# ALKALINITY REDUCTION BY CHLORIDE FORM ANION EXCHANGERS

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## 1.0 **Definition of Alkalinity**

By definition, alkalinity is an expression of the total basic forms of the alkali metals (i.e. sodium, potassium, etc.) and the alkaline earth metals (i.e. calcium, magnesium, etc.) present in a solution. These include the primary forms such as the hydroxides, carbonates and bicarbonates as well as the secondary forms such as the borates, silicates and phosphates.

Alkalinity and pH, although related, should not be used interchangeably. Some forms of alkalinity (i.e. hydroxides, phosphates, etc.) contribute more to pH than others (i.e. carbonates, silicates, etc.). Whereas pH is an intensity factor, alkalinity is a quantity factor.

## 2.0 **Determination of Alkalinity**

The concentrations of the primary forms of alkalinity are determined by titrating the sample with sulfuric acid to the phenolphthalein end point (i.e. P-point) and the methyl orange or methyl purple end point (i.e. M-point) as illustrated in Figure 1.

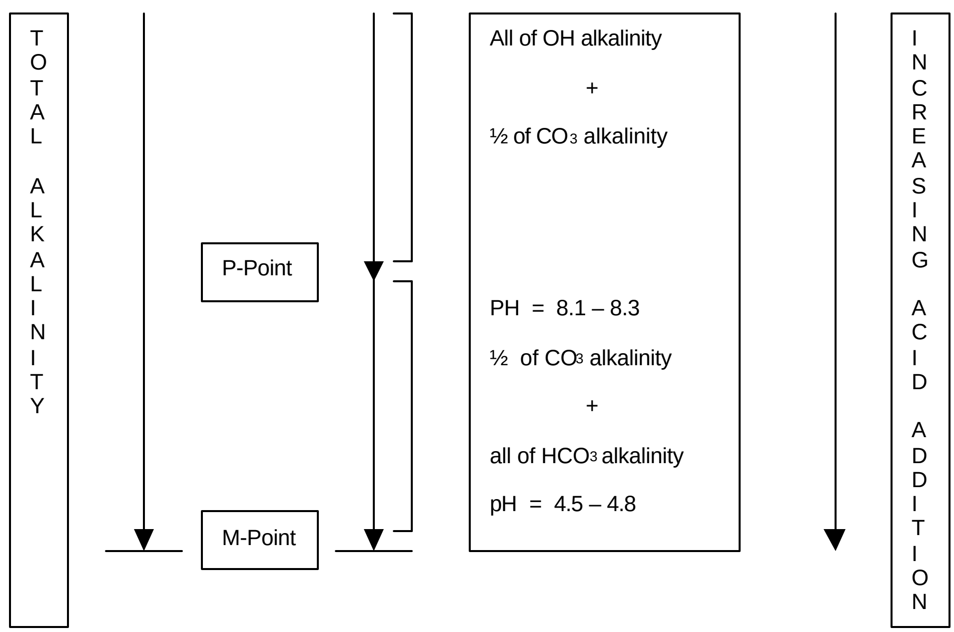


Figure 1: Titration of Primary Form Alkalinity

Primary form alkalinities at boiler water pH levels are given as follows:

a) OH alkalinity = 2 P-T
b) $CO_3$ alkalinity = 2 (T-P)
c) $HCO_3$ alkalinity = 0

At raw water pH levels, the alkalinity in most cases consists entirely of bicarbonate alkalinity.

If there is an appreciable amount of secondary form alkalinity, it can be precipitated by adding barium chloride to the sample. The hydroxide alkalinity remains and is measured directly by titration with acid to the P-point.

## 3.0 Alkalinity in Boiler Water

When boiler water chemical treatment is not practiced, hardness salts will precipitate onto the hot metal surfaces to form scale and/or baked on sludge. As these deposits become thicker, a greater heat driving force is required. This means higher metal temperatures, possibly resulting in tube rupture.

