APPLICATION OF CARBON DIOXIDE TO REDUCE WATER-SIDE LIME SCALE IN HEAT EXCHANGERS

PETER W. HART*, GARY W. COLSON, JEFFERY BURRIS

The MWV mill in Evadale, TX, has been experiencing significant lime-scale problems with its peroxide bleaching stage heat exchanger. Typically, the exchanger has had to be removed from service after 20 to 30 days of operation and cleaned (hydroblasted) to remove lime scale. Carbon dioxide was applied to the water side of the heat exchanger in an effort to buffer and to lower the water pH. By lowering the pH of the mill water from approximately 8.5 to less than 7.5, the solubility of calcium carbonate in the water was substantially increased, effectively eliminating lime scale formation in the heat exchanger.

INTRODUCTION

The MWV pulp mill in Evadale, TX, has a long history of plugging heat exchangers with formation of lime scale. Excessive scale formation has resulted in significant capital, maintenance, and operating costs over the years. Complete plugging of tubes has resulted in equipment failure, which has forced pulp mill and bleach plant processes to operate at suboptimal temperature conditions. Multiple heat exchangers are currently operating with several hundred plugged tubes as a direct result of scale formation. Analysis has determined that the primary component of the plugging material is lime scale, a form of calcium carbonate (CaCO₃).

In general, the formation of process scale within heating and cooling equipment would not be a noteworthy occurrence, except that these heat exchangers are plugging on the water side instead of on the process side of the tubes. The Evadale mill uses moderately hard ground water in its heating and cooling water systems. Typically, the pH of this water is approximately 8.3–8.5. The overall hardness of the water was determined to be 50.6 mg/L as CaCO₃, with Ca⁺ contributing 39.5 mg/L as CaCO₃ to the total. Manganese made the next largest contribution to hardness, 11.1 mg/L as CaCO₃.

Scale build-up in piping systems, which often occurs in hard water areas or in alkaline processes and effluent streams, severely restricts flow, which increases head loss and necessitates piping replacement or off-line cleaning [1]. Both of these force process areas to operate in a suboptimal manner, which negatively impacts the economic performance of the mill.

Water systems may be chemically treated either to discourage scale formation in naturally hard or oversaturated water or to encourage scale formation in naturally corrosive waters. Potable water systems typically treat water by controlling to a pH level that allows only a small amount of scale to form in the distribution system to prevent pipe corrosion. In corrosive waters, treatment involves forcing scale formation by adding lime or caustic [2]. Methods to prevent scale formation from hard or oversaturated water tend to be more difficult and costly.

Potential solutions

Water-side scale formation can be minimized by adding a strong mineral acid to the process water [3]. Another method is to add phosphate scale inhibitors to the water system [4]. Both methods are relatively problematic. The use of strong...
mineral acids can result in large pH swings in the water system, resulting in significant increases in corrosion within the water distribution system or in process heat exchangers. Premature equipment failure may occur because of the increased corrosion levels resulting from pH swings. The addition of phosphate-based antiscalers increases the operating cost of the system, resulting in economic difficulties. Other potential methods of controlling water hardness exist, for example, ion exchange systems, reverse osmosis systems, and ultrafiltration methods, but their capital and operating costs are prohibitive [5].

One potential method of controlling the pH of a water system to a level low enough to prevent scale formation without subjecting the system to the excessive pH swings associated with the use of strong mineral acids is the use of carbon dioxide [6]. Several successful laboratory and field tests have been performed by the U.S. Army Construction Engineering Research Laboratory [3]. These tests were conducted in locations with potable water of high hardness and low total dissolved solids content. More recently, carbon dioxide has been used as a method of lowering alkaline process wastewater pH [7].

CHEMISTRY OF THE SYSTEM

In a water system, as the pH of the system drops, the solubility of lime scale increases. Equation 1 shows the chemical equilibrium between CO₂ and lime scale:

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\text{CaCO}_3 (s) + \text{CO}_2 (g) + \text{H}_2\text{O} \leftrightarrow \text{Ca}^{2+} (\text{aq}) + 2 \text{HCO}_3^- (\text{aq}) \tag{1}
\]

The concentration of HCO₃⁻ is highly pH-dependent and tends to be at its maximum at a pH of approximately 8.3, which is roughly the same pH as the mill water system. At a pH near 8.3, the mill water system is uniquely suited to force lime scale out of solution and to form scale. Using the solubility constant, K_{sp}, of calcium carbonate and fixing the pH of the solution, it is possible to calculate the molar solubility of calcium carbonate in water. Figure 1 shows the solubility of lime scale as a function of pH. As can be seen in Fig. 1, as the pH drops from around 8 to around 6, the solubility of lime scale in water increases 20-fold.

