Operational and Financial Studies of Hydrogen Peroxide versus Hydrated Lime and Hydrogen Peroxide versus Sodium Hydroxide at Two Pennsylvania Mine Drainage Treatment Sites

Brent Means[1], Richard Beam and Don Charlton

Abstract

The Pennsylvania Department of Environmental Protection (PA DEP) oversees a number of mine drainage treatment trust funds. Recent financial market conditions have reduced revenue generation needed to pay for treatment. Cost-reduction evaluations were performed at two sites: the Mon-View Mathies and LTV Banning facilities. At Mon-View, 20% sodium hydroxide solution (w/w) was used for treatment and at Banning hydrated lime ($Ca(OH)_2$) was used. The evaluations consisted of characterizing chemical consumption and costs, pilot testing alternative treatment strategies and conducting a cost and treatment performance comparative analysis.

The evaluation of the original Mon-View sodium hydroxide system showed hydroxylation and ferrous iron (Fe(II)) removal were the dominant alkali-consuming reactions and calcite formation was minor. The actual NaOH dose was less than half the theoretical dose required to neutralize all alkali-consuming reactions. The treatment process utilized influent alkalinity contained in the mine drainage to aid in neutralization and saves $108 per day in NaOH costs. While this treatment scheme effectively utilized influent alkalinity, avoidable hydroxylation reactions doubled alkali consumption and increased costs. The evaluation of the original LTV Banning hydrated lime system showed the daily $Ca(OH)_2$ cost was $569, of which $190 was spent on hydroxylation reactions, $39 on Fe(II) removal and $340 on calcite formation. Unlike Mon-View, this treatment system did not utilize influent alkalinity and dosed at the theoretical rate required to neutralize alkali-consuming reactions. A small portion of alkali added actually contributed to Fe(II) removal, which was the sole parameter targeted for treatment. The evaluations showed significant chemical costs as a result of alkali consumption due to hydroxylation and calcite-formation reactions.

Year-long hydrogen peroxide (H_2O_2) field trials were conducted at each site to eliminate costs due to hydroxylation and calcite formation. At Mon-View, a 35% H_2O_2 dosing rate of 14 gallons per day achieved effluent concentrations of total iron similar to NaOH treatment. The H_2O_2 reduced the daily chemical cost by 34% and produced a yearly cost savings of $25,500. At Banning, a treatment strategy of 50% H_2O_2 and flocculent aids were used; however, the H_2O_2 treatment produced a difficult-to-settle iron floc that discharged elevated suspended solids. The treatment scheme was modified to a combination of 50% H_2O_2 and hydrated lime, with the lime serving as a settling agent. Dosing rates of 25 gallons per day and 1.2 tons per day produced acceptable effluent and a yearly savings of $120,000. Cost savings are expected at other net alkaline mine drainage sites treating for iron.

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1.0 Introduction

Ensuring perpetual treatment of coal mine drainage (CMD), post bankruptcy, is a challenging task for state programs. PA DEP inherited treatment responsibilities after the bankruptcy of LTV Steel Corporation (LTV) in 2001 and Mon-View Mining in 2005. LTV operated nine treatment facilities, with flow rates ranging from 925 to 4,500 gallons per minute (gpm), and Mon-View Mining operated a single facility. During bankruptcy proceedings, PA DEP used historical treatment cost data to calculate the perpetual treatment liability for each site. In both cases, the assigned assets were less than the amount requested by PA DEP resulting in partial funding of the perpetual liability. Liquid assets were placed in a growth income trust, whose revenue is utilized to pay for the ongoing operation and maintenance of mine drainage treatment facilities. The trust is financially managed by a third party, the Clean Streams Foundation, and PA DEP conducts oversight and approves all trust expenditures.

To further stress the already underfunded trusts, the onslaught of The Great Recession limited revenue generation and contributed to dramatic fluctuations in commodity pricing. Pricing for sodium hydroxide, the treatment chemical used at Mon-View, tripled over two years. PA DEP, with assistance from OSM, responded to the situation by performing cost-reduction evaluations at two sites, the Mon-View treatment site and the LTV Banning treatment facility. The Banning site was selected from the nine LTV sites based on its relatively high annual costs and because a second plant, the Euclid facility, which is essentially the same design as Banning, is operated in conjunction with Banning in order to control the mine pool. Consequently, any cost reduction strategies realized at Banning could be applied to Euclid as well. The major costs at Mon-View consisted of labor, treatment chemical and sludge disposal. The major costs at Banning were pumping, labor and treatment chemical. Since annual chemical costs were a large percentage of the overall costs, the cost-reduction evaluation focused on evaluating whether the current chemical selection and usage were optimized and the most cost-effective option available. A five step methodology was used in the cost-reduction evaluation: 1) Measure the current chemical dosing rates, 2) Quantify treatment process chemistry to identify the chemical fate of alkali treatment reagents, 3) Develop alternative treatment strategies, 4) Pilot test alternative treatment strategies, and 5) Perform a cost and performance evaluation between treatment strategies.

