

Correction for Ammonia/Amine Effect on pH When Using Phosphate Treatment

ABSTRACT

The current HRSG chemistry guide (ASME 2012) has an equation for the required correction for the effect of ammonia on boiler water or evaporator water pH and calculated sodium (Na) to phosphate (PO_4) mole ratios. Controlling this sodium alkalinity associated with phosphate is more complicated than the old method of just staying within the pH/ PO_4 control box. Rigorous calculation of the ratio can be necessary to avoid corrosion of evaporator and boiler tubes. This is of greatest concern in units that have high tube metal temperatures and high underdeposit concentration of boiler water due to such factors as high operating pressure, high heat flux and/or thick, porous waterside deposits.

WHAT IS THE Na: PO_4 RATIO?

The sodium-to-phosphate (Na: PO_4) mole ratio is the ratio of the moles of sodium alkalinity associated with orthophosphate species and hydroxide present to the moles of orthophosphate present. The free caustic concentration is sodium alkalinity present in excess of the amount corresponding to a 3.0:1 Na: PO_4 mole ratio. Small amounts of free caustic can be accurately estimated from the sodium-to-phosphate mole ratio and phosphate concentration.

The Na: PO_4 mole ratio cannot be calculated based on boiler water sodium analysis results unless all cationic and anionic species present also are quantified and the sodium concentration is adjusted to obtain the sodium concentration associated just with orthophosphate and hydroxide (measure and subtract the calculated amount of sodium associated with chloride, fluoride, bromide, sulfate, nitrate and nitrite). Also, potassium will behave in an equivalent manner as sodium and would need to be treated as an equivalent amount of sodium. These analyses on every sample are generally not practical. When this direct calculation method for the Na: PO_4 mole ratio using incomplete results of boiler water has been performed, it has produced erroneous and misleading estimates of the Na: PO_4 mole ratios or free caustic levels.

WHY IS THE RATIO IMPORTANT?

The Na: PO_4 mole ratio allows one to know the amount of free caustic or – if no caustic is present - the balance of sodium alkalinity to phosphate. High or low levels can contribute to corrosion on tube surfaces.

Large amounts of free caustic (NaOH) can cause caustic gouging under deposits – particularly in boilers with circulation problems or high heat flux (Jacklin, 1964, Klein (1962)). Free caustic also can carry over into the steam and cause corrosion and stress corrosion cracking of turbine components.

Low sodium-to-phosphate mole ratios can cause phosphate gouging of boiler and HRSG tube surfaces. This is most common in boilers operating over 2000 psig, but it has occurred in a 1500 psig boiler (Selby, 1993).

If boiler water is just evaporated to dryness, the resultant solid will be a concentrated form of the material present in the water. There have been boilers and HRSG units that have displayed this type of hideout, but

it is much less common. Typical hideout will liberate free caustic into the bulk boiler water while forming a lower Na:PO₄ ratio phosphate compound on tube surfaces.

Noll (1964) found that free caustic is generated above a ratio of 2.85:1 for 1235 psi boilers and above a ratio of 2.65 for 3000 psi boilers. At the time, it was suggested to treat these as maximum values to avoid caustic formation. Significant increases in corrosion were not expected until the sodium-to-phosphate mole ratio decreased below about 2.2:1 (Economy, 1975). However, subsequent experience and research found that other corrosion mechanisms can be experienced at sodium-to-phosphate mole ratios less than 3.0:1 – depending on the temperature and concentration mechanisms at tube surfaces.

At low sodium-to-phosphate mole ratios, the reaction of phosphate with magnetite can form an iron phosphate compound (e.g., Maricite). Tremaine (1993) presented data indicating the ratios at which Maricite would be expected. Maricite formation has been associated with significant cases of phosphate gouging (also called acid phosphate corrosion). Whenever something starts to consume iron oxide as a reaction product, it induces the formation of more magnetite and promotes corrosion. Therefore, close monitoring and control of the sodium-to-phosphate mole ratio is desired to avoid initiating this mechanism.

Careful monitoring of the sodium-to-phosphate mole ratio and free caustic can be used to detect hideout. If the tendency for hideout and caustic production increases, this indicates an increase in the underdeposit concentration mechanism. If hideout increases at a fixed concentration of phosphate, this may indicate that the boiler or HRSG needs to be chemically cleaned. However, circulation problems and high heat flux can similarly increase concentration mechanisms on tube surfaces and lead to increased hideout.

SODIUM-TO-PHOSPHATE MOLE RATIO CONTROL LIMITS

This paper is most useful for plants that operate with high ammonia (or amine) and low phosphate. For high-pressure HRSG plants with duct firing, the minimum suggested sodium-to-phosphate mole ratio is 2.8 (ASME 2012). The maximum limit corresponds to 1 ppm of free caustic above a sodium-to-phosphate mole ratio of 3.0:1. More caustic may be permitted for lower pressure HRSG units in industrial settings.

