Passive Mixing to Improve Calcium Oxide Dissolution

B. R. Leavitt, PE, PG[1], Tim Danehy[2], and Bryan Page[2]

Abstract: Water-powered dosers have been used for many years to feed pebble quicklime (CaO) or, more recently, hydrated lime ($Ca(OH)_2$) into mine drainage treatment facilities where electric power is not available. Lime utilization at these facilities has historically been poor when pebble lime is used due to the low solubility, high density, and large particle size of the pebble lime. This has resulted in the use of mixing channels downstream of the dosers to provide for contact time with the treated water. Two passive technologies one old and one new have been combined to improve pebble lime utilization. The Manor treatment facility, near Clearfield, Pennsylvania, has been modified to include a MixWell, inspired by diversion wells and a TROMPE driven air lift mixer "A-Mixer" to enhance lime dissolution. The result of this modification is an estimated 40 to 57 percent reduction in lime usage, leading to a project cost savings of $12,000 to $17,000 per year in lime cost.

Introduction

Pebble Quicklime

Pebble Quicklime is derived from the heating of limestone to convert the calcium or magnesium carbonate into the respective oxide. Depending on the limestone source, there are varying ratios of Calcium and Magnesium oxide. In addition to the Calcium / Magnesium oxide, there is also an inert component which does not contribute to acid neutralization. Pure pebble quicklime has a neutralization equivalent of 0.56 tons per ton of acidity ($CaCO_3$ equivalent) compared to hydrated lime which has a neutralization equivalent of 0.74 tons per ton of acidity. In addition, its higher density 55 to 60 pounds per cubic foot vs. 30 to 40 pounds per cubic foot allows for more alkalinity to be delivered on a per truck basis and it also allows for a smaller product silo.

When site, budgetary or other conditions limit the use of passive technology, water-powered dosers have been deployed to deliver pebble quicklime to neutralize acid mine drainage. These water-powered systems are sometimes referred to as semi-active. The solubility of pebble quicklime is somewhat limited, 1.33 g/L, while hydrated lime is somewhat more soluble at 1.76 g/L. Before it can dissolve in water, pebble quicklime has to be converted from Calcium oxide to calcium hydroxide, a process called slaking.

The slaking equation is:

$$CaO + H_2O \rightarrow Ca(OH)_2 \qquad (1)$$

This is an exothermic reaction commonly confined to a slaker where the elevated temperatures promote the slaking process. Limited quantities of water are used to keep the temperature elevated. If excessive amounts of water are used, then the lime is said to be "drowned" and the slaking reaction is inhibited by a coating of calcium hydroxide on the particle surface that restricts water penetration thereby restricting the

---

[1] Consulting Hydrogeologist 2776 S-Bridge Rd Washington, Pa. 15301

[2] BioMost Inc. 434 Spring Street Ext. Mars, PA 16046

reaction. This is the typical state of the reaction at most semi-active treatment sites. To overcome this limitation, the pebble quicklime is allowed to be deposited in long channels where the dissolution can proceed slowly. This can lead to low lime utilization at the treatment site due to un-dissolved lime that is buried in the channel or lime that has absorbed carbon dioxide from the air and has converted back to calcite.

Manor Mine

The Manor Mine is located in north central Pennsylvania12 miles northeast of the town of Clearfield. The mining took place in the Lower Kittanning seam in an up-dip direction. The mine closed circa 1970 and the portals have been sealed. The mine discharge emanates from a wet seal installed about 2004. Under a consent agreement, Pennsylvania Department of Environmental Protection (PADEP) has been managing the operations and a treatment plant at Manor since 2004. Prior to the recent modification, treatment consisted of calcium oxide addition using a water wheel (Aquafix) to regulate dosing. A mixing channel 300 feet in length with a vertical drop of 20 feet was provided to allow for mixing and dissolution of the pebble quicklime. The treated water was allowed to cascade for aeration and then was allowed to settle in three baffled ponds before discharging. As a result of this process, significant quantities of lime were deposited in the mixing channel and in the first settling pond. This reduced the storage capacity of the settling pond and resulted in the disposal of large amounts of unused lime along with the cost of lime sludge removal.

Due to difficulties with the plant operation, BioMost Inc. was hired to redesign the plant with a view to improving lime utilization and overall system operation. Two new concepts for lime mixing were designed and installed at the Manor facility.

The first device is called a MixWell, a modification of a diversion well concept. Raw water is directed into a large diameter vertical pipe where it is discharged at the bottom. A slurry of pebble quicklime in mine water is directed into the MixWell where the dense calcium oxide particles descend to the bottom where they are agitated by the incoming raw water. Either abrasion or exposure to low pH water or a combination thereof enhances the breakdown of the large particles and hence the lime utilization efficiency. Unlike a diversion well, there is not a thick bed of material to be suspended, and the lime is added on a continuous basis instead of batch mode as is typical of diversion wells.