This paper presents the results of the cost-reduction evaluation. First, the history and treatment configuration for each site is presented. Second, the methodologies used to perform the cost-reduction evaluation are presented. Lastly, the results of cost-reduction evaluation are presented.

2.0 Site Description

2.10 Mon-View Mathies – The Mon-View Mine is located near the Town of Monongahela, PA. The 12,835 acre underground mine complex, operated since 1944, mined the Pittsburgh Coal Seam using both conventional and longwall mining techniques until its abrupt closure in 2001. A mine pool quickly developed and iron-laden water started to gravity drain from an unreclaimed portal. The discharge flow ranges from 300 to over 2,000 gpm and quickly responds to precipitation events because of the subsidence features caused by the longwall mining techniques and historic room-and-pillar mining that occurred under shallow cover. The mine is currently 60% flooded (Ziemkiewicz et.al, 2004).

The Mon-View facility treats mine water that can be classified as "net alkaline" (Cravotta and Kirby, 2004). Table 1 shows the influent pH is 6.8 and contains 385 mg/L of alkalinity (as $CaCO_3$). Total iron is the only parameter targeted for treatment. Both Table 1 and visual inspections show the water is partially oxidized and contains suspended iron hydroxide as it emanates from the mine portal. The total and dissolved iron concentrations are 46 and 34 mg/L, respectively. As the gravity discharge emanates from the mine portal, a 1,200 foot pipe conveys the water to ponds and a wetland. A 20% NaOH solution (w/w) is added directly into the conveyance pipe for pH adjustment. The turbulence and retention time within the pipe acts as a reaction tank that mixes the NaOH with the mine drainage to increase pH and promote Fe(II) oxidation. During the treatment evaluation, the retention time between NaOH addition and the pipe outlet was measured at 3.5 minutes. The conveyance pipe discharges the water to two oxidation/settling ponds and a wetland, configured in series. The wetland discharges the final effluent to the receiving stream, Mingo Creek, a trout-stocked fishery.

2.20 LTV Banning – This underground mine complex is located near West Newton, PA, and was operated as early as 1889 by the Pittsburgh Coal Company. The mine was then operated by Republic Steel Corporation and finally by LTV until closure in 1982. Mine water treatment began while the mine was still in operation in the mid-1960s as a result of legislative requirements enacted in 1966 by the Commonwealth of PA which required all active underground mine operators to obtain discharge authorizations and treat all water pumped or otherwise discharged from their operations.

The Pittsburgh Coal Seam was mined at this site by room-and-pillar methods. The Banning Mine complex and associated mine pool encompasses a 28,000 acre area and is 43% flooded (Ziemkiewicz et.al, 2004). Two treatment plants, Banning and Euclid, pump the mine complex at a combined pumping rate of 6,500 gpm to prevent an artesian discharge into the Youghiogheny River Basin. The Banning mine pool must be maintained at an elevation below 775 mean sea level in order to prevent a breakout of the mine pool that would occur immediately adjacent to the Youghiogheny River in the Town of West Newton, located approximately one mile downstream. Euclid pumps from the deepest part of the mine and Banning pumps from a 150 foot shallower section located two miles from Euclid.

The Banning facility treats net alkaline mine water containing an influent pH of 6.8 and alkalinity of 394 mg/L as $CaCO_3$ (Table 1). Total iron is the only constituent targeted for treatment and Table 1 shows its concentration ranges from 10 to 18 mg/L. The Banning facility pumps at 2,310 gpm and uses $Ca(OH)_2$ slurry that is made on site using bulk delivery hydrated lime and treated effluent as slurry makeup water. The raw water is pumped to a rectangular reaction tank where $Ca(OH)_2$ slurry is added and pneumatically mixed for twenty minutes. After the reaction tank, the water flows to a flocculation tank and is then discharged to a circular clarifier having a retention time of approximately forty minutes. The precipitated sludge is continuously siphoned from the clarifier bottom and returned to the mine by injection boreholes.

Site	Sample Date	Alkali Reagent	Flow	Field pH	Field Alkalinity	Ca - D	Ca - T	Fe - D	Fe - T	Mg - D	Mg - T	Mn - D	Mn-T	Na - D	Na - T	Sulfate	Cl-	TDS @ 105 C
Mon-View Untreated	8/10/2010	20% NaOH (w/w)	396	6.86	385	96.5	100	34.8	46.3	37.5	39.7	1.34	1.41	448	468	948	86.5	1858
Banning Untreated	7/28/2011	$Ca(OH)_2$	2310	6.89	394	114	112	18	18.0	37.8	37.4	0.42	0.42	434	432	888.1	119.9	1918

* Flow = gpm, all concentrations in mg/L, Alkalinity =mg/L as $CaCO_3$, D = Dissolved, T = Total

Table 1: Untreated water quality characteristics at Mon-View and Banning.

3.0 Methodology

This section describes the methods used to measure flow and alkali dosing rates at both sites. In addition, this section describes the methods used to compute the chemical consumption due to alkali-consuming reactions encountered during the treatment process. The method used to validate the computed consumption is also presented.

