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*Help Instruction File:*

# Decarbonation Module Overview

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Provided by the Office of Surface Mining Reclamation and Enforcement (OSMRE), the Pennsylvania Department of Protection (PADEP), the U.S. Geological Survey's (USGS) and the West Virginia Department of Environmental Protection (WVDEP).

# Decarbonation Module Overview

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## 1.0 Objective

In the AMDTreat program, the Decarbonation Module is considered an ancillary treatment component of a mine drainage treatment facility. Decarbonation is the process of transferring dissolved carbon dioxide ( $\text{CO}_{2(\text{aq})}$ ) from mine water to the atmosphere to reduce acidity and lower alkali chemical consumption. This module provides guidance on sizing and estimating the performance of various Decarbonation systems configured as continuous stirred and plug flow reactors.

The objectives of the overview are to (1) Provide an understanding of the application of Decarbonation in mine drainage treatment and (2) Provide an overview of the Decarbonation Module to guide users in developing a cost estimate to construct this type of treatment system component. This module, as well as most of the other AMDTreat modules, can also be applied to reverse cost model existing systems and system components to establish and evaluate future financial and investment decisions. The information is presented in two sections, **Overview and Application** and **Decarbonation Module Overview**.

## 2.0 Overview and Application

The Overview and Application section is organized into three parts: (1) Purpose and Understanding of Decarbonation, (2) Equipment and Typical Treatment Configurations, and (3) Application.

### 2.1 Purpose and Understanding of Decarbonation

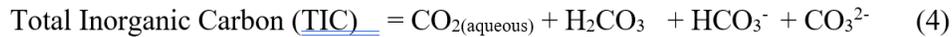
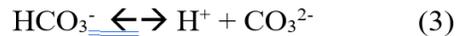
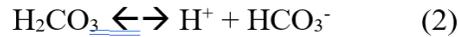
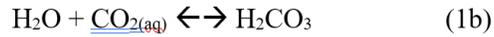
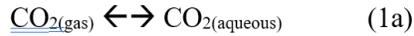
To understand decarbonation, this section will be divided into three subsections. The subsections are: What is Inorganic Carbon and how is it distributed in water?, How does Inorganic Carbon affect the treatment of mine drainage?, and What factors control how Inorganic Carbon is transferred from mine drainage to the atmosphere (decarbonation)? .

#### 2.1.1 What is Inorganic Carbon and how is it distributed in water?

A fundamental difference between organic and inorganic carbon is organic carbon is produced by living things. Organic carbon forms the basic organic compounds in living things and contains a carbon-hydrogen bond (e.g. Methane -  $\text{CH}_4$ ). Inorganic Carbon is created by inorganic processes (e.g. volcanos, mineral dissolution, etc.) and lacks the carbon-hydrogen bond (e.g. graphite (C), carbon dioxide ( $\text{CO}_2$ ), carbon monoxide (CO), and bicarbonate ( $\text{HCO}_3^-$ )). It is important to note the hydrogen atom in bicarbonate is bonded to oxygen and not to carbon, thus it still meets the definition of inorganic carbon.

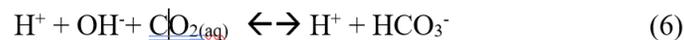
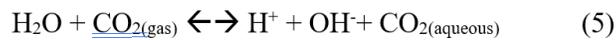
In natural waters, the common inorganic carbon species are carbonic acid ( $\text{H}_2\text{CO}_3$ ), bicarbonate ( $\text{HCO}_3^-$ ), and carbonate ( $\text{CO}_3^{2-}$ ). Total Inorganic Carbon (TIC) is the summation of these three inter-related species. They are inter-related because all three share carbonate as the “base” ion species. The difference between species is just the number of hydrogen atoms bonded to the oxygen contained in the carbonate ion. Carbonate is a deprotonated (lose a proton/ $\text{H}^+$ ) version of bicarbonate and bicarbonate is a deprotonated form of carbonic acid. So, what defines each species is the number of protons ( $\text{H}^+$ ) bonded to the  $\text{CO}_3^{2-}$  ion. Not only do all three species share a common base species in the carbonate ion, they also contain a molecule of  $\text{CO}_2$ . The fact that all three TIC species contain a molecule of  $\text{CO}_2$  shows that TIC is just a measurement of dissolved  $\text{CO}_2$  species in water.

The link between atmospheric CO<sub>2(g)</sub> dissolving into water to form the aqueous TIC species or exsolving (outgassing) from the water to the atmosphere is described by the following equations and the pictorial in Figure 1:



When disequilibrium exists between the atmosphere and a water body gaseous carbon dioxide will dissolve (undersaturated conditions) or exsolve (supersaturated conditions). When undersaturated, gaseous carbon dioxide dissolves to form aqueous carbon dioxide (Equation 1a) and a small portion of CO<sub>2(aq)</sub> will hydrate to form carbonic acid (Equation 1b). The combined concentrations of CO<sub>2(aq)</sub> and H<sub>2</sub>CO<sub>3</sub> (sometimes indicated as H<sub>2</sub>CO<sub>3</sub>\*) will be used interchangeably and referred to as carbonic acid. Carbonic acid can deprotonate twice, first to form bicarbonate (Equation 2) and then to form carbonate (Equation 3). Bicarbonate and carbonate are major components of alkalinity since they can accept protons (H<sup>+</sup>). Since pH is a measurement of the concentration (activity) of H<sup>+</sup> in solution, the incorporation of hydrogen ions by bicarbonate or carbonate will moderate decreases in pH resulting from the addition of CO<sub>2</sub> or other acid to the water.

By examining Equations 1 through 3, one may conclude that simply dissolving gaseous carbon dioxide into water will increase alkalinity since it appears to form bicarbonate and carbonate. In other words, one may suspect a treatment strategy to neutralize acidic mine drainage is to simply purchase a canister of gaseous CO<sub>2</sub> and inject it into the water to produce bicarbonate and carbonate alkalinity. However, dissolving CO<sub>2</sub> will not inherently, by itself, produce alkalinity. To conceptualize this point, it is useful to recast the model of CO<sub>2(g)</sub> dissolving into water by using the following equations:



Equations 5 & 6 show CO<sub>2(aq)</sub> reacting with hydroxyl ions (OH<sup>-</sup>) to produce bicarbonate. Dissolving CO<sub>2</sub> into water simply converts existing hydroxyl alkalinity into bicarbonate alkalinity, thus dissolving CO<sub>2</sub> into water does not inherently change the overall concentration of alkalinity but changes the form of

alkalinity from hydroxyl to bicarbonate while also decreasing the pH. Dissolving  $\text{CO}_{2(g)}$  into water will lower pH because as the concentration of hydroxyl is lowered, the concentration of protons ( $\text{H}^+$ ) will increase proportionally (to maintain the constant ionic product of water,  $K_w = [\text{H}^+][\text{OH}^-]$ ).

Equations 1 through 4 show dissolving gaseous  $\text{CO}_2$  into water will increase the concentration of the aqueous  $\text{CO}_2$  species and, hence, TIC, however, further explanation is needed to understand how the concentration of each carbonate species will change. Carbonate is a polyatomic ion and the number of protons ( $\text{H}^+$ ) bonded to the  $\text{CO}_3^{2-}$  ion defines the TIC species. The dependence on proton reactions to form  $\text{CO}_2$  species illustrates a pH dependence. Protonated species, like  $\text{H}_2\text{CO}_3$  will form in solutions with high concentrations of  $\text{H}^+$  (low pH) and deprotonated species, like  $\text{CO}_3^{2-}$ , will form in solutions with lower concentrations of  $\text{H}^+$  (high pH).  $\text{HCO}_3^-$  will form within the range of the other two species. Figure 2 relates pH to the distribution of inorganic carbon among the three species. The graph shows  $\text{H}_2\text{CO}_3$  dominates at  $\text{pH} < 6.35$ ,  $\text{HCO}_3^-$  dominates within the range of  $6.35 < \text{pH} < 10.32$ , and  $\text{CO}_3^{2-}$  dominates at  $\text{pH} > 10.32$ . The graph also shows at a pH of 6.35 the concentrations of  $\text{H}_2\text{CO}_3$  and  $\text{HCO}_3^-$  are equal and at a pH of 10.32 the concentrations of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  are equal. At all pH values, the sum of the three aqueous species equals TIC.

### 2.1.2 How does Inorganic Carbon affect the treatment of mine drainage?

The previous discussion focused on explaining the interplay between  $\text{CO}_{2(g)}$  and water and how TIC is distributed in water. Coal mine drainage in the eastern U.S. contains concentrations of  $\text{CO}_{2(aq)}$  that are supersaturated compared to atmospheric conditions. The reaction between acidic mine water and carbonate minerals, or their byproducts, is the major source of  $\text{CO}_{2(aq)}$  found in mine water (Equation 7). Since elevated concentrations of  $\text{CO}_{2(aq)}$  are common in eastern coal mine drainage it is important to understand its effect on the treatment of mine drainage.