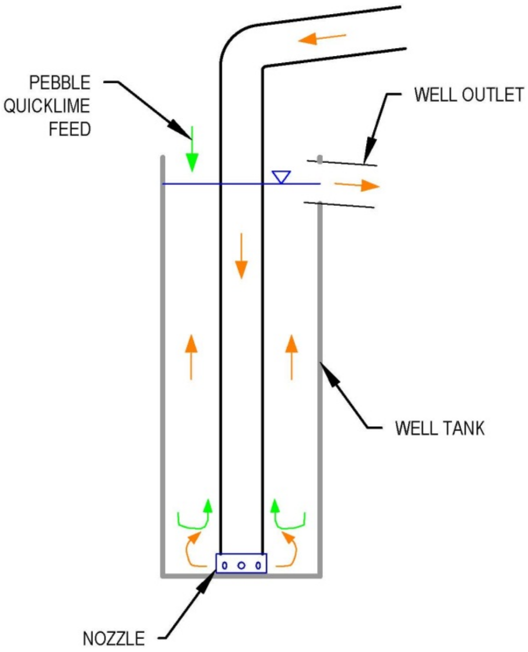

Figure 1. MixWell diagram.

Figure 2. MixWell in operation.

The second device is called an "A-Mixer" derived from an airlift mixer. This device consists of a large tank to provide residence time. In the center of the tank is a vertical pipe suspended off the bottom of the tank and rising to just below the normal water level in the tank. An air pipe, with an air distributor (diffuser), is suspended in the middle the vertical pipe and is connected to a source of compressed air. In this case, a Trompe, which is located below the treatment plant discharge, was installed to provide the compressed air. Air is bubbled up through the vertical pipe inducing water flow through the pipe. This causes a convective-like circulation in the tank that keeps small lime particles suspended and available for dissolution.

This paper evaluates the effectiveness of these two devices in terms of individual unit operation and the combined effect on lime utilization.

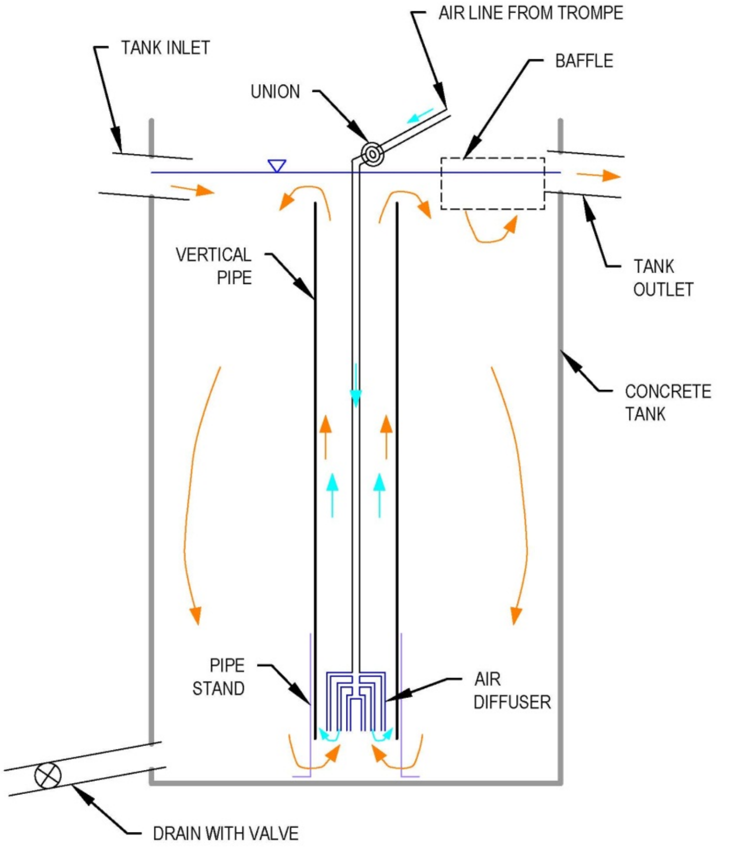

Figure 3. A-Mixer diagram.

Figure 4. A-Mixer in operation.

Raw Water

Water discharging from the Manor Mine ranges in flow from 78 to over 500 gallons per minute. The raw mine water contains the following constituents:

Table 1. Raw Water Quality at Manor Mine.

Parameter	Date						Units
Date	1-6-12	1-16-12	1-23-12	1-31-12	2-7-12	2-21-12	
pH Field	3.48	3.43	3.53	3.38	3.45	3.69	S. U.
Acidity	466	468	458	445	422	417	mg/L
Iron	233	201	231	183	210	203	mg/L
Aluminum	19.3	22.3	15.6	12.9	11.4	16.8	mg/L
Manganese	3.62	2.99	3.13	3.23	3.43	3.40	mg/L
Calcium	166	140	160	138	145	141	mg/L
Magnesium	43.3	49.7	51.7	54.1	44.9	45.7	mg/L

Field Investigation

Water from the modified treatment plant was sampled at four locations: Raw water; MixWell outflow, A-Mixer inflow; and A-Mixer outflow. Note, due to site conditions, the A-Mixer is located down-gradient of the MixWell. The influent of the A-Mixer travels approximately 150 feet along the existing mixing channel prior to entering the A-Mixer. With the exception of the raw water, these samples were quite complex in that they contained calcium oxide/hydroxide particles in suspension along with a suspension of ferrous hydroxide floc, which is actively trying to oxidize to ferric hydroxide. Special procedures had to be taken to get a representative sample from these three locations. Field filtered samples were desired so that the dissolved lime could be separated from the lime that was still in particulate form. A 0.45-micron filter was used for this purpose. The presence of the ferrous hydroxide floc greatly inhibited this filtration. To help avoid this problem, these samples were allowed to sit for 10 minutes before filtering so that the suspended particles could settle.

