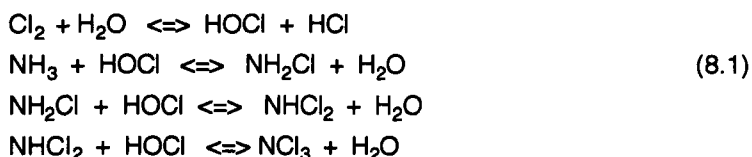


8. BREAKPOINT-CHLORINATION

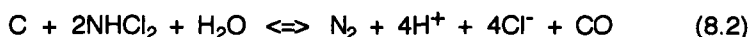
8.1. Principles of Breakpoint-chlorination

Chlorine can oxidize ammonia according to the following reaction scheme:



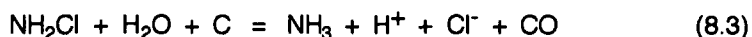
Activated carbon is able to adsorb chloramines, and so a combination of chlorination and adsorption on activated carbon can be applied for removal of ammonia.

The most likely reaction for chloramine on activated carbon is a surface oxidation:

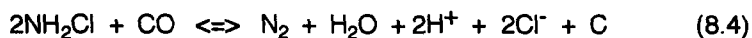


Furthermore, it is important to know that the $\text{Cl}_2/\text{NH}_3\text{-N}$ oxidized mole ratio is 2:1, for oxidation by this pathway.

The mono-chloramine reaction with carbon appears more complex. On fresh carbon the reaction is most probably:



After this reaction has proceeded to a certain extent, partial oxidation of mono-chloramine is observed, possibly according to the equation:



It has been observed that activation of fresh carbon is necessary before

mono-chloramine can be oxidized.

However, the reaction of chlorine with ammonia or amino compounds presents a problem in the practice of chlorination of waste water containing such nitrogen compounds.

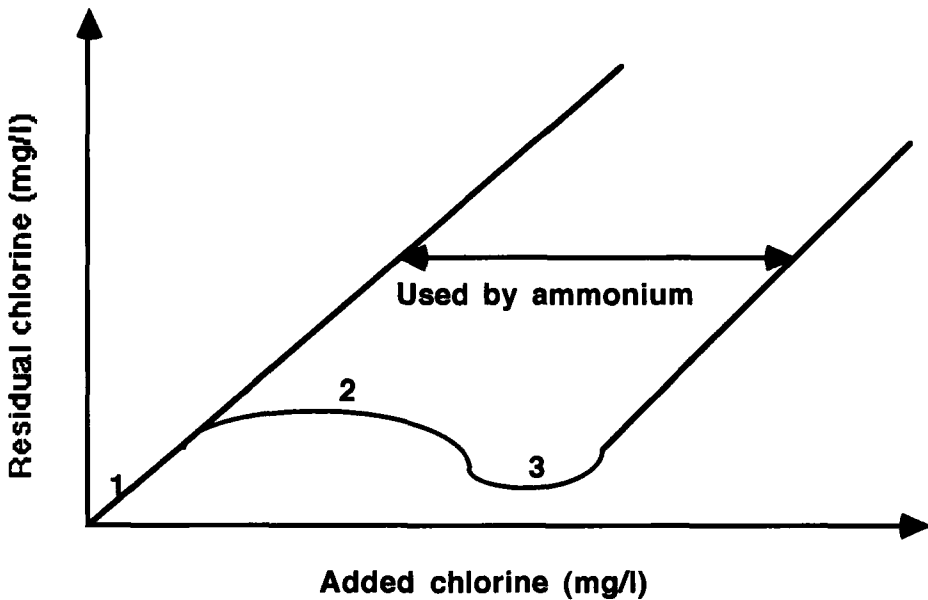
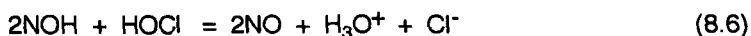
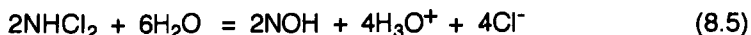


Fig. 8.1. Breakpoint chlorination.

