

Calculations to Manage Phosphate and Caustic Treatment

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ABSTRACT

Phosphate and/or caustic (NaOH) treatment boiler water treatment is often employed to reduce the risk of corrosion.

This paper describes empirical calculations for proper control of phosphate and caustic treatment which could be incorporated into an Excel spreadsheet which includes several calculations, of which the most important are:

1. Boiler water ammonia corrected pH
2. Sodium to phosphate molar ratio
3. Free sodium hydroxide concentration
4. Amount of phosphate and/or caustic to dose for a specific concentration at the current operating pressure

This can also be used to calculate how much caustic must be added to an AVT treated boiler to achieve a desired pH-value.

INTRODUCTION

Several chemistry regimens are employed today such as:

- All-volatile treatment, under reducing conditions (AVT(R))
- All-volatile treatment, under oxidizing conditions (AVT(O))
- Oxygenated treatment (OT)
- Phosphate treatment (PT)
- Caustic treatment (CT)

AVT and OT are more precisely feedwater treatments, whereby no solid alkali is added to the boiler water. AVT can be either reducing or oxidizing, which is dictated by the metallurgy.

PHOSPHATE TREATMENT

Phosphate treatment has been used for over 80 years and is currently still used in many boilers today. PT has evolved over the years from "coordinated phosphate treatment", which was introduced in 1942 [1] as "congruent phosphate treatment" to address corrosion issues thought to be caustic gouging experienced with coordinated treatment. Congruent phosphate operated at lower sodium to phosphate molar ratios ranging from 2.2 to 2.6, which resulted in "phosphate hideout" and acid phosphate corrosion.

Equilibrium phosphate (EPT), developed at Ontario Hydro in the 1980s by Jan Stodola [2], uses only tri-sodium phosphate (TSP) and low levels of caustic ($\leq 1.0 \text{ mg} \cdot \text{L}^{-1}$ NaOH) for pH control. In 2004 [3] Electric Power Research Institute (EPRI) developed their phosphate continuum (PC), which is a low or high concentration of phosphate and a low concentration caustic based on operating pressure. EPRI's 2011 phosphate treatment (PT) guideline [4] employs phosphate in the range of $0.2\text{--}3.6 \text{ mg} \cdot \text{L}^{-1}$ with up to $1.0 \text{ mg} \cdot \text{L}^{-1}$ of NaOH for boilers up to 10.34 MPa (1500 psi) and $0.2\text{--}1.5 \text{ mg} \cdot \text{L}^{-1}$ with up to $1.0 \text{ mg} \cdot \text{L}^{-1}$ of NaOH for boilers up to 17.24 MPa (2500 psi) using only tri-sodium phosphate and caustic. The pH control range for phosphate and caustic treatment is pH due to solid alkali excluding ammonia which EPRI established in 1994 [5].

CAUSTIC TREATMENT

Caustic treatment using higher concentrations of caustic was applied to low-pressure drum boilers in the 1950s successfully. As operating pressures increased in the 1960s, application of caustic treatment at the concentrations employed on lower pressure boilers resulted in caustic gouging and boiler tube failures. As a result, caustic treatment was abandoned in the US

for AVT and various forms of phosphate treatment. However, in the United Kingdom caustic treatment continued to be used and refined so the problems associated with phosphate treatment, such as phosphate hideout, could be avoided.

It is imperative to limit caustic to avoid caustic gouging and carry-over and subsequent deposition on the steam turbine.

INDUSTRY LIMITS FOR PHOSPHATE AND CAUSTIC TREATMENT

In 1994 EPRI introduced guidelines for pH control due to solid alkali only, which continues today. Therefore, the influence ammonia has on the measured pH of the sample must be determined and subtracted from the measured pH to determine the pH due to solid alkali when employing PT and CT. Various methods have been used to determine the "ammonia corrected pH", such as tables and curves provided by EPRI [5].