For low-pressure industrial boilers, lower minimum sodium-to-phosphate ratios are permitted and sometimes advised. Lower minimum sodium-to-phosphate mole ratios are suggested when there is a large potential for caustic contamination in the system. The lower ratio can neutralize more caustic contamination and provide more time to respond to the contamination. The minimum sodium-to-phosphate mole ratio limit is never below 2.2, and the minimum increases with increasing operating temperature. For industrial boilers, the top sodium-to-phosphate ratio can be as low as 2.8:1 or above the 3.0:1 ratio and be controlled up to some fixed level of free caustic.

Relatively small errors in Na:PO₄ mole ratios (e.g., 0.1-0.3) can significantly alter the interpretation of the results and the proper response by the water treatment operator. The risks of improper control include phosphate gouging corrosion (from low Na:PO₄ mole ratios) and caustic attack from elevated free caustic levels.

Establishment of suitable chemistry limits for a particular facility is beyond the scope of this paper, but considers the following factors.

- Drum pressure.
- Carryover experience.
- Tube deposit/condition history.
- System design and materials of construction.
- Makeup quality.
- Contamination sources.

GRAPHICAL METHODS OF ESTIMATION

Typically, the Na:PO₄ mole ratio was estimated by measuring boiler water pH and phosphate and using graphs relating pH, phosphate and Na:PO₄ mole ratio to obtain an estimate of the Na:PO₄ mole ratio. The graphs generally assumed no ammonia was present. For high level phosphate treatments, especially in mixed metallurgy systems in which feedwater ammonia concentration is controlled to 0.3 ppm as NH₃ or less, this graphical method provided reasonably accurate estimates of the Na:PO₄ ratio. However, for lower level phosphate treatments – especially in all-ferrous systems in which feedwater ammonia concentration is above 1 ppm as NH₃ – use of the graphs without adjustment for the effect of ammonia to obtain Na:PO₄ ratio produced inaccurate and misleading results.

An example of this was at a plant with a 2600 psig all-ferrous system visited in 1997 in which boiler water phosphate was maintained between 0.5 and 1.5 ppm as PO₄ and feedwater pH was maintained at about 9.4 units. Disodium phosphate was being fed in an effort to suppress pH because the Na:PO₄ mole ratio obtained using the graphical method was well above 3.0. However, when the impact of the boiler water ammonia concentration of 0.65 ppm as NH₃ was included, a Na:PO₄ mole ratio of about 2.0 was obtained. Clearly, the graphical method was producing inaccurate estimates leading to inappropriate treatment decisions and maintenance of less than optimal boiler water chemistry.

To overcome this shortcoming of the graphical method, some have used graphs relating pH, phosphate and Na:PO₄ mole ratio constructed with an assumed ammonia concentration representative of typical boiler water ammonia levels. This method worked reasonably well, but it provided erroneous estimates when the ammonia concentrations varied from the assumed value.

APPROXIMATE CALCULATION METHODS

Others have used a simplified mathematical model to estimate the Na:PO₄ mole ratio based on measured boiler water pH and phosphate and ammonia concentrations. (Verib 2002 and Verib 2003) The simplified mathematical model provided by Mr. George Verib was a vast improvement over the graphical methods or methods that did not consider ammonia. However, Hull demonstrated that the Verib method also experienced errors under conditions of high ammonia and low phosphate. A review determined much of the error was due to a small difference in the basicity constant used to develop the Verib method.

RIGOROUS CALCULATION METHOD

Given the widespread access to computers, there is little justification for compromising accuracy for the sake of simplicity in calculating Na:PO₄ mole ratios. It is recommended to use spreadsheets or other programs to calculate Na:PO₄ mole ratio based on measured boiler water pH and phosphate and ammonia

content using the more rigorous models. A detailed presentation and explanation of the model was presented by Hull (2006).

LIMITATIONS ON ALL METHODS

The rigorous method was based on standard analytical chemistry principles and a number of assumptions. However, all of these assumptions apply to the preceding methods mentioned.

1. All pH values and constants are referenced to 25°C.
2. All phosphate is truly dissolved.
3. The only cations present are hydrogen, sodium and ammonium (although we present information on the effect of amines later).
4. Solutions are sufficiently dilute that activity coefficients are equal to one.
5. Equilibrium is achieved.
6. 1 ppm is essentially equal to 1 mg/L.

The preceding assumptions generally are valid for power cycles utilizing any of the following chemicals.