Figure 8.1 shows the residual chlorine as a function of the chlorine applied. Between points 1 and 2 in the figure, mono- and di-chloramine are formed. The oxidation processes with chlorine occurring between points 2 and 3 give a decline in residual chlorine. Point 3 is called the breakpoint. It corresponds to a stoichiometric ratio of chlorine to ammonium-N of 7.6. It is sufficient to add this amount of chlorine for ammonium removal, provided that the waste water does not contain other components, that are oxidized by chlorine. A ratio of chlorine to ammonium-N of 8-10 is, however, required in most cases in practice. Addition of chlorine in this interval probably produces free nitrogen gas as the predominant product of oxidation. Fair et al (1968) even propose that the reaction involving the formation of NOH as an intermediate, followed by the formation of nitric oxide, NO, could explain the observations between points 2 and 3:

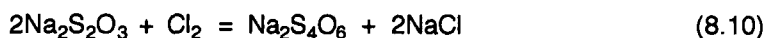


In total:



Further addition of chlorine beyond the breakpoint gives an increasing residue of free chlorine. Chlorine doses below the breakpoint requirement can be used to oxidize ammonia if chlorination is followed by contact with activated carbon (Bauer and Vernon, 1973).

When accidental overdosing of chlorine has occurred or after an intentional addition of large quantities of chlorine to accelerate disinfection, it will be desirable to remove the excess chlorine. This is possible with a reducing agent, such as sulfur dioxide, sodium hydrogen sulfite or sodium thiosulfate:



Oxidative degradation by chlorine is limited to a small number of compounds. Nevertheless, oxidation of these compounds contributes to overall reduction of BOD_5 in wastes treated with chlorine. A disadvantage is that chlorinated organic compounds may be formed in large quantities. A variety of chlorine compounds is applied in waste water treatments. For these compounds the available chlorine can be calculated, and is generally expressed as percentage chlorine having the same oxidation ability. Data for the different chlorine-containing compounds are given in Table 8.1.

It can be seen that the actual percentage of chlorine in chlorine dioxide is 52.5, but the available chlorine is 260%. This is, of course, because the oxidation state of chlorine in chlorine dioxide is +4 which means that five electrons are transferred per chlorine atom, while Cl_2 only transfers one electron per chlorine atom.

Hypochlorite is obtained by the reaction of chlorine with hydroxide in aqueous solution:

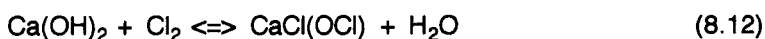


Table 8.1

Actual and available chlorine in pure chlorine-containing compounds

Compound	Mol. mass	Chlorine equiv. (moles of Cl_2)	Actual chlorine (%)	Available chlorine (%)
Cl_2	71	1	100	100
Cl_2O	87	2	81.7	163.4
ClO_2	67.5	2.5	52.5	260
NaOCl	74.5	1	47.7	95.4
CaClOCl	127	1	56	56
$\text{Ca}(\text{OCl})_2$	143	2	49.6	99.2
HOCl	52.5	1	67.7	135.4

Chlorinated lime, also called bleaching powder is formed by reaction of chlorine with lime:



A higher content of available chlorine is present in calcium hypochlorite, $\text{Ca}(\text{OCl})_2$. Chlorine dioxide is generated in situ by the reaction of chlorine with sodium chlorite:



8.2. Process Variables

In the removal of ammonia with a dose of chlorine followed by contact with activated carbon, pH determines the major chlorine species. The studies reported herein indicate that a pH value near 4.5 should be avoided, because NHCl_2 predominates and thus 10 parts by weight of chlorine are required for each part of $\text{NH}_3\text{-N}$ oxidized to N_2 . At a slightly higher pH and using acclimated and activated carbon, the portion of mono-chloramine increases and the chlorine required per unit weight of $\text{NH}_3\text{-N}$ oxidized should approach 7.6 parts, ignoring the chlorine demand resulting from other substances. However, further testing should be used to verify this conclusion in each case.