Calcium and magnesium may be precipitated in a sludge form, which is both non-adherent to the hot metal surfaces and easily removed with manual blowdown by adding phosphate and alkalinity to the water. An excess of these chemical types are maintained in the boiler water to drive the reactions to completion as follows:

a) $10\ Ca^{++} + 6\ PO_4^{---} + 2\ OH \rightarrow \underline{3\ Ca_3(PO_4)_4 \cdot Ca(OH)_2}$

Calcium + Phosphate + Hydroxide Alkalinity → Calcium Hydroxyapatite

b) $Mg^{++} + 2\ OH^- \rightarrow \underline{Mg\ (OH)_2}$

Magnesium + Hydroxyde Alkalinity → Magnesium Hydroxide

c) $3\ Mg^{++} + 2\ OH^- + 2\ SiO_3^{--} + H_2O \rightarrow \underline{2\ Mg\ SiO_3 \cdot Mg(OH)_2 \cdot H_2O}$

Magnesium + Hydroxide Alkalinity + Silicate + Water → Serpentine

For boilers operating within the pressure range of 0 – 300 psig, the prescribed concentration of total alkalinity and hydroxide alkalinity as suggested by the American Boiler Manufacturers Association are 700 ppm as $CaCO_3$ maximum and 100 – 350 ppm as $CaCO_3$, respectively. Consistent hydroxide concentrations substantially less than 100 ppm will not drive the above reactions to completion, whereas hydroxide alkalinity concentrations substantially greater than 350 ppm could result in stress corrosion cracking, also known as caustic embrittlement.

In most cases, raw water alkalinity is low enough that boiler water alkalinity may be controlled by the addition of caustic or soda ash. Both chemicals add to the hydroxide alkalinity, as well as the total alkalinity. However, soda ash, although it is safer to handle than caustic, releases carbon dioxide when heated, thus resulting in return line corrosion.

If the raw water has a high alkalinity (i.e. enough to result in a feedwater total alkalinity of more than 10 ppm as $CaCO_3$, the return line corrosion will be excessive as illustrated by the following equations:

a) $2\,NaHCO_3 + \text{Heat} \rightarrow Na_2CO_3 + H_2CO_3$

Sodium Bicarbonate + Heat → Soda Ash + Carbonic Acid

b) $Na_2CO_3 + H_2O + \text{Heat} \rightarrow 2\,NaOH + H_2CO_3$

Soda Ash + Water + Heat → Caustic + Carbonic Acid

c) $H2CO_3 \rightarrow H_2O + CO_2$

Carbonic Acid → Water + Carbon Dioxide

d) $Fe + 2H_2CO_3 \rightarrow Fe(HCO_3)_2 + H_2$

Iron + Carbonic Acid → Ferrous Bicarbonate + Hydrogen

Also the blowdown, as well as the make-up, will be excessive, even without the addition of extra alkalinity, in order to limit the alkalinity to the prescribed concentration. Therefore, some method of reducing the alkalinity must be used. Chloride anion dealkalization is one such method.

## 4.0 **Chloride – Anion Dealkalizer**

### 4.1 Comparison with Other Dealkalizing Systems

The various systems, which reduce alkalinity in a water supply by ion exchange, are illustrated in Table 1.

As indicated all of these systems, with the exception of the chloride anion system, require acid resistant material as well as a decarbonator, both of which add to the capital cost of the installation.

With the exception of the sodium cycle with acid post mix system, the chloride anion dealkalizer is the only system which does not offer a reduction of raw water solids, thus no savings in make-up requirements are normally realized; however, if a boiler is being operated at a low solids level merely to limit alkalinity, then reduction of raw water alkalinity will result in reduced make-up requirements.

Thus, the advantage of reduced make-up without having to handle acid makes dealkalization by a chloride anion exchanger very attractive to small plant operators.