The impact on understanding the interplay between  $\text{CO}_{2(aq)}$  and pH is profound when treating mine drainage. When an alkali chemical, such as hydrated lime ( $\text{Ca}(\text{OH})_2$ ), is added to mine drainage the resultant increase in pH (Equation 8) causes the TIC species to redistribute to maintain equilibrium conditions (Equations 9 & 10). This will cause deprotonation of TIC species as pH is increased and a release of acidity that will cause pH buffering and additional chemical consumption (Equation 11).

Calcium Hydroxide dissolves in water to increase the hydroxyl concentration and, thus, pH increases:



TIC species redistribute to establish equilibrium conditions as pH is increased. To illustrate this point, assume pH 6.3 mine drainage was dosed with Calcium Hydroxide to achieve pH 11. At a pH of 6.3, Figure 2 shows 50% of the TIC species is bicarbonate and 50% is carbonic acid. At pH 11, there is

virtually no carbonic acid and there is less bicarbonate, but more carbonate than at pH 6.3. To achieve equilibrium at the higher pH, carbonic acid and bicarbonate must deprotonate to form carbonate, thereby increasing the carbonate concentration while decreasing the concentration of carbonic acid and bicarbonate.

Carbonic acid fully deprotonates to produce carbonate and releases two moles of acidity ( $H^+$ ):



Bicarbonate deprotonates to increase the concentration of carbonate and releases one mole of acidity:



The deprotonation of carbonic acid and bicarbonate releases acidity that requires an additional dose of  $Ca(OH)_2$  to neutralize the acidity to prevent pH drop and maintain pH 11 conditions:



The amount of acidity released depends on the initial pH and the final pH since pH determines how TIC is distributed among the species. Any change in the distribution of species between the initial and final pH must be achieved by protonation ( $pH_{final} < pH_{initial}$ ) or deprotonation ( $pH_{final} > pH_{initial}$ ) of the species. Assume pH 3 mine drainage is increased to pH 8.4. At pH 3 TIC is in the form of carbonic acid and at pH 8.4 it has all deprotonated to produce bicarbonate. Inversely, of pH 8.4 mine drainage is decreased to pH 3, bicarbonate must protonate to produce carbonic acid. If pH 8.4 mine drainage is treated to pH 12.3, all bicarbonate must deprotonate to produce carbonate. For more complicated conditions, say a pH 3 water is treated to pH of 9.5, a large portion of the carbonic acid deprotonates to produce bicarbonate and a smaller portion deprotonates to produce carbonate (Figure 2). Speciation modeling provides a method to predict the amount of acidity released as pH is changed.

For example, assume a 1000 gallon/minute (gpm) acid mine discharge will be dosed with  $Ca(OH)_2$  to increase the pH from 4.0 to 8.4 for treatment. Assume the mine drainage contains a TIC of 30 mg/L and temperature of 12° C. The red line in Figure 3, noted as “Line #1”, represents the plot location of the pH 4.0 untreated mine water on the TIC distribution graph. The purple line (line #2) represents the treatment pH end point of 8.4. The figure shows the percent distribution of the three inorganic carbon species for a given pH. Thus, the graph shows almost 100% of the TIC is in the form  $H_2CO_3$  at the pH of the untreated water but ~ all of it deprotonates and converts to  $HCO_3^-$  as the water is treated to a pH of 8.4.

As  $Ca(OH)_2$  is added,  $H_2CO_3$  deprotonates to form  $HCO_3^-$  and release  $H^+$ . The acidity released during the species transformation consumes additional  $Ca(OH)_2$  as shown in Equation 11. This release of acidity as pH is adjusted during mine drainage is a major cause of increased chemical consumption and cost.

Thus far, the description of the TIC system and its effect on treatment has been described qualitatively; however, it can be quantitatively described as well. For example, consider the previously described 1000 gpm discharge containing a pH of 4 and TIC of 30 mg/L (as C). This solution contains a H<sub>2</sub>CO<sub>3</sub> concentration of 155 mg/L (as H<sub>2</sub>CO<sub>3</sub>). The deprotonation of H<sub>2</sub>CO<sub>3</sub>, to produce HCO<sub>3</sub><sup>-</sup>, as the pH is increased to 8.4 will release 125 mg/L of acidity (expressed as CaCO<sub>3</sub>) in producing HCO<sub>3</sub><sup>-</sup>. Given a flow of 1,000 gpm, an acidity of 125 mg/L (expressed as CaCO<sub>3</sub>), and a unit cost of \$160/ton for Ca(OH)<sub>2</sub>, equates to an annual chemical cost of \$34,910 to just neutralize CO<sub>2</sub>-based acidity.

One strategy to minimize this nuisance reaction is to first decarbonate the water before adding chemical to adjust pH. The process of decarbonation is to remove CO<sub>2(aq)</sub> from mine drainage and exsolve it to Earth's atmosphere as CO<sub>2(g)</sub>. Lowering the initial TIC concentration will proportionally lower the acidity and corresponding base required for neutralization. If the aqueous concentration of CO<sub>2</sub> is greater than the equilibrium concentration with respect to the atmosphere in contact with the water, Equation 1 will proceed to the left (reactants side). Thus, H<sub>2</sub>CO<sub>3</sub> will dissociate into CO<sub>2(g)</sub> that can escape into the atmosphere; all associated aqueous carbonate speciation reactions (Equations 1-3) would go to the left and lower the TIC.

### 2.1.3 What factors control how Inorganic Carbon is transferred from mine drainage to the atmosphere (decarbonation)?

The pressure of Earth's atmosphere is 1.0 atmosphere at sea level and is made up of a collection of gases, mostly nitrogen (N<sub>2</sub>) and oxygen (O<sub>2</sub>). It is useful to define the percent by volume, which corresponds to the partial pressure of each of the individual gases. The volumetric percentage of Carbon Dioxide in the atmosphere is 0.04% and, therefore, the partial pressure of CO<sub>2(g)</sub>, is 0.0004 atmospheres. Henry's Law relates the partial pressure of a gas in an atmosphere above a liquid (P<sub>CO2</sub>) to the equilibrium concentration of that gas dissolved into a liquid (C<sub>CO2</sub>) by using a gas-specific constant called Henry's constant (k<sub>H</sub>) (Equation 12a). Henry's Law accounts for differences in the solubilities of various gases as a function of its partial pressure:

$$C_{CO_2} = k_H P_{CO_2} \quad (12a)$$

Where:

k<sub>H</sub> has the units of  $\frac{mol_{gas}}{L*atm}$

While we will be using the form shown in Equation (12a), note you may see the following form in some text books:

$$C_{CO_2} = \frac{P_{CO_2}}{k_H} \quad (12b)$$

Where:

k<sub>H</sub> has the units of  $\frac{L*atm}{mol_{gas}}$

The partial pressure of CO<sub>2(g)</sub> is 0.0004 atmospheres and a table of constants in a chemistry textbook indicates  $k_H$  for the CO<sub>2</sub>/water system is .034 moles/L atm. Thus, the concentration of H<sub>2</sub>CO<sub>3</sub> (CO<sub>2(aq)</sub>) in equilibrium with the atmosphere is ~ 0.84 mg/L, which is significantly less than the 155 mg/L calculated in the hypothetical mine drainage scenario previously presented. Therefore, there is a driving force to transfer CO<sub>2</sub> from the water to the atmosphere to achieve equilibrium. This water is suitable for decarbonation since a concentration gradient exists that favors transferring gas from water to the atmosphere. However, the analysis thus far does not consider the amount of time it will take for decarbonation or whether the cost of decarbonation (capital, electrical, etc.) is more than the cost of adding chemical to neutralize the CO<sub>2</sub> acidity as presented in Equation 10.

The paragraphs above have shown the hypothetical mine drainage is susceptible to decarbonation but the mechanisms and factors that affect decarbonation have not been identified. To understand the factors, imagine that Figure 4 represents carbonated mine drainage emerging at the surface and being held in a shallow pond. Also, imagine the red circles represent CO<sub>2</sub> molecules in the air and water and assume the concentration of CO<sub>2(aq)</sub> is greater than the concentration allowed by Henry's Law when the water is equilibrated to atmospheric conditions. In this disequilibrium example, there is a concentration gradient, indicated by the upward arrow, so particles will "diffuse" in the direction of high to low concentration to achieve equilibrium. Diffusion can be thought of as the random movement of particles by natural means and not due to the movement of the fluid (advection). At equilibrium, the concentration gradient would be 0 and there would not be a driving force for the net transfer of gas molecules from or to the water.