3.10 Flow and chemical dosing rates – The gravity flow rate at Mon-View was measured using a Marsh McBirney Model 2000 ultrasonic flow meter. The pumping rate at Banning was measured using an unobtrusive Greyline PT400 Portaflow ultrasonic flow meter secured to the pumping pipeline away from turbulent zones.

Alkali dosing rates were quantified using two methods. The first method entailed using the measured flow rate and collecting the dispensed chemical for a specified time period to determine the dosing rate. The authors recognized that dosing variability exists over short time frames. Therefore, measured dosing rates were validated by collecting a series of water samples directly before and after chemical addition to measure the mass increase in calcium [Ca] and sodium [Na]. The increases were expressed in terms of the treatment chemicals and adjusted for reagent purity to compute dosing. Results from both methods agreed ($<$ 10% difference) with the chemical purchasing records for each site.

3.20 Computed chemical consumption due to Fe(II), hydroxylation and calcium carbonate (CaCO₃) formation – The alkali requirement to achieve a desired target treatment pH is a function of the total hydroxyl-consuming reactions that occur when pH is adjusted. Identifying the reactions responsible for hydroxyl consumption is important for predicting alkali requirements and for developing treatment strategies to reduce avoidable consumption. Since both of these waters are circumneutral pH net alkaline, the common hydroxyl-consuming reactions encountered during treatment include Fe(II) removal, hydroxylation of aqueous species and calcite ($CaCO_3$) formation.

3.21 Consumption due to Fe(II) removal – Fe(II) is commonly removed from CMD by adding alkali chemical to a targeted treatment pH of between 7.5 and 8.5. Within this pH range, Fe(II) is removed by two different mechanisms occurring simultaneously. The removal mechanism, ferrous hydroxide formation ($Fe(OH)_2$) (Equation 1), is the dominant mechanism at the upper end of the pH treatment range. The other mechanism, Fe(II) oxidation (Equation 2), is the dominant reaction at the lower end of the pH treatment range.   Figure 1 shows that dissolved Fe(II) concentrations in excess of 10 mg/L will persist at a treatment pH of 8.5, if $Fe(OH)_2$ formation is the sole control of iron solubility. Field experience and treatment performance data show dissolved iron is routinely below 0.5 mg/L at a treatment pH of 8.5. A combination of both Fe(II) removal mechanisms occurring simultaneously explains the discrepancy between theory and field observations. In addition to $Fe(OH)_2$ formation at pH 8.5, rapid Fe(II) oxidation at air saturation will reduce the dissolved Fe(II) concentration by half in less than ten seconds using rate constants reported by Dempsey et al (2001). Figure 1 shows that Fe(II) oxidation will further reduce the residual dissolved Fe(II) concentration, due to $Fe(OH)_2$ solubility, to less than 0.5 mg/L.

$$Fe^{2+} + 2OH^- = Fe(OH)_2 \qquad\qquad (1)$$

$$Fe^{2+} + .5H_2O + .25O_2 + 2OH^- = Fe(OH)_3 \qquad (2)$$
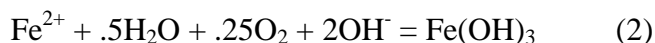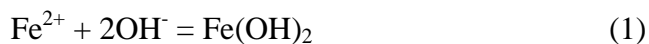
NaOH and $Ca(OH)_2$ consumption due to Fe(II) removal was determined by collecting total and dissolved water samples at the influent and effluent of the reaction tank. Sample results were used to quantify Fe(II) removal and Equations 3 and 4 were used to compute the NaOH and $Ca(OH)_2$ consumption due to Fe(II) removal.

$$\text{NaOH consumption (ml/L)} = (C_{\text{Fe initial}} - C_{\text{Fe reactor effluent}}) * 0.006 \qquad (3)$$

$$Ca(OH)_2 \text{ consumption (mg/L)} = (C_{\text{Fe initial}} - C_{\text{Fe reactor effluent}}) * 1.33 \, / \, \% \text{ purity}_{Ca(OH)2} \qquad (4)$$
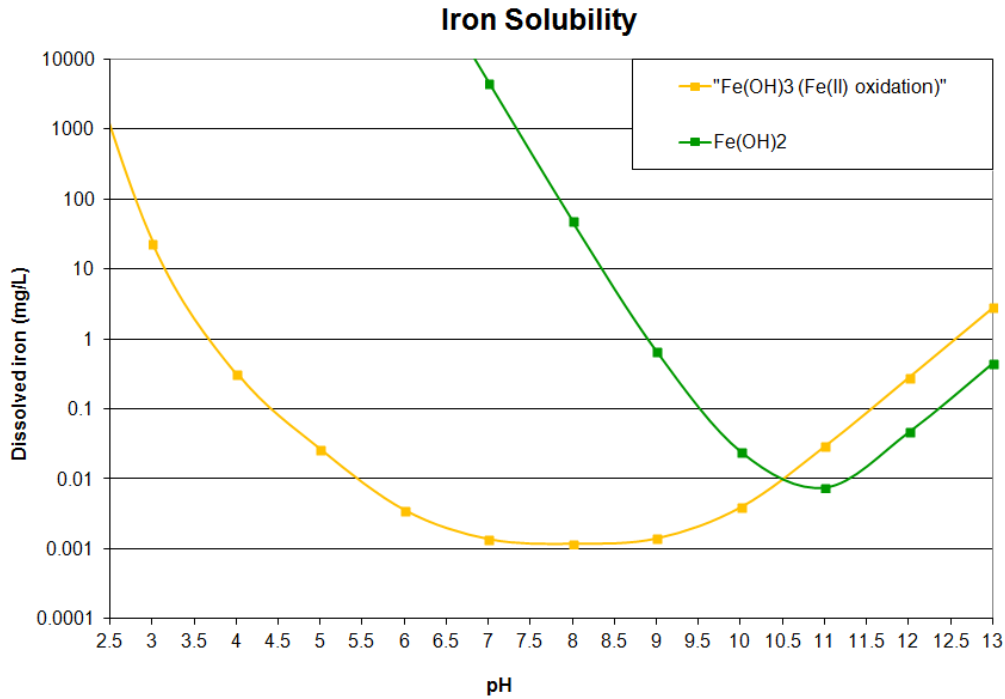