- Sodium Phosphates
- Ammonia
- Hydrazine (Present at sufficiently low levels not to appreciably affect ratios.)
- Carbohydrazide (Present at sufficiently low levels not to appreciably affect ratios.)

While the model estimates the Na:PO₄ mole ratio, if boiler water contains significant amounts of potassium alkalinity (hydroxide or potassium phosphate), the estimated Na:PO₄ mole ratio would include the moles of potassium alkalinity. It is cautioned that a high potassium to sodium ratio can result in very high corrosion rates in parts of boilers and superheaters.

WATER ANALYSES METHODS

There is an old adage about computer programs: garbage in, garbage out. Errors in the analytical results will result in erroneous estimates of the sodium-to-phosphate mole ratios, free caustic and pH without ammonia.

Phosphate

The form of phosphorus of interest is dissolved orthophosphate. In most power plants and industrial facilities, phosphate is determined by colorimetric test procedures. However, ion chromatography also may be used in some facilities with more advanced laboratories. In both cases, the standard methods report the results as PO₄, and these readings can be used directly in the calculation. A few tips in analyses are provided in the following list.

- Do not test for total phosphate as this will include other organic and complex phosphates.
- Filter all samples during condenser leaks to eliminate false positive readings from precipitated hardness phosphate. (See following discussion.)
- Filter samples if significant amounts of iron are present as this can cause positive interference.

For units experiencing condenser leaks or intrusion of other sources of hard water (i.e., contains calcium and magnesium), suspended hardness phosphates can be present in the boiler water. In at least one spectrophotometric phosphate procedure, a portion of these suspended hardness phosphates can redissolve and produce a false high phosphate concentration. Therefore, samples should be filtered (preferably in a 0.45 μm filter) before phosphate testing during condenser leaks.

pH

The pH needs to be measured accurately and at a temperature of 25°C (77°F). Higher or lower temperatures change the pH, and the ability to correct readings back to 25°C varies significantly. While there are ways to mathematically adjust for the effect of temperature on pH, in all cases, the best approach is to have sample temperatures rigidly controlled. Most good online analyzers have a means for adjusting for the effect of temperature on the electrodes and user-selected adjustments for the effect of temperature on the solution chemistry. However, it is common to see online monitors in plants still on factory default settings rather than on settings appropriate for the particular sample stream.

Ammonia

In the model, it talked about total ammonia as the sum of free ammonia and ammonium ion. However, this is just called the ammonia nitrogen as NH_3 in standard analytical procedures. There also is a test for total nitrogen (i.e., Kjeldahl method), which should not be performed for the ammonia test as it can include other organic amines – which behave much differently than ammonia.

There was a time when most power plants programmed their own spectrophotometers to provide ammonia readings as ppm or mg/L of ammonia as NH_3 , which has a molecular weight of 17.0306 g/mole. When the sodium phosphate ratio formulas were developed, this was the basic assumption.

Most power plants that perform bench tests for ammonia have spectrophotometers with preloaded procedures. A common default presentation of ammonia test results is ammonia nitrogen expressed as $\text{NH}_3\text{-N}$ (Hach 2005). What this means is the ammonia concentration is expressed as just nitrogen with a molecular weight of 14.0067 g/mole.

With older models, the procedure would have factors used to convert these $\text{NH}_3\text{-N}$ values to other units. For example, to convert from $\text{NH}_3\text{-N}$ to ammonia as NH_3 , one procedure instructs multiplying by 1.22 (although a more exact factor would be 1.2159).

More modern versions of the spectrophotometers allow the user the option of setting the instrument up to display the readings as NH_3 instead of $\text{NH}_3\text{-N}$. Some allow presentation as NH_4^+ , but this would not be useful for the task at hand.

Formulas presented in the HRSG chemistry consensus (ASME (2012) and calculations discussed in the development work (Hull, 2006) were based on the ammonia readings being reported as ammonia as mg/L of NH_3 . Therefore, either the meter should be set up to provide results in these units or the readings as mg/L of $\text{NH}_3\text{-N}$ should be multiplied by 1.2159 to convert to mg/L as NH_3 prior to use in the sodium-to-phosphate ratio formulas.

Amine

The standard models assume that no amines other than ammonia are present. The use of amines other than ammonia will tend to result in the overestimation of Na:PO_4 mole ratios, unless the amine concentration is determined and the model is adjusted to include the amine. This section discusses estimating the amine level. A subsequent section provides guidance for modifying the spreadsheet calculation methods if other amines are present in the boiler water.

Unfortunately, rarely is there a good means of quantifying the concentration of amine in boiler water samples at most nonnuclear power plants or industrial facilities. Nuclear power plants, typically, will have a degreed chemist onsite and often will have ion chromatograph (IC) units set up to quantify the levels of amines present in steam generator samples. IC units are more prevalent in nonnuclear power plants than in the past, so this may be a viable option at facilities with the necessary equipment and expertise.