Try to think of the factors that would help increase the rate of transfer of CO<sub>2</sub> molecules from the mine drainage pond to the atmosphere in a passive manner (without adding energy). Intuitively, one can imagine the rate of transfer will depend on the magnitude of the concentration (pressure) gradient (more particles = more likely to transfer). Furthermore, one can imagine the larger the surface area of the pond/air interface, the easier it would be to transfer CO<sub>2</sub> molecules as the random motions have more of a chance to move across the interface. In addition, one could also imagine a shallow pond would be more efficient at transfer than a deep pond since a shallow pond would quicken transfer by minimizing the distance molecules can randomly move away from the interface surface. While the example is focused on CO<sub>2</sub> molecules, one could imagine molecules with less mass, therefore atomic weight, (i.e. O<sub>2</sub>) would increase the rate of transfer as well since they move more quickly.

The factors that affect the passive transfer of molecules between air and water are represented in Fick's Law. Fick's Law describes the rate of passive diffusion of molecules in response to a concentration gradient. Fick's law can be expressed in several ways as shown in Equations 13 through 15. Equation 10 describes the "net rate" of particles moving through an area in response to a change of pressure (particles in a volume) over a distance. The rate of diffusion represents the amount of gas transported over time and is governed by several variables including: (1) the concentration/pressure gradient ( $P_1 - P_2$ ), (2) the surface area of the interface where the transfer takes place (air/water interface)( $S_{area}$ ), and (3) the Diffusion Coefficient which is specific to the gas/liquid system ( $D_{CO_2}$ ).

$$\text{Diffusion Rate (Velocity of Particles)} = \frac{(P_1 - P_2) * S_{area} * D}{\text{Gradient distance}} \quad (13)$$

$$\frac{Velocity}{Area} = \frac{(P_1 - P_2)}{Gaident\ distance} * D \quad (14)$$

$$Flux = Gradient * D \quad (15)$$

The Diffusion Coefficient describes the quantity of a gas that is moving through a cross section per unit time when the concentration gradient is unity (units of L<sup>2</sup>/Time). The Diffusion Coefficient is not only a proportionality constant but also incorporates characteristics like molecular weight and solubility. Graham's Law (16) provides the link between molecular weight (MW) and Diffusion Coefficient showing D is inversely proportional to the square root of the molecular weight of the gas.

$$Diffusion\ Coefficient\ \&\ Particle\ Velocity = \frac{1}{\sqrt{MW}} \quad (16)$$

Thus, heavier molecules, like CO<sub>2</sub>, will diffuse slower than lighter molecules, like O<sub>2</sub>. The Diffusion Coefficients for CO<sub>2</sub> and O<sub>2</sub> in water are 1.91 and 2.42 (cm<sup>2</sup>/sec @ 25C), respectively, which shows O<sub>2</sub> diffuses about 1.26 times faster than CO<sub>2</sub>. This makes sense since the O<sub>2</sub>/CO<sub>2</sub> ratio of 1/√MW of the gases is 1.3, which is very similar to the ratio of diffusion coefficients.

Notice Equations 12 through 14 describe steady state diffusion since the diffusion rate or flux of gas being transferred is not changing as a function of time, thus the rate of diffusion is constant and is at steady state. One reason why the rate of diffusion is constant is because the concentration gradient (P<sub>1</sub> - P<sub>2</sub>) is constant with time. When decarbonating mine drainage, the concentration gradient will change with time since decarbonation will continuously lower the concentration of CO<sub>2(aq)</sub> as gas is outgassed to atmosphere. Therefore, a more robust model that considers a variable rate is required to model decarbonation and size decarbonation reactors.

In addition to needing a non-steady state diffusion equation (rate changes with time) to model decarbonation, we need to consider non-passive mechanisms to transfer CO<sub>2</sub>. Instead of relying on the random motion of molecules, why not add an advective component (transfer mechanism due to bulk fluid motion) to a decarbonation system to drive molecules in a direction to promote transfer. Moreover, instead of designing a decarbonation system with a fixed distance (concentration gradient) between the bottom of the fluid and the transfer interface like shown in Figure 4 (e.g. pond), why not create a short transfer distance to increase the gradient by either injecting compressed atmospheric air to create bubbles in mine drainage (Figure 5) or creating water droplets and splashing them into the air. Creating either small air bubbles in water or small water droplets in air will increase the transfer surface area and enhance the rate of transfer. In either case, the cumulative surface area of the bubbles or water droplets will be orders of magnitudes greater than the transfer surface area of a pond or ditch, the rate of transfer will be greater by orders of magnitude.

Both the enhanced transfer due to convection/mixing processes and the fact that the rate of transfer will change with time requires a modified version of Fick's Law:

$$\frac{d[C_{CO_2(aq)}]}{dt} = -k_{La} * (C_i - C_s) \quad (17)$$

Where:

$d[C_{CO_2(aq)}]/dt$  = the rate of change in the concentration of  $CO_{2(aq)}$  (moles  $L^{-1} sec^{-1}$ )

$-k_{La}$  = "bulk" volumetric (gas) transfer coefficient ( $sec^{-1}$ )

$C_i$  = Initial Concentration of  $CO_{2(aq)}$  (moles  $L^{-1}$ )

$C_s$  = Saturation Concentration of  $CO_{2(aq)}$  under atmospheric conditions (moles  $L^{-1}$ )

This non-steady state equation shows the rate of  $CO_2$  transfer changes with time and depends on both the concentration gradient and the gas transfer coefficient. The gas transfer coefficient is considered a "bulk" coefficient since it contains both " $k_L$ " which represents the mass transfer coefficient that describes the transport of gas to the atmosphere and " $a$ " which represents the gas-liquid exchange area per unit volume of liquid (e.g. bubble surface area). Furthermore,  $k_L$  represents a host of mechanisms that affect transfer, such as diffusion, advection, mixing effects, and the type of reactor used (batch, plug flow, stirred). It is impracticable to be able to separate and quantify all of the individual mechanisms that affect  $k_L$  and  $a$ , thus gas transfer coefficients are empirically derived by measuring the performance of operating decarbonation devices. Transfer coefficients are process and equipment specific and it may be difficult to scale the performance of a decarbonator at one site into the design of a decarbonator for another site.

The AMDTreat team used Equation 16 and empirically measured gas transfer coefficients for a variety of combinations of different mechanical devices (surface aerators, bubble diffusers) paired with different chemical reactor designs (continuous stirred, plug flow). Water samples were collected to characterize the change in  $CO_2$  concentration in the decarbonation unit and dye testing was used to determine retention time (Figures 6 and 7). The information was used to determine the gas transfer coefficient for different types of decarbonation equipment. This will be further discussed in Section 2.2, Equipment and Treatment Configurations.

## 2.2 Equipment and Treatment Configurations

Decarbonation is the process of transferring  $CO_2$  from the water to the air, the reverse of carbonation. The decarbonation module offers the ability to model and predict decarbonation performance using different decarbonation devices paired with different chemical reactor designs. The two primary methods for mechanical decarbonation involve either pumping compressed air into water or pumping water into the air. Both processes enhance the transfer mechanism by creating small particles of air or water with large surface areas. AMDTreat offers the ability to model both approaches using several different decarbonation units.

### 2.2.1 Decarbonation Reactors

AMDTreat can model several decarbonation devices configured as continuous stirred or plug flow reactors (Table 1). Users may also use their own Custom option to enter a transfer coefficient and model the performance as either a plug flow (PFR) or continuous stirred reactor (CSTR). Recall, the default transfer coefficients provided represent the performance of both the decarbonation device and reactor as a system. A key difference between PFR and CSTR is that the concentration of  $\text{CO}_{2(\text{aq})}$  changes with retention time (or distance along the flow path) in a PFR but is assumed to be a constant average concentration in a CSTR because the CSTR is assumed to be instantaneously and completely mixed. Therefore, every drop of high  $\text{CO}_{2(\text{aq})}$  influent water entering the CSTR is instantly diluted to the average concentration of the entire reactor. Furthermore, the  $\text{CO}_{2(\text{aq})}$  concentration of the CSTR is assumed to be the same as the effluent concentration since the reactor is assumed to be completely mixed. In other words, the concentration gradient between the water and atmosphere is relatively low and constant throughout the entire volume in a CSTR. In a PFR, a large concentration gradient may result from the initially elevated  $\text{CO}_{2(\text{aq})}$  concentration in influent to the reactor, which results in greater potential for gas transfer upon aeration. As the  $\text{CO}_2$  is removed, the concentration gradient decreases as a function of distance or volume (retention time) through the PFR. Because the initial gradient between  $\text{CO}_{2(\text{aq})}$  in the solution versus  $\text{CO}_{2(\text{aq})}$  in equilibrium with the solution is relatively high, the same aeration rate in a PFR results in a gas transfer rate that will be greater than that for a CSTR of similar volume (using the same aeration technology). For this reason, PFR is the preferred reactor choice for decarbonation.

Decarbonation Device	Default $k_{La}$ ( $\text{sec}^{-1}$ )	Plug Flow Reactor	Continuous Stirred Reactor
<b>Surface Aerator</b>	0.00067	NA	x
<b>Fine Bubble Diffuser Aerator</b>	0.00116	x	NA
<b>Maelstrom Oxidizer</b>	0.03195	x	NA
<b>Custom</b>	User Specified	x	x

Table 1: Combination of decarbonation devices, reactor types, and default gas transfer coefficients used in AMDTreat. The Custom option allows users to enter a customized  $k_{La}$  for either a plug flow or continuous stirred reactor decarbonation system.

