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## Another Solution from NORIT Americas Inc.

# Declorination with Activated Carbon

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*Dechlorination with Activated Carbon* The most common method of maintaining biologically safe drinking water supplies is by using some form of residual chlorine disinfectant. Many end users require removal of this disinfectant from the water. Granular activated carbon (GAC) is the most effective and reliable technology for dechlorination. Free chlorine is removed by a catalytic reaction which occurs on the particle surface and in the macropores. An additional benefit of GAC treatment is the removal of organic compounds, often responsible for unpleasant taste and odors in the source water.

American Norit Company produces several carbons ideal for this application, the GRANULAR DARCO® series, the NORIT® granular series, and the pelletized NORIT® ROW 0.8. These carbons have a combination of high external particle surface and a large number of macropores for rapid dechlorination. The large transitional pore surface area is especially effective for adsorbing the dissolved organic compounds which create unpleasant tastes and odors.

*Chlorine Halving Value* The efficiency of a given carbon for dechlorination is normally expressed in terms of chlorine halving value. The halving value represents the depth of the GAC layer required to reduce the original chlorine concentration by 50% under uniform test conditions. For example, consider a carbon with a halving value of 5 cm being used to treat water containing a free chlorine concentration of 8 ppm. A carbon layer of 5 cm will reduce the free chlorine level to 4 ppm and a further 5 cm layer will reduce the free chlorine level to 2 ppm, and so on until the desired level is reached.

Halving value is a measure of the dechlorination rate of an activated carbon. A lower number indicates superior performance. A description of the Chlorine Halving Value analytical procedure is available in Table A. However, system variables such as flow rate and allowable pressure drop dictate a compromise to a GAC grade which possesses both acceptable halving value and good hydraulic characteristics.

There are a number of important variables which may affect the halving value of individual activated carbons.

1. Chemical nature of free chlorine, in order of increasing halving value, e.g.
   a). chlorine gas
   b). hypochlorites
   c). chloramine and dichloramine
   d). chlorine dioxide
2. Activated Carbon Particle Size (smaller average particle size decreases the halving value).
3. pH of the water to be dechlorinated (higher pH increases the halving value).
4. Temperature (higher water temperatures decrease the halving value).
5. Nature of the water to be treated (halving value is increased if the water is high in dissolved organics).
6. Linear flow velocities (higher flow velocities increase the halving value).

*Chemical Form of Disinfectant* Residual chlorine for biological control can be added to water in several forms. The most common method is direct chlorination by injecting chlorine gas. Chlorine

*TABLE A*

*Chlorine Halving Value Procedure — A glass column 40mm I.D. is filled with 100mm of carbon and is saturated with water by boiling and subsequent cooling. Fines are removed by washing. About 25 liters of solution are prepared by adding sodium hypochlorite to obtain 5 mg/l concentration. The column is fed at a rate of 36 m/hr (superficial velocity) for 35 minutes. At this point, samples of chlorine are taken upstream and downstream of the column. The chlorine concentration is determined immediately either iodometrically or otherwise. The height of the carbon layer is measured to the nearest mm and the half value length is calculated:*

$$HVL = \frac{0.301h}{\log (a/b)}$$

*where*

$h$ = *height of carbon bed*
$a$ = *influent chlorine conc.*
$b$ = *effluent chlorine conc.*

### *GAC DECHLORINATION PERFORMANCE**

| *Rank* | *Half-Length Value* | *(cm)* |
|---|---|---|
| *1.* | *Lignite* | *2.60* |
| *2.* | *Peat* | *2.63* |
| *3.* | *Bituminous Coal* | *2.73* |
| *4.* | *Coconut Shell* | *2.96* |

| *Rank* | *Dechlorination Number*** | |
|---|---|---|
| *1.* | *Peat* | *13.00* |
| *2.* | *Lignite* | *8.70* |
| *3.* | *Bituminous Coal* | *6.90* |
| *4.* | *Coconut Shell* | *6.00* |

**Tests were performed with standard 12x40 mesh GAC with a 1.0 mm (GMD) particle diameter.*

***g $Cl_2$/kg GAC/hr*

may also be added as a solid in the form of sodium hypochlorite. Some municipal systems are using chlorine dioxide. To reduce the formation of disinfectant byproducts more plants are using chloramines. In this case, direct chlorination with chlorine gas is followed by injecting ammonia to produce monochloramine. Activated carbon will catalytically reduce these chlorine-based disinfectants. There are, however, important adsorber design differences depending on the chemical form of the disinfectant.