Particle Size Analysis

Pebble quicklime samples were taken from the AquaFix feeder at the Manor site. These samples were sieved through a 10, 60, 80, 200, and 325 mesh screens. Effluent from the MixWell and the A-Mixer were also wet sieved through the 10, 60, and 80 screens; finer screens were blinded by the ferrous hydroxide floc. Figure 5 shows the particle size distribution of the raw lime product. Figure 6 shows the particle size contained in the effluent water from the MixWell. Figure 7 shows the particle size contained in the effluent from the A-Mixer. It was not possible to sieve the entire flow from the MixWell, consequently, a mass balance based on particle weight was not possible.

The graphs show continued degradation of the particle size as it moved through the system. Over 60 percent of the raw lime was retained on the number 10 sieve. Effluent from the MixWell had no material on the number 10 sieve and 80 percent of the material retained on the number 60 sieve. Effluent from the A-Mixer had between 40 to 55 percent retained on the number 60 sieve with a similar range being retained on the number 80 sieve.

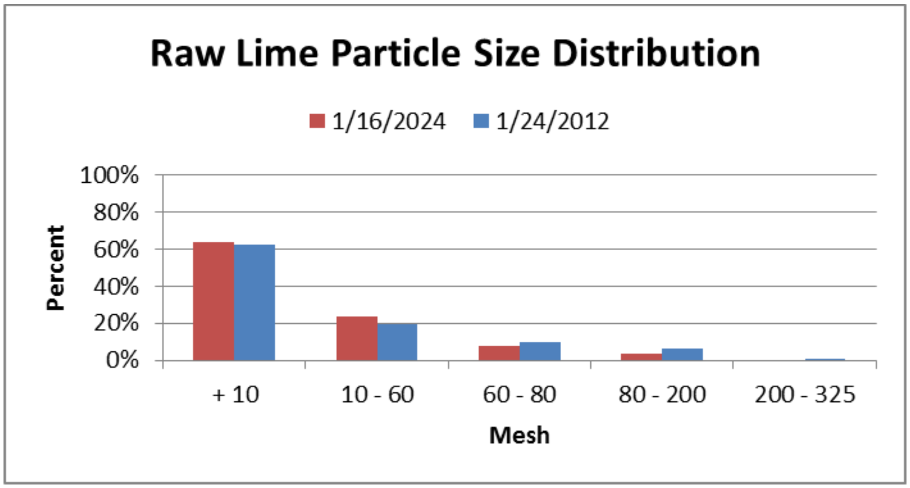

Figure 5. Pebble Quicklime particle size.

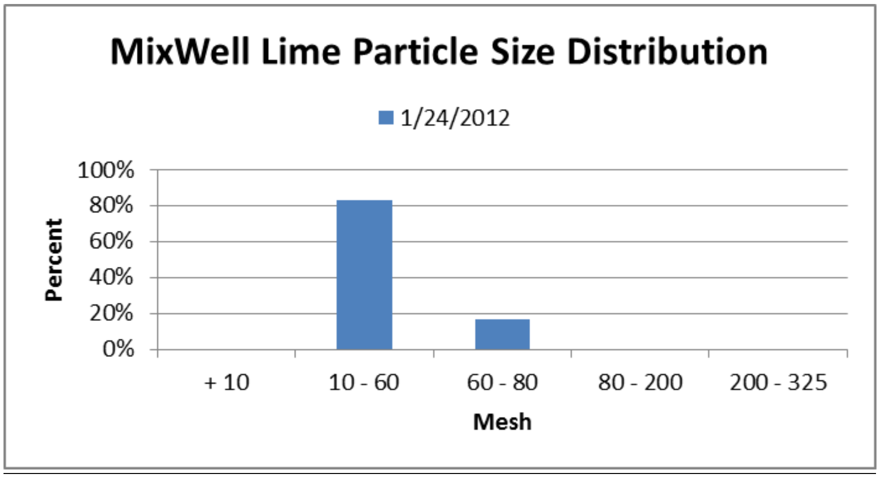

Figure 6. MixWell discharge particle size.