### 2.2.2 Decarbonation Approaches

#### 2.2.2.1 Mixing Water into Air

##### 2.2.2.1.1 Surface Aerators

Surface aerators include a large collection of aeration devices, which include floating aerators, fountain, and spray aerators. All these devices pump or push water to the surface to create small droplets of water that mix with the air to cause transfer. Some of the devices have specially designed splash guards or nozzles to promote the formation of small droplets. Floating surface aerators are common decarbonation devices at mine drainage treatment facilities. Floating aerators are relatively inexpensive, and ponds and reactors can easily be retrofitted to install a surface aerator. They can be installed in PFRs (Figure 8) and in CSTRs (Figure 9), however, the decarbonation module in AMDTreat only offers the ability to model surface aerators installed in a CSTR tank. Users input the desired retention time and AMDTreat selects a

tank depth based on the flow rate. AMDTreat estimates the cost to purchase and install a tank based on user input and selections and does not attempt to evaluate whether the design can achieve the predicted performance.

The AMDTreat team collected field data and calculated  $K_{La}$  for several sites using surface aerators for decarbonation. Empirical data were collected on the rates of  $CO_2$  outgassing during an aeration experiment at one AMD site described by Cravotta (2015) and at several active or passive treatment AMD sites in Pennsylvania that employed various aeration or other treatment technologies. Values for  $k_{L,CO_2}$  were estimated from the linear slope of  $\ln(C_0 - C_s)/(C_t - C_s)$  versus  $t$ , where  $t$  is elapsed time during the aeration experiment or travel time between measurement points. Either dye tests were used to determine retention time or residence time was computed by dividing the estimated water volume by the measured flow rate. No attempt was made to explicitly consider the effects of water depth, wind, and other hydrodynamic parameters on the gas exchange rates or solute transport (e.g. Rathbun, 1998; Zappa et al., 2003). The empirical values corrected to 20 °C for  $k_{L,CO_2}$  which resulted in a default  $K_{La}$  for surface aerators of  $0.00067 \text{ sec}^{-1}$ . Users can use the “custom” option in AMDTreat to input a customized  $K_{La}$  and model decarbonation in either a PFR or CSTR configuration. When choosing a customized  $K_{La}$  it is recommended that the user validates the selection based upon field testing of similar equipment designs or available verifiable performance data.

#### 2.2.2.2 Mixing Air into Water

##### 2.2.2.2.1 Fine Bubble Diffuser Aerator

Fine bubble diffuser aerators are available in many different configurations and styles. In mine drainage treatment, compressed air blowers push air through a grided piping network installed in the bottom of a tank or pond reactor (Figures 10 & 11). Diffuser disks or tubes installed throughout the piping network transform the compressed air into bubbles less than a millimeter in diameter (Figures 12 & 13). Typically, a check valve separates the diffuser head from the piping network. When applied to mine drainage treatment scenarios, the diffuser heads are susceptible to fouling with scale or precipitate. Flexible head aids in cleaning. The head is typically constructed of a flexible material such as EPDM rubber to aid in removing scale. Some designers opt for larger orifices (larger bubbles) to help prolong and manage clogging issues with iron hydroxide.

AMDTreat assumes the bubble diffuser system consists of a grided piping network installed in the bottom of a rectangular tank constructed of either concrete or bolted or welded steel and configured as a CSTR. The AMDTreat team collected field data and calculated  $K_{La}$  for several sites using bubble diffusers for decarbonation (Figure 14). The field-collected data was used to develop a default  $K_{La}$  for bubble diffusers of  $0.00116 \text{ sec}^{-1}$ . Users can use the “custom” option in AMDTreat to input a customized  $K_{La}$  and model a bubble diffuser decarbonator in either a PFR or CSTR configuration.

AMDTreat estimates the cost to purchase and install a tank based on user input and selections and does not attempt to evaluate whether the predicted performance can be achieved with the selected design. Users may want to use the decarbonation option in the PHREEQ-N-AMDTreat model to help predict performance.

#### 2.2.2.2.2 Maelstrom Aerator (Oxidizer)

The Maelstrom's official trade name is the Maelstrom Oxidizer and is manufactured and marketed by Somerset Environmental Solutions (SES) (Figures 15 & 16). The name "Maelstrom Oxidizer" implies its primary function is to oxidize ferrous iron. While it can accelerate iron oxidization, the primary geochemical function is gas exchange which has a secondary effect of accelerating iron oxidation as exsolving  $\text{CO}_{2(\text{aq})}$  will increase pH. The Maelstrom is typically sized for one minute of retention time configured as a PFR where water enters one side of the tank and flows to the other side. It is a popular decarbonation device in the Appalachian coal fields because of its small footprint, ease of installation, and effectiveness. Most other decarbonation devices require engineering to properly size and design the decarbonation device, tank, and foundation. Maelstrom is a turn-key system that is offered in four standard sizes and can be combined in various sizes to achieve the needs of a site. The cost typically covers all the componentry and the installation of the system on a foundation.

The Maelstrom consists of three parts, the compressed air blower, the plenum box, and the decarbonation tank. The blower compresses atmospheric air (Figure 17) and forces the compressed air into a 0.5 ft height plenum box. The plenum is physically the bottom part of the decarbonation tank system and serves to distribute air to the numerous air tubes in the overlying decarbonation tank (Figure 18). The air flows to the top of the air tube and down between the tube and tube housing before exiting to the water through the stainless-steel air nozzle band (Figure 19). The relatively large orifices on the band are shaped to cause airflow countercurrent to water flow which creates violent mixing between the air bubbles and water. While the air orifices are relatively large, fouling due to calcite, aluminum, and iron scale does occur and requires periodic maintenance (Figure 20). Maintenance usually involves using a cordless driver to remove a bolt that attaches the air tube housing to the air tube. The housing is removed, and the orifices are pressured washed to remove the scale. One benefit is the maintenance can occur while the system continues to operate. The need for maintenance is visually monitored by visually inspecting changes in water level in each row of air tubes in the tank. Figure 21 shows a drop in water level due to the lack of air volume caused by a clogged section of air tubes. The water flow in Figure 21 is from the top of the photo to the bottom.

Some opt to house the blower in an acoustic-silencing housing to lower noise levels in situations where noise is a concern (Figures 17 & 22). Adding a variable frequency drive (VFD) to the electrical control panel provides the ability to control the blower motor speed which controls horsepower and airflow (Figures 23 & 24). This allows operators to calibrate the system to achieve the optimal cost-savings (decarbonation/HP). Neither of these options are included in the AMDTreat cost estimates for the Maelstrom.

The default  $K_{La}$  used in AMDTreat for the Maelstrom is  $0.03195 \text{ sec}^{-1}$ . The typical height of Maelstrom units is 5.0 ft (plenum-0.5, water depth-2.5, air allowance-0.5, & freeboard-1.5 ft)

#### 2.2.1.2.3 Custom Decarbonation

AMDTreat provides the option for users to enter a custom  $K_{La}$  to model decarbonation configured as a continuous stirred or plug flow reactor. When choosing this option it is recommended that the user validates the selection based upon field testing of similar equipment designs or available verifiable performance data.

## 3.0 Decarbonation Module Overview

### 3.1 Layout and Workflow

In general, inputs are on the left-hand side of the module and calculated outputs are on the right. The module inputs on the left-hand side are arranged into five sections: (1) *Water Quality and Flow Input*, (2) *Equipment and System Installation*, (3) *Annual Cost Input* (4) *Other Capital Items*, and (5) *Other Annual Items*. The workflow is for users to begin at the top left-hand side and continue down on the left-hand side entering all the appropriate input parameters.

Module output is provided on the right-hand side of the module. Module outputs are arranged into four sections: (1) *Sizing Summary*, (2) *Capital Cost*, (3) *Annual Cost*, and (4) *Net Present Value*. The *Sizing Summary* section provides the calculated Decarbonation Design Output, Water-Quality Output, Hydrated Lime Savings Assessment (if selected as part of the input), and Decarbonation Tank Sizing Summary information. The estimated cost to install and operate the decarbonation tank, along with the user specified components, is provided under the *Capital Cost* and *Annual Cost* headings. The final output section includes the *Net Present Value* (NPV) analysis. This section provides an estimate of the total cost to operate and maintain this treatment system component for a defined time period.

A general overview of the module input and output sections is presented below, however users are directed to the numerous tool tips located in the module that provide additional detailed information, such as definitions of terminology. In most cases, the tool tips are accessed by selecting the information icon (  ) in each of the subheadings in the module.