Figure 1: *Solubility of Fe(OH)$_2$ and Fe(OH)$_3$, considering OH$^-$, CO$_{2(aq)}$*
and SO$_4^{2-}$ aqueous complexing.

3.22 Consumption due to hydroxylation – Hydroxylation is defined herein as the reaction of hydroxyl ion (OH$^-$) with aqueous species to form water and other aqueous species. For example, as $Ca(OH)_2$ dissociates in solution, hydroxylation of anions, cations and aqueous complexes occur as represented in Equations 5 through 8:

Hydroxylation of anion:
$$H_2CO_3 + OH^- = HCO_3^- + H_2O \qquad (5)$$

$$HCO_3^- + OH^- = CO_3^{2-} + H_2O \qquad (6)$$
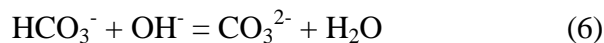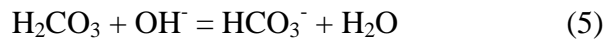
Hydroxylation of cation:
$$Mg^{2+} + OH^- = MgOH^+ \qquad (7)$$

Hydroxylation of aqueous complexes:
$$CaHCO_3^+ + OH^- = CaCO_{3(aq)} + H_2O \qquad (8)$$

6

Generally, the hydroxylation of anions and aqueous complexes yield water as the product, whereas the hydroxylation of cations will yield hydroxyl complexes.

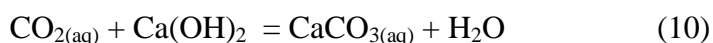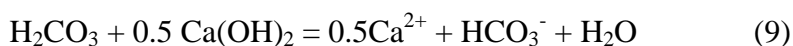Aqueous speciation modeling was used to compute alkali consumption due to hydroxylation reactions. Geochemist Workbench software (Bethke, 2008; Bethke and Yeakel, 2012) was used to speciate both the untreated mine drainage entering the reactor tank and the treated mine drainage leaving the reaction tank. Changes in concentrations of aqueous species undergoing hydroxylation between the two sampling points were noted and the equivalent amount of alkali addition required to provide the OH^- for hydroxylation was calculated. For example, speciation modeling shows alkali addition in the reaction tank causes a decrease of H_2CO_3 and increase in HCO_3^- and CO_3^{2-} concentrations as the water equilibrates to the increased pH condition. Concentrations of complexes, like $CaCO_{3(aq)}$, also increase. The $Ca(OH)_2$ dose required for the increase in species like HCO_3^- and $CaCO_{3(aq)}$ can be computed from the following relationship:

$$H_2CO_3 + 0.5\ Ca(OH)_2 = 0.5Ca^{2+} + HCO_3^- + H_2O \qquad (9)$$

$$CO_{2(aq)} + Ca(OH)_2 = CaCO_{3(aq)} + H_2O \qquad (10)$$

The total NaOH and $Ca(OH)_2$ consumption due to hydroxylation were computed by tracking changes in modeled concentrations for nineteen species prone to hydroxylation reactions.

3.23 Consumption due to $CaCO_3$ formation – Calcite formation increases consumption of both NaOH and $Ca(OH)_2$. $CaCO_3$ formation is caused by a single mechanism in NaOH treatment systems and by two mechanisms in $Ca(OH)_2$ systems. Both mechanisms increase the alkali requirement by consuming OH^- to precipitate $CaCO_3$. The first mechanism affects both NaOH and $Ca(OH)_2$ systems and is termed the "dissolve-precipitate" mechanism. In this mechanism, $Ca(OH)_2$ dissolves into mine drainage and increases $[Ca^{2+}]$ and $[OH^-]$ until the solution becomes supersaturated and induces $CaCO_3$ precipitation. Elevated aqueous CO_2 species concentrations in CMD can cause $CaCO_3$ precipitation to occur at a treatment pH as low as seven. Equation 11 shows the $CaCO_3$ precipitation will buffer against pH increase and consume hydroxyl.

