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IDENTIFICATION AND TESTING OF AMINES FOR STEAM GENERATOR CORROSION AND FOULING CONTROL

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ABSTRACT

AECL and EPRI have been evaluating candidate amines for control of corrosion and fouling in recirculating nuclear steam generators. To permit an unambiguous ranking of the suitability of the candidate amines, the characteristics of base strength, volatility, price, steam generator fouling, cost of associated condensate and blowdown polishing, toxicity and ecotoxicity have been summarized in a single numerical index.

The majority of the data required for the calculation of the index is available in the literature. The effect of amine on steam generator fouling has been measured using a recirculating loop at AECL under flow boiling conditions. The loop results coupled with steam generator modelling indicate a significant reduction in steam generator fouling rates when optimized chemistry is used. The calculated reduction in the cost of steam generator fouling and corrosion control for several amines and amine mixtures is given.

INTRODUCTION

As a rule, pressurized water reactor (PWR) and pressurized heavy water reactors (PHWR) use an all-volatile water treatment (AVT) in the steam cycle (secondary heat transport system). The main ingredient of this treatment is an organic amine used to adjust the pH. The most commonly-used amines are monoethanolamine (ETA), morpholine (MPH) and ammonia (NH₃). The latter is becoming less popular because of its high volatility, yet it is universally present as a product of decomposition of other amines, thus contributing to the overall pH. Other still less common "alternative" or "advanced" amines include 2-amino-2-methyl-propanol (AMP), dimethylamine (in a mixture with ETA), and 3-methoxypropylamine (3MPA).

The main purpose of adding the amine is to control corrosion throughout the steam cycle by providing an adequately alkaline pH at all locations of interest. Many moderately strong and volatile amines can provide adequate pH when dosed in sufficient quantities. However, since steam generator (SG) fouling is an endemic and very costly problem in nuclear power plants, there is also a desire to optimize the water chemistry for SG fouling control.

SG fouling involves deposition of iron corrosion products, mostly magnetite, and other impurities on the SG

tube bundle (on the SG shell side, where boiling occurs). The deposits are detrimental because of possible:

- creation of flow-restricted or liquid-deficient zones, where aggressive chemistry may develop, resulting in under-deposit or crevice corrosion,
- detrimental effects on heat transfer, resulting in degradation of plant thermal performance,
- flow blockages, resulting in an increased pressure drop and, in extreme cases, level oscillation.

Fouling management may involve: station outages (e.g., for inspection and cleaning), station de-rating and, in extreme cases, steam generator replacement. As an example of the magnitude of the cost associated with SG fouling, one may consider the following figures: the cost of replacement power during an outage--US\$1 million per day, the cost of removal of crud from SGs--US\$3,200 per kg (based on chemical cleaning performed when the crud loading on tubes reaches 0.1 kg/m²), the cost of SG replacement--\$200 million per plant (the SG itself costs US\$10-25 million each). Over the last 20 years, 27 US PWRs have replaced 85 SGs, and an additional 13 PWRs are currently in the process of replacing 34 SGs over the next 5 years. Power plants have been de-rated by as much as 10% due to SG fouling.

Atomic Energy of Canada Limited (AECL) and Electric Power Research Institute (EPRI) have been evaluating candidate amines for corrosion and SG fouling control (Klimas et al. 2002, Turner et al. 1997, 1999, 2001). Since any of a large number of amines or other additives can be considered for water chemistry control, one must state at the beginning that the driving force for the selection of the amine(s) is a minimization of the overall cost of the control of corrosion and fouling in the power plant. While fouling control has been the main focus of our work, all the relevant amine selection criteria must be identified and satisfied, and thereafter the overall cost minimized.

IDENTIFICATION OF AMINES

Amine Selection Criteria

The following fundamental selection criteria for amines have been identified:

- Corrosion control
 - Strong base
 - Low volatility (~1:1 water-steam partition coefficient)