*Chlorine Removal* Chlorine may be added as chlorine gas or as sodium or calcium hypochlorite. Normally, levels of 1-5 ppm chlorine are added at the water purification plant with the goal of having a residual 0.1 ppm reaching the consumer. Some bottling plants may super chlorinate the water to over 10 ppm. In water, free chlorine reacts to form hypochlorous acid.

$Cl_2 + H_2O \longrightarrow HCl + HOCl$

Chlorine + water ⟶ hydrochloric acid + hypochlorous acid

The hypochlorous acid disassociates in water to form the hypochlorite ion ($OCl^-$). This is the active disinfectant form of free chlorine.

Activated carbon is often used as an adsorbent to retain dissolved organic compounds which impart tastes and odors to the water. In the case of dechlorination it is not adsorption, but a chemical reaction, which removes the hypochlorous acid. The C* represents the surface of the activated carbon in this simplified expression of the dechlorination reaction.

$HOCl + C^* \longrightarrow HCl + C^*O$

This reaction is relatively rapid. The chlorine concentration can be cut in half every few seconds with 99% removal in under 60 seconds.

*Chloramine Removal* Hypochlorous acid has been the primary disinfectant for many years. It is a very strong oxidant which reacts with naturally occurring dissolved organic material to produce trihalomethanes (THM). There are limited data which indicate THM's are carcinogenic. The EPA has placed maximum limits on this type of compound. In order to meet these regulations, many municipal water purification plants have switched from direct chlorination to the less chemically aggressive chloramines. Chloramines still provide residual biocide protection while generating much lower levels of THM's.

The switch to chloramines has created problems for industrial and commercial operations which dechlorinate their water. While activated carbon catalytically removes both chloramines and hypochlorous acid, chloramines require much more reaction time. Most GAC adsorbers in dechlorination service were initially designed to remove hypochlorous acid. When local municipalities change to chloramines, these adsorbers are usually undersized.

Chloramines may be present as mono-, di-, and tri-chloramine. At normal pH levels, the monochloramine is the predominant chemical form. There are two reactions taking place to remove monochloramine.

1. $NH_2CL + H_2O + C^* \longrightarrow NH_3 + HCL + C^*O$
2. $2NH_2Cl + C^*O \longrightarrow N_2 + C^* + 2HCl + H_2O$

Initially, only the first reaction takes place. When surface oxides have built up, the second reaction occurs, converting the ammonia to elemental nitrogen. Early in the life of a GAC bed, a 5-10 minute retention time will remove over 95% of the chloramines. However, at equilibrium, Empty Bed Contact Times (EBCT) of 25-30 minutes may be required.

*Particle Size Effects* The smaller the GAC particles are, the faster the dechlorination rate. A disadvantage of smaller particles is higher pressure drop. Generally, a 12x40 mesh GAC is more than twice as effective as an 8x30 mesh GAC. Likewise, a 20x40 mesh GAC is up to 50 percent more effective than a 12x40 mesh GAC; see Figure 1. However, the smaller 20x40 mesh GAC has about double the pressure drop of 12x40 mesh GAC and 4 times the pressure drop of 8x30 mesh GAC.