For a facility in which the amine feed rates, operating pressure, operating temperatures, deaerator venting rates, makeup rates, extent of condensate polishing (which removes amines), and blowdown rates are fairly constant, it may be possible to have routine samples sent to an outside laboratory for analysis of the amine concentrations in the boiler water and to use these values in the formula. However, this is not a reliable control if onsite personnel have no way to verify the readings.

We recall seeing an old spectrophotometric procedure for morpholine. However, it is not carried in current standard references.

Another hypothetical approach is proposed for evaluation to estimate amine levels: measure the total amount of nitrogen compounds (as N); measure the ammonia nitrogen (as N); and then, calculate the nitrogen (as N) due to the amine by difference. If the ammonia concentration was determined as NH_3 , it can be converted to $\text{NH}_3\text{-N}$ by multiplying by 0.82244. The amine concentration would be the amine nitrogen (as N) times the amine molecular weight divided by the molecular weight of nitrogen (14.0067). Table 1 provides the molecular weights (MW), the multiplication factors to convert from amine nitrogen as N to the amine, and the basic dissociation constants for three common amines. The basic dissociation constant is the dissociation constant for water divided by the acid dissociation constant for the amine. Acid dissociation constants are available from standard references such as Lange's Handbook of Chemistry.

Table 1

| Amine | MW g/mole | ppm Amine / ppm N* | Basic Dissociation Constant, K_{bam} |
|-----------------|----------------------|-------------------------------|---|
| Cyclohexylamine | 99.1772 | 7.08069 | 4.4000E-4 |
| Ethanolamine | 61.0842 | 4.36107 | 3.1876E-5 |
| Morpholine | 87.1224 | 6.22005 | 2.1550E-6 |

* Multiply amine as N by factor to get amine.

It is not known if the standard procedures for total nitrogen would be able to properly detect all of the nitrogen associated with the amine compounds in Table 1. An evaluation would be needed to determine

the recoveries of the analytical methods for the specific amines used. In systems that use more complex amines, the amines can decompose to other amines, which would render this approach inaccurate.

In power plants using urea for NO_x control, urea contamination can enter the condensate in some system designs – which would cause false positive errors. Also, facilities receiving process condensate could have other sources of organic nitrogen, which would cause positive interference with this approach.

We would be interested if any attendees have methods or experience quantifying amines onsite. Rapid determination of the amine concentration is the main limitation for correcting for the effect of amines on the Na:PO₄ mole ratio with phosphate treatment programs.

MODIFYING FORMULATION FOR AMINES

The formulas can be modified to include the effect of other amines in addition to ammonia. In Appendix A of Hull (2006), an equation (Equation 27) is presented for the sodium ion concentration in moles/L. Assuming that the amine is monovalent (has only one dissociation constant), the formulas are fairly easy to modify. The extent to which the amine dissociates in solution is essentially the amount it will behave as sodium in the water sample, raise the pH, and cause a false high bias in the sodium-to-phosphate ratio if not considered.

For each additional amine considered in addition to ammonia, the right side of the equation would be reduced by the following factor to decrease the predicted sodium alkalinity to a more representative value.

$$[\text{Amine}] K_{\text{bam}} / ((K_{\text{w}}/H) + K_{\text{bam}})$$

Where;

$$[\text{Amine}] = \text{mole /L of amine} = [\text{mg/L amine} / \text{MW}/1000] \text{ (e.g., mg/L as ethanolamine} / 61084.2)$$

K_{bam} = basic dissociation constant for amine (see Table 1, e.g. 3.186E-5 for ethanolamine).

K_{w} = water dissociation constant = 1.008E-14

$$H = 10^{-\text{pH}}$$

If using the formulas presented in the HRSG chemistry consensus document, the negative of the above factor would be included in the large bracketed { } sodium-to-phosphate ratio formula on Page 25 of that reference (ASME 2012). This factor would be included for each additional amine in addition to ammonia. This methodology only works for amines with a single amine group. The formula to calculate the sodium-to-phosphate mole ratio, which includes correction for the combined effect of ammonia and one other primary amine (such as ethanolamine), is provided in Appendix A

COMPUTER METHODS OF CALCULATION

There are two common methods for rigorous calculation of the Na:PO₄ mole ratios:

- a spreadsheet program (e.g., Excel) in which data are entered and the calculations automatically performed and logged with the data;

- and, a program with prompts the user to enter the data and provide the results (e.g., a Basic computer program, MS QBasic).

