**Decarbonating at the St. Michael Treatment Plant: Effect on Cost, Sludge, and Sedimentation**

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**Extended Abstract**

 Rosebud Mining’s St. Michael mine drainage treatment plant was retrofitted for decarbonation to reduce CO2 (aq) -based acidity before pH adjustment with slaked lime. The retrofit process included a comprehensive decarbonation evaluation and selection process. The evaluation included field-measuring CO2 (aq) mass transfer coefficients for various operating diffused-air and surface aerator decarbonation units, configured as both plug flow and continuous-stirred reactors. The selection process entailed using the CO2 (aq) mass transfer coefficients to predict decarbonation, and corresponding lime reduction, as if the decarbonation units were installed at St. Michael. The predicted results were used as the basis for a cost/benefit analysis to identify the time period for financial return.

 Based on the evaluation results, Rosebud Mining selected the Maelstrom Oxidizer decarbonation system because the concentration of CO2 (aq) was predicted to be reduced from 189 mg/L to 16 mg/L with 46 seconds of hydraulic retention, possessed a compact size for retrofit, and would result in a quick financial payback.

 Four Maelstrom Oxidizers were installed in August 2014. At a total flow of 3600 gpm, the four units reduced CO2 (aq) as predicted from 189 mg/L to 18 mg/L with each unit possessing 46 seconds of hydraulic retention and 3250 CFM of air flow. The pebble lime dose decreased from 10.1 tons/day to 3.8 tons/day.

 An unanticipated consequence of decarbonation was decreased sedimentation performance in the clarifier due to decreased calcite formation and solids loading. The combination of changing the sludge recirculation ratio, implementing a two-staged polymer dosing scheme, and increasing the sludge wasting frequency returned sedimentation performance to pre-decarbonation levels.

 Considering lime savings and additional electrical and polymer costs, the net annual cost savings exceeds $300,000 USD at the 3600 gpm pump rate.

**Background**

 Rosebud Mining operates the Mine 78 underground coal mine near Johnstown, Pennsylvania. Mine 78 is located on the Upper Freeport bituminous coal seam, which is positioned 160 ft above the abandoned and flooded St. Michael mine. Hydraulic head pressure forces water from the St. Michael mine pool up and into the overlying Mine 78 coal reserves. Rosebud developed a plan to pump and treat the St. Michael mine pool to dewater and gain access to Mine 78 coal reserves that could last for thirty years.

 Rosebud installed dewatering pumps in an existing mine shaft and constructed a 14.4 MGD mine drainage treatment plant near the town of St. Michael. The treatment plant uses two slakers to convert pebble CaO to a Ca(OH)2 slurry and two 225-ft diameter clarifiers, which operates in parallel. The plant uses a sludge densification process developed by Bethlehem Steel and first described by Kostenbader and Haines in two publications (Kostenbader and Haines 1970; Haines and Kostenbader 1970) and later by Bosman (1974). The process involves pumping accumulated sludge from a clarifier to a conditioning tank where it is mixed with Ca(OH)2 slurry before being discharged to the reaction tank to react with untreated mine drainage. Previous investigators concluded this conditioning step adjusts the surface charge on FeOOH precipitate causing dissolved constituents to precipitate on the surface of the recycled sludge. The process results in improved precipitate particle growth and a less hydrated sludge. In addition, they determined recirculated solids act as seed particles promoting precipitation and particle agglomeration (Wee, Yong, Gan et al. 2005). Sludge densities of up to 30 weight % can be achieved with this process (Zick et al. 1999). The densification process can improve sedimentation and lower costs by eliminating or reducing polymer dose and reducing episodic de-sludging.

 The plant commenced operation in July 2013. The discharge permit required a total iron concentration of < 3.0 mg/L at the outfall; however, the dense sludge process was able to routinely achieve an effluent total iron of 1.5 to 2 mg/L without polymer addition. The plant consumed 33 tons of CaO per day at a daily lime cost of $4,620 (2013 USD) when operated at the maximum capacity of 10,000 gpm. The high lime consumption prompted a cost-reduction evaluation that recommended retrofitting the plant for a decarbonation step before pH adjustment with conditioned sludge. This paper details the analysis and results of retrofitting the plant. First, the effect of total inorganic carbon species on alkali chemical consumption is reviewed. Second, the evaluation method used to analyze and select a decarbonation unit is presented. Lastly, the results of installing the decarbonation unit and its effect of lime consumption and treatment performance are presented.

**Total Inorganic Carbon**

 Charles Cravotta sampled 100 mine drainage discharges in Pennsylvania and found the drainage is commonly supersaturated with carbon dioxide, with a median partial pressure that is 100 times that of the atmosphere. Probable sources of carbon dioxide in underground coal mine drainage include the oxidization of mine gases, such as methane, (Eq.1), reactions between acid mine drainage and carbonate minerals (Eq. 2), and reactions between acidic mine drainage and carbonate–rich water infiltrating into the mine (Eq.3).