### 3.2 Module Inputs

**3.2.1 Water Quality and Flow Input:** The user specifies the design flow in this section. Normally the design flow is used to design the components of the treatment facility and represents the maximum flow of the mine drainage discharge or pumping well. This flow rate is used to calculate the tank retention time for the tank size that has been selected in the next module input section. If the treatment system only experiences the maximum flow for a small percentage of the time, it may be appropriate to use the 50 or 75 percentile flow as the design flow to avoid excess capital and annual costs.

### 3.2.1.1. Raw pH, Temperature, Alkalinity, and TIC:

AMDTreat offers users two methods to calculate the concentration of CO<sub>2(aq)</sub> for the raw water. Users can use the radio button to select either the Alkalinity or TIC method. Both methods require users to specify the raw pH and temperature, and either define the alkalinity or TIC concentration. AMDTreat uses this information to speciate the water and calculate the concentration of CO<sub>2(aq)</sub>. Please note, users must use the TIC method to compute CO<sub>2(aq)</sub> if the raw pH is < 4.5 (~ no alkalinity).

Users must be aware that the accuracy of this model is highly sensitive to the accuracy of the initial input parameters used to calculate CO<sub>2(aq)</sub>. Field-measured pH, alkalinity, and temperature is required, and it is important to try to obtain an in-situ measurement of pH to minimize accidental exsolving CO<sub>2</sub> during measurement, causing pH change. The use of laboratory alkalinity values may result in artificially low results due to consumption by iron oxidation or calcite precipitation during sample transport. TIC samples must be carefully collected. The 125 ml amber glass bottles (w/septum) must be filled and capped underwater, as far below the surface as possible, in a manner to avoid exsolution of CO<sub>2</sub>.

### 3.2.2 Decarbonation System Equipment and Installation:

A decarbonation system consists of the decarbonation unit and a tank. Users make selections under the three subsections to size the decarbonation system. In the Decarbonation Systems Options section, users specify the desired decarbonation retention time and specify the type of decarbonator and reactor design. It is important to note the Maelstrom is a premanufactured turn-key system that does not require user-specified design options. Instead, AMDTreat uses the design flow and determines the optimal number and sizes of Maelstrom units (Table 2). The design retention time for a Maelstrom unit is ~ 1 minute. The cost of the purchase and installation for the Maelstrom estimated by AMDTreat includes a concrete foundation.

Tank Size (LxWxH)(ft)	Tank Volume (gal)	Blower HP	Blower CFM
5 x 5 x 5	300	5	400
5 x 10 x 5	600	10	1,000
10 x 10 x 5	1,200	20	2,000
5 x 15 x 5	1,850	30	3,000

\*Maelstrom is sized for a 1 min. retention time; thus a 300-gal tank is sized for flows up to 300 gpm  
Table 2: Characteristics of Maelstrom decarbonation units.

For non-Maelstrom decarbonation systems, the Non-Maelstrom Decarbonation Tank & Equipment Input section is used to specify the tank construction material, protective coating and depth and freeboard dimensions. AMDTreat sizes the tank in a square configuration. The protective coatings help to prevent corrosion and increase the longevity of the tank. It is standard to use coatings to protect equipment materials in the treatment of mine drainage and the type of coating affects the default equipment lifecycle used in the Net Present Value section of this module. Additionally, this section allows users to select and include the cost of stairs, hand railing, and a catwalk for the decarbonation tank. The stairs are assumed to be positioned at 37 degrees from horizontal and each section reaches 12 ft vertically. The catwalk is assumed to span across the entire tank. Users can opt

to include a variable frequency drive (VFD) to control the speed of the decarbonation motor. This provides the ability to optimize decarbonation while controlling electricity costs. Furthermore, a VFD can offer the treatment system additional performance flexibility with respect to varying the amount of CO<sub>2</sub> removal in order to achieve a desired effluent alkalinity concentration. For example in certain scenarios or during seasonal conditions, allowing a certain amount of aqueous CO<sub>2</sub> to remain in the raw water will allow for higher alkalinities in the effluent which in turn may be more desirable in achieving water quality restoration goals in the watershed.

The water depth within the tank is assigned by AMDTreat based on the design flow (Table 3) and users specify the tank freeboard in this section. The total tank height is the summation of the water depth and the freeboard depth.

Flow (gpm)	<500	>500 < 1500	>1500<3000	>3000<4500	>5000
<b>Tank Depth (ft)</b>	3	5	10	15	20

Table 3: Default water depth based on design flow used by AMDTreat to size decarbonation tank.

For additional information on catwalk, hand railing, stairs, and protective coatings, please refer to the Reaction Tank help file. The Reaction Tank module uses the same equipment as Decarbonation, except for the tank geometry and lack of a Fiberglass option in Decarbonation.

The Non-Maelstrom Decarbonation Tank Foundation section is used to cost the tank foundation. Users specify the load-bearing capacity of the soils for the site along with the unit cost to purchase, deliver, and form a rebar-reinforced foundation. The load-bearing capacity of the solids changes the foundation area. Please see the Reaction Tank help file to learn more about how soil quality affects foundation sizing. The foundation area is assumed to be the footprint of the tank plus a one-ft apron and AMDTreat estimates the capital cost.

### 3.2.3 Annual Cost Input: This section contains the unit costs that effects estimate of annual costs.

*3.2.3.1 Aerator Operational Time:* Some mine drainage treatment systems do not continuously operate. For example, many underground mines have pump and treat systems that are designed to maintain a certain mine pool elevation to prevent a surface discharge. During dry climatic conditions, a mine pool may not have to be pumped for weeks until it fills to an elevation that triggers pumping. The Operational Time annual cost input provides users with the ability to specify the period of time the decarbonation system operators. The operational time will affect the annual electricity cost.

*3.2.3.2 Electrical Unit Cost:* Users must specify the unit cost of electricity for the site they are interested in evaluating. The true cost of electricity includes taxes, transmission, and distribution fees, therefore, one should take the total cost of a monthly electrical bill and divide by the kWh used to determine the electrical unit cost. This cost is used to calculate the annual electrical cost of all electrical components in the treatment system. In the case of decarbonation, it is used to estimate the cost to operate the decarbonation blower.

**3.2.3.3 Hydrated Lime Cost Savings Assessment:** Users can opt to have AMDTreat perform a cost evaluation for decarbonating mine drainage. The cost evaluation consists of estimating the annual hydrated lime requirement to treat to a user-specified treatment pH and comparing that cost to the cost of first decarbonating mine drainage and then adding hydrated lime to the same treatment pH. The non-decarbonation cost, which consists of the annual hydrated lime cost, is compared to the decarbonated treatment cost, which includes both the electrical cost to operate the decarbonation blower and the annual hydrated lime cost, to calculate the net annual savings. This provides the user with an overall estimate of cost savings. See the help file sections for Post Decarbonation Solution and Hydrated Lime Savings Assessment (part of the Sizing Summary section) for additional information.

**3.2.4 Other Capital Items:** The *Other Capital Items* section allows users to capture the capital cost of equipment and other items that are not included in this module. For example, in some cases users may want to include the cost of adding steel gridding across the entire top of the decarbonation tank to allow complete access instead of a catwalk. This can be accounted for here in the *Other Capital Items* section to capture the capital cost.

**3.2.5 Other Annual Items:** The *Other Annual Items* section allows users to capture the cost of other annual items that are not included in this module. For example, users could include the annual subscription cost to conduct electronic surveillance on the treatment system in the *Other Annual Items* section.

## 3.3 Module Outputs

**3.3.1 Sizing Summary:** The Sizing Summary section displays important calculated module outputs, such as estimates of  $\text{CO}_{2(\text{aq})}$  concentrations, prediction of post-decarbonation pH, decarbonation tank dimensions, and estimated blower airflow and horsepower.

**3.3.1.1 Decarbonation Design Output:** This section provides an estimate of the calculated retention time for the decarbonation tank, an estimate of the % of  $\text{CO}_{2(\text{aq})}$  removed by the simulated decarbonation system, and provides the gas transfer coefficient ( $K_{\text{la}}$ ) used to model the decarbonation system. The % of  $\text{CO}_{2(\text{aq})}$  removed is calculated by first speciating the water based on the user-specified pH, Temp and either the specified alkalinity or TIC concentration. Next AMDTreat assigns a  $K_{\text{la}}$  based on the decarbonation unit selected, an integrated form of Equation 12 is used to predict the final  $\text{CO}_{2(\text{aq})}$  concentration after decarbonation. The % removal is determined from the initial and final  $\text{CO}_{2(\text{aq})}$  concentrations.

**3.3.1.2 Water Quality Output:** This section provides the results of the speciation calculations for the pre and post-decarbonated water based on user-specified values for pH, Temperature, and either alkalinity or TIC. monitored to understand how sensitive speciation calculations are to user input and selections. This section is subdivided into two sections, *Initial Solution* and *Post Decarbonation Solution*.