$$Ca^{2+} + OH^- + CO_{2(aq)} = CaCO_{3(s)} + H^+ \qquad (11)$$

The other mechanism, termed recarbonation, occurs when hydrated lime particulates adsorb $CO_{2(aq)}$ to create a $CaCO_3$ shell around hydrate particulates before they can dissolve (Wiersma, 1996).

$$Ca(OH)_{2(s)} + CO_{2(aq)} = CaCO_{3(s)} + H_2O \qquad (12)$$

Consumption due to $CaCO_3$ formation was computed by examining the difference between total and dissolved total inorganic carbon (TIC) concentrations across the reaction tank. TIC was determined by collecting water samples and by field-measuring pH, dissolved alkalinity and temperature.

3.30 Validation of consumption analysis using alkalinity accounting – The alkali chemical dose was measured by conducting a mass balance analysis of [Ca] and [Na] concentrations at the influent and effluent of the reaction tank. Identifying the geochemical pathway of the alkali consumption was determined by tracking the changes in hydroxyl-consuming species, by speciation modeling and water sampling, at the influent and effluent of the reaction tank. The understanding of the system was validated by performing a mass balance accounting of the alkalinity inputs and consumption within the

reaction tank. Alkalinity inputs consist of the influent alkalinity of the untreated mine drainage and from hydrate dosing. Alkalinity consumption is caused by the three hydroxyl-consuming reactions noted above. Subtracting the alkalinity consumption from the alkalinity inputs will predict the effluent alkalinity of the reactor tank. Agreement between computed and measured effluent alkalinities validates an understanding of the consumptive processes.

$$\text{Alkalinity}_{\text{Effluent Computed}} = (\text{Alk}_{\text{Influent}} + \text{Alk}_{\text{from Ca(OH)2 Dosing}}) - \text{Alk}_{\text{Consumption}} \qquad (13)$$

4.0 Cost Reduction Evaluation Results and Discussion

4.10 Measured flow and chemical dosing rates – The results of the flow and dosing measurements and water sampling are shown in Table 2. The measured flow rates at Mon-View and Banning were 396 gpm and 2,310 gpm, respectively. The measured NaOH dosing rate at Mon-View was 122 gallons per day and the $Ca(OH)_2$ dosing rate at Banning was 3.7 tons per day. During the Mon-View evaluation in August 2010, the average unit cost of NaOH was $0.95 per gallon and during the Banning evaluation in October of 2012, the unit cost of $Ca(OH)_2$ was $160 per ton.

4.20 Computed chemical consumption due to Fe(II), hydroxylation and $CaCO_3$ formation – Water sampling results used in the analysis are provided in Table 2. The computed consumption due to the different reactions is shown in Table 3. The results show significant amounts of chemical are consumed by hydroxylation and, at Banning, calcite precipitation. Only 3% of the sodium hydroxide addition went towards calcite formation at Mon-View, as opposed to 60% of the hydrated lime addition at Banning. The results show $340 per day worth of hydrated lime is being consumed by calcite formation at Banning. X-ray defraction analysis and field application of acid to fresh precipitate confirmed the presence of calcite at both sites and affirms the analysis. In addition, the calcium activity diagram in Figure 2 shows the untreated water at both sites is unsaturated with respect to calcite and becomes supersaturated as pH is increased after alkali dosing. The diagram shows Banning treated water is much more saturated than Mon-View, which supports the analysis that less consumption due to calcite occurs at Mon-View.

Table 4 shows the computed daily costs for the reaction analysis compared against the actual costs determined from measured dosing. The good agreement between computed and actual costs at Banning indicates that alkalinity consumption at Banning is solely from chemical addition and the treatment system is not taking advantage of the influent alkalinity. On the other hand, the cost analysis at Mon-View shows the computed costs are double the actual costs. In this case, the sodium hydroxide dose is less than theoretically required for complete reaction neutralization because the treatment process uses the influent alkalinity in the treatment process. This efficient use of influent alkalinity and chemical saves $116 per day at Mon-View. For these reasons, Mon-View is operated as a more efficient treatment system than Banning.

Table 5 provides the results of the alkalinity accounting method that was used to validate the consumption analysis. The results show the predicted effluent alkalinity differed less than 10% for observed alkalinity for both sites, which provides confidence in the alkalinity consumption analysis.