- No increase in general corrosion
- Introduction of no amine-specific corrosion issues (e.g., flow-accelerated corrosion)
- Products of thermal decomposition introduce no corrosion issues
- SG fouling control
 - Low deposition rate for magnetite particles
 - High rate of deposit removal
 - Low rate of deposit consolidation
 - No increase in fouling by hematite particles, or other less common fouling species.
- Amine cost
 - Low price
 - Readily available
 - Low concentration required for use (implying a high base strength, low volatility, and low molecular mass)
 - Low thermal decomposition rate in deoxygenated water at temperatures up to 280°C
- Condensate and blowdown polishing costs (in plants employing condensate and blowdown polishing)
 - Compatible with ion-exchange resins
 - Low molar concentrations required (implying a high base strength and low volatility)
- Safety and environmental considerations
 - Not a carcinogen or otherwise extremely hazardous substance (as defined and listed by an appropriate environmental protection agency or equivalent)
 - Low toxicity to humans (lethal dose 50% kill, $LD_{50} \leq$ that for ammonia; the threshold limit value—time-weighted average, $TLV-TWA \leq$ that for ETA).
 - Good biodegradability and low ecotoxicity (“inherently biodegradable” strongly preferred).
 - Low concentration required for use
 - Products of degradation no more hazardous than the parent chemical or ammonia
 - Already used in industry
 - Acceptable to the regulator
- Social aspects
 - No practical diversion routes for production of controlled substances, like illicit drugs, chemical weapons, etc.

- Tolerable odour at the anticipated (non-toxic) concentrations
- Other practical considerations
 - Sufficient solubility
 - No excessive foaming at low concentrations
 - Safety/convenience of storage, handling, and dosing to the feedwater
 - Commonly used (so that extensive data are available)

Amine Index

A numerical “amine index” can be defined for direct comparison of the economics of the application of various amines for corrosion and fouling control. This index has been termed “combined comparative amine index for corrosion and fouling control.” The index is “combined” because it permits an unambiguous and quantified ranking of candidate amines taking into consideration the relevant amine characteristics: base strength, volatility, price, specific effect on steam generator fouling, cost of associated condensate and blowdown polishing, toxicity and ecotoxicity, etc. The index is “comparative” because it is useful only for selection between two or more candidate amines; therefore, the costs which are considered constant (or undetermined) on the change of the identity of the amine are eliminated from the index.

The index can only be calculated for amines (or amine mixtures) that pass the toxicity, ecotoxicity, social, and other basic practical requirements for the application in a steam cycle. The index depends on the station design and its operating parameters (e.g., blowdown rate).

The index, \$I\$, can be expressed as a sum of the partial non-constant costs:

$$\$I = \$A + \$B + \$C + \$D \quad (1)$$

The cost of the amine, \$A\$, is calculated as the amine usage (in kg per EFPY of 1000 MW station) times the price of the amine (dollars/kg). The usage is primarily determined by the required amine concentration (see the next section), operation of condensate polishing (if any), the SG blowdown rate, and the rate of decomposition of the amine.

The comparative cost of fouling, \$B\$, is estimated for one amine on the basis of the known or estimated cost of fouling for another (“standard”) amine, the factor for fouling prevention for both of the amines, and the ratio of the corrosion product transport rates for the two amines. The factor for fouling prevention is discussed in Section “Effect of Amine on Fouling”.

For stations that use condensate polishing (not all do) and operate the IX beds in the protonated form, the cost of polishing, \$C\$, can be calculated using:

$$\$C = \frac{F \cdot Y \cdot C}{M_M} \cdot \frac{\$IX_{Reg}}{IX_{Cap}} \quad (2)$$

where F is the flow through the polisher and C is the difference in the amine concentration in water coming to and from the IX bed. For stations that operate the IX bed in the amine form, the requirement for the amine is that the resin selectivity for the main cationic impurity (usually sodium) over the amine is acceptable.

Where applicable, the cost of blowdown polishing, \$D, can be calculated using a formula analogous to (2), but with the blowdown flow rate used in place of F.

The majority of the data required for the calculation of the index is available in the literature and can be readily applied to evaluate the acceptability and economics of switching a plant to an alternative amine.

On the basis of the literature data and the amine selection criteria, the following potentially-interesting amines were removed from further consideration as candidates for use in nuclear power plants: azeridine, azetidine, cyclohexylamine, quinuclidine (QND), 3-hydroxyquinuclidine (3HQ) (Klimas et al., 2002).

The most difficult to evaluate are the following contributors to the combined amine index:

- the required amine concentration, and
- the effect of the amine on SG fouling.

Amine Concentration

The critical parameter for the evaluation of the amine index is the concentration of the amine required in the SG final feedwater. The required concentration depends on the amine strength, volatility, station design, and the pH requirements for the individual plant components so that they meet their design lifetime (40-60 years for CANDU® NGSs). Example concentrations can be calculated from the requirement stated in the following form: "the required amine concentration is the minimal concentration of the amine (mg/kg) in the final feedwater which is required to maintain a pH of 1 pH unit above the neutral point everywhere in the steam cycle". Here, the 1 pH unit above the neutral point is arbitrary, but it would be considered satisfactory for most components with low-velocity flow (e.g., <5 m/s). Note that some stations may have specific requirements for high pH in components constructed of carbon steel with a very low chromium content (e.g., <0.02%) which experience high-velocity flow (e.g., primary steam separators, condensate lines, SG tube support plates), or for a low pH in the condenser constructed of copper-

based alloy, or specific requirements for SG crevice neutralization if ingress of acidifying species (e.g., chlorides or sulfates) is an issue. Such special requirements need to be specified before the required amine concentrations can be established.