Control of the phosphate concentration is straight forward since the chemist can measure the phosphate (PO_4) residual, however addition of caustic for pH control is less precise, relying on experience, tables and charts, and educated estimates. When operating a unit on AVT and an excursion occurs the chemist must take corrective action to avoid damage to the boiler, which usually requires a temporary transitioning to PT or CT.

Some chemists in the industry have developed various tools to more accurately determine the sodium to phosphate molar ratio and ammonia corrected pH. This paper discusses such a tool, the calculations used, and how to integrate the calculations into the unit supervisory control and data acquisition (SCADA) or distributed control system (DCS) to manage PT and CT.

The EPRI [4] and International Association for the Properties of Water and Steam (IAPWS) [6] limits for phosphate treatment are listed in [Table 1](#) and the limits for caustic treatment are listed in [Table 2](#).

It is important to note, as mentioned earlier, that the pH is the ammonia corrected pH. Determining the phosphate concentration is simple. Measuring the pH with ammonia and solid alkali is simple, however determining the pH due to solid alkali is more challenging as is determining the free sodium hydroxide concentration. For many years plant chemists relied upon tables, curves, and algorithms from EPRI or other sources to control phosphate and caustic treatment pH and free sodium hydroxide. The analytical tool calculates the ammonia corrected pH, sodium to phosphate molar ratio, and free sodium hydroxide concentration.

CALCULATIONS TO MANAGE PHOSPHATE AND CAUSTIC TREATMENT

Phosphate and Caustic Treatment Management Calculation

The phosphate and caustic management calculation was developed to aid the station and corporate chemist to more precisely control phosphate and caustic treatments. Unit operating and chemistry data is entered into the Excel spreadsheet and the following parameters are calculated:

	EPRI [4]	EPRI [4]	IAPWS [6]
Drum pressure	10.34 MPa (1500 psi)	17.24 MPa (2500 psi)	17.24 MPa (2500 psi)
Specific conductivity [$\mu\text{S} \cdot \text{cm}^{-1}$]	> CACE	> CACE	< 8
CACE [$\mu\text{S} \cdot \text{cm}^{-1}$]	< 32	< 15	< 10
pH [–]	9.2–9.8*	9.0–9.6*	9.0–9.3*
Phosphate as PO_4 [$\text{mg} \cdot \text{L}^{-1}$]	0.2–3.6	0.2–1.5	0.3–1.5
NaOH [$\text{mg} \cdot \text{L}^{-1}$]	0–1.0	0–1.0	–

* Solid alkali pH (ammonia corrected pH)

Table 1:
EPRI and IAPWS phosphate treatment limits.
CACE conductivity after cation exchange

	EPRI [4]	EPRI [4]	IAPWS [6]
Parameter	10.34 MPa (1500 psi)	17.24 MPa (2500 psi)	17.24 MPa (2500 psi)
Specific conductivity [$\mu\text{S} \cdot \text{cm}^{-1}$]	< 9	< 12	3.5–9.5
Cation conductivity [$\mu\text{S} \cdot \text{cm}^{-1}$]	< 9	< 18	< 9
pH [–]	9.1–9.4*	9.1–9.4*	9.1–9.5*
NaOH [$\text{mg} \cdot \text{L}^{-1}$]	0.5–1.0	0.5–1.0	0.5–1.2

* Solid alkali pH (ammonia corrected pH)

Table 2:
EPRI and IAPWS caustic treatment limits.