8

Mon-View: Results of Original 20% Sodium Hydroxide (w/w) Treatment Configuation

Sample Location	Sample Date	Flow (gpm)	Chemical	Dosing (gal/day)	Daily Chemical Cost*	Field pH	Field Alkalinity	Ca - D	Ca - T	Fe - D	Fe - T	Mg - D	Mg - T	Mn - D	Mn-T	Na - D	Na - T	SO_4^{2-}	Cl^-	TDS @ 105 C
Reaction tank Influent	8/10/2010	396	20%			6.86	400	96.5	100	34.8	46.3	37.5	39.7	1.3	1.4	448	468	948	87	1858
Reaction tank Effluent	8/10/2010	396	NaOH	122	$ 116	7.22	385	95.5	102	4.306	46.2	37.2	40.8	1.3	1.4	475	515	919	89	2024
Final Effluent	8/10/2010	396	(w/w)			7.48	375	94.3	97.2	1.1	1.09	35.7	39	1.1	1.2	454	502	948	88	1920

* 20% NaOH = $.95/gal

All values in mg/L, Alkalinity = mg/L as $CaCO_3$, D = Dissolved, T = Total

Banning : Results of Original Hydrated Lime Treatment Configuation

Sample Location		Flow (gpm)	Chemical	Dosing	Daily Chemical Cost*	Field pH	Field Alkalinity	Ca - D	Ca - T	Fe - D	Fe - T	Mg - D	Mg - T	Mn - D	Mn-T	Na - D	Na - T	SO_4^{2-}	Cl^-	TDS @ 105 C
Reaction tank Influent	7/28/2011	2310				6.89	394	114	112	18	18.0	37.8	37.4	0.42	0.42	434	432	888	120	1918
Reaction tank Effluent	7/28/2011	2310	$Ca(OH)_2$	3.77 tons/day	$ 603	8.28	310	87.5	256	0.026	16.9	37	40	0.04	0.42	440	444	929	121	1844
Final Effluent	7/28/2011	2310				8.25	306	71.5	92	<.020	1.0	32.6	39.3	0.03	0.04	390	462	905	121	1920

* $Ca(OH)_2$ = $160/ton

All values in mg/L, Alkalinity = mg/L as $CaCO_3$, D = Dissolved, T = Total

Table 2: Sampling and dosing results for evaluating original Mon-View and Banning Treatment Systems.

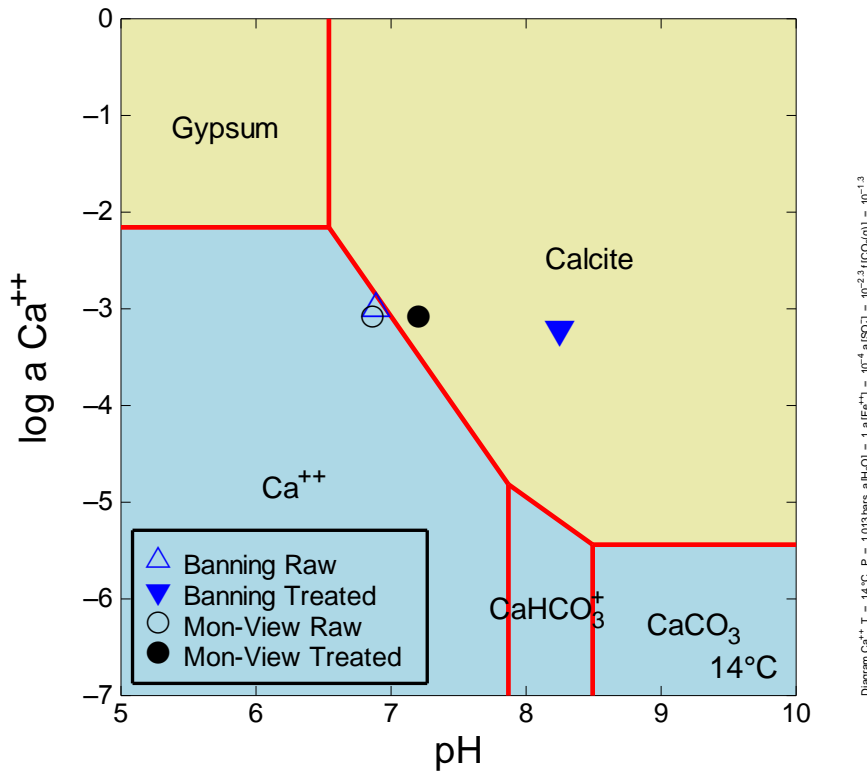|	Mon-View	Banning
Fe(II) removal	62	33
Hydroxylation	57	109
Calcite Formation	5.5	195
Total Computed Consumption	124.5	337

*values expressed as mg/L as $CaCO_3$

Table 3: Computed alkali consumption.

Figure 2: Calcium activity diagram for untreated and treated water. Diagram assumptions: T = 14º C, log a[Fe(II)] = -4.0, log a[SO_4^{2-}]= -2.3, log f[$CO_{2(g)}$]= -1.3

	Mon-View	Banning
Fe(II) removal	$112	$ 61
Hydroxylation	$102	$ 190
Calcite Formation	$ 10	$ 340
Computed Daily Chemical Cost	$224	$ 591
Actual Daily Chemical Cost	$116	$603

Table 4: Chemical costs due to hydroxyl-consuming reactions.

	Mon-View	Banning
Influent Alkalinity	400	394
Measured Alkali Dosing	65	252
Total Alkalinity Inputs	465	646
Computed Alkali Consumption	125	337
Calculated Effluent Alkalinity	340	309
Measured Effluent Alkalinity	375	310
Percent (%) Difference	-9%	-.3%

All values = mg/L as $CaCO_3$

Table 5: Validation of computed alkali consumption through alkalinity accounting.