The effects of particle size on GAC bed pressure drop are demonstrated in Figure 2 for GRANULAR DARCO® grades typically used for dechlorination. Pressure drop characteristics for GRANULAR DARCO® activated carbons are described by the following equation, which should be used at high flow rates or where high/low water temperatures significantly affect viscosity.

$$\Delta P = 129 \frac{uVL}{D_p^2 D_c^2}$$

Where:

$\Delta P$ = pressure drop in inches of water
$u$ = viscosity in centipoise
$V$ = flow rate in gallons per minute
$L$ = GAC bed height in feet
$D_p$ = geometric mean particle diameter (GMD) in millimeters
$D_c$ = column diameter in inches
Granular Darco 12x20 GMD = 1.20 mm
Granular Darco 12x40 GMD = 0.92 mm
Granular Darco 20x40 GMD = 0.63 mm
Granular Darco 20x50 GMD = 0.55 mm

*pH Effect* The pH of the water being treated has an important effect on dechlorination halving value. GAC is very effective for removing HOCl which is the primary form of chlorine in water below pH 7. At pH of 8.5 and higher, however, the chlorine exists primarily as the hypochlorite ion ($OCl^-$). As Figure 3 illustrates, GAC efficiency drops off sharply at high pH. While it may take less than 20 seconds of contact time for 99% chlorine removal at a pH of 7, it could require over 3 minutes for the same chlorine reduction at pH greater than 9. This can be an important consideration for the designer.

If source water pH fluctuates, there may occasionally be chlorine breakthrough which indicates the need for a larger adsorber. The adsorber should be designed to accommodate the highest expected pH during normal operation.

*Temperature Effect* At higher temperatures, the dechlorination reaction is faster. Figure 4 shows the effect of water temperature on efficiency. For example, dechlorination halving value at 35°F is double the value at 88°F, requiring twice the GAC bed volume to achieve the same effluent chlorine level. It is a good practice to design the GAC adsorber for winter water temperatures.

*Impurities* Generally, impurities in the source water shorten the life of a GAC bed. Suspended solids and colloidal material will plug up the macropores and increase pressure drop. Regular backwashing will remove some of this material. Organic compounds, typically