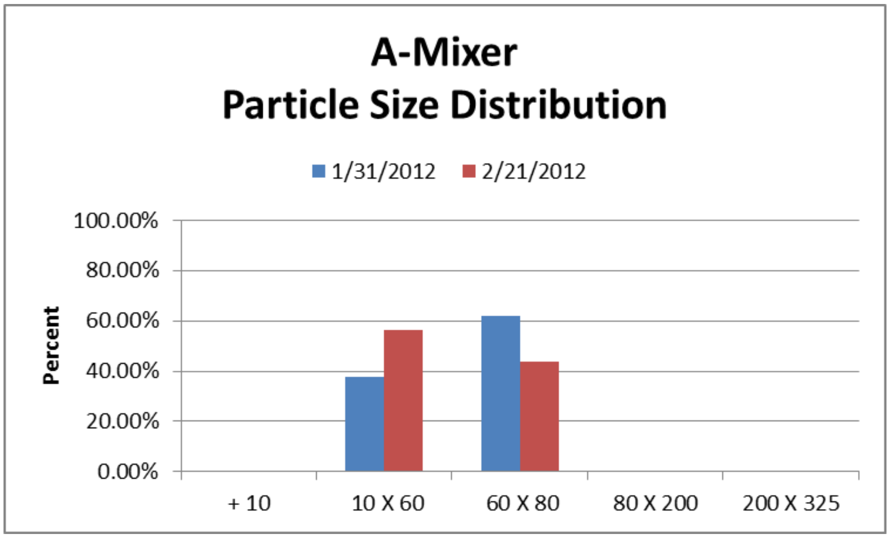

Figure 7. A-Mixer discharge particle size.

Note that all of the raw lime that was retained on the number 10 screen was reduced to minus 10 mesh by the MixWell.

pH

Water pH was measured, in the field, at four locations: raw water; effluent from the MixWell; influent into the A-Mixer; and effluent from the A-Mixer. Figure 8 is a graph of these data measured on four different dates. The pH was substantially increased in the MixWell. Two of the plots showed an increase in pH as the water crossed the lime bed and two of the plots show a pH decrease as the water traversed the lime bed. Three of the plots show a slight increase in pH in the A-Mixer and one of the plots shows no change in pH.

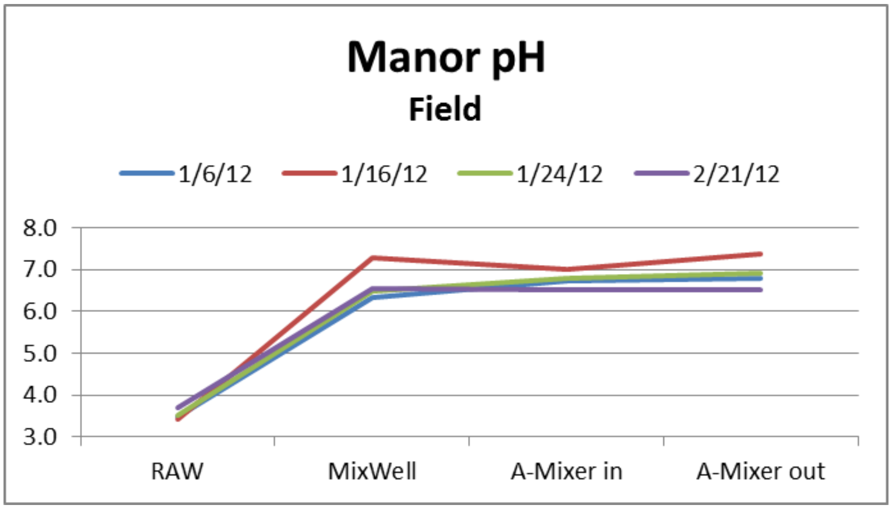

Figure 8. Manor water pH.

The chemistry driving the pH rise in the MixWell is straight forward. The pebble quicklime dissolved raising the pH and some of the dissolved ferrous iron precipitated as ferrous hydroxide floc. Between the MixWell discharge and the A-Mixer inlet was about 150 feet of the existing mixing channel. In the mixing channel; minor amounts of additional raw/other water was added, lime was dissolved, and some ferrous iron was oxidized. As a consequence the pH was variable depending on lime dosing. The pH in the A-Mixer was also complicated, a steady to slightly rising pH was observed but this must be viewed in relationship to the dissolved iron data.

Dissolved Oxygen

A plot of the DO data is shown in Figure 9. As soon as the pebble quicklime was added to the raw water nearly all available oxygen was consumed. As the water flowed over the lime channel, oxygen was reintroduced, but it was again consumed in the A-Mixer even though air was also being added.