4.30 Alternative treatment strategy and pilot testing – The results show the majority of the alkali addition is being consumed by nuisance reactions when pH is adjusted for Fe(II) removal. To avoid pH adjustment, the evaluation team sought a cost effective oxidant as an alternative treatment strategy. Hydrogen peroxide (H_2O_2) would solely target Fe(II) and avoid hydroxylation and calcite reactions. H_2O_2 consumption calculations predicted a significant cost savings over the alkali chemicals. Year-long pilot testing of H_2O_2 was conducted at both sites. Pilot testing consisted of using 330-gallon totes and a peristaltic pump to meter H_2O_2 dispensing into mine drainage.

5.0 Cost and Treatment Performance Comparative Analysis

The evaluation team developed a strategy to collect data for the comparative analysis. Both treatment systems were sampled the day of the conversion to the H_2O_2 pilot test to characterize treatment directly before H_2O_2 implementation. The goal was to collect performance data for both treatment chemicals in a short timeframe before flow or chemistry changed. Once H_2O_2 was dispensed, the effluent was

monitored for pH, alkalinity and total and dissolved [Na] and [Ca] to identify when the effects of NaOH and $Ca(OH)_2$ treatment were removed. During this time, the treatment system was calibrated to optimize H_2O_2 dosing and treatment performance. This flushing and calibration processes took six days at Mon-View and one and one-half days at Banning. During the six days, the flow increased at Mon-View from 396 to 420 gpm while the dissolved iron remained constant. The pump rate at Banning remained constant and the dissolved iron concentration decreased by 7.4 mg/L.

5.10 Mon-View – A 35% H_2O_2 dosing rate of 14 gallons per day was required to achieve a total iron effluent concentration within 0.4 mg/L of the NaOH treatment (Table 6). While preserving treatment performance, the use of H_2O_2 reduced the daily chemical cost from $116 to $46 per day, which is a yearly cost savings of $25,500. Assuming a net rate of return of five percent, the trust fund could save $226,422 over the next decade.

5.20 Banning – The Banning Treatment System required a long and complicated calibration process because of two reasons. First, the clarifier contained a short circuit that reduced the retention time from forty to five minutes. The short circuit did not drastically affect treatment performance during hydrate treatment but created a large iron plume that discharged a total iron concentration of 5 mg/l during H_2O_2 treatment. The configuration of the flume that conveyed water to the center well had to be reconfigured to correct the short circuit. Secondly, the oxidation of Fe(II) by H_2O_2 creates a particle that is extremely small and difficult to flocculate. After fixing the short circuit, the effluent total iron concentration ranged from 3 to 5 mg/L, even after using various poly-aluminum chloride coagulants and anionic polymers. Only a treatment combination of 50% H_2O_2 and $Ca(OH)_2$ would produce an effluent iron concentration similar to the $Ca(OH)_2$-only treatment. The H_2O_2 was injected into the pumping pipeline at a dosing rate that fully oxidized Fe(II) before being discharged to the reaction tank. Hydrated lime was added to the reaction tank and served as a flocculation aid.

A dosing rate of 25 gallons per day of 50% H_2O_2 and 1.2 tons per day of $Ca(OH)_2$ were required to achieve a total iron effluent concentration identical to the $Ca(OH)_2$-only treatment (Table 7). The combination of H_2O_2 and $Ca(OH)_2$ lowered the treatment costs from $603 to $275 per day, which is a yearly cost savings of $120,000. Assuming a net rate of return of five percent, the trust fund could save $1.1 million over the next decade.

Mon-View: Results of Original 20% Sodium Hydroxide (w/w) Treatment Configuation																				
Sample Location	Sample Date	Flow (gpm)	Chemical	Dosing (gal/day)	Daily Chemical Cost*	Field pH	Field Alkalinity	Ca - D	Ca - T	Fe - D	Fe - T	Mg - D	Mg - T	Mn - D	Mn-T	Na - D	Na - T	SO_4^{2-}	Cl^-	TDS @ 105 C
Reaction tank Influent	8/10/2010	396	20%	122	$ 116	6.86	385	96.5	100	34.8	46.3	37.5	39.7	1.3	1.4	448	468	948	87	1858
Reaction tank Effluent	8/10/2010	396	NaOH			7.22	400	95.5	102	4.306	46.2	37.2	40.8	1.3	1.4	475	515	919	89	2024
Final Effluent	8/10/2010	396	(w/w)			7.48	375	94.3	97.2	1.1	1.09	35.7	39	1.1	1.2	454	502	948	88	1920

