Breakpoint chlorination for chloramine control using activated carbon

Chloramines are increasingly recognised as a viable alternative to traditional chlorine compounds to provide a sterilising effect in potable water. However, the inadvertent formation of chloramines can cause significant concern when appropriate measures are not in place to manage their deleterious effects.

**Background**

Chloramines are of concern to a variety of water users. Where water is used for the production of beverages, or medical use, such as dialysis, the presence of chloramines is considered unpleasant to taste and harmful in respective cases. The use of traditional sterilising agents, particularly sodium hypochlorite can cause inorganic chloramines to form in water, where ammonia is present. This reaction is represented by the following equation with its respective reaction rate constant (at 25°C C = 298 K) (Morris, 1967):

\[
\text{NH}_3 + \text{HOCl} = \text{NH}_2\text{Cl} + \text{H}_2\text{O}
\]

\[
(k_{298} = 6.1 \times 10^{-6} \text{ M}^{-1} \text{ sec}^{-1})
\]

As ammonia has more than one hydrogen that can be replaced by a chlorine atom, it reacts with an excess of hypochlorous acid to form dichloramine (Morris, 1967; Gray et al., 1979):

\[
\text{NH}_2\text{Cl} + \text{HOCl} = \text{NHCl}_2 + \text{H}_2\text{O}
\]

\[
(k_{298} = 3.4 \times 10^{-6} \text{ M}^{-1} \text{ sec}^{-1})
\]

Dichloramine is relatively unstable it rapidly decomposes to form monochloramine. In this form, it is relatively difficult to remove by adsorption and requires the use of specially prepared adsorbents with a high surface reactivity. This can add to the overall cost of treatment as these materials are more considerably more expensive to manufacture.

Standard activated carbons however do have a capacity for the removal of trichloramine that can be achieved by ensuring sufficient chlorine is added to force the creation of this more stable form of chloramine. This reaction proceeds as follows (Morris and Isaac, 1983):

\[
\text{NHCl}_2 + \text{HOCl} = \text{NCl}_3 + \text{H}_2\text{O}
\]

\[
(k_{298} = 2.1 \text{ M}^{-1} \text{ sec}^{-1})
\]
**Breakpoint chlorination**

The determination of the point where the level of chlorine necessary to achieve this is known as Breakpoint Chlorination. Once the breakpoint is achieved, any additional chlorine added in excess of the breakpoint determined will be present as free chlorine and will be removed by activated carbon in the normal dechlorination process.

If ammonia is known to be present, and its concentration can be determined, a calculation can be made of the quantity of chlorine necessary for addition to form dichloroamine, that can be readily oxidised to trichloramine. This is particularly effective at acidic pH ranges (pH <3) where only trichloramine is formed. However, this may prove to be problematic and treatment at neutral pH are often preferred.

In this case, chlorine dose must be increased in the ratio of 5:1 to 10:1 at pH 7 to form the desired chloramine species. Chlorination at ratio levels below 5:1 preferentially forms monochloramine, which, due to its high stability cannot be oxidised by the addition of increased chlorine. In order to be certain of effective conversion, the normal recommended ratio is 12.5mg Cl/mg NH₃ [EPA Guidance Manual - Alternative Disinfectants and Oxidants, 1999].

pH value also has a significant determining factor on the formation of chloramines with the rate optimised in the range of 6 - 9.

**Control of excess chlorine following breakpoint chlorination**

Please refer to Jacobi Carbons Technical Bulletin “JACOBI-TIS-AQUASORB-DECHLORINATION CALC-A4-ENG-A0813” available from your local sales office or appointed representative.