**Initial Solution (raw water):** This section provides the results of using the user specified values to speciate the raw water. The calculated value for the  $\text{CO}_{2(\text{aq})}$  concentration represents the amount of  $\text{CO}_2$  available for decarbonation. If the “Alkalinity” method (under the Water Quality & Flow Input section) was selected to estimate  $\text{CO}_{2(\text{aq})}$

concentrations, then the water is speciated and the TIC concentration is calculated and shown in this subsection. If the “TIC” method (under the Water Quality & Flow Input section) was selected to estimate  $\text{CO}_{2(\text{aq})}$  concentrations, then the water is speciated and the Alkalinity concentration is calculated (if present in the water) and shown in this subsection.

*Post Decarbonation Solution:* This section provides estimates of the pH, TIC,  $\text{CO}_{2(\text{aq})}$ , and Alkalinity after decarbonation has been simulated using the user-selected decarbonation device. It is important to note this section provides estimates assuming the solution solely consists of water and TIC species and does not consider the effect other reactions, such as iron oxidation or aluminum hydrolysis, will have on the post decarbonation pH, alkalinity, or TIC. Users are encouraged to use the PHREEQ-N-AMDTreat tool to model the behavior of complex solutions in a decarbonation scenario. The decarbonation model is a simple tool that provides a rough estimate of the effect decarbonation will have on a carbonated solution.

*3.3.1.3 Hydrated Lime Savings Assessment:* This section provides an estimate of the annual net savings of decarbonating mine drainage. This section is only active if the *Hydrated Lime Cost Saving Assessment* is checked under the *Annual Cost Input* section. The concentration of  $\text{CO}_{2(\text{aq})}$  outgassed is provided under the *Water Quality Output* section by comparing the pre and post-decarbonation concentrations. This section recasts the concentration outgassed in terms of the acidity that would be released and consumed by an alkali chemical to achieve the treatment pH. The  $\text{Ca}(\text{OH})_2$  Savings is the value for  $\text{CO}_2$  Acidity Outgassed recast in terms of Hydrated Lime and the  $\text{Ca}(\text{OH})_2$  Cost Savings represents the chemical savings due to decarbonating the  $\text{CO}_2$  instead of neutralizing it during alkali addition. Cost to Operate Decarbonation Blower is calculated by using the blower HP and the unit cost of electricity to estimate the cost of Decarbonation. The Net Cost Savings is the  $\text{Ca}(\text{OH})_2$  Cost Savings minus the Cost to Operate the Decarbonation Blower.

*3.3.1.4 Non-Maelstrom Decarbonation Tank Sizing Summary / Maelstrom Decarbonation Tank Sizing Summary:* The last section in the Sizing Summary provides specifications and dimensions for the Decarbonation System. If a Maelstrom is selected, this section is titled Maelstrom Decarbonation Tank Sizing Summary and provides the number and size of tanks estimated by AMDTreat for the design flow, along with the total blower HP and airflow. If a decarbonation system other than a Maelstrom is selected, this section will be titled Non-Maelstrom Decarbonation Tank Sizing Summary and will display the tank dimensions along with blower estimates.

**3.3.2 Capital Cost:** This section provides the estimated costs for the selected decarbonation components. If Maelstrom was selected, a single cost will be provided since Maelstrom is a turn-key system and the purchase cost includes the decarbonation system, foundation, and installation. For all other decarbonation units, users can either specify the installation costs or estimate the installation cost as a percentage of the capital cost.

**3.3.3 Annual Cost:** The annual cost section provides an estimate of the annual cost to operate and maintain the Decarbonation system. The annual operation and maintenance cost can be either specified or estimated as a percentage of the capital cost. Similarly, the annual Electric cost can be specified or

estimated based on kW requirements of the electrical componentry and the specified unit cost of electricity.

**3.3.4 Net Present Value:** The Net Present Value (NPV) section determines the cost to operate a treatment system component over a specified time period. The NPV calculates the present-day financial investment required to generate the income to pay for future operation and equipment/materials replacement costs. Both **Financial Variables** and **Cost Categories** are required to calculate the NPV.

*3.3.4.1 Financial Variables* - The *Term of Analysis*, *Inflation Rate*, and *Rate of Return* are three variables used in the NPV calculations. The default values for these terms are shown under the *Net Present Value* section of each module. Users must access the *Net Present Value* menu at the top of the main user interface to change the default values as they would apply to all modules used for an entire treatment system. While NPV is determined for each AMDTreat module activated by the user, the goal is to determine a total NPV for an entire mine drainage treatment system project (a collection of cost estimates for individual modules creates a treatment system project in AMDTreat). Therefore, single values for *Term of Analysis*, *Rate of Return*, and *Inflation Rate* are applied to all modules and cannot vary between modules.

- Term of Analysis: The time period used by the NPV calculation to determine the financial investment required to pay for all future costs of the treatment system.
- Inflation Rate: Represents the average price increase of goods and services over time. AMDTreat uses the inflation rate to calculate the future cost of the annual operation and maintenance (O&M) and recapitalization items.
- Rate of Return: Describes the expected profit on an investment.

*3.3.4.2 Cost Categories* - For each treatment module, AMDTreat provides a list of recommended equipment and materials that require recapitalization. In addition, AMDTreat provides recommendations (default values) for life cycle and replacement percentage. Users can click on the default values for *Life Cycle* or *Replacement Percentage* and use the +/- buttons to change the default values. In addition, users can select *Custom Cost* and enter a new cost to represent the current cost of the equipment. Users can add new recapitalization items or deactivate/delete existing items for calculating the NPV.

An example of how the recapitalization variables are used to determine NPV is to consider the following hypothetical scenario. Assume a vertical turbine pump has a life cycle of 50 years but requires the pump motor to be rebuilt every 20 years. Assume the present-day cost to purchase the motor is \$500,000, and the cost to remove, rebuild, and reinstall the pump motor is \$20,000. Now assume we want to determine the amount of investment required today (NPV) to generate the income to pay for the future cost of rebuilding the pump motor over a 50-year *Term of Analysis*, which is also equal to the life cycle of the pump. Assume an *Inflation Rate* of 5.0% and *Rate of Return* of 8.1%. The goal is to place the money in a relatively secure investment vehicle to generate 8.1% annually. The NPV will calculate the size of investment required to generate income for future costs.

There are several ways to model the replacement cost. One way is to replace 4% of the present-day cost of the pump (4% of \$500,000 = \$20,000) with a life cycle of 20 years. If the *Term of Analysis* is 50 years, then the entire pump would not require recapitalization since the life cycle of the pump is 50 years. However, the motor would require two replacements (50 years / 20 years = 2.5 rounded down to 2).

To determine the NPV to recapitalize rebuilding of the motor, AMDTreat calculates the future cost to rebuild the motor at each life cycle, 20 and 40 years. The program uses the *Inflation Rate* to inflate the present-day default cost to rebuild the motor in 20 and 40 years from now. While the present-day cost to rebuild the pump motor is \$20,000, the future cost to rebuild the motor in 20 years at a 5.0% *Inflation Rate* is \$53,065 and \$140,799 in 40 years (Equation 17). Assuming an 8.1% *Rate of Return*, the 50-year NPV for the pump is \$17,422. In other words, an initial investment of \$17,422 is needed at an annual *Rate of Return* of 8.1% to generate the investment income required for the two motor rebuilds over the 50-year life cycle of the pump.

Cost to rebuild pump motor in 20 years =

$$\text{Present Day Cost} \times (100\% + \text{Inflation Rate})^{20} = \$20,000 \times (100\% + 5\%)^{20} = \$53,065 \quad (17)$$

- Annual Operation and Maintenance Cost: By default, AMDTreat transcribes the annual O&M cost from the Annual Cost section to the NPV section. The program assumes the module is being used to first estimate the annual cost for a treatment system component, so it automatically transcribes the annual cost to the NPV section. If this is not the case or the user wants to use some other annual cost, the “Use Custom” box can be selected to allow the user input of a different annual cost to utilize in the NPV calculation.
- Recapitalization Cost: Certain treatment system components, especially mechanical and water conveyance equipment, require periodic replacement. The recapitalization cost of an item is an estimate of the amount of money required to pay for future replacement costs for the item. In addition to the Financial Variables described above, three additional values are required to calculate the NPV of recapitalization costs, the Present-Day Equipment Cost, the Life Cycle, and the Replacement Percentage.
- Default Cost: This represents the current cost to purchase the equipment or material.
- Life Cycle: The time frame between equipment or material replacement is termed as its Life Cycle. Some equipment manufacturers provide recommended life cycles for their equipment to provide consumers with an estimate of how long the equipment is expected to be operational. Some life cycles, such as those used for treatment media (limestone), are based on best professional judgement. Some operators prefer to periodically purchase and replace equipment before failure to preserve the continuity of operations, while others wait until failure to replace an item.
- Replacement Percentage: The Replacement Percentage is an adjustment factor to the Default Cost to accommodate situations where the entire piece of equipment or all of the

material does not require recapitalization. For example, a passive treatment component may be designed to contain enough limestone to neutralize the acidity load for 20 years, however, the accumulation of metal hydroxide precipitates within the void space of the limestone layer may require that 25% of the limestone be replaced every 7 years to prevent hydraulic failure such as plugging or short-circuiting. For this scenario, the initial cost of the limestone making up the limestone layer is discounted by 75% and assigned a life cycle of 7 years to determine the amount of money required to cover the cost of replacing 25% of the limestone layer every 7 years over the Term of Analysis.