The spreadsheet program data (pH, phosphate, and ammonia) and results (Na:PO₄ mole ratio, free caustic) are located in parallel columns. Log sheet data can be copied into the spreadsheet for rapid assessment of large collections of data. Some clients prefer to incorporate spreadsheets into their electronic log sheets for automatic calculation of the ratios and free caustic. In either case, the ratios and free caustic values can be graphed or trended versus load, date, or other chemistry parameter(s) to evaluate hideout or cycle contamination. The advantage of the spreadsheet is that it can be used to rapidly process large collections of data.

For the Basic program, the operator fills in the pH, phosphate, and ammonia. The Na:PO₄ mole ratio, free caustic (ppm as NaOH), and the ammonia-free pH are displayed automatically on the same screen. These results can be manually entered on the log sheets or computerized spreadsheets for tracking and graphing. Some versions of these programs and spreadsheets also include calculations of the minimum theoretical conductivity, which is discussed in the paper by Hull (2006).

INTERPRETATION OF RESULTS

Na:PO₄ mole ratios above 3.0 indicate that free caustic is present. Under these conditions, the reported free caustic residual should be used for chemistry control. An example of measured and calculated values is provided in Table 2.

Table 2 - Example of Calculations for Unit on Equilibrium Phosphate Treatment

| Measured Parameters | | | Calculated Values | |
|---------------------|---------------------|---------------------|--------------------------|----------|
| pH | ppm PO ₄ | ppm NH ₃ | Na:PO ₄ Ratio | ppm NaOH |
| 9.4 | 0.5 | 0.3 | 5.43 | 0.51 |
| 9.5 | 1.0 | 0.3 | 4.43 | 0.60 |
| 9.7 | 0.5 | 0.3 | 4.91 | 1.21 |

The above data show that the Na:PO₄ mole ratio can follow a different trend than the free caustic residual. If the Na:PO₄ mole ratio is above 3.0, the free caustic residual is much more relevant for control purposes. The Na:PO₄ mole ratio is most useful when ratios are less than 3.0.

The calculated free caustic residual will be either positive (Na:PO₄>3) or negative (Na:PO₄<3). The negative value shows how much caustic would have to be added to boiler water to achieve an Na:PO₄ mole ratio of 3.0.

The Na:PO₄ ratio is sometimes a negative value. This would be caused by acidic contamination that converts sodium alkalinity to neutral sodium salts and suppresses pH. This condition would also presume a higher ammonia concentration as shown in the following list in which phosphate, pH and ammonia are measured and the ratio is calculated.

- PO₄: 0.5 ppm
- pH: 9.2

- NH_3 : 1.0 ppm as NH_3
- Na:PO_4 : -0.84

EXAMPLES OF USING A SPREADSHEET

Facility A and B examples were included in the Hull paper (2006). More recent results are presented for Facility C.

Facility A, 1800 psig HRSG

Figure 1 presents a graph of the calculated Na:PO_4 mole ratios for the high-pressure (HP) section of a three-pressure HRSG (maximum operating pressure up to ~1800 psig) at Facility A over a one-year period. Note that Facility A did not operate very often during the year and does not have duct burners. Usually, only one of the two HRSG units was in service at a time, and the HP drum pressure was below 1400 psig when only one HRSG was in service (estimated about 20 days' operation above 1400 psig per unit). Also, since the sample conditioning system was rather poor (hot cooling water), much of the error in these readings may be due to high sample temperatures which caused a low pH bias and subsequent underestimation of Na:PO_4 mole ratios.

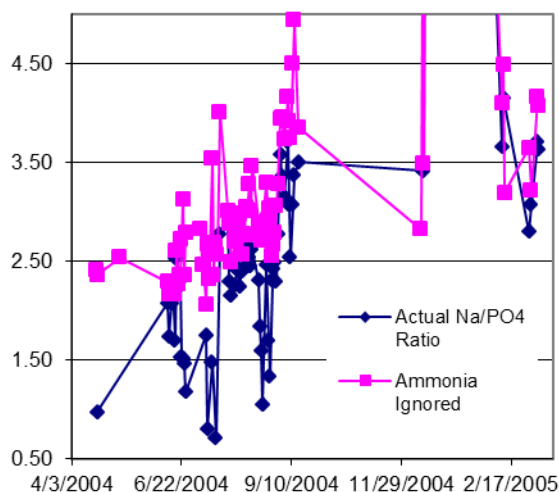


Figure 1
Sodium-to-phosphate Mole Ratio vs. Time, Facility A HRSG 1 HP Drum

The upper curve in Figure 1 shows the much higher ratios calculated when ammonia was not included in the calculation. While Facility A tested for ammonia, there appeared to be a general lack of understanding of the effect of ammonia on the allowable pH control range for the boiler water. Ignoring the ammonia effect resulted in low to satisfactory Na:PO_4 mole ratios. However, inclusion of measured boiler water ammonia levels in the calculations resulted in excessively low Na:PO_4 mole ratios during much of the first half of the review period. During the middle and end of the review period, high Na:PO_4 ratios were noted (up to 7.5). We have truncated the top of the graph to provide slightly better resolution at the lower Na:PO_4 mole ratios.