FIG. 1

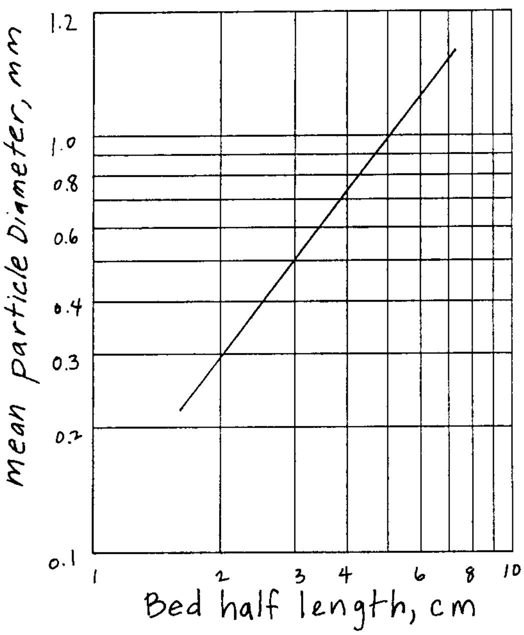


FIG. 2

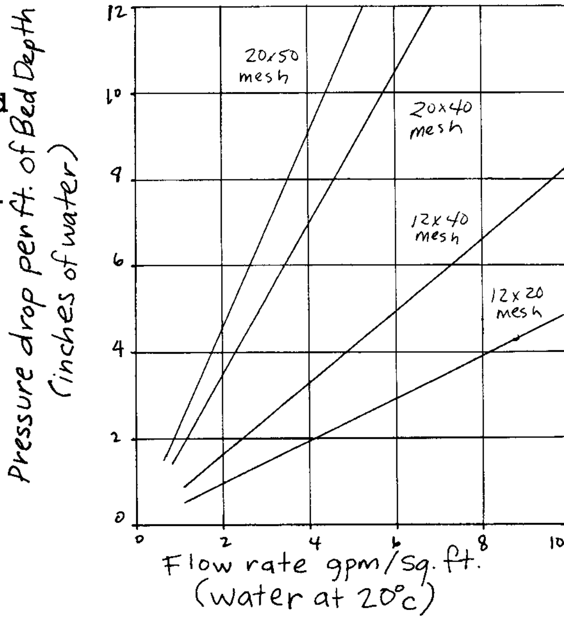
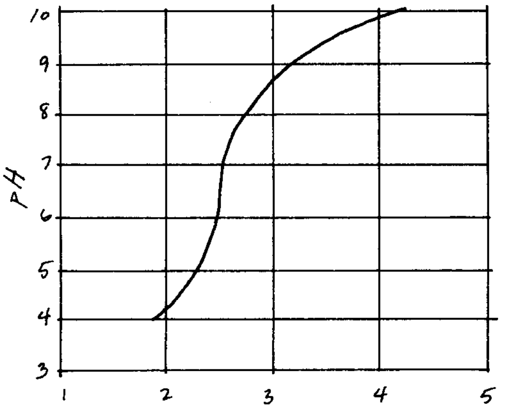
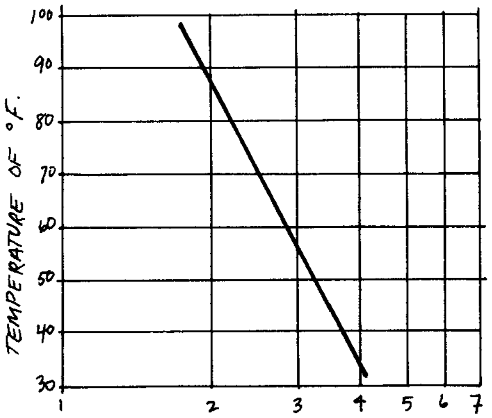


FIG. 3



Chlorine Halving Value-cm
Granular Darco 12x40

FIG. 4



Chlorine Halving Value-cm
Granular Darco 12x40

causing taste and odor, are adsorbed onto the carbon. They reduce the dechlorination efficiency of the GAC because they form a thin molecular coating over the carbon surface. Some of the smaller organic molecules are eventually oxidized by incoming chlorine. However, many of the larger compounds are not easily oxidized. Large pore volume activated carbon grades like the GRANULAR DARCO® series, the NORIT® granular series and NORIT® ROW 0.8, are less susceptible to fouling with organic impurities due to their high adsorption capacity. In systems with very clean source water, GAC beds will effectively dechlorinate for many years; see Figure 5. Most waters, however, contain at least small quantities of dissolved organics which usually deplete the GAC bed in 1-3 years.

*GAC Adsorber Startup Procedure* American Norit GAC grades are delivered in bags, super sacks, and bulk trucks. Sufficient GAC should be ordered to fill the adsorber 2/3 to 3/4 full. Do not overfill the adsorber: leave sufficient freeboard to allow for bed expansion during the backwash step.

### *Charging the Adsorber*

1. Prior to charging the adsorber with GAC, it should be filled with water under hydraulic pressure to check for gasket leaks. After a successful pressure test, drain the adsorber and open the top manway. If the adsorber is equipped with a bed support screen over the outlet line or distributor, then skip to step 4.
2. Many adsorbers use GAC bed support media, for example, gravel or anthracite. Some manufacturers design the adsorbers to take layers of graded support media. The larger media goes in first; each layer should be leveled before adding the next smaller size of support media. The particle size of the top layer of media should be 1-3 mm. Support media should cover the top of the outlet distributor to a depth of 4 inches.
3. After loading the support media, it should be backwashed to remove any fine material or impurities. Backwash the support media at a flow rate of 15-20 gpm/sq. ft.
4. Before charging the GAC, partially fill the adsorber with water to a level of 2 feet above the support bed or screen. Maintain a water level over the GAC bed while charging, as this will cushion the impact as GAC is poured in. Fill 2/3 to 3/4 of the available volume with GAC, leaving sufficient room for bed expansion during the backwash.
5. Allow the GAC to soak for at least 8 hours to remove air from the pores of the activated carbon.