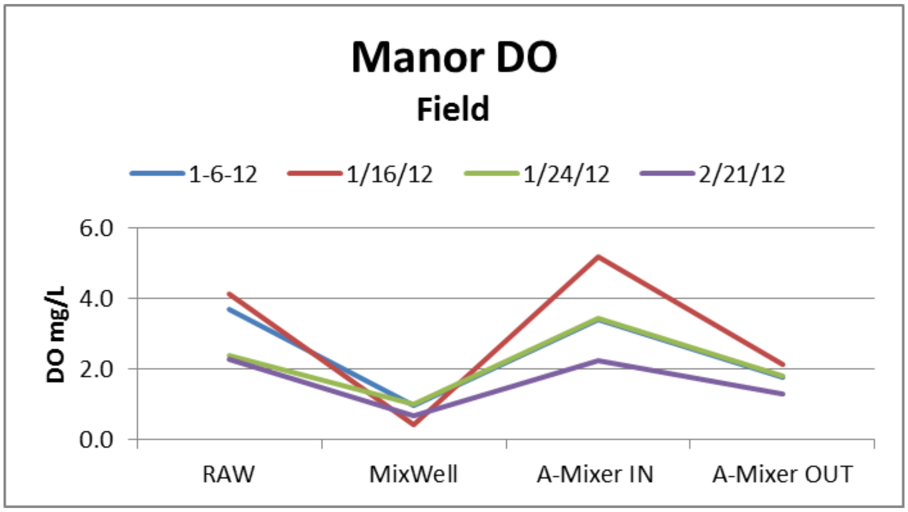

Figure 9. Dissolved oxygen

These drops in DO concentration were attributed to ferrous iron oxidation to ferric iron (equation 1) or alternatively, ferrous hydroxide oxidation to ferric hydroxide (equation 4). The ferrous oxidation reaction consumed oxygen and generated acidity by the following two equations:

$$Fe^{+2} + \frac{1}{4} O_2 + H^+ \rightarrow Fe^{+3} + \frac{1}{2} H_2O \qquad (2)$$

When the ferric iron precipitated, three moles of acidity were generated for each mole of iron. This equation will be useful when we consider iron precipitation in the A-Mixer.

$$Fe^{+3} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \qquad (3)$$

The net reaction is that two moles of acidity were created for each mole of iron oxidized and precipitated. This oxidation reaction was pH limited and was only expected to be significant above a pH of 7.

A second reaction may also be occurring. Ferrous hydroxide also known as green rust has been observed in all parts of the semi-active treatment system. This ferrous hydroxide can be converted to Ferric hydroxide without the generation of acidity.

$$Fe(OH)_2 + \frac{1}{2} H_2O + \frac{1}{4} O_2 \rightarrow Fe(OH)_3 \qquad (4)$$

In this case the addition of oxygen was the only requirement as all of the other reactants were present. At pH lower than 7, this was expected to be the dominant reaction in the A-Mixer.

Alkalinity

Figure 10 shows the alkalinity measured in the field for the treatment system. As expected, alkalinity rose as the pebble quicklime was added in the MixWell. The alkalinity then decreased in the lime channel as oxygen reacted to convert ferrous iron into ferric hydroxide. Alkalinity was again given a slight boost in the A-Mixer despite the introduction of air in the system.

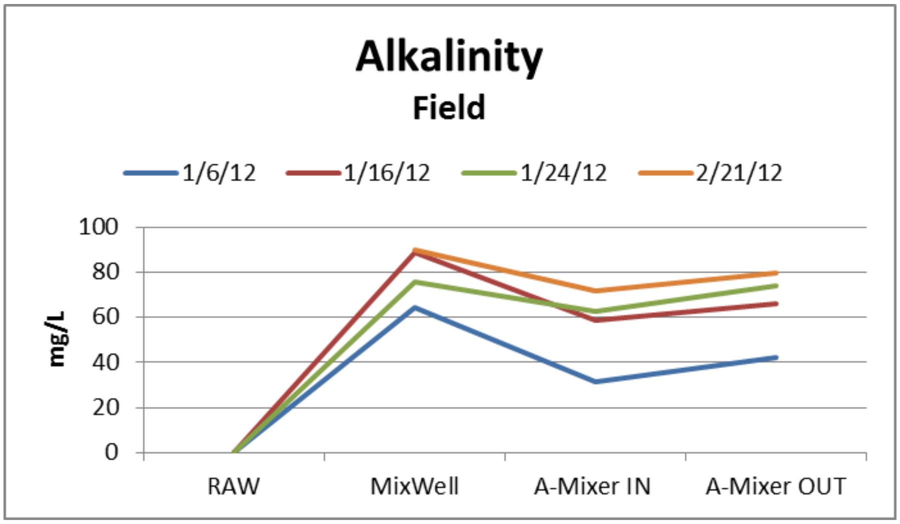

Figure 10. Manor field alkalinity.

Dissolved Iron

Samples for dissolved iron were taken at each of the four sampling locations. These samples were allowed to sit for 10 minutes while the floc settled, then the supernatant was field filtered using a 0.45-micron filter. Figure11 shows a significant decrease in dissolved iron as the water traversed the treatment system.

