

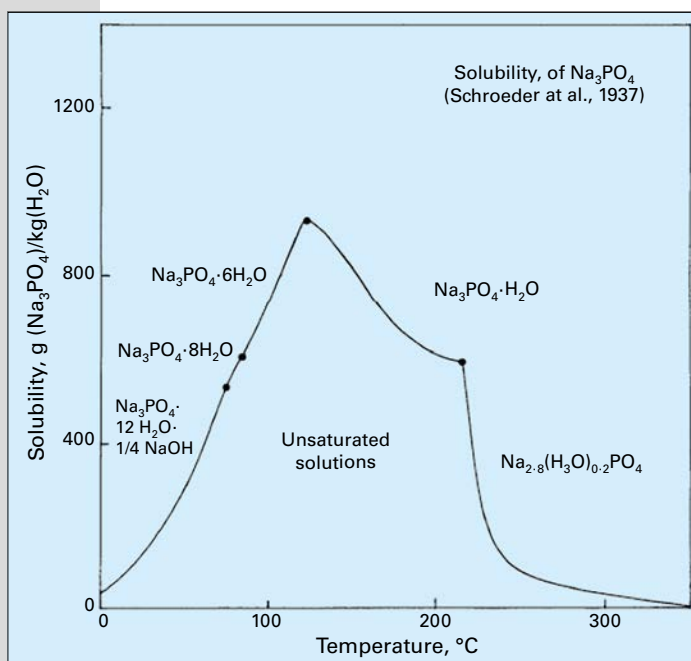
## Considerations for the Control of the Dosing of Trisodium Phosphate ( $\text{Na}_3\text{PO}_4$ ) in Boiler Water

### INTRODUCTION

In the recent past, various organizations have been trying to establish a more or less full automatization of the dosing control for the phosphate boiler water treatment (typically called PT), similar to the well-established and well-functioning automatic dosing control of ammonia. Although this may sound easy, as nowadays very reliable instruments and sampling systems are available, it is relatively difficult to implement, especially for PT, as the entire phosphate chemistry is very complex compared to that of ammonia. Therefore a safe and reliable automatic control of PT involves a lot of traps and risks which must be considered. The most common and challenging issues in this respect are described here. Although this list may not be complete, it could be used to reconsider the idea of fully automated control of phosphate dosing

### BACKGROUND

The utilization of phosphate salts for boiler water treatment is more than 90 years old. The initial purpose was to prevent the formation of hard calcium scales on heat transfer surfaces at a time when boilers were mainly operated with non-demineralized water containing salts and hardness. Over the decades various types of phosphate treatment have been developed and applied, from pure  $\text{Na}_3\text{PO}_4$  (TSP) through to the so-called "coordinated phosphate treatment, the "congruent phosphate treatment (CPT)," and the "equilibrium phosphate treatment," in order to overcome various negative effects experienced so far. These are – among others – caustic embrittlement, hydrogen damage, caustic under-deposits, caustic gauging, and of course the notorious effect of "hideout – hideout return." These various phosphate treatments have turned out to be very challenging and not very successful as the phosphate chemistry is quite complex.



The phenomenon of hideout with increasing load and pressure (a decrease in phosphate and an increase in pH) and hideout return when the unit load decreases (an increase in phosphate occurring with a pH depression) makes such an automatic control extremely difficult, especially in units with flexible operation and frequent load changes (see also [Figure 1](#)).

Figure 1:  
The solubility of trisodium phosphate in high-temperature water as a function of temperature (source: EPRI [2]).

Other problems, notably acid phosphate corrosion (APC), arise as a result of the use of mono- and di-sodium phosphate in a vain effort to "chase" hideout so as to maintain the control point within the CPT range. APC occurs in units experiencing phosphate hideout problems, and thus the mechanism is most often active in high-pressure boilers operating at or above about 10.3 MPa.