*Backwashing* Prior to putting a new GAC charge into service it should be backwashed to remove any fines generated during shipping and loading the GAC. Start backwash slowly (i.e. 2-3 gpm/sq. ft.). This will flush out any air trapped in the bed. Continue increasing backwash flow rate to achieve 30-40% bed expansion; see Figure 6 to determine proper flow rate for your GAC grade. Continue backwashing for one hour. After backwashing, adjust valves for normal downflow operation. In ultra pure water applications it may be necessary to drain the first bed volume of downflow water to remove any fines trapped in the bottom of the adsorber.

The backwash curves in Figure 6 show fluidization of GRANULAR DARCO® grades over a broad range of bed expansions in water at

20 C (68°F). When water gets cold, the viscosity increases significantly which in turn increases bed expansion. If back flush rates are not reduced at low water temperatures, then GAC may be washed out of the adsorber. The following equation provides required flow for 30% bed expansion.

$$F = 10.9\frac{A D_p}{u}$$

F = gallons per minute
A = cross section flow area in square feet
$D_p$ = geometric mean particle diameter (GMD) in millimeters
u = viscosity in centipoise (Table B).

If the water being filtered contains suspended solids, it may be necessary to periodically backwash the adsorber. Normally a 15-30 minute backflush with 30-40% bed expansion is sufficient to remove trapped solids from the GAC bed.

Backwashing is effective for removing dirt and debris which build up on the top few inches of the GAC bed. Normally, backwashing is triggered by increasing pressure drop, although some units are on automated timers. Backwashing does not regenerate the GAC bed: adsorbed organics will stay on the activated carbon.

*Sterilization* Activated carbon can become fouled with biological growth after being in service for several months. To avoid this, the bed should be sterilized periodically. Sterilizations can be accomplished by steaming, washing with sodium hydroxide, or super chlorinating the GAC bed. Steaming is generally the most effective sterilization procedure.

*Steam Sterilization* Caution: Make sure all equipment exposed to steam and hot condensate are compatible with the high temperatures.

1. Isolate the adsorber and drain it.
2. Hook up a low pressure steam line to the inlet side of the adsorber and open steam valve.
3. When steam starts to come out of the drain line, continue steaming for one hour. Always control steam rate with the valve on the steam line. Never cut back on steam flow rate with the drain valve, it may over pressure the adsorber. Avoid blowing steam through the adsorber at high velocity.
4. After steaming, the adsorber should be backflushed for 30 minutes. An option to steaming is to run hot water through the GAC bed. When the effluent reaches 180 °F, discontinue hot water wash and start backflush.

*Super Chlorination* When steam is not available or equipment is not compatible with higher temperatures, super chlorinating the GAC bed will sterilize it.

1. Isolate the adsorber, drain it, and close the drain valve.
2. Using 2.5% hypochlorite solution (common household bleach), pour one gallon per 25 cubic feet of GAC bed into the top of the adsorber.
3. Partially open the backflush valve and slowly fill the adsorber with water to 1-2 feet over the GAC bed.
4. (Optional) If an air source is available, hook it to the backwash line and let it bubble up through the column. Do not vigorously blow air up through the GAC bed. The goal is to gently stir the hypochlorite solution; do not agitate the GAC bed.
5. Soak the GAC bed in hypochlorite solution eight hours, then drain the bed.