Laboratory studies at Blue Plains in Washington (Pressley et al., 1970 and 1973), in which buffered distilled ammonia nitrogen solutions of 20 mg/l concentrations were subject to breakpoint-chlorination dosages, showed a definite optimum pH for breakpoint in the range of pH 6 to 7. The chlorine dosage at optimum pH levels were found to be 8:1 (chlorine to ammonium-N).

The reaction rate has not been measured quantitatively, but it has been noted that the reaction is very rapid (Morris, 1965). The optimum pH for the reaction rate is 8.3, but at pH 6-7 the reaction is completed in 0.2 seconds.

There is no evidence that normal variations in the temperature of waste water effluents and initial mixing conditions affect the nitrogen removal by this process.

Organic nitrogen is to a certain extent removed by the breakpoint-chlorination according to Brown and Caldwell (1975), while Taras (1953) has reported a very slow reduction of amino acids.

Nitrate and nitrogen chloride are occasionally found in the effluents from the breakpoint-chlorination process.

An increasing level of pretreatment decreases the amount of chlorine required to achieve breakpoint, as demonstrated in Table 8.2, where results reported by Pressley et al. (1973) and Brown and Caldwell (1975) are summarized. Increase of total dissolved solid will generally imply a higher chlorine to ammonium-N ratio.

The application of activated carbon for dechlorination is recommended, as it serves several functions other than removal of residual chlorine. Carbon, as demonstrated in Section 8.1, can effectively catalyze the chemical reactions and

remove soluble organics through adsorption.

Table 8.2.

Effect of Pretreatment on Chlorine:ammonium-N breakpoint ratio.

Type of water	pH	Initial N conc. mg/l	Final N conc. mg/l	Breakpoint-ratio
Buffered water	6-7	20	0.1	8:1
Raw waste water	6.5-7.5	15	0.2	9:1 - 10:1
Secondary effluent	6.5-7.5	11.2	0.1	8:1 - 9:1
Tertiary effluent	6.5-7.5	9.2	0.1	8:1
Lime clarified raw waste water, filtered	7.0-7.3	11.2	0.1	9:1

Stasuik et al., (1973) has studied the required contact time for complete dechlorination of both free and combined chlorine. They found that 10 minutes were sufficient.

8.3. Design of Breakpoint-Chlorination Units

The design of breakpoint-chlorination follows the stoichiometric relations already presented in Sections 8.1 and 8.2. The amounts of chlorine, and other chemicals including acids and bases for pH-adjustment and sulfur dioxide for dechlorination, can be calculated from these relations.

The design of the adsorption unit is mainly based on empirical relations:

- A hydraulic application rate of $\leq 0.1 \text{ m}^3/\text{m}^2$ is recommended.
- 50 000 - 100 000 m^3 waste water can be dechlorinated per m^3 of activated carbon between two regenerations of activated carbon.

The spatial requirements are low due to the high rate of the chemical

reactions involved in the breakpoint chlorination and the various dechlorination processes.

The TDS (total dissolved solid) increment as a result of break point chlorination can be found from the figures in Table 8.3.

Table 8.3.

Ratios of total dissolved solids (TDS) to ammonium N - removed for the application of different chemicals by break point chlorination

Chemical Addition	TDS increase : ammonium-N removed
Chlorine gas	6.2 : 1
Sodium hypochlorite	7.1:1
Chlorine gas+lime for neutralization of all acidity	12.2:1
Chlorine gas+sodium hydroxide for neutralization of all acidity	14.8:1

8.4. Application of Breakpoint-Chlorination for Removal of Nitrogen

Complete removal of the 25-40 mg per liter ammonium-N is far too costly by this method. Chlorine costs about 38-45 US cents per kg, which means that the chlorine consumption alone will cost about 14 US cents per m³ waste. When the capital cost and the other operational costs are added the total treatment cost will be as high as 30-45 US cents per m³, which is considerably more expensive than other nitrogen removal methods.

