ALKALINITY CONTROL

PURPOSE: To aid in formation of desirable sludge and to maintain a protective coating of iron oxide on steel surfaces.

* * * * * * * * * * * * * *

The total alkalinity of boiler water includes all dissolved components that are capable of reacting with acid: These are most commonly hydroxide (OH^-), carbonate (CO^{-2}), bicarbonate (HCO^-), phosphate (PO^{-3}), and silicate (SiO^{-2}). Among these alkaline components, the hydroxide is most important from a chemical control standpoint; it is measured directly by pH determination or by titration.

Boiler water must contain a certain amount of causticity (i.e. Hydroxide alkalinity in order to accomplish three things:

1. To maintain a protective coating of iron oxide over the metal and thereby prevent certain types of corrosion.

2. To provide a proper environment for precipitation of desirable sludge materials.

3. To keep silica in solution so as to avoid deposition of silica scales.

Excessively high concentrations of hydroxide alkalinity may result in foaming difficulties or caustic corrosion of the boiler steel. Caustic alkalinity may also cause caustic embrittlement of boiler steel under some conditions. Alkalinity control is correct when the boiler water contains enough hydroxide to secure the desired benefits without inviting trouble associated with aggressively high concentrations of caustic. The P (Phenolphthalein) alkalinity test provides a sound basis for control of the alkalinity in boiler water. pH determination is also widely used for this purpose where a low level alkalinity is to be maintained.

Hydroxide alkalinity in boiler water may come from a variety of sources. It may be added directly in the form of caustic soda (sodium hydroxide). When soda ash is fed as a water conditioning chemical, it decomposes under boiler steaming conditions, producing sodium hydroxide (plus carbon dioxide which goes off with the steam).

Sodium hydroxide and/or sodium carbonate may be present as excess treating chemicals in the effluent from a lime-soda softener; the use of such pre-treating equipment automatically provides the alkali required for alkalinity control in the boiler water. Most raw waters contain bicarbonate (HCO^-). So does effluent waters from sodium cycle and from most sodium-acid cycle zeolite softeners. Under boiler water conditions, bicarbonate decomposes first to carbonate and then to carbon dioxide. The carbon dioxide leaves the boiler with the steam and forms carbonic acid in the condensate system. The sodium that was attached to the bicarbonate reacts to form alkalinity. In all cases it is the boiler water hydroxyl alkalinity, as measured by the OH alkalinity test (it can also be determined by running the P Alkalinity and the Total Alkalinity test and using the formula 2P-T = OH Alk) or pH value, that concerns us, regardless of whether this hydroxide is added as such or represents the decomposition product of soda ash or alkaline components in raw water or treated makeup water.

Maximum and minimum P alkalinity and OH Alkalinity values (and/or pH) limits are specified for proper control of boiler water alkalinity in your plant. Alkalinity concentrations below the specified minimum may result in corrosion difficulties or the formation of objectionable sludge or scale. Whenever boiler water alkalinities fall below the recommended minimum, do not hesitate to increase the feed of alkali (caustic products as NaOH or KOH) or to increase the total alkalinity of the treated water if a softener is involved. Alkalinities above the specified maximum may result in foam-type carry over or localized caustic embrittlement corrosion, and they may complicate protective measures employed to prevent caustic embrittlement. When boiler water alkalinities rise above the recommended maximum, reduce the feed of alkali bearing materials or reduce the total alkalinity of the treated water if a softener is used. In an emergency, increase the blow down rate if necessary to bring boiler water alkalinity under control.

Sodium hydroxide is the preferred approach, as the break down components does not form carbon dioxide. Carbon dioxide will carry off the steam and form carbonic acid in the condensate return lines.

To determine the potential for alkalinity development in a boiler, the attached chart should be used. Keep in mind, that the OH^- ion is what does the work in the boiler. This is the ion that allows the extension and charge release when dispersants are added to the boiler, the ion that forms the protective magnetite barrier and the ion that allows for metal precipitation in the boiler in a desired form (calcium& magnesium are metals).

Ions	*P = 0*	*P < T/2*	*P = T/2*	*P > T/2*	*P = T*
(OH)	0	0	0	2P - T	T
CO_3	0	2P	T	2(T - P)	0
HCO_3	T	T - 2P	0	0	0

To reference this chart, consider;

P = Phenolphthalein Alkalinity
T = Total Alkalinity or Methyl Orange Alkalinity (M Alk)
OH = Hydroxyl Alkalinity
CO_3 = Carbonate content of the water
HCO_3 = Bicarbonate content in the water

Where P = 0, all of the alkalinity that is measured by titration is bicarbonate alkalinity

Example: P Alk = 0, T Alk = 122 ppm, Bicarbonate alkalinity = 122 ppm

If P<T/2, Example would be P Alk = 10 ppm and T Alk = 40 ppm

OH Alkalinity = 0 ppm
Carbonate = 2P, 2X 10 ppm = 20 ppm of the alkalinity is carbonate
Bicarbonate = T – 2P, 40 ppm – 2X10ppm = 20 ppm.of the alkalinity is bicarbonate

If P = T/2, P alkalinity = 30 ppm, T Alkalinity = 60 ppm

OH Alkalinity = 0 ppm
Carbonate Alkalinity = T = 60 ppm
Bicarbonate Alkalinity = 0 ppm
In this case, you have water that has alkaline pH, which has neutralized the hydrogen ion, preventing bicarbonate ions from being present in the water.

If P > T/2, usually the case for boiler water chemistry. Example P Alk = 300, T Alk = 400 ppm

OH = 2P-T = [(2 X 300 ppm) - 400 ppm] = 200 ppm as hydroxyl alkalinity
Carbonate = 2(T-P) = 2(400 – 300) = 200 ppm
Bicarbonate = 0 ppm

If P=T, This is found with dealkalyzer discharge or where all of the alkalinity comes from Alkalinity builders that are added to the water. Example; P Alk = 300 ppm, T Alk = 300 ppm

OH = T = 300 ppm
Carbonate = 0 ppm
Bicarbonate = 0 ppm