20% NaOH = $.95/gal, all values = mg/L, alkalinity = mg/L as $CaCO_3$

Mon-View: Results of Pilot Testing 35% H_2O_2																				
Sample Location		Flow (gpm)	Chemical	Dosing (gal/day)	Daily Chemical Cost*	Field pH	Field Alkalinity	Ca - D	Ca - T	Fe - D	Fe - T	Mg - D	Mg - T	Mn - D	Mn-T	Na - D	Na - T	SO_4^{2-}	Cl^-	TDS @ 105 C
Reaction tank Influent	8/16/2010	420		14	$ 46	6.85	385.0	94.4	103	32.8	46	35.3	40.2	1.3	1.4	438	492	953	89	1840
Reaction tank Effluent	8/16/2010	420	35% H_2O_2			6.74	332.1	93.6	101	3.46	44.1	35.5	38.8	1.3	1.4	447	470	970	90	1800
Final Effluent	8/16/2010	420				7.2	326.0	93.3	93.6	0.04	1.41	35.1	35.5	1.3	1.3	433	428	949	89	1846

* 20% NaOH = $.95/gal, 35% H_2O_2 = $3.30, all values = mg/L, alkalinity = mg/L as $CaCO_3$

Table 6: Results of the cost and treatment performance comparative analysis: Original NaOH treatment versus H_2O_2 pilot test.

Banning : Results of Original Hydrated Lime Treatment Configuation

Sample Location		Flow (gpm)	Chemical	Dosing	Daily Chemical Cost*	Field pH	Field Alkalinity	Ca - D	Ca - T	Fe - D	Fe - T	Mg - D	Mg - T	Mn - D	Mn-T	Na - D	Na - T	SO_4^{2-}	Cl^-	TDS @ 105 C
Reaction tank Influent	7/28/2011	2310	$Ca(OH)_2$	3.77 tons/day	$ 603	6.89	394	114	112	18	18.0	37.8	37.4	0.42	0.42	434	432	888	120	1918
Reaction tank Effluent	7/28/2011	2310				8.28	310	87.5	256	0.026	16.9	37	40	0.04	0.42	440	444	929	121	1844
Final Effluent	7/28/2011	2310				8.25	306	71.5	92	<.020	1.0	32.6	39.3	0.03	0.04	390	462	905	121	1920

$Ca(OH)_2$ = $160/ton; All values = mg/L, alkalinity = mg/L as $CaCO_3$

Banning: Results of Pilot Tesing a combination of both 50% H_2O_2 and Hydrated Lime

Sample Location		Flow (gpm)	Chemical	Dosing	Daily Chemical Cost*	Field pH	Field Alkalinity	Ca - D	Ca - T	Fe - D	Fe - T	Mg - D	Mg - T	Mn - D	Mn-T	Na - D	Na - T	SO_4^{2-}	Cl^-	TDS @ 105 C
Reaction tank Influent	10/23/2012	2300	50% H_2O_2	25 gal/day	$ 275		469.4	89.4	89.5	10.6	10.8	31.2	31	0.278	0.272	426	446	675	112	ND
Reaction tank Effluent	10/23/2012	2300	&	and 1.2		7.5	587	107	137	0.081	10.8	28.2	32.6	0.166	0.284	396	440	677	112	ND
Final Effluent	10/23/2012	2300	Hydrated	tons/day			565.2	117	121	0.026	1.0	29.5	30.7	0.144	0.162	416	428	702	113	ND

* 50% H2O2 = $3.30/gal and $Ca(OH)_2$ = $160/ton; All values = mg/L, alkalinity = mg/L as CaCO3

Table 7: Results of the cost and treatment performance comparative analysis: Original Ca(OH)₂ treatment versus H₂O₂ and Ca(OH)₂ pilot test.

5.30 Comparative Analysis Summary – Because of the significant cost savings, a full-scale H_2O_2 treatment system was installed at Mon-View. The system consists of a tank, two diaphragm metering pumps, dispensing lines and safety equipment. As an added safety precaution, the tank was enclosed in a concrete block structure. The range of the diaphragm pump can treat flows from 300 to 2,200 gpm with $Fe(II)$ concentrations up to 37 mg/L. The capital and installation cost of the entire H_2O_2 system was $25,000. The cost savings predicted during the year-long pilot testing has translated to the full-scale system and the payback of the capital cost occurred within a year.

The Banning site is still using a combination of totes of H_2O_2 in conjunction with $Ca(OH)_2$. Approval has been granted to implement a full-scale H_2O_2 system during 2013. Approval has also been granted to evaluate the Euclid treatment facility where the estimated savings, using H_2O_2, are estimated at over $200,000 per year.

It is important to note H_2O_2 contains chemical safety issues that are much different than hydrated lime and other typical mine drainage treatment chemicals. Safety concerns must be considered alongside cost savings before making a final treatment decision. Both sites are visited daily by the treatment operator and human access is controlled by perimeter fencing and entrance gates. Hydrogen peroxide may not be recommended for remote and unattended mine drainage treatment sites.

6.0 Conclusions

This study showed that treatment of net alkaline mine drainage by alkali addition can result in significant chemical costs due to hydroxylation and calcite-formation reactions. Hydrogen peroxide can provide significant cost savings if dissolved $Fe(II)$ is the sole constituent of concern. However, thorough pilot testing and careful consideration of H_2O_2, safety issues are required before deciding on a final treatment strategy.

7.0 Acknowledgements

8.0 References

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