FIG. 5

7ph @ 70°F
using an 8 x 30 carbon mesh

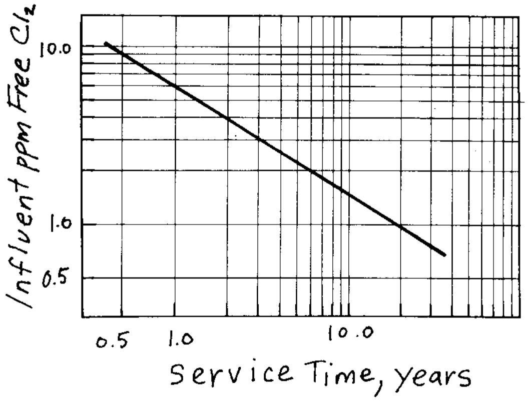
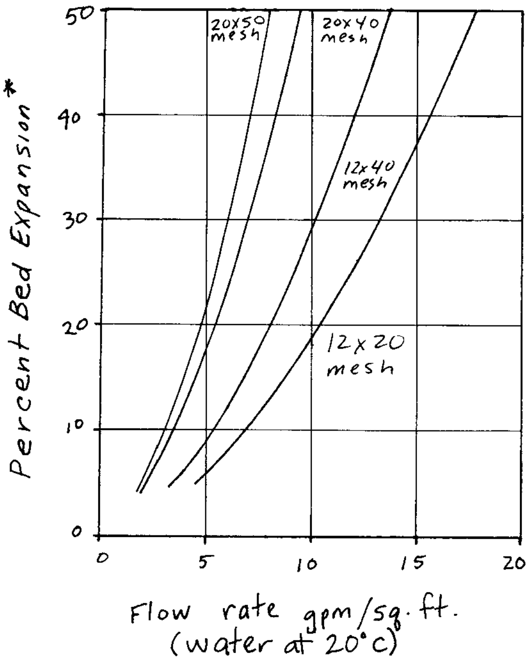


FIG. 6



* Expansion is expressed as percent of the backwashed and settled bed depth.

*TABLE B*

*VISCOSITY OF WATER*

| *Temp. F* | *Cp* |
|---|---|
| *0* | *1.79* |
| *40* | *1.55* |
| *50* | *1.31* |
| *60* | *1.12* |
| *70* | *0.98* |
| *80* | *0.86* |
| *90* | *0.76* |
| *100* | *0.68* |

6. Backflush the adsorber for at least 30 minutes before putting it back into service.

*GAC Adsorber Design* This section will describe what information is required and how to use it to design a GAC adsorber for dechlorination service. The designer needs to know:

1. Flow rate (gpm)
2. Disinfectant type (chlorine or chloramine)
3. Temperature
4. pH
5. GAC mesh size

Multiply the flow rate by correction factors A, B, C, & D to get the size of GAC bed required.

Flow Rate × A × B × C × D = cu. ft. GAC

CORRECTION FACTORS

| A | | B | | C | | D | |
|---|---|---|---|---|---|---|---|
| form | factor | pH | factor | Temp °F | factor | mesh | factor |
| chlorine | 1.0 | 5 | 0.8 | 40 | 1.47 | 12x20 | 2.0 |
| chloramine | 3.0 | 6 | 0.9 | 50 | 1.29 | 12x40 | 1.0 |
| | | 7 | 1.0 | 60 | 1.14 | 20x40 | 0.75 |
| | | 8 | 1.1 | 70 | 1.00 | 20x50 | 0.68 |
| | | 9 | 1.35 | 80 | 0.88 | | |
| | | 10 | 1.6 | 90 | 0.77 | | |

Once the GAC bed volume is known, then the vessel dimensions can be chosen. The chart in Figure 7 can be used to select a vessel. Follow these steps:

1. In the Maximum Flow Rate Column, find a value close to, or exceeding, the design flow rate.
2. In the second column, find the minimum vessel diameter.
3. The third column provides the cross section area of the vessel. Divide the GAC bed volume by the cross section area to get necessary bed depth. If the bed depth is over eight feet, go to the next larger vessel diameter.
4. In the bed volumes section, find the required vessel height. This chart is calculated to provide an additional 50% of the GAC bed height for backflush bed expansion.