Hideout in high-pressure boilers is caused by reversible reactions between aqueous phosphate and magnetite that result in the formation of the sodium iron phosphate compound ( $\text{NaFePO}_4$ ) and an iron(III) phase, sodium iron hydroxy phosphate ( $\text{Na}_4\text{Fe}(\text{OH})(\text{PO}_4)_2 \times 1/3\text{NaOH}$ ) [1].

Many more details can be found in the various literature, such as EPRI [2] or IAPWS TGD4-11(2015) [3], as well as the VGB standard S-010 [4] and many other published papers. These provide very valuable details and it is highly recommended to study them.

### PRINCIPAL CONSIDERATIONS FOR APPLICATION

Boiler water treatment by means of sodium phosphate is permitted by all recognized standards and organizations. Of course under certain conditions its use is also necessary or at least highly recommended, as it may reduce certain risks, such as too low pH-values in the boiler water caused by the volatility of ammonia, which may result in, for example, flow-accelerated corrosion (FAC). The original reasons for its use 90 years ago, such as preventing the formation of hard calcium scales, are no longer valid in almost all units since fully demineralized water is used. Therefore, the use of phosphate should no longer be seen as the "overall standard" for the treatment of boiler water, and it should only be used when really needed, for example to securely establish a pH-value high enough to avoid FAC. This situation is not present in each and every boiler and it very much depends on the operating pressure and the resulting distribution coefficient for ammonia under the given operating conditions, which is likely the case in low-pressure and intermediate-pressure boilers of heat-recovery steam generators (HRSGs).

With increasing operating pressure, the distribution coefficient of ammonia becomes increasingly favorable, so that the absolute need to dose phosphate decreases. Also, in parallel, the temperature in the evaporator becomes more favorable with respect to possible FAC risks, so that in boilers with high or very high operating pressure (e.g. >120 bar) the need for phosphate is even lower. In other words, the benefit of a treatment with phosphate becomes increasingly lower, the higher the operating pressure is.

On the other hand, with high pressure the risks of hideout – hideout return, as well as all the other risks mentioned above, increase and in boilers with a very high operating pressure (>150–160 bar) the so-called vaporous carry over of sodium phosphate increases significantly. This effect leads to a significant impairment of the steam purity, leading to critical deposits in the superheater, as well as on the steam turbine. In other words, the disadvantages of this treatment may become greater than the advantages. Consequently, the application of this treatment should be scrutinized and questioned critically. Often it must be observed that this type of treatment has been chosen solely based on tradition (...*"this is our standard"*...) without a detailed technical justification, which should never be done.

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## PROCESS CONSIDERATIONS

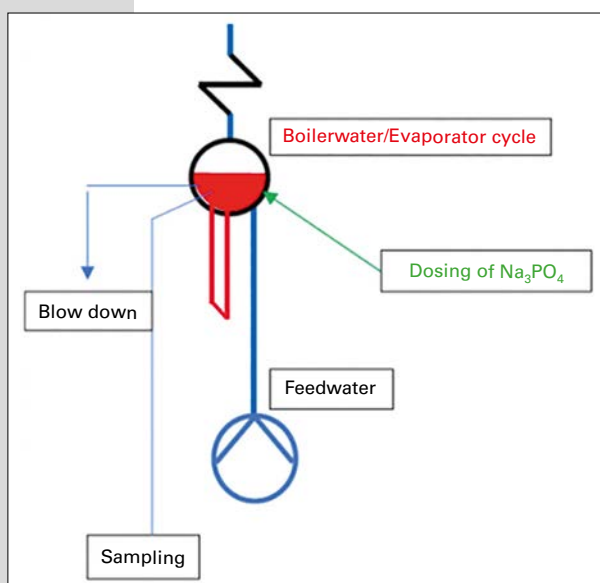
### Evaporator Cycle and Monitoring

The treatment with phosphate is used only within the evaporator cycle, which always contains a fixed volume which needs to be treated and which does not change. Therefore, it is different from the dosing of ammonia in condensate and feedwater, where a signal from the mass flow is used in addition to the monitored chemical parameters, such as pH-value or specific conductivity, to control the dosing rates.