It is possible to use chlorine to oxidize ammonium compounds to free nitrogen, but this process involves even higher chlorine consumption and, is therefore, even more expensive.

The formation of organic chlorine compounds is another crucial disadvantage of this process, because discharge of these compounds should be

avoided due to their high toxicity.

The method has, however, two advantages:

- 1) By using sufficient chlorine it is possible to obtain a very high efficiency.
- 2) The low spatial requirement makes it particularly suitable for certain applications, including addition to an existing facility, where nitrogen removal is required, but space constraints exist.

This means that the method has found application mainly *after other ammonium removal methods*, where high efficiencies are required. This is the case when the waste water is reclaimed, for example in the two plants shown in Figs. 7.19 and 8.2. As can be seen, it is necessary to use several treatment processes to achieve a sufficient water quality after the treatment. Chlorination and treatment on activated carbon are used as the last treatment to assure good ammonium removal and sufficient disinfection of the water. An additional chlorination is even used after the treatment on activated carbon to ensure a chlorine residue in the water supply system. Note that the solution in Fig. 7.19, where the major portion of ammonium-nitrogen is removed by stripping before the residue of ammonium-N is removed by breakpoint-chlorination, is preferable, because the operating costs become more limited due to the pronounced lower consumption of chlorine.

It should be mentioned in this context that ozonation, which is a disinfection process widely used for treatment of water and related to chlorination, is able to oxidize amines. It is possible by ozonation to oxidize amines completely to nitrite and nitrate, provided that ozone is used in a ratio to the concentration of amines slightly above the stoichiometric ratio; see Elmghari-Tabib et al., 1982.

Ozone is also able to oxidize ammonia to nitrate. This process is catalyzed by the presence of bromide ions; see Haag et al., 1984.

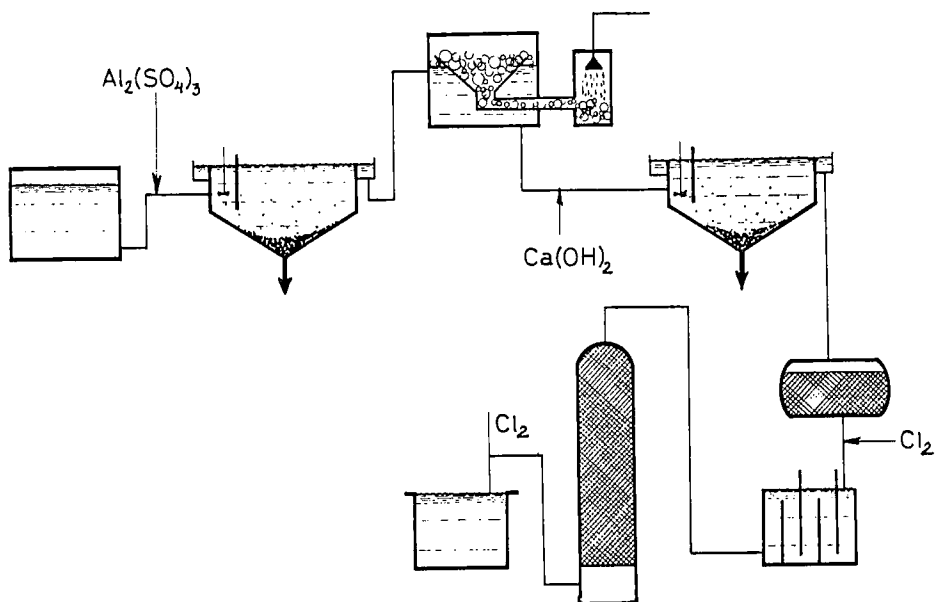


Figure 8.2. Production of potable water from waste water in Windhoek, Namibia.