The sudden increase in lime-scale solubility with a drop in pH from 8 to 6 suggests that a small decrease in the pH of the mill water system might be sufficient to minimize or eliminate the lime-scale problem in the mill heat exchangers. Equilibrium modeling was carried out to determine the amount of carbon dioxide that would be required to lower the pH of the mill water system sufficiently. Figure 2 shows the carbon dioxide dosage profile and the resulting pH of the mill water system. The addition of approximately 38 mg/L of carbon dioxide should be sufficient to lower the pH of the mill water from 8.5–8.6 to about 7.0. Only about 10 ppm of carbon dioxide would be required to lower the mill pH to about 7.5. Estimates from the solubility limits suggest that the vast majority of the lime-scale problems in the bleach plant heat exchangers should be minimized or eliminated at an operating pH of 7.5. With a 7.5 pH target, potential corrosion issues should be substantially reduced.

MILL-SCALE IMPLEMENTATION

As a result of the favorable predictions from theoretical understanding and modeling of the mill system, it was decided to attempt to use carbon dioxide in the mill water going into the heat exchanger in the peroxide stage of the pine bleach plant. This heat exchanger typically plugs with lime scale to the point that it has to be removed from service within 20–25 days of being put into service. The scale forms on the water side of the exchanger and starts forming near the exit. The mill started the trial by adding pure liquid CO₂ to the water side of the exchanger. Three initial application concerns were identified: 1) the CO₂ must be injected properly into the water so that it has time to mix and to drop the pH before the heat exchanger; 2) the CO₂ must be uniformly diffused in the water. Otherwise, there is a risk of localized carbonic acid attack on mild steel; and 3) CO₂ will gas out of the water where there is high agitation in the system, at which point the pH will return to its starting value, and scale formation will occur at or slightly after this location in the system.

The CO₂ injection system consists of CO₂ storage, distribution piping, electric and pneumatic control panels, and a gas/liquid contactor. Carbon dioxide addition is controlled by means of a simple on/off or modulating proportional control system that uses a pH control signal to regulate the flow of CO₂ by means of a control valve [8].
To ensure that the process experiences uniform CO₂ mixing and that the rate of corrosion of the heat exchanger tubes is not increased, a coupon rack was installed in the mill water system to determine the corrosion rate. A scaling potential monitor was also installed to provide a better prediction of the impact of CO₂ on scale formation.

Initial mill-scale trials targeted a pH of approximately 7.1 to 7.2 instead of the 7.5 pH target that was determined by modeling to be a potential operating point. The lower pH target was initially used as a method of validating the process concept. A result of using the lower pH target was an approximate doubling of the amount of CO₂ required to maintain the system target pH conditions. Future optimization will therefore be required.

SCALE MONITORING

An effort was made to monitor the amount of scale formation occurring in the process system. Side-stream scaling-rate monitors, as shown in Fig. 3, were supplied and installed by Buckman. These monitors consisted of detachable steel rods inside glass tubes. The rods were electrically heated to enhance the rate of scale deposition. Process fluid was taken as a slip stream and passed through the glass tubing over the heated rods. An effort was made to match the flow rate of the process fluid over the heated rod to that of the actual fluid passing through the heat exchanger tubes. Because calcium carbonate solubility is inversely proportional to temperature, lime scale will form preferentially on the heated steel rods before it forms in the heat exchanger. After a specified amount of time, the steel rods can be disconnected from the system, and the weight of scale deposited can be determined gravimetrically. A rough rate of scale formation can then be predicted from these data.

MILL PROCESS RESULTS

The mill operators routinely monitored the system pH, the pressure drop across the heat exchanger, and the resulting pH of the water system. The potential scaling rate was monitored and predicted by the scaling monitor. Under typical mill conditions, this heat exchanger would be by-passed after approximately 20–30 days of running time due to excessive pressure drop resulting from heavy lime scale build-up. After 29 days of operation, no increase in pressure drop was noted across the heat exchanger, which indicated that lime scale build-up was not occurring. To date, the scale monitoring probes have not predicted scale formation in this system. After more than 180 days of operation, the heat exchanger was taken out of service and inspected during a routine fibre-line shutdown. No process scale was observed.

CONCLUSIONS

Typically, extreme scale formation on the water side of the heat exchanger has
forced mill personnel either to by-pass the heat exchanger or to shut it down and to remove the scale mechanically after as little as 25–30 days of operation. At the time of this writing, the mill has successfully operated the heat exchanger for more than 180 days with no indication of significant scale build-up. Pressure drop across the heat exchanger has not increased substantially, and the slip-stream scaling-rate monitors have not predicted a significant amount of potential scale formation. The system pH has been successfully maintained between 7.1 and 7.5 with the addition of approximately 27 ppm CO₂ based on the water flow to the heat exchanger. The mill is still successfully controlling scale formation using CO₂ application to the water side of the heat exchanger. The use of CO₂ appears to be an excellent method for controlling scale build-up on the water side of heat exchangers. Pressure drop across the exchanger has been maintained at “just cleaned” levels even after several months of operation.

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REFERENCES