The volatility and base strength have been measured or calculated for many amines at temperatures up to 300°C (Cobble et al., 1992). On the basis of these data, the required amine concentration can be calculated using a steam cycle model coupled with a chemical equilibrium code. Table 1 shows the calculated concentrations required to maintain a pH of 1 pH unit over the neutral point everywhere in a CANDU-6 steam cycle (crevices and the primary steam separators were not considered) for a number of amines. Table 1 demonstrates that MPH requires approximately 9 times the concentration compared to ETA in order to maintain the required pH_T conditions. The following amines are found to require relatively low concentrations to maintain the specified pH_T in the steam cycle: 4-aminobutanol (4AB), diaminopropane (DAP), diaminoethane (DAE), and 5-aminopentanol (5AP). The required concentrations are 4 to 5.3 times lower than that for ETA, or 35 to 47 times lower concentration than that for MPH. Table 2 lists the pH values resulting from the application of the amines at the concentrations given in Table 1. For mixtures containing dodecylamine (DDA), the concentration of DDA was taken at 1.2 mg/kg.

Table 1. Calculated Concentration of the Amine in the Final Feedwater Required to Maintain a pH_T of 1 pH Unit Above the Neutral Point in the Steam Cycle.

Amine Name	Abbreviation	Amine Concentration	
		mg/kg	Relative to ETA
Ethanolamine	ETA	8.0	1.00
Ammonia	NH ₃	55	6.9
Morpholine	MPH	70	8.8
Dimethylamine	DMA	25	3.1
Pyrrolidine	PYRR	10	1.3
3-Hydroxyquinuclidine	3HQ	3.0	0.38
Dipropylamine	DPA	24	3.0
Methylamine	MA	15	1.9
3-Methoxypropylamine	3MPA	55	6.9
4-Aminobutanol	4AB	1.5	0.19
5-Aminopentanol	5AP	2.0	0.25
Diaminoethane	DAE	2.0	0.25
Diaminopropane	DAP	1.5	0.19

Table 2. Calculated pH_T and pH_T of the Neutral Point at 15 Locations in the CANDU-6 Steam Cycle. The locations are: 1-condenser, 2-deaerator, 3-SG, 4-high pressure turbine drain, 5-moisture separator, 6 to 11-low pressure turbine drains (6 stages), 12-high pressure heater (shell side), 13-15-low pressure heaters (shell side).

Amine	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
ETA	9.4	7.1	6.6	7.1	7.2	7.1	7.7	8.2	8.4	8.6	8.9	7.1	7.2	7.7	8.3
NH3	10.1	7.6	6.6	6.9	6.9	6.9	7.3	7.7	8.0	8.3	8.6	7.2	7.8	8.3	8.8
MPH	9.5	7.2	6.6	7.0	7.0	7.0	7.5	7.9	8.2	8.5	8.8	7.0	7.4	7.8	8.4
DMA	10.3	7.8	6.6	6.9	7.0	6.9	7.3	7.8	8.1	8.4	8.8	7.4	8.1	8.5	9.0
PYRR	9.8	7.5	6.6	7.0	7.1	7.0	7.5	8.0	8.3	8.6	9.0	7.2	7.7	8.1	8.6
3HQ	9.0	6.9	6.6	7.1	7.1	7.1	7.7	8.1	8.2	8.4	8.6	7.0	6.9	7.3	7.9
DPA	10.0	7.6	6.6	6.8	6.8	6.8	7.2	7.6	7.9	8.3	8.7	7.2	7.8	8.2	8.7
MA	10.2	7.7	6.6	7.0	7.0	7.0	7.5	8.0	8.2	8.6	8.9	7.3	7.9	8.4	8.9
3MPA	10.0	7.5	6.6	7.1	7.1	7.1	7.6	8.2	8.4	8.8	9.2	7.2	7.7	8.2	8.8
4AB	8.9	6.8	6.7	7.1	7.1	7.0	7.6	8.0	8.1	8.3	8.5	6.9	6.8	7.2	7.8
5AP	9.0	6.9	6.6	7.1	7.1	7.0	7.7	8.1	8.2	8.4	8.6	6.9	6.8	7.2	7.9
DAE	9.1	6.9	6.6	7.1	7.1	7.1	7.6	8.1	8.2	8.4	8.7	7.0	7.0	7.4	8.0
DAP	9.0	6.9	6.6	7.1	7.1	7.1	7.7	8.1	8.2	8.4	8.7	7.0	6.9	7.3	7.9
ETA+DDA	9.5	7.1	6.6	7.1	7.2	7.1	7.7	8.2	8.4	8.6	8.9	7.1	7.2	7.7	8.3
DAE+DDA	9.2	7.0	6.6	7.1	7.1	7.1	7.6	8.1	8.2	8.4	8.7	7.0	7.1	7.5	8.1
$pH_{neutral}$	6.9	5.7	5.6	5.7	5.7	5.6	5.8	6.0	6.1	6.2	6.4	5.7	5.8	6.0	6.3