If the Na:PO₄ ratio is above 3.0, the free caustic alkalinity (ppm NaOH) calculation must be used for monitoring and control. Figure 2 presents the calculated free caustic over the the same time period. The free caustic level was high (1-8.5 ppm) on about six days. The high caustic levels (>1 ppm) are believed to have been due to a makeup system upset. It appeared that they had just started to operate in the trace caustic region (0-1 ppm) at the end of the review period. Negative values for free caustic were not graphed.

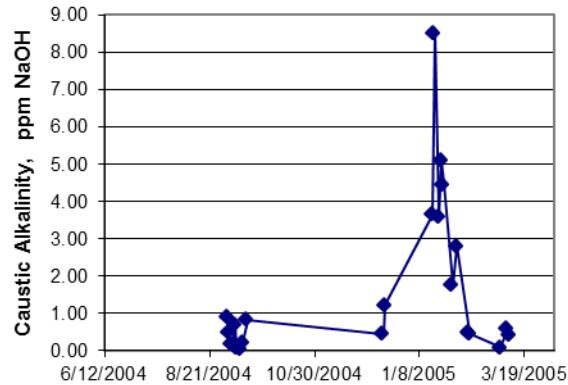


Figure 2
Free Caustic, ppm NaOH,
Facility A, HRSG 1, HP Drum

Facility B, 1800 psig HRSG

Facility B had a three-pressure HRSG unit, which operated with drum pressures of 840-1800 psig. While the Na:PO₄ mole ratios were significantly better than those for Facility A, a significant number of the readings were lower than the target (>2.7) for the HP drum sample. Note that this control range was a little more liberal than the current HRSG chemistry consensus document. This unit did not have duct burners, and so was not subject to the same heat flux and underdeposit concentration concerns for which the current HRSG consensus document was developed. Despite fairly high phosphate levels, no hideout trend was noted when data were graphed versus turbine load.

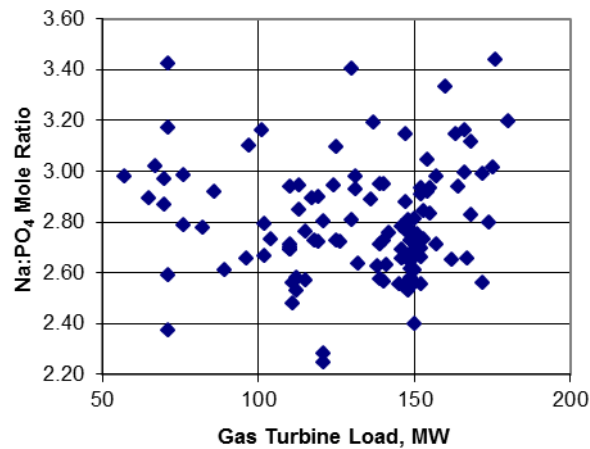


Figure 3
Ratio vs. Load, HP Drum, Facility B

Figure 4 presents a graph of the free caustic in the HP drum blowdown versus the gas turbine load. Only one reading was slightly above the 1 ppm free caustic limit. Note that the calculated free caustic values often were slightly negative. This just indicates the amount of caustic which could enter the boiler before free caustic would be present. During low pH upsets, this value can be used to indicate the amount of caustic that would have to be added to achieve 3.0 ratio and restore pH.

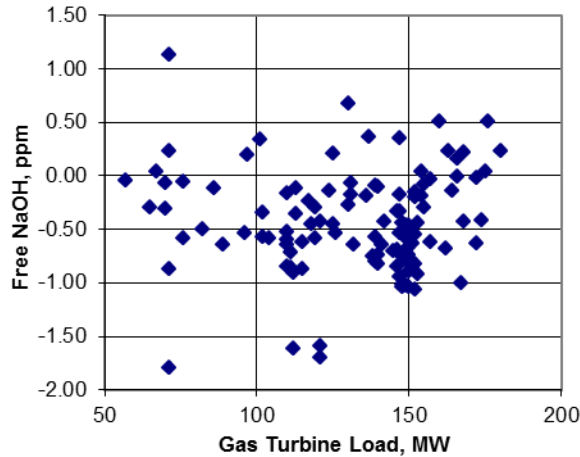


Figure 4
Free Caustic vs. Load, HP Drum, Facility B

Figure 5 presents a graph showing the error in the Na:PO₄ mole ratio for the data from Facility B if ammonia levels in the boiler water were ignored. As indicated in Figure 5, the error from ignoring ammonia in Na:PO₄ mole ratio estimates increased from about 0.1 at phosphate concentrations of 6 ppm to an error of about 0.5 as phosphate approaches 2 ppm. The huge effect of ammonia on the ratios is well established in the literature, but this information does not always reach the water treatment operators.