Phosphate losses are mainly determined by the blowdown. However, in most plants this blowdown rate is not measured or indicated and depends on the various individual settings during operation, and even more strongly on the current operating situations and conditions. For example, during start-up the blowdown is usually higher due to a temporarily higher blowdown rate for maintaining the correct water level by dumping the so-called swell water. Also, load changes may cause significant changes in blowdown rates. These changes will consequently result in changes in the phosphate concentration within this evaporator cycle, but it should be kept in mind that it will take a certain amount of time until this change in concentration is present homogeneously. This already causes a certain time delay until this effect is detected and measured correctly and in a representative manner.

In addition to this unavoidable delay in stable and representative conditions, a further delay due to the sampling line should be considered as well. These sample lines are usually very long and may have a length of easily 100m or more, which is another delay factor for monitoring.

The automatic control of a phosphate dosing system will be affected significantly by these unavoidable delays and changes, resulting in more or less strongly fluctuating operation of the dosing rates and in the end a fluctuating phosphate concentration and pH-value in the boiler water. Keeping in mind the complex chemistry of phosphate, as well as the possible risks involved with it, as described in the previous section, this is definitely an unwanted situation which should absolutely be avoided.



In addition, it is also clear that a continuous dosing of phosphate is not at all required, since all guidelines allow a certain range between a lower and an upper value, which may be used to the full extent. Experience has also demonstrated that a re-dosing is required only for a very short time (typically 15–30 min), perhaps every second or third day, if the boiler blowdown is adjusted to a reasonable low level (which should be done in any case for other reasons).

Figure 2:  
Schematic of a drum boiler.

### Cycling Operation

Units in cycling operation while utilizing phosphate treatment have experienced frequent phosphate hideout problems, where the concentration of the phosphate in the boiler seems to "disappear and reappear" as the unit makes significant load changes. When the phosphate "disappears," operations or also an automatic dosing control would typically try to correct the situation by adding more phosphate, which will usually result in an overfeed situation when the load changes again and the phosphate "reappears."

Cycling also often results in temporary drum-level control problems that can result in mechanical carryover of phosphate and sodium from the drum to the superheater sections and the steam turbine, leading to potential deposition and corrosion. Flexible plants operating in a cycling mode should rather use an all-volatile treatment (AVT) chemistry, as this will reduce at least these risks to a lower, reasonable level.

### Low-Load Operation

Drum boilers with natural circulation may sometimes experience stagnant or nearly stagnant conditions during low-load operation due to the low steam production resulting in a low circulation number. This may lead, as experienced in several cases, to a partial dry-out in certain limited and smaller areas of the evaporator. This may result in the creation of a strong alkaline environment locally on the metal surface, resulting in alkaline corrosion. Therefore, it is recommended to monitor the boiler water chemistry very closely during these periods, and it might also be advisable to reduce or stop the dosing of TSP.

### Considerations for the Sampling System

It is obvious that the entire sampling system needs to fulfill certain important requirements to avoid false readings and thus an incorrect signal input to the dosing system. By experience it is also known that samples from boiler water may more frequently cause a blockage due to a higher load of iron oxide particles compared to other samples like live steam. This is especially true during start-up and/or cycling operation.

In case of an interrupted sample flow, the cells of the various monitors may either be filled with old sample or they may run empty. Both situations will create completely false signals, which may lead to an overdosing or at least a very incorrect dosing rate, which of course creates risks for the boiler. Consequently, the instruments installed should have the capability of self-diagnosis coupled with a modern information technology, such as PROFIBUS or the like, to prevent false readings from being accepted as true and to ensure that the control room immediately becomes aware that maintenance is urgently necessary. Also, certain other hardware features such as backpressure regulators and a flushing facility (upstream pressure reducing valve with an automated valve) are required, as this will help to establish stable and representative sample conditions.