When selecting the amine concentration, requirements for neutralization of acidic crevices could also be considered. Table 3 shows example pH_T values calculated for a model SG crevice in the presence of 3 common impurities (chloride, sulfate, acetate) and the concentrations of amine in the feedwater as listed in Table 1.

Table 3. Calculated pH_T in Model Crevices Neutralized with Amines. The assumed impurity was: (1) 3 $\mu\text{g}/\text{kg}$ of Cl^- , (2) 3 $\mu\text{g}/\text{kg}$ of SO_4^{2-} , and (3) 300 $\mu\text{g}/\text{kg}$ of CH_3COO^- .

Amine	(1)	(2)	(3)
ETA	5.1	1.4	6.7
NH3	4.5	0.1	6.1
MPH	4.8	0.7	6.4
DMA	4.4	-0.1	5.9
PYRR	4.7	0.4	6.2
3HQ	5.2	1.6	6.8
DPA	4.6	0.3	6.1
MA	4.6	0.2	6.1
3MPA	4.7	0.6	6.3
4AB	4.9	0.8	6.6
5AP	5.2	1.6	6.8
DAE	5.1	1.4	6.7
DAP	5.2	1.4	6.7
Crevice pH with no amine	3.9	-1.2	5.4
$pH_{neutral}$	5.6	5.6	5.6

The results in Table 3 demonstrate that, as expected, the most volatile amines (DMA, NH₃, MA, DPA) have a limited capacity for neutralization of acidic crevices. The

least volatile of the amines considered (4AB, 5AP, DAE, DAP, ETA) are more effective at neutralizing acidic crevices.

It is recommended that similar pH calculations be performed for any other considered candidate amines and amine mixtures.

Effect of Amine on SG Fouling

The effect of amines on SG fouling can be divided into two major parts: (1) the effect of the amine on the transport of the corrosion products with the feedwater into the SG, and (2) the specific effect of the amine on SG fouling.

The effect of amine on the corrosion product transport is thought to be amine unspecific (Sawochka, 2003) for popular water-treatment amines like ETA, MPH or NH₃. In general, the experience is that the higher the pH, the lower the corrosion product transport into the SG, regardless of the nature of the amine. Thus, assuming a similar target pH in the feedwater train for two amines, no specific effect of the amine on the corrosion product transport would be expected. Note that usage of an amine which produces a lower pH in a portion of the feed train may result in an increase of the corrosion rate at this location, with a subsequent increase of corrosion product transport to the SG and a higher rate of SG fouling. Also, some amines could be expected to have a specific effect on corrosion rates and therefore on the corrosion product transport, e.g., filming amines (e.g., DDA) are known to inhibit flow-accelerated corrosion (FAC).

The effect of the amine on the corrosion product generation can be evaluated from the station design data (materials, piping area, flow velocities, etc.), the distribution

of pH_T throughout the feedtrain (e.g., Table 2), and the dependence of the corrosion rates on pH_T . For the application in the amine index, the crud concentration in the final feedwater is of interest. Under steady-state operation, this concentration can be reasonably expected to be proportional to the overall rate of production of the corrosion products in the steam cycle.

The amine effect on SG fouling has been found experimentally to be amine specific, i.e., different amines produce varying fouling rates at constant high-temperature pH_T and thermohydraulic conditions. It is treated in detail in the experimental section of this paper.

The rate of accumulation of crud in a SG (kg/s) can be described using the following equation:

$$\frac{dM}{dt} = K_f \rho A C_{SG} \quad (3)$$

It is assumed that the concentration of crud in the SG is uniform and equal to the crud concentration in blowdown. The value of $K_f \rho$ (kg/m²s) is termed the normalized fouling rate because it can be calculated by normalizing the fouling rate per unit area to unit mass fraction of crud. Equation (3) uses as an overall normalized fouling rate for the entire SG. The value of $K_f \rho$ depends on the chemistry and thermohydraulic conditions. Its dependence on the amine identity has to be evaluated experimentally.

