FREE VS CAPTIVE ALKALINITY-INTRODUCTION AND BACKGROUND.

Phosphate, added to a boiler, precipitates calcium hardness as calcium phosphate. Early work indicated that the calcium phosphate would precipitate in at least two distinct forms. The finely divided talc-like material was identified as hydroxyapatite. Ca5(PO4)30H. The sticky, more dense calcium phosphate was identified as Whit lockite Ca3(PO4)2' The obvious difference between these two forms is the hydroxide substitution in the hydroxyapatite. It was clear that a minimum amount of hydroxide alkalinity was required to force the formation of hydroxyapatite rather than the Whit lockite. For' this reason, among many others, a free hydroxide residual in the bulk boiler water became a standard control consideration. As boiler pressures reach 42Kg/cm2 silica starts to volatilize which makes a maximum limit on silica residual mandatory. With lower silica levels, lower phosphate levels became essential to prevent the formation of magnesium phosphate. Free hydroxide increases the solubility of silica. This minimizes volatilization and also decreases the chance for formation of complex silica scale. With decreasing silica concentrations in the boiler water, magnesium phosphate reappeared as a common troublesome deposit. This led to the development of "Precision Control". This new treatment scheme consisted of maintaining a phosphate boiler water residual of between 2 and 4 ppm with a hydroxide residual of between 4 and 8 ppm. This treatment program was successful in eliminating the formation of magnesium phosphate and handled silica excursions very well. The likely cause of localized corrosion failures in high heat transfer area was thought to be due to caustic. If caustic concentrated on the metal surfaces, it was capable of dissolving the protective magnetite layer. This caused metal loss as the magnetite dissolved as rapidly as it formed from the base boiler metal. Since caustic was the suspect cause of this corrosion, it was commonly called caustic gouging, a misnomer that persists even today. To combat this caustic-related problem, boiler water technologists commenced treatment with a technique known as captive alkalinity. Theoretically, this approach precludes the presence of free caustic alkalinity in the boiler water, primarily with the use of acid phosphates. Despite very high quality feed water boiler tube failures in boilers operated at 42kg/cm2 or greater are still common due to localized metal loss. The affected areas show smooth, rolling gouges. These types of failures were thought to be related to caustic gouging and limited to pressures exceeding 70 kg/cm2. In reality, any chemical in the boiler water is capable of causing this problem at boiler pressures as low as 42 kg/cm2, particularly acid sulfates and chlorides, in addition to sodium hydroxide. Since the mechanism is the same regardless of the chemical, it is correctly named "concentrating film attack". Today, concentrating film attack is still the most common cause of water wall tube failures in higher-pressure boilers. Precision Control Precision control involves the maintenance of small residual of orthophosphate, 2-4 ppm, and 4 to 8 ppm of sodium hydroxide. Precision control was devised originally as a means of preventing the formation of magnesium phosphate sludge on generating surfaces and reducing the concentration of soluble silica in the boiler water. Boiler operators found that the traditional high levels of phosphate resulted in the formation of adherent deposits when evaporators carried over or condenser leaks developed. This was because the phosphate competed with silica for magnesium and deposition of obnoxious magnesium phosphate occurred. It was also found that at low phosphate concentrations, the magnesium precipitated almost exclusively as the less adherent magnesium silicate. Maintenance of a free hydroxide residual provided further assistance in deposit control because the sludge tended to remain fluid in the alkaline water. Co-ordinated Phosphate pH Control The introduction of free hydroxide to high-pressure boilers was shown to be associated with accelerated corrosion, which sometimes occurred on high temperature metal surfaces or beneath deposits of corrosion products. This phenomenon, commonly called "caustic attack", but more properly concentrating film attack and characterized by large pits or grooves gave rise to the popularity of the Coordinated Phosphate-pH Control Method. The theory of this treatment was that if boiler water pH were maintained at or below the pH, which existed due to equilibrium conditions representing sodium to phosphate ratio of 3:1, then no free hydroxide would be present in the bulk boiler water. This Coordinated Phosphate-pH Control had been originally developed for the prevention of caustic embrittlement. Congruent Control Unfortunately, caustic attack continued to occur in high-pressure boilers even though Coordinated Phosphate-pH Control was practiced. This was shown to be due to precipitation of disodium phosphate from a Tri-Sodium phosphate" solution at high temperature, with the net result being the generation of sodium hydroxide in the supernatant liquid. They found the congruent composition, those at which the liquid and solid phases are the same; correspond to mol ratios of Na to PO4 of 2.85 at 3000C (90 kg/cm2) and 2.65 at 3650C (200 kg/cm2). In captive alkalinity programs, pH rather than sodium is the primary control of sodium since it is easier to measure than sodium. In captive alkalinity programs, phosphate is used primarily as a pH control agent, while in Precision Control programs phosphate acts more as a deposit control agent. This form of captive alkalinity, requiring very low sodium to phosphate ratio is typically not very practical for many industrial plants, unless condensate returns approach 90%, and condensate polishers are employed. Since Congruent Control offers very little protection against silica volatilization and scale formation, and is very susceptible to an unexpected ingress of excess sodium, it is not the best choice for industrial plants and cogeneration facilities. Conversely, Congruent Control was designed for tightly controlled systems with the highest quality feedwater and typically, greater than 98% condensate returns, blow- down rates approximating one-half percent or less and sodium levels of less than 50 ppb in the feedwater. PRECISION VS. COORDINATED PHOSPHATE-PH CONTROL Selecting one program over the other involves a complete understanding of the following parameters Ø The impact of, and the ability to control, sodium in the pre-boiler system. Ø Silica control in the makeup pretreatment system. Ø History of pretreatment upsets/condensate contamination Ø Use of polymers as boiler water dispersants Ø Base-loaded versus load following steam demand. Testing and control considerations Ø Causes and consequences of hideout This is an extract from the original paper published by Wex technologies Pvt. Ltd on the subject. Incase you wish to receive the full paper do write us or e- mail your request to wextech@vsnl.net