#### *3.3.4.3 Rationale for Recapitalization Recommendations:*

Recapitalization recommendations are based on either manufacture recommendations (per discussions with manufactures) or professional experience of the AMDTreat Team. In either case, the recommendations may not apply to all situations. Users are encouraged to customize the recapitalization assumptions to their treatment scenario. AMDTreat Team members located in Pennsylvania and West Virginia have a collective experience in design, funding, and/or operation/maintenance for over 100 passive treatment systems. The AMDTreat Team held discussions on personal experience to develop a list of recapitalization recommendations. Users may have different experience and opinions than those listed.

By default, AMDTreat includes a list of six recapitalization items for a non-Maelstrom decarbonation system and one for a Maelstrom system. The only recapitalization item for a Maelstrom is for the Blower. Users can delete or modify any of the default Recapitalization items by either deselecting the item or by setting the Replacement % to zero. If the item is deselected the Total Cost for the item will still be shown but the cost will be subtracted from the NPV Cost, shown in the NPV Heading. For example, the default value for the lifecycle of the aerator/blower is 10 years due to experience with decarbonation systems. However, users may opt to periodically rebuild the blower motor instead of purchasing new. In this case, users could opt to add a recapitalization cost to rebuild the motor every 10 years and replace the entire blower unit every 30 years. Users are free to fully customize the replacement items, including adding new items or deleting default items.

**Decarbonation Tank:** The Life Cycle of a steel reaction tank depends on how well the bottom of the tank is protected from ground moisture, how often it is sandblasted and painted, and whether the tank is vandalized. After considering the condition and life of many steel tanks, the AMDTreat team feels 35 years is a good estimate as long as the tank is on a concrete or gravel foundation or on wooden cribbing to prevent contact with ground moisture. A much longer Life Cycle may be appropriate if the tank is cleaned, primed, and painted when corrosion becomes visible. Concrete reaction tank Life Cycle is defaulted to 75 years based upon observations of existing systems that AMDTreat members have observed. This assumption is only valid if protective coatings are periodically reapplied.

The default Life Cycle for a fiberglass tank is 25 years. This value was determined after discussing tank longevity with chemical distribution companies and tank manufactures assuming the tank would be placed outside and open to the atmosphere.

**Catwalk & Stairs with Handrails:** The default Life Cycle of both the Catwalk and Stairs with handrails is set at 20 years at 100% Replacement. These are safety and access items so the user should consider if the life cycle value needs adjusted.

**Tank Protective Coating:** This item would only apply to the concrete and steel tanks. The fiberglass tank would not have a protective coating on the tank. Depending on the specific coating (Alkyd, Epoxy, or Zinc/Urethane) selected the default Life Cycle will be different.

**Decarbonation Aerator/Blower:** The default Life Cycle is 10 years and at 100% Replacement after surveying several treatment operators.

**Variable Frequency Drive:** The default Life Cycle is 20 years and at 100% Replacement.

### 3.4 Assumptions of Design Sizing and Costs

AMDTreat is a cost estimation model that uses assumptions to provide treatment sizing and both capital and annual cost estimates. While there are many assumptions in the program, the assumptions that follow are important for the Decarbonation module.

1. AMDTreat assumes the gas transfer coefficients assigned to each of the decarbonation devices are representative of that type of device and scalable. This is not the case since the specifics on the decarbonation devices and tanks are not known and are not represented in AMDTreat. The transfer coefficients were measured by the Team at numerous locations and a representative coefficient was selected for a type of decarbonation system. These coefficients may not apply to your situation. A prudent approach would be to visit a site with a desired decarbonation system, measure the transfer coefficient, and use the coefficient and AMDTreat to model different sizing scenarios.
2. The effect of Decarbonation on species concentrations assumes an ideal solution containing only water and TIC species. Mine drainage is a complex solution and various reactions can occur during Decarbonation that will affect results. This module should be used for approximation only. Fully scale geochemical models, like PHREEQ-N-AMDTreat or other codes should be used to fully predict solution changes.

When choosing a Custom Decarbonation option AMDTreat team recommends that the user validates the selection based upon field testing of similar equipment designs or available verifiable performance data. 5.0 Figures

## 4.0 Figures

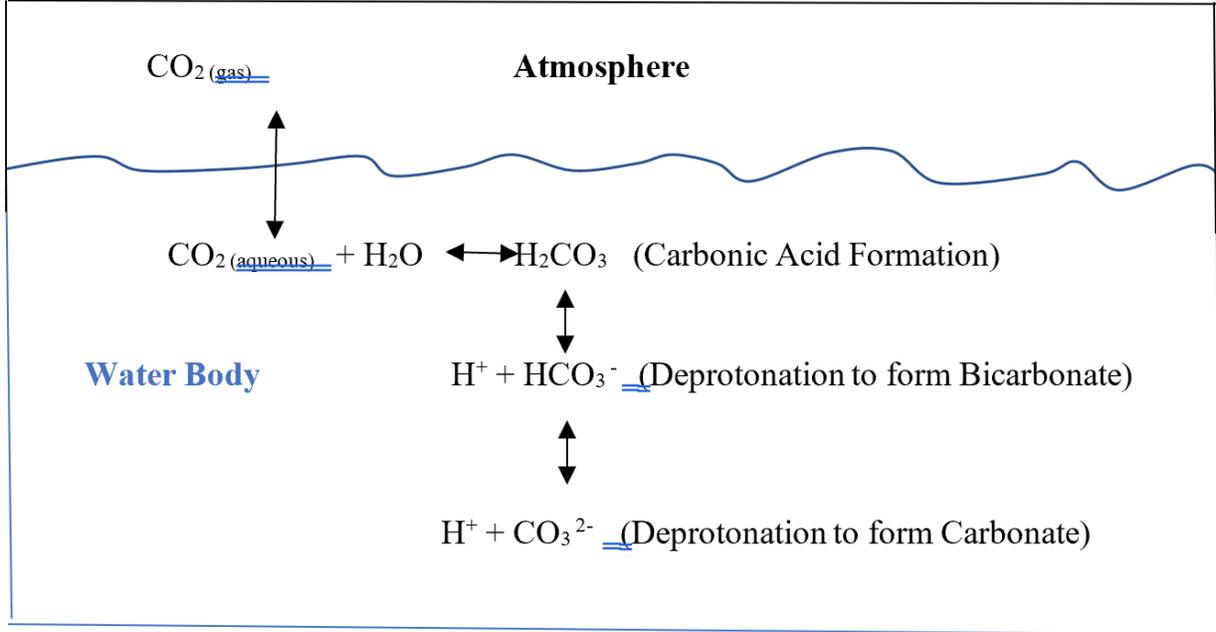


Figure 1: Relationship between gaseous and aqueous carbon dioxide species.

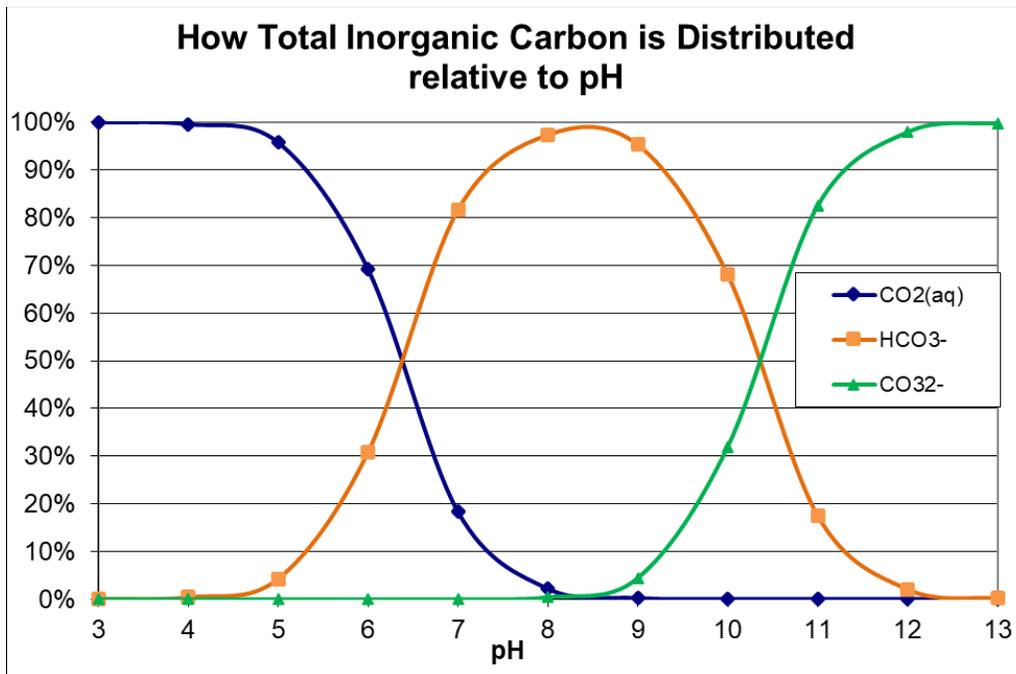


Figure 2: Distribution of TIC based on pH.