The crud source is the SG feedwater, and the sinks for the crud are: SG fouling, blowdown, and moisture carry-over. Thus, one can write a mass balance for non-volatile species:

$$\frac{dM}{dt} = C_{feed} F_{feed} - b C_{SG} - c C_{SG} \quad (4)$$

Using (3) to eliminate C_{SG} from (4) and re-arranging yields:

$$\frac{dM}{dt} = \frac{C_{feed} F_{feed} K_f \rho A}{K_f \rho A + b + c} \quad (5)$$

The above equation represents the rate of crud accumulation in the SG as a function of the SG independent operating parameters. Thus, the SG fouling rate depends on the magnitude of the normalized SG fouling rate, which is chemistry-dependent.

An important parameter describing SG fouling is the blowdown efficiency, E_{bld} . The blowdown efficiency for an impurity is defined as the ratio of the rate of discharge of the impurity with the blowdown (including moisture carryover) to the rate of impurity ingress to the SG with the feedwater. Dividing (5) by the rate of transport of crud into the SG one obtains:

$$E_{bld} = \frac{b + c}{K_f \rho A + b + c} \quad (6)$$

An alternate parameter describing SG fouling is the factor for fouling reduction by blowdown, $f_{red,bld}$, which is defined as the ratio of the rate of the ingress of the impurity into the SG to the rate of its accumulation in the SG. It can be readily shown that:

$$f_{red,bld} = \frac{1}{1 - E_{bld}} \quad (7)$$

From Equations (6) and (7), both the blowdown efficiency and factor for fouling reduction depend on the normalized fouling rate; therefore, they are chemistry-dependent. Thus, SG chemistry can be optimized for a maximum blowdown efficiency.

The comparative cost of fouling, \$B, for two amines can be calculated as:

$$\$B_2 = \$B_1 \frac{f_{red,bld,1} \cdot C_{feed,2}}{f_{red,bld,2} \cdot C_{feed,1}} \quad (8)$$

where the indices 1 and 2 refer to the first and the second amine, respectively. Equation 8 assumes that the cost of fouling management is proportional to the rate of the accumulation of crud in the SG.

LOOP TESTING

The specific effect of the amine and crud type on the fouling rate under SG operating conditions was measured in a water recirculating loop at the AECL Chalk River Laboratories for several amines and cruds. As the fouling substrate, nuclear steam generator quality tubing UNS N06600 (“Alloy 600”) was used. The arithmetic average roughness height of the fouling surface was approximately 1.2 μm . The loop thermohydraulic conditions are listed in Table 4, and chemistry conditions in Table 5. The flow direction was vertically upwards, and the channel diameter was 10.7 mm. The test loop has been described in detail elsewhere (Turner and Klimas, 2000, Klimas and Pietralik, 2002, Klimas et al., 2002).

Magnetite (particle diameter $\sim 0.2 \mu\text{m}$, Figure 1) was used as the fouling species in most of the tests. It was manufactured using a method described by Sugimoto and Matijevic (1980). Two tests employed magnetite with a surface purposely contaminated with silica (a common station impurity). Two tests used a crud collected in a Canadian NGS SG (85% magnetite and 15% hematite, particles 0.1-10 μm , volume average diameter 1.6 μm). Several tests used hematite, which was either commercial grade (“Fisher Scientific”, 0.1 μm diameter) or manufactured at AECL ($\sim 0.2 \mu\text{m}$ diameter). Lepidocrocite was manufactured at AECL (rods, 0.2 μm length, aspect ratio ~ 10). Fresh ferrous precipitates were allowed to form in the loop during the test by a continuous injection of ferrous acetate at a rate very low compared with the loop flow rate. For all types of crud, a radiotracer (^{59}Fe , half-life

44.6 days) was employed for on-line monitoring of the rate of crud buildup at several locations on the heated test section using high-efficiency (high-purity Ge monocrystal) γ -ray detectors. These on-line data were calibrated after the test by a precise determination of the radioactivity distribution along the test section.

Table 4. Loop Thermohydraulic Conditions.

Parameter	Unit	Value
Pressure (Absolute)	MPa	5.7
Saturation Temperature	$^{\circ}\text{C}$	272
Water Temperature at Test Section Inlet	$^{\circ}\text{C}$	180
Mass Flux	$\text{kg}/\text{m}^2\text{s}$	300
Heat Flux	kW/m^2	230
Steam Quality	-	-0.3 to 0.55

Table 5. Loop Chemistry Conditions.