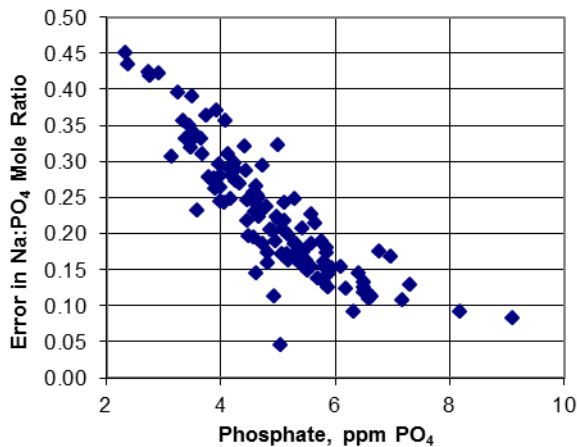


Figure 5
Error in Ratio (If Ammonia Is Ignored) vs. Phosphate Concentration, Facility B

Facility C, 2000 psig Boiler

Figures 6-8 show an evaluation for a 2000 psig drum type boiler on low level phosphate 0.75-1.5 ppm treatment with ammonia. They routinely monitored pH, phosphate and boiler water ammonia and used a spreadsheet to track their control. They maintained 0.33-0.45 ppm of ammonia in the boiler water during this period of review. Control was very good, and they had a very small fluctuation in the level of free caustic in the boiler water. As indicated in Figure 8, if they did not correct for ammonia, the free caustic values would have been overestimated by about 0.4 ppm and they may have responded prematurely thinking that they had high caustic in the boiler water.

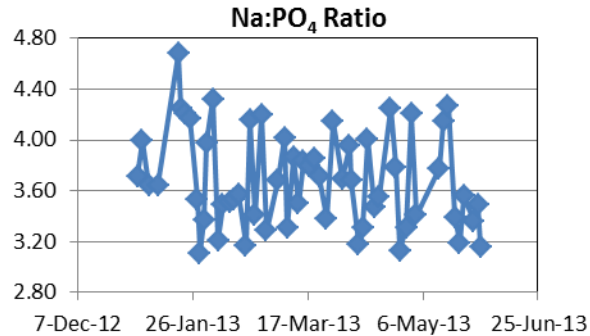


Figure 6
Na:PO₄ Ratios in Boiler Water

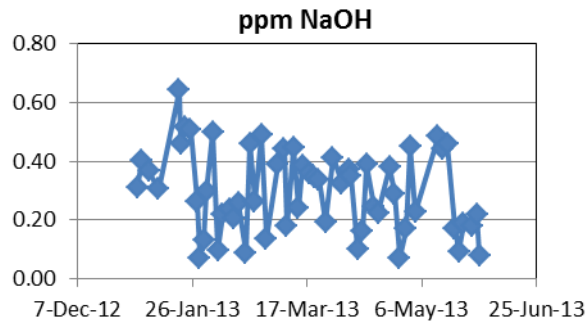


Figure 7
Calculated Free Caustic in Boiler Water

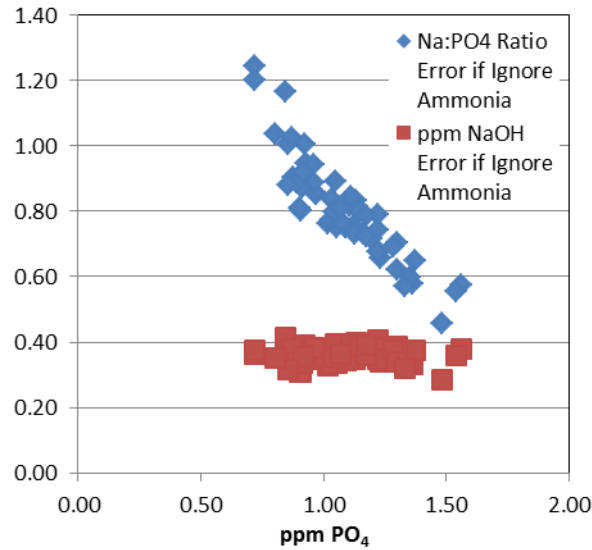


Figure 8

Relative Error in Na:PO₄ Ratio and ppm NaOH vs. ppm PO₄ if Ignore Ammonia

Example of Amine Correction

As the spreadsheet was just updated to reflect the amine correction developed for this paper, it was considered desirable to provide some hypothetical examples to demonstrate the effect of ethanolamine on the sodium-to-phosphate mole ratio. Table 3 shows the separate and combined effect of ammonia and ethanolamine on the estimated sodium-to-phosphate mole ratio with 1.5 ppm of phosphate present.