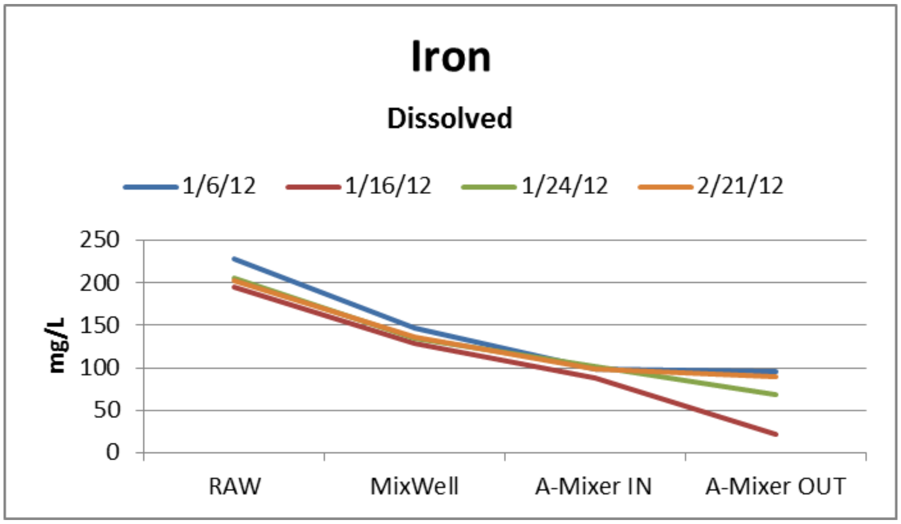

Figure11. Dissolved Iron in the Manor treatment system.

Dissolved iron concentrations within the A-Mixer dropped on two dates, 1/16/12 and 1/24/12, but were stable on the other two dates when there was no change in dissolved iron concentration. This variation was correlated with the pH of the A-Mixer inlet. The pH was between 6.8 and 7.0 on the days that showed a decrease in dissolved iron. The pH was below 6.8 on the days that dissolved iron remained unchanged.

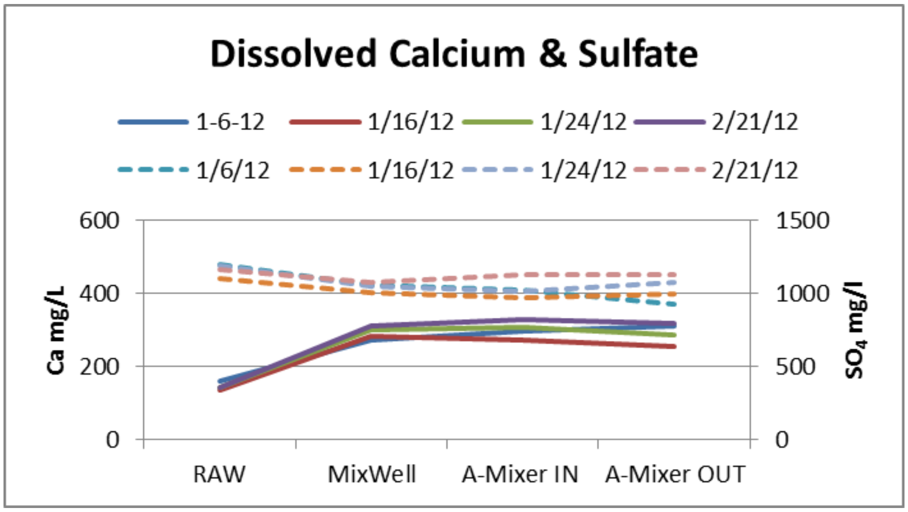

Figure 12. Calcium and Sulfate concentrations.

Sulfate & Calcium

Sulfate concentrations in the raw water ranged from 1095 to 1192 mg/L and the dissolved calcium values ranged from 134 to 159 mg/L. Figure 12 is a plot of the Sulfate and Calcium data across the treatment system. Note that the calcium increase resulting from the MixWell corresponded to a Sulfate decrease at the same time. This suggested gypsum precipitation in the MixWell. There was little consistent change in these dissolved constituents throughout the rest of the treatment system.

Discussion

It is clear from Figures 8, 10, and 12 that the MixWell was doing the bulk of the pebble quicklime dissolution, and that gypsum precipitation was occurring in the MixWell. On January 6, the MixWell contributed 75 percent of the calcium added during the treatment process.

Efforts to use calcium to measure system performance of the A-Mixer were frustrated by spatial, temporal, and possibly gypsum and calcite variations across the site. As a consequence, on one sampling trip the calcium increased in the A-Mixer and on three occasions the calcium level decreased. This decrease occurred even though alkalinity increased.

Figure 13 shows a picture of the raw lime and Figure 14 shows the material taken from the bottom of the MixWell (MixWell Sludge). Note the percentage of “dark matter” or grit concentration relative to the white calcium oxide. These heaver grit particles can help with the mechanical degradation of the pebble quicklime, but at some point the grit must be drained from the system when it becomes excessive. Note also the rounded surface of the pebble quicklime (lower left). This rounding can be from abrasion or chemical dissolution of the particle surface. The pebbles on the lower right also show the effects of abrasion and include gypsum pebbles.

Note the black particles that are present in the two effluent samples in Figures 15 & 16. These particles are the inert components of the pebble quicklime product. Manufacturer-provided data indicate that the pebble quicklime product has a calcium oxide content of 94.4 percent and a lime index of 92.3 percent. This indicates that about six percent of the product is grit. As the lime dissolves, the percentage of grit in the remaining particles increases.