FIG. 7

| MAXIMUM FLOW RATE (GPM) | VESSEL DIAMETER (INCHES) | AREA (SQ. FT.) | GAC BED VOLUME (CU. FT.) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | 4 | 5 | 6 | 8 | 10 | 12 | VESSEL HGT. (FT) |
| | | | 2.7 | 3.3 | 4 | 5.3 | 6.7 | 8 | BED HGT. (FT) |
| 6.3 | 12 | 0.79 | 2.1 | 2.6 | 3.2 | 4.2 | 5.3 | 6.3 | NOTICE 50% FREEBOARD TO ALLOW FOR BACKFLUSH BED EXPANSION. |
| 8.6 | 14 | 1.07 | 2.9 | 3.5 | 4.3 | 5.7 | 7.2 | 8.6 | |
| 11 | 16 | 1.40 | 3.8 | 4.6 | 5.6 | 7.4 | 9.4 | 11 | |
| 14 | 18 | 1.77 | 4.8 | 5.8 | 7.1 | 9.4 | 12 | 14 | |
| 17 | 20 | 2.18 | 5.9 | 7.2 | 8.7 | 12 | 15 | 17 | |
| 25 | 24 | 3.14 | 8.5 | 10 | 13 | 17 | 21 | 25 | |
| 39 | 30 | 4.91 | 13 | 16 | 20 | 26 | 33 | 39 | |
| 57 | 36 | 7.07 | 19 | 23 | 28 | 37 | 47 | 57 | |
| 77 | 42 | 9.62 | 26 | 32 | 38 | 51 | 64 | 77 | |
| 101 | 48 | 12.6 | 34 | 42 | 50 | 67 | 84 | 101 | |
| 157 | 60 | 19.6 | 53 | 65 | 78 | 104 | 131 | 157 | |
| 226 | 72 | 28.3 | 76 | 93 | 113 | 150 | 190 | 226 | |
| 308 | 84 | 38.5 | 104 | 127 | 154 | 204 | 258 | 308 | |
| 402 | 96 | 50.2 | 136 | 166 | 201 | 266 | 336 | 402 | |
| 509 | 108 | 63.6 | 172 | 210 | 254 | 337 | 426 | 509 | |
| 628 | 120 | 78.5 | 212 | 259 | 314 | 416 | 526 | 628 | |

Some source waters are high in dissolved organic material. These compounds, which often impart unpleasant tastes and odors to the water, are adsorbed onto the carbon. Eventually the organic loading will interfere with dechlorination. Cold water temperatures will also reduce dechlorination efficiency. If the adsorber is designed for 60°F operation, there may be chlorine breakthrough when a cold snap forces source water temperatures down to 40°F. Likewise, increase in water pH from 8 to 9 will reduce dechlorination efficiency 20%.

For locations where source water properties can deviate significantly from design conditions, increasing GAC bed volume provides a greater margin of safety. It is generally more economical to increase bed volume with greater bed depth. If the resulting bed depth exceeds 8 feet, then go to the next larger vessel diameter.

This general design information is based on experience with GAC in dechlorination applications and is intended to provide guidelines to help the designer specify the proper size of a GAC adsorber. This design information is conservative for most applications; however, no warranties are expressed or implied. When the source water has high pH excursions, low winter temperatures, or high levels of organic contamination, the designer may choose to improve the margin of safety. Contact your American Norit Representative for more information concerning the use of GAC in your specific applications.

*Adsorber Vessel* Materials of construction are determined by vessel size, service pressure, and sterilization method. Generally stainless steel, coated carbon steel, or fiberglass vessels are adequate. Small adsorbers can be constructed from plastic, but water line service pressure generally limits them to 24 inches in diameter. Carbon steel vessels can be plastic or rubber lined, or simply painted with several coats of epoxy. For lined/coated carbon steel and fiberglass tanks, be sure to specify materials compatible with the sterilization method, i.e. steaming or super chlorinating.

Adsorbers in dechlorination service should be designed for down flow operation. If the inlet line comes through the top head of the adsorber, directing flow directly onto the GAC bed, then it should be baffled so flow does not disturb the bed. An inlet line entering the top side of the adsorber does not need to be baffled. The bottom of the adsorber should be equipped with a distributor to pick up the treated water.