Table 3: Effect of Ammonia and Ethanolamine on Na:PO₄ Ratio

| Phosphate | pH | Ammonia | Ethanolamine | Na:PO ₄ Ratio |
|-----------|-----|---------|--------------|--------------------------|
| 1.5 | 9.2 | 0 | 0 | 3 |
| 1.5 | 9.2 | 0.28 | 0 | 2.45 |
| 1.5 | 9.2 | 0 | 1 | 2.31 |
| 1.5 | 9.2 | 0.28 | 1 | 1.76 |

When ethanolamine is present in the blowdown sample, the actual sodium-to-phosphate mole ratio can be noticeably less than predicted by conventional methods that ignore ethanolamine – even when significant phosphate concentrations are present. The estimated sodium-to-phosphate mole ratios due to 1-5 ppm of ethanolamine with 2-10 ppm of phosphate are shown in Tables 4 and 5.

Table 4: Effect of Ethanolamine on Na:PO₄ Ratio
(2-5 ppm PO₄)

| Ethanol-amine, mg/L | Sodium-to-phosphate (Na:PO ₄) Mole Ratio | | |
|---------------------|--|--------------------------------|--------------------------------|
| | pH 9.5, 2 mg/L PO ₄ | pH 9.6, 3 mg/L PO ₄ | pH 9.7, 5 mg/L PO ₄ |
| | | | |

| | | | |
|---|------|------|------|
| 0 | 3.51 | 3.27 | 2.96 |
| 1 | 3.12 | 3.04 | 2.84 |
| 2 | 2.73 | 2.81 | 2.72 |
| 3 | 2.34 | 2.58 | 2.6 |
| 4 | 1.96 | 2.35 | 2.48 |
| 5 | 1.57 | 2.12 | 2.36 |

**Table 5: Effect of Ethanolamine on Na:PO₄ Ratio
(10 ppm PO₄)**

| pH | Sodium Phosphate (Na:PO ₄) Ratio With 10 mg/L PO ₄ | |
|------|--|--------------------------|
| | No Ethanolamine | With 5 mg/L Ethanolamine |
| 10.1 | 3.21 | 3.05 |
| 10 | 2.96 | 2.77 |
| 9.9 | 2.76 | 2.54 |
| 9.8 | 2.6 | 2.34 |
| 9.7 | 2.48 | 2.18 |

SUMMARY

The paper reviewed the use of a rigorous calculation method to determine the Na:PO₄ mole ratios and free caustic in boiler water samples from boiler water, pH, phosphate and ammonia data. Guidance on adapting formulas for use when other amines also are present is provided.

REFERENCES

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Appendix A

The following sodium-to-phosphate mole ratio formula includes terms to account for the effect of one organic amine with ammonia on the boiler water pH. The parenthetic example in the variable listing is for ethanolamine. Mixtures of ethanolamine and ammonia have commonly been used with heat recovery steam generators.

$$R = (1/P_t) \{ K_w/H + 3P_t/D + 2HP_t/DK_3 + H^2P_t/((DK_3)K_2) - H - A_t K_b / [(K_w/H) + K_b] - A_m K_{bam} / [(K_w/H) + K_{bam}] \}$$

Where:

R = Sodium-to-phosphate ratio

H = Hydrogen ion concentration = $10^{-\text{pH}}$

A_t = Ammonia concentration in moles/L = (ppm NH_3) / (17,030.61)

A_m = Amine concentration in moles/L (e.g. ppm ethanolamine / 61,084.2)

P_t = Phosphate concentration in moles/L = (ppm PO_4) / (94,971.4)

K_w = Dissociation constant for water = 1.008×10^{-14}

K_b = Dissociation constant for ammonia = 1.7742×10^{-5}

K_{bam} = Basic dissociation constant for organic amine (e.g. 3.1876E-5 for ethanolamine)

K_1 = First dissociation constant for phosphoric acid = 7.1121×10^{-3}

K_2 = Second dissociation constant for phosphoric acid = 6.2373×10^{-8}

K_3 = Third dissociation constant for phosphoric acid = 4.571×10^{-13}

D = Ionization fraction = $H^3 / (K_1 K_2 K_3) + H^2 / (K_2 K_3) + H / K_3 + 1$

The same, separate equation from the referenced paper and the HRSG consensus document can be used to calculate the amount of free sodium hydroxide:

$$\text{ppm free NaOH} = (R-3) \times (\text{ppm PO}_4) \times 0.42139$$