Figure 13. Raw Quicklime.

Figure 14. MixWell Sludge.

Figure 15. MixWell Discharge.

Figure 16. A-Mixer discharge.

The MixWell and A-Mixer discharges were wet sieved. This limited the particle size that could be captured to screens that were not blinded by the ferrous floc (+ number 80 screen). In addition, the 12-inch sieves were not large enough to capture the entire flow; consequently, a mass flow rate was not possible. Because of this, we did not compare the size of the piles in Figures 15 and 16. Figure 7 showed a particle size reduction between the MixWell discharge and the A-Mixer discharge. It is suspected that more lime was dissolved in the A-Mixer when the inlet pH was greater than 7 as the acidity from the dissolved ferrous iron was released. This suspicion was based on the drop in dissolved iron that occurred when the pH was greater than 7, combined with an increase in pH at the same time. Figure 17 shows this relationship on the January 16 sampling date: the dissolved iron dropped from 88 to 22 mg/L while the pH rose from 7.1 to 7.38. Water with lower pH did not benefit from the dissolved iron reduction. At the higher pH, oxygen reacted more quickly with the ferrous iron converting it to ferric iron. This process released acidity that was neutralized by the remaining undissolved quicklime particles being held in suspension by the A-Mixer. The net result was that when the inlet pH was maintained at or above 7, iron oxidation in the A-Mixer occurred rapidly thereby releasing acidity into the water. This acidity was immediately neutralized by the suspended calcium oxide particles, which led to a higher outflow pH and a higher alkalinity.

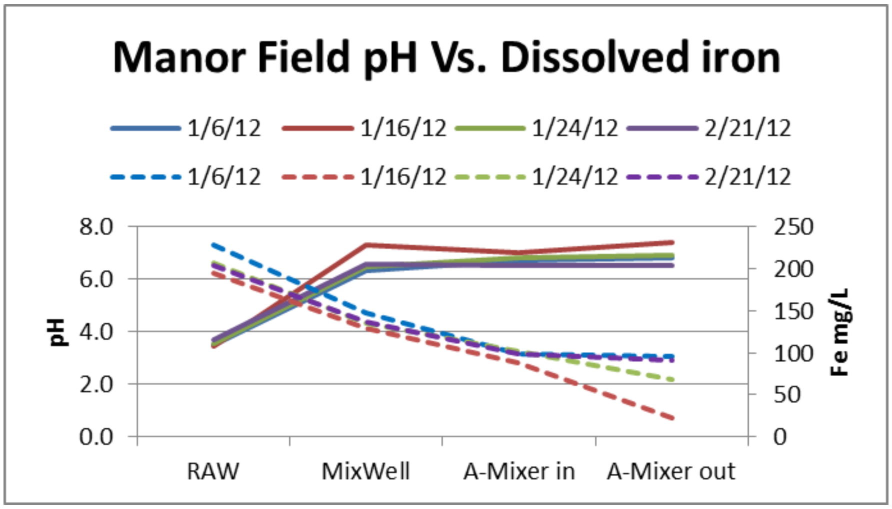

Figure 17. pH compared to dissolved iron.

The proof of the technology is based on the lime utilization rate. Three approaches were taken to establish this rate. First, the acidity of the mine water was used to calculate the amount of pebble quicklime required to neutralize that acidity. This calculated value was then compared with the actual amount of pebble quicklime added. On three occasions, pebble quicklime was captured from the lime auger over a one-minute period and these samples were weighed and used to compute the lime efficiency. On 2-21-12, the lime feed was not captured. Instead, the lime delivered per revolution on the prior sampling was used to calculate the lime added for this date. Consequently it is not known if the lime dosage on this date was an accurate reflection of the actual lime dosage. The lime dose on this date was further complicated by the system being down for several days prior to the sampling event. It is believed that the operator was overdosing in an effort to raise the pH in the settling ponds. The lime efficiency in excess of 100 percent may be due to higher quality pebble quicklime being delivered than was reported on the lime analysis, or it could represent some amount of under treatment in the system. These data are shown in Figure 18. Also in Figure 18 is a plot of the lime utilization rate based on the stoichiometric amount of calcium needed to treat the mine water. This approach is confounded by gypsum and possibly calcite formation within the system. The formation of gypsum or calcium, if taken into account, would increase the reported lime utilization rate.