- 1 Ammonia distribution ratio
- 2 Feedwater pH
- 3 Feedwater ammonia concentration as NH_3
- 4 Boiler water ammonia concentration as NH_3
- 5 Ammonia corrected pH
- 6 Sodium to phosphate molar ratio
- 7 Boiler water free sodium hydroxide (NaOH)

The calculations require the following data inputs:

■ Data inputs

- Drum pressure
- Boiler water pH
- Boiler water phosphate
- Boiler water cation conductivity
- Boiler water specific conductivity
- Feedwater cation conductivity
- Feedwater specific conductivity

■ Calculated values for boiler water (BW) ammonia concentration

- Ammonia distribution ratio
- Feedwater pH
- Feedwater ammonia
- Boiler water ammonia

■ Calculated values for phosphate and caustic treatment management

- Ammonia corrected pH
- Sodium to phosphate molar ratio
- Boiler water free sodium hydroxide concentration

Table 3 illustrates the analytical spreadsheet including the data inputs and the subsequent calculations.

Calculated Values for Boiler Water Ammonia Concentration

The equations for calculating the following parameters are reviewed:

- Ammonia distribution ratio
- Feedwater pH
- Feedwater ammonia
- Boiler water ammonia

Ammonia distribution ratio calculation The algorithm, Eq. (1), to calculate the ammonia distribution ratio, D_A , shown below, was derived from the ammonia distribution versus pressure curve [7].

$$D_A = -1.79553 \times \ln(p_D) + 16.0404 \quad (1)$$

The algorithm calculates the ratio of steam/water for ammonia at the drum pressure, p_D , entered in the data input.

Data Inputs		
Parameter	Unit	Value
Drum Pressure, p_D	[psig]	2 400
Boiler Water pH, pH_{BW}	[–]	9.40
Boiler Water PO_4 , C_{BWP}	[$\text{mg} \cdot \text{L}^{-1}$]	1.00
Boiler Water Cation Conductivity, CACE_{BW}	[$\mu\text{S} \cdot \text{cm}^{-1}$]	3.00
Boiler Water Specific Conductivity, SC_{BW}	[$\mu\text{S} \cdot \text{cm}^{-1}$]	9.0
Feedwater Cation Conductivity, CACE_{FW}	[$\mu\text{S} \cdot \text{cm}^{-1}$]	0.10
Feedwater Specific Conductivity, SC_{FW}	[$\mu\text{S} \cdot \text{cm}^{-1}$]	4.0
Calculated Values for BW Ammonia Concentration		
Ammonia Distribution Ratio (Steam/ H_2O), D_A	[–]	2.07
Feedwater pH, pH_{FW}	[–]	9.15
Feedwater NH_3 , C_{FWA}	[$\text{mg} \cdot \text{L}^{-1}$]	0.44
Boiler Water NH_3 , C_{BWA}	[$\text{mg} \cdot \text{L}^{-1}$]	0.21
Calculated NH_3 Corrected pH, $\text{Na}:\text{PO}_4$ Ratio, and Free NaOH		
NH_3 Corrected Boiler Water pH, pH_{AC}	[–]	9.29
Sodium to Phosphate Molar Ratio ($\text{Na}:\text{PO}_4$)	[–]	3.92
Boiler Water Free NaOH, C_{BWS}	[$\text{mg} \cdot \text{L}^{-1}$]	0.39

Table 3:
Analytical spreadsheet to manage phosphate and caustic treatment. The data inputs may be taken from the continuous analyzers or grab sample analysis.

Feedwater pH calculation This calculation, Eq. (2) shown below, uses the current EPRI equation [4] for calculating feedwater pH, pH_{FW} , due to ammonia using the specific conductivity, SC_{FW} , and cation conductivity, CACE_{FW} , values of the feedwater sample.

$$\text{pH}_{\text{FW}} = 8.55 + \text{Log}(\text{SC}_{\text{FW}} - 0.25 \times \text{CACE}_{\text{FW}}) \quad (2)$$

Feedwater ammonia concentration calculation Eq. (3), shown below, uses the dissociation constant of water, K_w , the basicity constant for ammonia, K_b , along with the calculated hydrogen ion $[\text{H}^+]$ concentration, and the molecular weight of the NH_3 molecule to calculate the ammonia concentration in the feedwater, C_{FWA} [8].