Table 1 - _Dealkalizer Systems using Ion Exchangers

| | **Decarbonator Required** | **Acid Required** | **Raw Water Solids Reduced** |
|---|---|---|---|
| Sodium cycle exchanger with acid post mix | Yes | Yes | No |
| Split Stream<br>- Hydrogen cycle exchange and raw water<br>- Sodium and hydrogen Cycle exchangers | <br>Yes<br>Yes | <br>Yes<br>Yes | <br>Yes<br>Yes |
| Hydrogen cycle exchanger (strong and weak acid) | Yes | Yes | Yes |
| Mixed bed or mono bed hydrogen-sodium cycle exchanger | Yes | Yes | Yes |
| Chloride cycle anion exchanger | No | No | No |

4.0 **Chloride – Anion Dealkalizer** (continued)

4.2 <u>Principle of Operation</u>

A chloride anion dealkalizer is usually preceded by a sodium cycle softener for the production of water of sufficient quality for make-up to low pressure boilers.

Regenerated with brine, a sodium cycle softener favourably exchanges calcium and magnesium for sodium as follows:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | ( | $HCO_3)_2$ | | | | | $2NaHCO_3$ |
| | Ca | ( | | | | | | |
| $Na_2Z$ + | | ( | $SO_4$ | $\rightarrow$ | Ca | ) | Z + | $Na_2SO_4$ |
| | Mg | ( | | | | ) | | |
| | | ( | $C1_2$ | | Mg | ) | | 2NaC1 |

| | | | | | |
|---|---|---|---|---|---|
| Sodium form cation resin | + | Calcium and/or Magnesium | )(Bicarbonate )(Sulfate $\rightarrow$ )(Chloride | Calcium and/or Magnesium form cation resin | + Sodium bicarbonate Sodium sulphate Sodium chloride |

A chloride anion dealkalizer, also regenerated with brine, utilizes strong base type II <u>anion</u> resin to exchange the alkalinity and sulfates in the softener effluent for chloride as follows:

| | | | | |
|---|---|---|---|---|
| | | $(NaHCO_3$ | $\rightarrow$ | (NaC1) |
| ZCL | + | | | |
| | | $(Na_2SO_4$ | $\rightarrow$ | (2 NaC1 |

| | | | |
|---|---|---|---|
| Chloride + form anion resin | Sodium bicarbonate and/or sodium sulphate | $\rightarrow$ | Sodium chloride |

Chlorides in the softener effluent pass through the dealkalizer unchanged.

Unfortunately, anion resin has a higher affinity for sulfates than for alkalinity. This results in reduced efficiency (i.e. due to the needless, but necessary exchange of sulphates for chlorides) and alkalinity leakage.

## 4.0 **Chloride – Anion Dealkalizer** (continued)

### 4.2 Principle of Operation (continued)

With high ratios of alkalinity to total anions (or low ratios of sulphate to total anions), the efficiency of ion exchange is increased and the leakage of alkalinity is reduced. For example, with ratios of alkalinity to total anions of 50 to 90%, the capacity and alkalinity leakage to be expected are 12 kilograins as $CaCO_3$ per cubic foot of resin and less than 10% of the raw water alkalinity, respectively.

If caustic is added to the brine regenerant of the dealkalizer, the free carbon dioxide contained in the influent is converted to the bicarbonate or carbonate and exchanged as such for chloride.

### 4.3 Operating Steps

The regeneration of a chloride anion dealkalizer is similar to that of a sodium cycle softener. However, the difference in densities between the two resin types (i.e. S.G. of 1.3 for sodium form cation resin versus S.G. of 1.1 for chloride form anion resin) means that anion resin is backwashed at a lower rate than cation resin in order to prevent resin carry-over.

The regeneration steps and suggested operating set points of a chloride anion dealkalizer are indicated in Table 2.