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## PARAMETERS TO BE MEASURED

As described in the previous sections, phosphate chemistry may be rather complex in a boiler with other contaminants present and with the risk of phosphate hideout processes occurring. A full description of the boiler chemistry cannot be attained without comprehensive analysis of the concentrations of sodium, phosphate, and all the other ionic species that may be present at significant concentrations. The necessary online parameters are listed below:

- **Specific Conductivity** measurement again provides a warning of deviation from the normal operation of the boiler. In boilers where high levels of phosphate hideout occur, there can be large increases in conductivity during periods of low-load operation.
- **pH** measurement is needed because it demonstrates that the phosphate present in the boiler water is appropriate to provide the necessary control over the risks of both acidic and alkaline corrosion. At low phosphate concentrations, the measured pH at 25°C can be significantly influenced by the ammonia concentration. The pH measurement alone is an insensitive indicator of corrosion risk in phosphate-dosed boilers.
- **Phosphate** measurement is necessary to enable unambiguous control of dosing in boilers that are subject to hideout and to allow the interpretation of the conductivity after cation exchange in terms of other contaminants.
- **Sodium** is necessary to gain a full picture of the boiler chemistry and to determine at any time the important [sodium]:[phosphate] molar ratio.

IAPWS [5] also recommends measuring conductivity after cation exchange, as it is of some value despite the complicating factor that results from the contribution of the phosphate anion. When potentially corrosive contaminants such as chloride are present, the conductivity after cation exchange rises appreciably more rapidly than the conductivity. However, it is acknowledged that measurements of conductivity and conductivity after cation exchange without additional information on phosphate and contaminant ion concentrations cannot yield a full and unambiguous understanding of the behavior of the boiler water. Complete interpretation of the measurement requires, at a minimum, knowledge of pH, and is simplified by knowledge of the phosphate concentration. The use of cation exchange by means of electro deionization (EDI) to reduce the maintenance requirements for cation exchange resin when analyzing boiler water can be beneficial.

## CONCLUSIONS & RECOMMENDATIONS

Complete understanding of phosphate chemistry in drum boilers requires a high level of attention to the analytical techniques by the plant chemist as well as a complete understanding of the complex chemistry of phosphate in boiler water and the different possible reactions.

Considering the relatively complex chemistry, the number of parameters needed for proper dosing control, as well as the different influencing factors from the process, it is pretty clear that a fully automatic control of phosphate dosing is rather difficult and would require a highly sophisticated, exhaustive hardware installation in conjunction with an ingenious control logic.

Such great effort in combination with the facts that a continuous dosing of phosphate is **not** required in the great majority of power stations and, based on experience, re-dosing is usually only required for a very short time (typically 15–30 min) perhaps every second or third day, a fully automatic dosing control becomes very questionable.

In other words, I **would never recommend** this for the reasons laid down here, as it may create more risks than it eliminates.

[1] Dooley, R. B., Bursik, A., "PPChem 101 – Boiler and HRSG Tube Failures; Lesson 6: Acid Phosphate Corrosion", *PowerPlant Chemistry 2010*, 12(6), 368.

[2] *Cycle Chemistry Guidelines for Fossil Plants: Phosphate Continuum and Cautic Treatment, Final Report, January 2004. Electric Power Research Institute, Palo Alto, CA, USA, 1004188.*

[3] *Technical Guidance Document: Phosphate and NaOH Treatments for the Steam-water Circuits of Drum Boilers of Fossil and Combined Cycle/HRSG Power Plants, 2015. International Association for the Properties of Water and Steam, IAPWS TGD4-11(2015).*

[4] *Feed Water, Boiler Water and Steam Quality for Power Plants/Industrial Plant, 2011. VGB PowerTech Service GmbH, Essen, Germany, VGB-S-010-T-00;2011-12. EN.*

[5] *Technical Guidance Document: Instrumentation for Monitoring and Control of Cycle Chemistry for the Steam-water Circuits of Fossil-fired and Combined Cycle Power Plants, 2015. International Association for the Properties of Water and Steam, IAPWS TGD2-09(2015).*

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