$$\text{C}_{\text{FWA}} = \left\{ \frac{(K_w)^2}{[\text{H}^+]^2 \times K_b} - \frac{K_w}{K_b} + \frac{K_w}{[\text{H}^+]} - [\text{H}^+] \right\} \times 17000 \quad (3)$$

Boiler water ammonia concentration calculation Eq. (4), shown below, simply divides the calculated feedwater ammonia concentration determined by Eq. (3) by the ammonia distribution ratio determined by Eq. (1) to calculate the boiler water ammonia concentration, C_{BWA} .

$$\text{C}_{\text{BWA}} = \frac{\text{C}_{\text{FWA}}}{D_A} \quad (4)$$

Ammonia corrected boiler water pH calculation Eq. (5), shown below, to calculate the ammonia corrected pH, pH_{AC} , uses the measured boiler water pH, pH_{BW} , the calculated boiler water ammonia concentration, C_{BWA} , and the molecular weight of ammonium hydroxide to calculate the pH of the boiler water after subtracting the boiler water ammonium hydroxide concentration.

$$\text{pH}_{\text{AC}} = -\text{LOG} \left(\frac{10^{-14}}{10^{(\text{pH}_{\text{BW}}-14)} - \left(\frac{\text{C}_{\text{BWA}}}{17000} \times (-0.086 \times (\text{pH}_{\text{BW}})^2 + 1.146 \times \text{pH}_{\text{BW}} - 2.729) \right)} \right) \quad (5)$$

This is referred to as ammonia corrected pH, which must be done because when using phosphate or caustic treatment, the pH control limits are based on pH from solid alkali only excluding any contribution from ammonia.

Sodium to phosphate molar ratio ($\text{Na}:\text{PO}_4$) calculation It is important to know the $\text{Na}:\text{PO}_4$ ratio so the chemist can control the ratio in the proper range of ≥ 3.0 . As the $\text{Na}:\text{PO}_4$ ratio decreases below 3:1, the risk of acid phosphate corrosion increases, especially when the ratio is lower than 2.8:1.

$$\text{Na}:\text{PO}_4 \text{ Ratio} = \frac{(10^{(\text{pH}_{\text{AC}}-14)} + \frac{\text{C}_{\text{BWP}}}{47485.5}) \times 94971}{\text{C}_{\text{BWP}}} \quad (6)$$

where C_{BWP} is the measured boiler water phosphate concentration.

Boiler water free sodium hydroxide concentration calculation for phosphate treatment It is important to know the free sodium hydroxide concentration and to control it between 0 and $1.0 \text{ mg} \cdot \text{L}^{-1}$ when using phosphate treatment. If the concentration increases beyond $1.0 \text{ mg} \cdot \text{L}^{-1}$, the risk of caustic gouging increases. Eq. (7) calculates the free sodium hydroxide concentration, C_{BWS} , when using phosphate treatment.

$$\text{C}_{\text{BWS}} = (10^{\text{pH}_{\text{AC}}-14} - 10^{\text{LOG}(\{\text{C}_{\text{BWP}} \times 3 \div 94791\} - \{\text{C}_{\text{BWP}} \div 47395.5\} + 14)} - 14) \times 40000 \quad (7)$$

Eq. (8), shown below, can also be used to calculate the free sodium hydroxide concentration and can be used when using caustic treatment.

$$\text{C}_{\text{BWS}} = (10^{\text{pH}_{\text{AC}}-14} - 10^{\text{C}_{\text{BWA}}-14}) \times 40000 \quad (8)$$

INTEGRATION WITH DCS OR SCADA

If continuous monitoring is employed for all the data inputs required by the phosphate and caustic treatment management tool or the caustic treatment management tool, it is easy to integrate the equations used in the tool into the DCS or SCADA. Performing calculations in these software systems is quite easy; all you must do is follow the prescribed format for the software. Enter the equations and where values such as conductivity, pH, and phosphate are required enter the parameter tag identity. This will provide constant monitoring of the ammonia corrected pH, sodium to phosphate molar ratio, and free sodium hydroxide, thereby providing the chemist with tools to better control the chemistry. Some instrument manufacturers, e.g. Swan Analytical, provide analyzers that will monitor both the specific and cation conductivity and use this data to calculate the pH and ammonia. If you have such analyzers, you can use these values for the calculated feedwater pH and ammonia.