Table 2 - Regenerating Set Points for Chloride Anion Dealkalizer

| **Regeneration Step** | **Duration (Minutes)** | **Flow Rate** | **Regenerant Concentration** |
|---|---|---|---|
| 1. Backwash | 10 | 2-3 USGPM / $ft^2$ Bed area | Raw Water |
| 2. Regeneration | 20 – 30 | 0.5 USGPM / $ft^3$ resin | 5% NaC1 at 5 lb/$ft^3$ resin plus caustic at 0.5 lb/$ft^3$ resin |
| 3. Displacement Rinse | 15 | 0.5 USGPM / $ft^3$ resin | Softened water |
| 4. Fast Rinse | 15 – 20 | 2 USGPM / $ft^3$ resin | Softened water |

The service flow rate is 2 – 5 USGPM/$ft^3$ resin until an alkalinity leakage of greater than 10% of the raw water alkalinity occurs, at which time the resin should be regenerated.

4.0 **Chloride – Anion Dealkalizer** (continued)

4.4 Effluent Quality

The effluent quality of a chloride anion dealkalizer is summarized in Table 3.

Table 3 – Effluent Quality of a Chloride Anion Dealkalizer

| Effluent Quality | With Brine and Caustic Regeneration | With Brine only Regeneration |
|---|---|---|
| PH | 7 – 9.5 | 5.5 – 7.5 |
| Alkalinity | 5 – 10% of raw water alkalinity | 5 – 15% of raw water alkalinity |

As indicated, high alkalinity leakage at the beginning of the run may be remedied by increasing the salt dosage. High pH, carbonate and hydroxide leakage during the last half of the run may be remedied by reducing the amount of caustic in the regenerant.

Since the effluent of a chloride anion exchanger, when preceded by a sodium cycle softener, consists almost entirely of sodium chloride, the boiler water will also consist largely of sodium chloride, an environment which is not especially corrosive due to the absence of dissolved oxygen.

However, particular attention should be paid to magnesium leakage from a sodium cycle softener as it will combine with the chlorides in the chloride anion dealkalizer effluent to form magnesium chloride which can, in the absence of alkalinity, hydrolyze to form an acid condition in the feedwater as follows:

$$MgC1_2 + 2H_2O \rightarrow Mg(OH)_2 + 2\ HC1$$

Magnesium Chloride + Water → Magnesium Hydroxide + Hydrochloric Acid

Therefore, the magnesium hardness leakage should be maintained at less than 1ppm as $CaCO_3$ and softener overrunning must be avoided.

## 4.0 **Chloride – Anion Dealkalizer** (continued)

### 4.5 Design and Construction

If only the relative resin capacities are considered (i.e. 12 kgrns/$ft^3$ for anion resin versus 20 kgrns/$ft^3$ for cation resin), the dealkalizer vessel should be larger than the softener vessel. However, if there is a demand for alkaline soft water, the dealkalizer vessel will in fact be the same size or smaller than the softener vessel.

The dealkalizer brine tank, sized to contain sufficient brine and caustic for only a single regeneration, contains saturated brine from the softener brine tank. Caustic is dissolved and added to the former tank with each regeneration.

Due to the presence of oxygenated chloride and caustic, the more conventional materials such as copper and iron are inadequate for long term service.

The dealkalizer vessel, if constructed of steel, should be epoxy lined, however, the preferred material of construction is fibre reinforced plastic (FRP). Similarly, the preferred material for the brine tank is FRP or polyethylene. Piping and valves in and around the dealkalizer should be constructed of plastic such as PVC, CPVC, polyethylene, polypropylene, FRP, etc.

Dealkalized water should be directed via plastic piping and valves to the deaerator, except for the final 10 feet of piping which should be construction of carbon steel due to the higher temperature at this point, for the removal of oxygen. If it is directed to intermediate storage, these vessels should be epoxy lined.