CH4 + 2O2 → CO2(g) + 2H2O (1)

CaCO3 + 2H+ → CO2(aq) + Ca2+ + H2O (2)

H+ + HCO3- → CO2(aq) + H2O (3)

 Many abandoned underground coal mines are partially flooded and contain both a mine pool and a mine atmosphere. As mine gases oxidize, the mine atmosphere becomes saturated with CO2(g) many times above ambient atmospheric concentrations. CO2(g) dissolves into the underground mine pool according to Henry’s law:

CO2(aq) → KH PCO2 (4)

A small fraction of CO2(aq) reacts with water to form carbonic acid:

CO2(aq) + H2O → H2CO3 (5)

Both CO2(aq) and H2CO3 are often referred to as aqueous carbon dioxide. H2CO3 will dissociate into in two steps:

H2CO3 → HCO3- + H+ (6)

HCO3- → CO32- + H+ (7)

 Total Inorganic Carbon (TIC) refers to the sum of dissolved inorganic carbon species in water, mainly H2CO3, HCO3-, and CO32-. To properly understand the effect of dissolved carbon dioxide on treatment, one has to determine whether the treatment system acts as an *open* or *closed* system.

 Conventional treatment of mine drainage is typically accomplished by a rapid addition of a caustic chemical for acid neutralization and metal removal by hydroxide precipitation (Kuyucak, 1998). Because of the rapid pH adjustment, it is assumed no significant mass transfer of CO2(aq) occurs between the solution and atmosphere and TIC remains constant. The system is considered *closed* and a Bjerrum plot can describe the distribution and dominance of TIC species over a Ph range. Dosing mine drainage with a caustic chemical to increase the pH from 3.0 to 9.5, for ferrous iron and manganese precipitation, would result in the deprotonation of H2CO3 to form HCO3- (Eq. 6) and CO32- (Eq. 7) as carbonate equilibria shifts to reestablish equilibrium to the increased pH condition.

 The diprotic nature of carbonic acid can significantly increase caustic chemical consumption. The amount chemical consumption is increased depends on the concentration of CO2(aq) and on the treatment pH endpoint.

0.5Ca(OH)2 + H2CO3 → 0.5Ca2+ + H2O + HCO3- (8)

Ca(OH)2 + H2CO3 → Ca2+ + 2H2O + CO32- (9)

 Tom Jageman recognized the increased chemical costs caused by dissolved carbon dioxide in mine drainage and proposed decarbonating mine drainage prior to caustic chemical addition. Coal mining companies in Pennsylvania began decarbonating mine drainage by installing a floating surface aerator in a steel or concrete tank configured as a continuous stirred reactor (CSR). Decarbonation is achieved by the surface aerator pumping carbonated mine water to the surface of the tank where the water is broken into droplets under a deflector shield and sprayed into the air for gas transfer. The rate of CO2(aq) mass transfer from the liquid to gas phase (Stumm and Morgan 1996):

∆ CO2(aq)/time = -KLCO2, a (CO2(aq)atm – CO2(aq)raw) (10)

 The small droplets of water produced by the surface aerator increase the gas-liquid interfacial area per liquid volume ratio (a), which increases the mass transfer of carbon dioxide. In most cases, decarbonation systems were sized based on bench testing or from mimicking other treatment systems, both of which often resulted in unoptimized decarbonation systems.

**Methods**

Decarbonation Evaluation

 A three-step evaluation was used to select a decarbonation system at St. Michael: 1) determine field-measured bulk CO2(aq) gas transfer coefficients for various operating decarbonation systems, 2) predict decarbonation performance and lime reduction at St. Michael using the determined gas transfer coefficients, and 3) conduct a financial analysis to identify the most cost-effective decarbonation system.

Field-Measured Bulk Gas Transfer Coefficients

The performance of the decarbonation step used at Lancashire and Renton was evaluated by calculating the rate of CO2(aq) mass transfer from the liquid to gas phase (Stumm and Morgan 1996):

∆ CO2(aq)/time = -KLCO2, a (CO2(aq)atm – CO2(aq)raw) (11)

 *KL* and *a* were combined to compute a bulk mass transfer coefficient (KLCO2,a) for the surface aerator/tank system. Values for KLCO2,a were calculated by measuring field pH and temperature and collecting TIC and aqueous chemistry samples at the influent and effluent of the decarbonation tank. Geochemist Workbench was used to speciate the samples to quantify the decrease in CO2(aq) concentrations across the tank. Values for CO2(aq)atm were modeled by equilibrating the raw water with a partial pressure of carbon dioxide of 10-3.4 atm to simulate ambient atmosphere conditions. A differentiated form of equation (11) was used to model the decarbonation systems as continuous stirred reactors.

 The diprotic nature of aqueous carbonic acid can significantly increase the caustic chemical consumption during mine drainage treatment. When a caustic chemical is added to carbonated mine drainage, the increase in pH disrupts the carbonate equilibria and the reactions (Eq. 5 and 6) will shift to reestablish equilibrium. As pH is increased, H2CO3 and HCO3- will deprotonate, release acidity, and increase the caustic chemical consumption.

0.5Ca(OH)2 + H2CO3 → 0.5Ca2+ + H2O + HCO3-  (12)

The summation of H2CO3, HCO3-, and CO32- are referred to as total inorganic carbon (TIC). If a caustic chemical is added to acid mine drainage resulting in a pH increase, the equilibria between the different species changes. The concentration and dominance of these species is pH dependent in a closed system as illustrated in the Bjerrum plot.

Kuyucak, N. 1998. Mining, the environment and the treatment of mine effluents. Int. J. Environmental Pollution, Vol. 10, No. 2