CONCLUSION

Phosphate and caustic treatments are commonly used around the world. They have the advantage of providing alkalinity to neutralize acidic salts, thereby reducing the risk of internal corrosion. Historically, controlling the chemistry has been part science, part art, due to inadequate tools to determine key parameters such as ammonia corrected pH, sodium to phosphate molar ratio, and free sodium hydroxide concentration. That technical shortfall has been resolved with this calculation, allowing the chemist to more precisely monitor and control the boiler water chemistry whether it is phosphate with caustic treatment or just caustic treatment. If adequate continuous monitoring is available, the equations can be entered into the DCS or similar system to provide continuous monitoring of the key parameters for phosphate and caustic treatment resulting in improved chemistry control.

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THE AUTHOR



While preparing this article, the editorial team learned of the passing of Randy Turner, our friend and colleague for many years. Randy Turner's passing is a great loss to all of us, as a friend, as a member of the IAPWS community, and as a member of the international power plant chemistry family.

Together with the advisory board of the journal, we decided to publish this article in this issue of the journal, despite the sad circumstances. Please find a tribute to Randy on the following page.

Tribute to Randy Turner



Randy Carl Turner, Technical Director of SWAN Analytical USA, was a chemist, pioneer and teacher, and a very well-respected member of the international power plant chemistry community. Randy passed away on Friday, April 24, 2020, in Marietta, Georgia, USA.

Randy was born in Carrollton, Georgia, on October 8, 1954, and earned a bachelor's degree in chemistry from the University of West Georgia in 1978. Randy worked as a plant chemist for 17 years and as a corporate chemist for 16+ years for Southern Company, USA, supporting their fleet of fossil plants. Since 2012, he had been the Technical Director of Swan Analytical USA.

Randy was hard-working and dedicated to the advancement of the fields of power plant chemistry and water technologies. He authored and presented more than 20 papers on power plant chemistry at conferences and authored or coauthored papers published in industry journals. In addition to his work, he also served as the chairman of many professional committees, and received multiple awards in recognition of his contributions. He was a member of the Advisory Council for the International Water Conference (IWC), the International Association for the Properties of Water and Steam (IAPWS), the American Water Works Association (AWWA), the American Society of Mechanical Engineers (ASME), and the American Society for Testing and Materials (ASTM).

In the late 1980s, Randy was a chemist at Georgia Power's Hal B. Wansley power plant with supercritical units. In 1991 he was a member of a group at the Electric Power Research Institute (EPRI) which was then working on oxygenated treatment (OT). In July 1991, Randy Turner joined the team on a visit to supercritical plants in Germany. On November 1, 1991, he became a pioneer when Wansley Unit 1 was the first unit in the US to be converted to OT, an event also attended by a team of Soviet and German scientists.

Randy remained a member of the OT team at EPRI, which later had a technical exchange with 10 Japanese utilities that were also starting to convert supercritical units to OT. During these interchanges Randy became a teacher on the practical aspects of OT and conversions.

He also started publishing at this time with a first paper on the conversion to OT at Wansley at the 1992 International Water Conference (IWC-92-19). Randy continued to travel to various locations around the world, where he presented and taught at seminars and conferences.

Randy Turner's passing is a great loss to all of us, as a friend and as a member of the international power plant chemistry family. In the past years I have had the honor of traveling with him to various locations around the world where we've organized seminars and conferences. It was always a wonderful experience to spend time with this great teacher and friend.

Tapio Werder
Editor in Chief
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