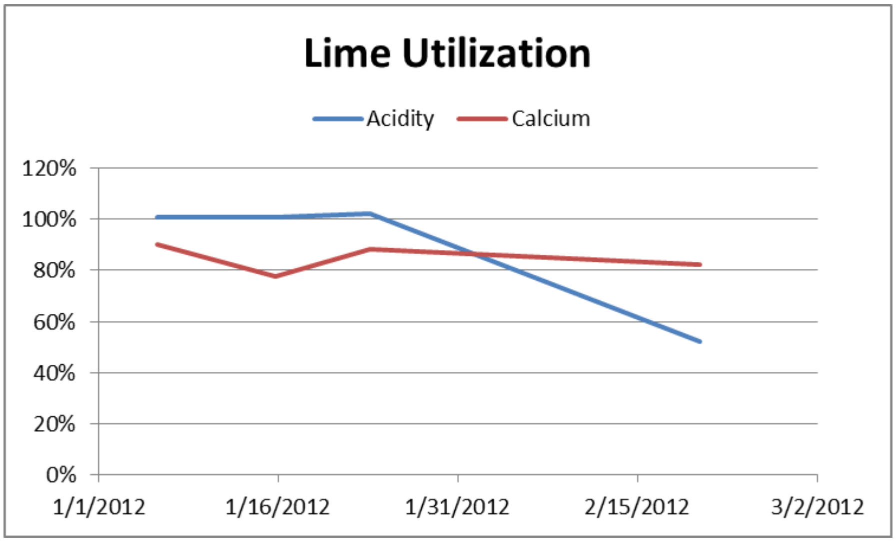

Figure 18. Lime Utilization based on initial acidity and stoichiometric calcium.

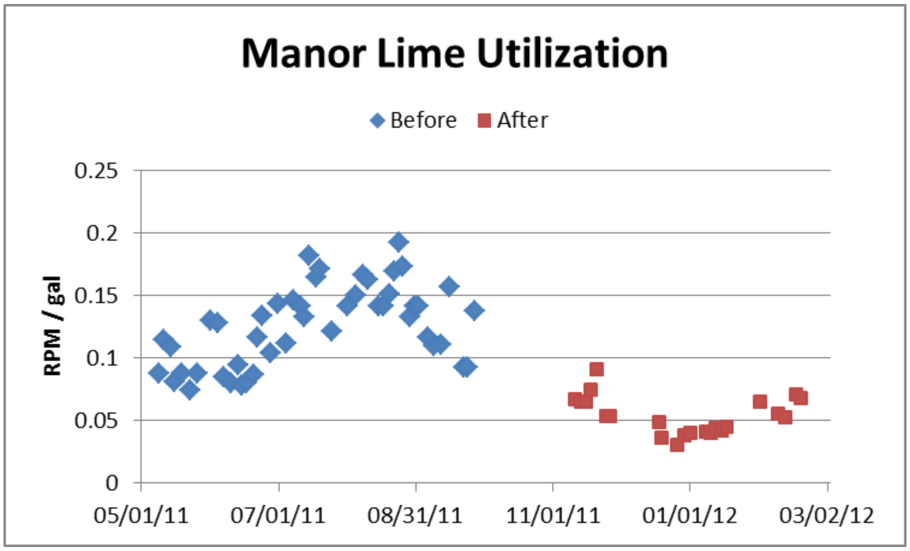

Figure 19. Lime Utilization at Manor before and after MixWell and A-Mixer construction.

The ultimate test of lime utilization is a comparison of the lime usage before and after the MixWell and A-Mixer retrofit. Plant personnel have adjusted the lime delivery of the plant so that their discharge criteria were maintained both before and after the plant retrofit. Using the plant log book, the flow rate and the Aquafix revolutions per minute (RPM) were recorded. The RPM data were divided by the flow data to yield a metric of RPM/gal. This metric was then plotted against time and graphed in Figure 19. The before and after data show a definitive improvement in the lime required. The average RPM/gal before the retrofit was 0.1255, while after the retrofit the RPM/gal was 0.0719. This indicates that the new plant was operating on 43 percent of the lime that was required prior to the rebuild. Before the retrofit, annual lime cost was $30,000. The indicated savings in lime cost is $17,100 per year. This did not include the cost of dredging and disposal of unused lime in the first settlement pond.

Conclusions

Passive mixing technology can have a very significant improvement in lime utilization where pebble lime is the source of the alkalinity.

The MixWell technology can be very effective at dissolving pebble quicklime and can reduce the particle size of its effluent.

The A-Mixer, if operated at pH 7 or above, can advance the oxidation of ferrous iron while maintaining pH across the system.

Acknowledgement

The authors gratefully acknowledge the Pennsylvania DEP, especially Mike Smith, Mario Carrrello and Eric Rosengrant for supporting our new technology. In particular we offer our thanks to Bill Gongaware and his crew, Kreug and Jeremy, who let us play with their water and supported our efforts at every turn. Thanks guys!

References

Aube, B. 2005, The Science of Treating Acid Mine Drainage and Smelter Effluents. Retrieved March 7, 2012, http://www.robertsongeoconsultants.com/rgc_enviromine/publicat/treatment%20science.pdf

Leavitt, B.R., 2011. Aeration of Mine Water Using a TROMPE: 2011 West Virginia Mine Drainage Task Force Symposium. Morgantown, West Virginia.

Leavitt, B.R., 2010. Air Lifting Mechanisms for Oxidation in Underground Mines: 2010 West Virginia Mine Drainage Task Force Symposium. Morgantown, West Virginia.

Skousen, J.G, & Ziemkiewicz P.F. "Acid Mine Drainage Control & Treatment" 1995, West Virginia University and the National Mine Land Reclamation Center.