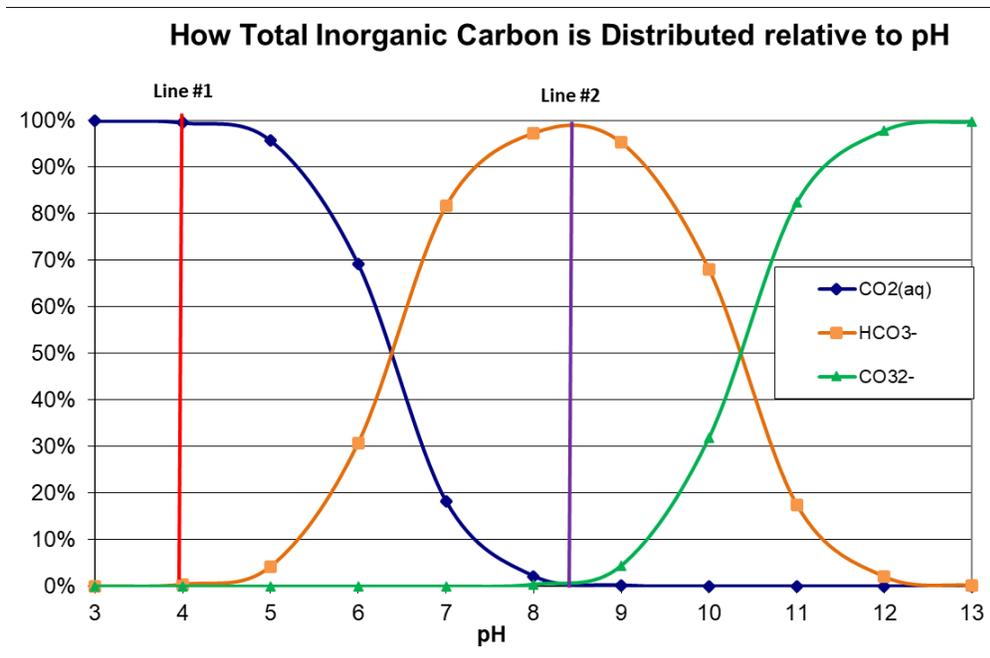


Figure 3: Deprotonation of TIC species when pH is raised during treatment.

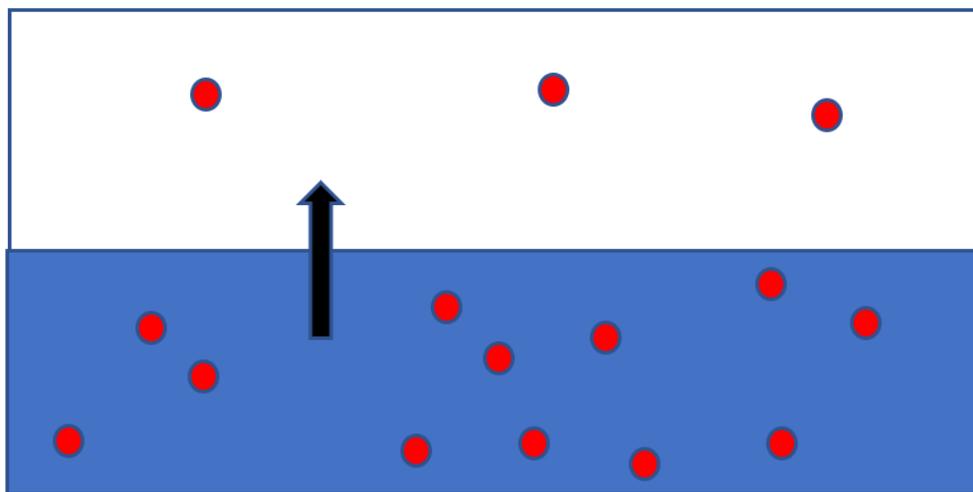


Figure 4: Depiction of a shallow pond containing carbonated mine drainage. Red circles represent CO<sub>2</sub> molecules.

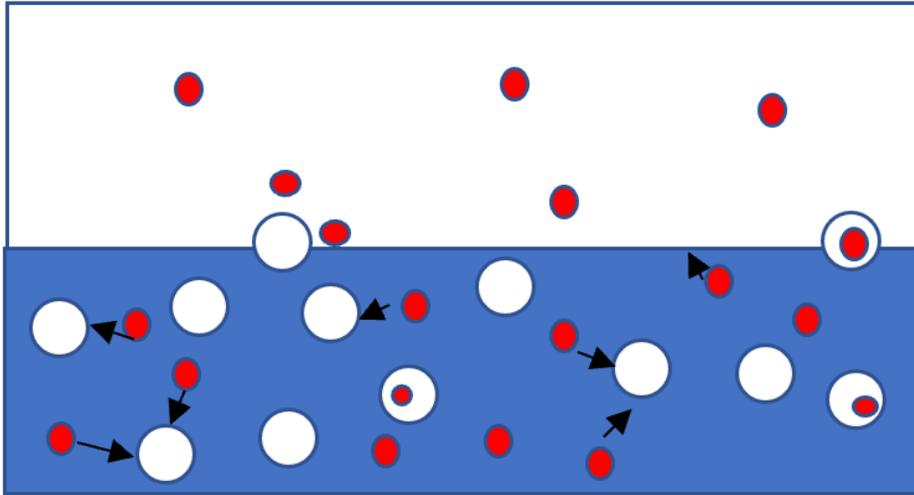


Figure 5: Pictorial showing the mixing of compressed air into the water, which changes the distance between the CO<sub>2</sub> molecules and the air/water interface (increases gradient), the air bubbles increase the overall surface area and enhance transfer.



Figure 6: Dye testing on a decarbonation unit to determine the CO<sub>2</sub> transfer coefficient.



Figure 7: Dye testing on a Maelstrom Oxidizer decarbonation unit to determine the  $\text{CO}_2$  transfer coefficient.



Figure 8: Two surface aerators in a plug flow reactor providing decarbonation.



Figure 9: A surface aerator mounted in a continuous stirred reactor pulling water to the surface and creating droplets under the splash hood. Note the bubble froth promotes strong gas transfer, however, better results would be seen with froth in a plug flow reactor.



Figure 10: Fine diffuser aeration system with a piping grid at the bottom of a tank and disk diffusers.



Figure 11: Fine diffuser aeration system with a piping grid at the bottom of a tank and tube diffusers.



Figure 12: Ethylene Propylene diene monomer (EPDM) rubber disk diffusers.



Figure 13: Ethylene Propylene diene monomer (EPDM) rubber tube diffusers.



Figure 14: Fine bubble diffuser decarbonation system configured as a plug flow reactor.



Figure 15: Maelstrom Oxidizer aerator unit. The blower enclosed in acoustic silencing housing is shown in the background and the aeration unit is shown in the foreground.



Figure 16: Maelstrom Oxidizer aerator unit used to decarbonate anoxic and carbonated underground mine drainage. Compressed air blower not visible in photos.



Figure 17: Compressed air blower housed in acoustic-silencing housing. Maelstrom is located in a residential area and noise was a concern. AMDTreat does not include the cost of acoustic housing.



Figure 18: Maelstrom decarbonation tank showing vertical baffles separating the rows of air tubes.



Figure 19: Photo showing the air tube (steel tube in tank) with air tube housing removed. Compressed air from the plenum flows to the top of the air tube and down in between air tube and housing before exiting through the stainless-steel air nozzle band.



Figure 20: Air Tube removed for maintenance. The air orifices on the stainless-steel band at the bottom of air tube are pressure washed to remove scale and precipitate from clogging orifices. Note the orifices are directional and results in half of the air tube forcing air horizontally and countercurrent to the water flow. This causes strong mixing between water/air that is optimal for gas transfer.



Figure 21: Notice reduced water levels within the red box of the Maelstrom on the right side of the photo. The reduced airflow reduces the water elevation and is a sign the stainless steel air nozzle banks are clogged and require cleaning.



Figure 22: Sixty HP blowers enclosed in acoustic building to reduce noise. The Maelstrom Tanks sit above the building on top of the steel structure.



Figure 23: Spencer blower and electrical panel with variable frequency drive control panel inside of building shown in Figure 22.



Figure 24: Variable Frequency Drive control panel provides the ability to control the blower output. This provides the ability to alter the decarbonation/horsepower ratio to optimize treatment costs.