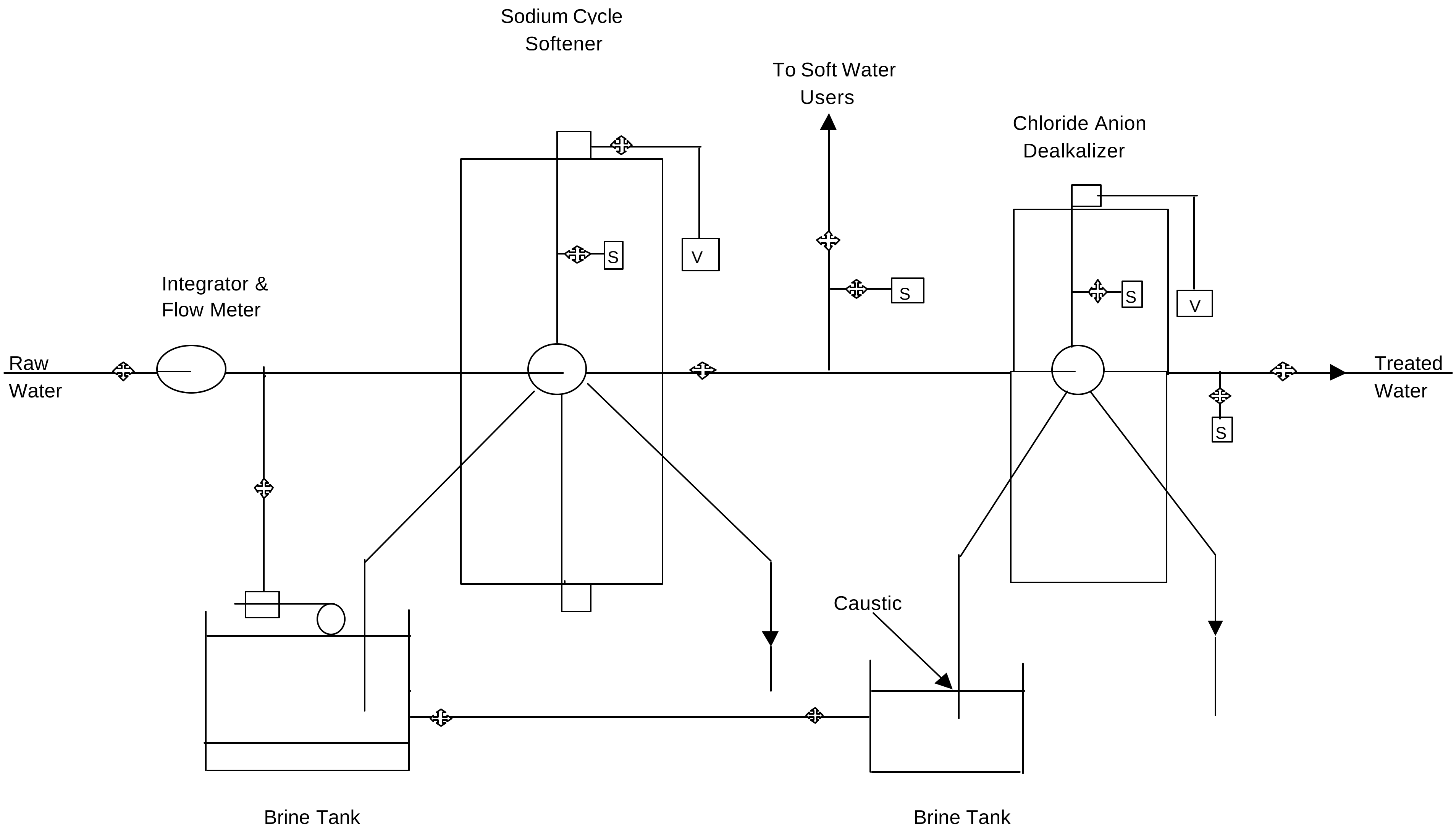


Figure 3: Arrangement of Sodium Cycle Softener - Chloride Anion Dealkalizer System