Parameter	Unit	Tests with Magnetite, Station Crud, and Ferrous Precipitates	Tests with Hematite, and Lepidocrocite
pH_{272} (at $X=0$)	pH unit	6.2	6.2
$[\text{O}_2]$	$\mu\text{g}/\text{kg}$	< 5 (below the detection limit)	~ 150
residual $[\text{N}_2\text{H}_4]$	$\mu\text{g}/\text{kg}$	25-100	0

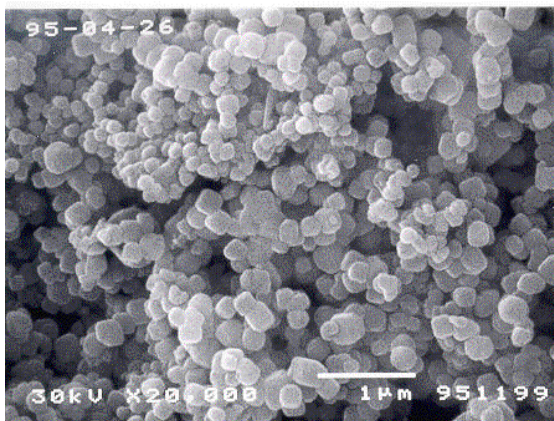


Fig. 1 Scanning Electron Microscopy Micrograph of Magnetite Used in the Majority of the Loop Tests

RESULTS

The specific effect of the amine on the normalized fouling rate by magnetite particles under typical steam generator operating conditions is shown in Figure 2. Average rates for all tests performed under the same thermohydraulic and chemistry conditions are shown,

together with the confidence interval (90%) to contain the mean. For tests with small number of data points, the confidence intervals were not calculated. The effect of amine on fouling of adiabatic surfaces is shown in Figure 3. The specific effect of crud type on fouling rates is shown in Figure 4.

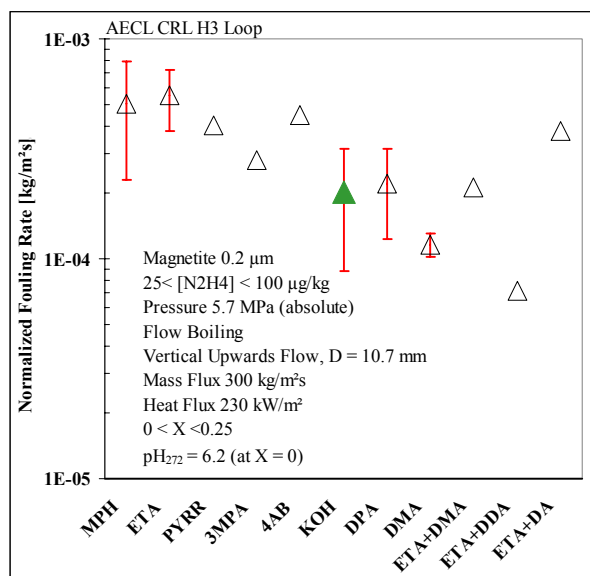


Fig. 2 Specific Effect of Amine on Fouling Rates Under Typical SG Operating Conditions

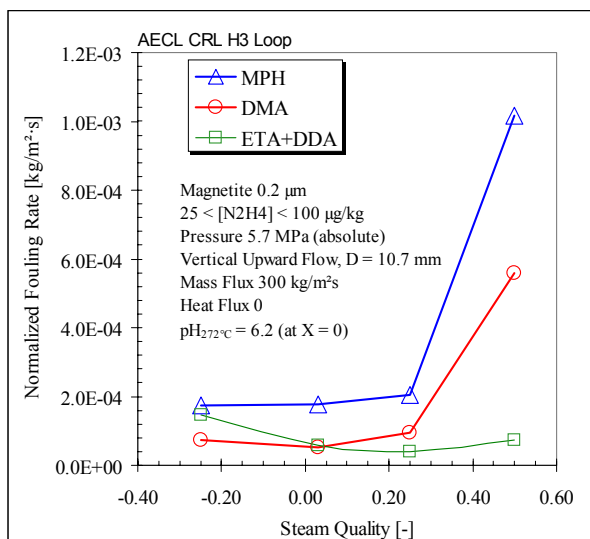


Fig. 3 Specific Effect of Amine on Fouling Rates Under SG Operating Conditions, Unheated Surfaces

