrosion cracking (Secondary side SCC) |
| CORD: | Chemical oxidizing reducing decontamination (Siemens decontamination process) | | | |
| | | | OLNC: | On-line noble chem. |
| | | | OPDA: | Oleyl propylene diamine |
| CS: | Carbon steel | | OSG: | Original steam generator |
| DC: | Degased conductivity | | PWR: | Pressurized water reactor |
| DMA: | Dimethlyamine | | RSG: | Replacement steam generator |
| ECP: | Electro Chemical Potential | | RWCU: | Reactor water clean-up |
| ECT: | Eddy current test | | SAM: | Self-assembling-monolayer |
| EDX: | Energy dispersive x-ray | | SC: | Specific conductivity |
| EOC: | End of cycle | | SCC: | Stress corrosion cracking |
| EPRI: | Electric power research institute | | SEM: | Scanning electron microscopy |
| ETA: | Ethanol amine | | SG: | Steam generator |
| FAC: | Flow accelerated corrosion | | SS: | Stainless steel |
| FW: | Feed water | | SAC: | Strong acid cation resins |
| GDR: | German Democratic Republic | | SBA: | Strong base anion resins |
| HOR: | Hide-out return | | TS: | Tube sheet |
| HP: | High pressure | | TSL: | Tube sheet lancing |
| HPWR: | Heavy water pressurized water reactor | | TTS: | Top of tube sheet |
| | | | USSR: | United Soviet Social Republic |
| HWC: | Hydrogen water chemistry | | VVER: | Water-water-energy-reactor (Russian: Wodo-wodjanoi energetitscheski reaktorn) |
| IEX: | Ion exchange resins | | | |
| KWU: | Kraftwerk union | | WBA: | Weak base anion resins |

# Unit conversion

| TEMPERATURE | | |
|---|---|---|
| °C + 273.15 = K | °C × 1.8 + 32 = °F | |
| T(K) | T(°C) | T(°F) |
| 273 | **0** | 32 |
| 289 | 16 | 61 |
| 298 | 25 | 77 |
| 373 | **100** | 212 |
| 473 | **200** | 392 |
| 573 | **300** | 572 |
| 633 | 360 | 680 |
| 673 | **400** | 752 |
| 773 | **500** | 932 |
| 783 | 510 | 950 |
| 793 | 520 | 968 |
| 823 | 550 | 1022 |
| 833 | 560 | 1040 |
| 873 | **600** | 1112 |
| 878 | 605 | 1121 |
| 893 | 620 | 1148 |
| 923 | 650 | 1202 |
| 973 | **700** | 1292 |
| 1023 | 750 | 1382 |
| 1053 | 780 | 1436 |
| 1073 | **800** | 1472 |
| 1136 | 863 | 1585 |
| 1143 | 870 | 1598 |
| 1173 | **900** | 1652 |
| 1273 | **1000** | 1832 |
| 1343 | 1070 | 1958 |
| 1478 | 1204 | **2200** |

| MASS | |
|---|---|
| kg | lbs |
| 0.454 | **1** |
| **1** | 2.20 |

| DISTANCE | |
|---|---|
| x (μm) | x (mils) |
| 0.6 | 0.02 |
| 1 | 0.04 |
| 5 | 0.20 |
| **10** | 0.39 |
| 20 | 0.79 |
| 25 | 0.98 |
| 25.4 | **1.00** |
| **100** | 3.94 |

| PRESSURE | | |
|---|---|---|
| bar | MPa | psi |
| **1** | 0.1 | 14 |
| 10 | **1** | 142 |
| 70 | 7 | 995 |
| 70.4 | 7.04 | **1000** |
| **100** | 10 | 1421 |
| 130 | 13 | 1847 |
| 155 | 15.5 | 2203 |
| 704 | 70.4 | **10000** |
| **1000** | 100 | 14211 |

| STRESS INTENSITY FACTOR | |
|---|---|
| MPa√m | ksi√inch |
| 0.91 | **1** |
| **1** | 1.10 |

| Radioactivity |
|---|
| **1 Sv** = 100 Rem |
| **1 Ci** = 3.7 × 10$^{10}$ Bq = 37 GBq |
| **1 Bq** = 1 s$^{-1}$ |