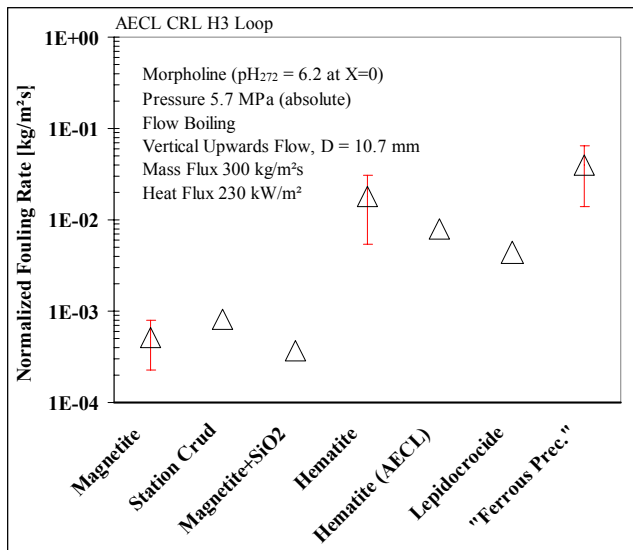


Fig. 4 Specific Effect of Crud Type on Fouling Rates under Typical SG Operating Conditions for Morpholine Chemistry

DISCUSSION

From Figure 2, the highest fouling rates under typical SG operating conditions are produced when pH is controlled with MPH or ETA, the lowest rates (average 7.4 times lower) when pH is controlled with a mixture of ETA and DDA. Comparing the fouling rates with those obtained in amine-free water (the same high-temperature pH_T adjusted with potassium hydroxide), it appears that DDA and DMA are fouling inhibitors whereas MPH and ETA are fouling enhancers. The effect of amine on fouling under forced-convective conditions (Figure 3) generally parallels that for flow boiling: the highest rates under forced convection were measured for MPH and significantly lower for ETA+DDA and DMA. DDA appears to be a particularly effective fouling inhibitor under forced convection at elevated steam quality. The mechanism by which the amine can affect fouling is still unknown. For both DDA and DMA, the low fouling rates were measured to be associated with high rates of deposit removal from the test section, which suggests that these amines reduce the consolidation rate of the deposited particles and/or enhance the particle re-entrainment rates. An amine-specific effect on particle deposition rate is also observed. The AECL fouling model which incorporates particle deposition (transport followed by attachment), re-entrainment of unconsolidated deposit, and deposit consolidation has been described elsewhere (Klimas et al. 2002).

Fouling rates can vary by 2 orders of magnitude depending on the type of crud (Figure 4). The lowest rates were measured when particulate magnetite was the fouling

species. Dissolved ferrous species and hematite particles appear to be particularly effective foulant species.

Using Equation (5) for CANDU SG, addition of DDA is predicted to reduce the rate of accumulation of crud in the SG by a factor of 3.7.

Employing Equations (1) and (7) one can evaluate the economics of application of an optimized amine mixture containing DDA. Example results are shown in Table 6, which suggest savings exceeding US\$1 million per year for a station currently employing MPH, 1% blowdown, and blowdown polishing. The reduction of the cost is mostly by DDA-specific effect on fouling.

Table 6. Example Results of Comparison of Economics of Application of DDA (US\$ Million per EFPY)

Amine and Feedwater Concentration	Fouling Cost	Blowdown Polishing Cost (1% Blowdown)*	Total Cost
MPH, 70 $\mu\text{g}/\text{kg}$	1.5	0.22	1.7
ETA, 8.0 $\mu\text{g}/\text{kg}$	1.5	0.18	1.7
ETA+DDA	0.38	0.18	0.56

* Assuming 40% blowdown recovery and the cost of regeneration of IX resin of US\$2000 per a 3500-equivalent bed.

Results in Tables 1 and 2 suggest that the corrosion and fouling management costs could be further reduced by substituting ETA with a stronger amine, e.g., DAE or 4AB. This could potentially reduce the cost of blowdown polishing and further optimize pH in the feedtrain, thus reducing the corrosion product transport into the SG and fouling (amine-unspecific effect).

CONCLUSIONS

The major conclusions from this work are summarized below:

1. Steam generator (SG) fouling rates by iron corrosion products are a strong function of water and surface chemistry. Fouling rates spanning more than three orders of magnitude under constant thermohydraulic conditions were measured in an experimental loop. Therefore, SG chemistry can be optimized for fouling mitigation. Loop measurements can provide hints on what SG chemistry conditions contribute to high fouling rates.
2. Dodecylamine (DDA) is an effective fouling inhibitor under SG operating conditions. It was loop tested as a mixture with ethanolamine (ETA).
3. Amines such as morpholine (MPH) and ETA appear to be fouling enhancers compared to amine-free water of the same high-temperature pH. These amines, when used on their own, produce normalized fouling rates 5-

- 10 times higher than those under water chemistry controlled with the mixture of ETA+DDA.
4. Modelling of SG fouling suggests that the rate of accumulation of crud in the SG would decrease by a factor of 3.7 if MPH was substituted with ETA+DDA (amine-specific effect on fouling).
 5. Further reduction of SG fouling can be achieved by optimizing the amine mixture so that appropriately high pH is achieved throughout the steam cycle (amine-unspecific effect on fouling).
 6. The suitability of amines and amine mixtures for corrosion and fouling control can be summarized with a single cost-based "amine index". Initial calculation of the amine index suggests that significant savings (over \$1 million per effective full-power year) would result by substituting MPH with a mixture of ETA+DDA in a standard 1000-MW plant that uses no condensate polishing (or polishers in the amine form), and a blowdown rate of 1% of the steaming rate with blowdown polishing.

NOMENCLATURE

\$A	the cost of the amine, \$/EFPY
\$B	the comparative cost of fouling, \$/EFPY
\$C	the cost of condensate polishing, \$/EFPY
\$D	the cost of blowdown polishing, \$/EFPY
\$I	the combined comparative amine index, \$/EFPY
\$IX _{Reg}	the cost of single regeneration or disposal of IX, \$/bed
A	surface area, m ²
b	blowdown rate, kg/s
C	mass fraction (kg/kg)
c	carry-over rate (kg/s)
E	efficiency, dimensionless
F	mass flow rate, kg/s
f	a factor, dimensionless
IX _{Cap}	capacity of IX bed for the amine (mol/bed)
K	kinetic rate constant, m/s
M	mass, kg
M _M	molecular mass, kg/mol
pH _T	pH at temperature different than the standard 25°C
T	temperature, K
t	time, s
X	thermodynamic steam quality, dimensionless
Y	duration of a year, s

Acronyms

AVT	all-volatile water treatment
CANDU®	CANadian Deuterium Uranium, a registered trademark of Atomic Energy of Canada Limited.
EFPY	effective full-power year of station operations
FW	SG feedwater
IX	ion exchange

NGS	nuclear generating station
PHWR	pressurized heavy-water reactor
PWR	pressurized water reactor
SG	steam generator (boiler)

Greek

ρ	mass density, kg/m ³
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Subscript

bld	SG blowdown
f	fouling
feed	SG feedwater
T	at a temperature different than 25°C

REFERENCES

- Cobble J.W., P.J. Turner, and T.O. Passell, *PWR Advanced All-Volatile Treatment Additives, By-Products, and Boric Acid*, Report TR-100755, Electric Power Research Institute, Palo Alto, CA, U.S.A., July, 1992.
- Klimas, S.J., D.A. Guzonas, C.W. Turner, and K. Fruzzetti, *Identification and Testing of Amines for Steam Generator Chemistry and Deposit Control*, Report 1002773, Electric Power Research Institute, Palo Alto, CA, U.S.A., December, 2002.
- Klimas, S.J. and J.M. Pietralik, *Two-Phase Forced-Convective Fouling Under Steam Generator Operating Conditions*, 4th Canadian Nuclear Society Steam Generator Conference, May 5-8, Toronto, Canada, 2002.
- Sawochka, S., *Corrosion Product Transport*, presented at the 2003 Steam Generator Secondary Side Management Conference, Savannah, GA, U.S.A., Feb.10-12, 2003.
- Sugimoto T. and E. Matijevic, *Formation of Uniform Spherical Magnetite Particles by Crystalization from Ferrous Hydroxide Gels*, Journal of Colloid and Interface Chemistry, Vol. 76, pp.227-243, 1980.
- Turner, C.W., D.A. Guzonas, S.J. Klimas, and P. Frattini, *Surface Chemistry Intervention to Control Boiler Tube Fouling*, Report TR-110083, Electric Power Research Institute, Palo Alto, CA, U.S.A., December, 1999.
- Turner, C.W., D.A. Guzonas, S.J. Klimas, and P. Frattini, *Surface Chemistry Intervention to Control Boiler Tube Fouling—Part 2*, Report 1006286, Electric Power Research Institute, Palo, Alto, CA, U.S.A., September, 2001.
- Turner, C.W. and S.J. Klimas, *Deposition of Magnetite Particles from Flowing Suspensions under Flow-Boiling and Single-Phase Forced-Convective Heat Transfer*, Can. J. Chem. Eng., vol.78, pp.1065-1075, 2000.
- Turner, C.W. S.J. Klimas, and P.L. Frattini, *The Effect of Alternative Amines on the Rate of Boiler Tube Fouling*, Report TR-108004, Electric Power Research Institute, Palo Alto, CA, U.S.A., September, 1997.