

OSM Contract Number S06PC12059

Applied Science Project

IN-situ Mitigation of Iron in a Net-alkaline Environment

IN MINE

Final Report

For:

U.S. Department of the Interior
Office of Surface Mining
Appalachian Region

By:

National Mine Land Reclamation Center
150 Evansdale Drive
NRCCE Building, Suite 202
PO Box 6064
Morgantown, WV 26506

Paul Ziemkiewicz, PhD, Director
Bruce Leavitt, P.E., P.G., Consultant
Richard Herd, Project Manager

November 23, 2009

Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

IN-situ Mitigation of Iron in a Net-alkaline Environment

IN MINE

Executive Summary

Hydrogen peroxide is a powerful oxidizing agent in liquid form. It is used at some acid mine drainage treatment plants instead of, or in addition to, mechanical aeration. Unlike oxygen derived from air, hydrogen peroxide reacts rapidly with ferrous iron in net alkaline water causing an immediate precipitate. Because it is a liquid, rather than a gas, it does not have to be compressed to be delivered to the bottom of a mine pool. Prior investigations have demonstrated, at bench scale, that *in situ* treatment of net alkaline mine water is possible. Hydrogen peroxide is more expensive than mechanical aeration, but the lower capital costs associated with an in situ treatment may offset the operating cost. In addition to evaluating the efficacy of hydrogen peroxide this study also investigates the hydrodynamics of flow in the mine.

The T&T / Ruthbelle mine complex, in Preston County West Virginia, consists of three mines: T&T #2, T&T #3, and Ruthbelle. On April 25 1994 a blowout at the T&T #2 pit mouth resulted in Environmental impacts to Muddy Creek and the Cheat River. A subsequent Consent Decree, with Coastal Coal, led to a hydrologic study of the mine complex and the injection of 80,845 tons of limestone sand as an *in situ* treatment. The State of West Virginia has had and continues to have the obligation of water treatment from this discharge.

The *in situ* use of hydrogen peroxide requires that the flow to be treated be concentrated in one or just a few mine entries. The mine map of T&T #2 was evaluated and a site was identified that met these criteria. A borehole, remaining from the Coastal project, was identified in the same entry, and site access permission was obtained from the property owner. Two holes were drilled into the mine in-by and out-by of this borehole. The upstream hole was for hydrogen peroxide injection and the downstream hole was for sampling of the mine water. A stainless steel submersible well pump was installed in the sampling well for this purpose. Electric service to the site was established by Allegheny Energy.

Hydrogen peroxide injection into the in-by well did not produce a dose response relationship with the sampling well despite high levels of peroxide addition. Review of the mine map indicated that the mine water might be flowing in a down dip entry 9.6 meters away from the current hole. The preexisting Coastal well was located between this entry and the sampling well, and was upgraded to serve as a peroxide injection well. The response to hydrogen peroxide addition into the Coastal well was significant and the initial effects of the addition were evident within 41 minutes. Field measurements of pH, oxidation reduction potential (ORP), and dissolved oxygen (DO) all responded to the addition of hydrogen peroxide.

Field titration of the raw mine water using pH, DO and ORP were conducted to establish the ferrous oxidation end point. ORP and pH both proved useful in determining this end point. One or both of these probes can be used to control the rate of hydrogen peroxide addition so that over treatment does not occur.

The hydrogen peroxide injection rate was controlled by a peristaltic pump. This injection rate was varied periodically and the effect of these different rates were measured at the sampling well. Water samples were also taken and measured for total, dissolved and ferrous iron. Based on these data, a dose response plot was created which showed a linear relationship with an R^2 value of 0.99 for both the dissolved and the ferrous iron data. This plot was used to calculate the dose required for complete ferrous iron oxidation, this number was then used to determine that the flow in the mine entry was 43 gallons per minute during the test.

The following conclusions and recommendations are offered:

In Situ oxidation of ferrous iron using hydrogen peroxide has been demonstrated. The reaction is rapid and proportional to dose.

Either pH, ORP, or both may be used to determine the completion of the oxidation process so that over treatment does not occur. These inputs can be used by a PLC to regulate the dose.

Hydrogen Peroxide addition does not affect the amount of carbon dioxide dissolved in the mine water. Ex-solution of that carbon dioxide will increase the pH of the raw mine water or the hydrogen peroxide treated mine water. This allows the treatment designer the ability to raise the pH at the mine discharge following *in situ* oxidation with hydrogen peroxide.

Hydrogen peroxide can be used to determine the volume of flow in an entry. Based on this calculation, it was possible to estimate the flow and water chemistry of the combined T&T #3 and Ruthbelle mines.

Injection of hydrogen peroxide into a point of concentrated flow was deemed essential during the project design, and this point was demonstrated when the designed injection well was not in the flow path. Had more reliance been placed on the indicated mine ventilation stoppings, the injection hole might have been located in a better spot.

The chemical cost of Hydrogen Peroxide treatment has been calculated to be \$0.0066 per mg/l ferrous per 1000 gallons. The estimated capital cost for a single site is \$36,000 although this number will vary with site specific conditions.

The travel time in the corridor from the Coastal injection well to the pit mouth is between 43.0 and 67.7 hours. Settling of the iron hydroxide precipitate has been demonstrated at bench scale, is indicated by laboratory analysis at the Livengood sampling well, but could not be confirmed at the T&T pit mouth. This is believed to be attributable to the high velocity in the test entry combined with the low pH of the Ruthbelle flow which resulted in the re-dissolution of the iron precipitate.

The effect of hydrogen peroxide addition on the ORP and the ferrous iron data at the pit mouth was observable.

Recommendations:

The water quality from the T&T #2 mine is net alkaline and low in aluminum, as a result it will not benefit greatly from additional alkalinity addition. On the other hand, the water joining the corridor

from Ruthbelle would benefit greatly from additional alkalinity. The potential addition of alkalinity to the sludge disposal water in T&T #3 should be investigated.

In Situ settlement of iron should be achievable if the location of the injection well is located further in-by the current location. This would provide fully flooded entries with slow water velocity to promote settling, it would provide storage volume for the sludge, and it should also be possible to avoid the complications associated with the limestone sand injection.

IN-situ Mitigation of Iron in a Net-alkaline Environment

IN MINE

Introduction

Hydrogen peroxide is known to react rapidly with ferrous iron in net alkaline water. (Ziemkiewicz 2001.) This reaction results in a drop in pH and precipitation of the iron. In slow moving waters, such as those that would be encountered in a flooded mine entry, the precipitated iron is expected to settle relatively quickly. This attribute was demonstrated at bench scale in Ziemkiewicz 2001. Additional bench scale testing showed that there was no detectable oxidation of pyrite due to the presence of the hydrogen peroxide.

The chemistry of water emanating from below drainage underground mine in the Pittsburgh coal seam has been shown to evolve from net acidic to net alkaline over time. As a result, there are large numbers of mine discharges that are net alkaline located in Pennsylvania and West Virginia. This net alkaline chemistry is well suited for in situ reaction with hydrogen peroxide.

The successful application of hydrogen peroxide in *in situ* treatment is dependent on identifying points of concentrated flow in the underground mine. The ideal condition would be a point in the mine where all of the flow is concentrated in one or two entries. Examples of this condition can include: mine to mine transfers via entry or borehole; or restriction in the mine caused by internal barriers, mining conditions, or, in the case of older mines, water drainage entries.

This purpose of this project is to demonstrate the effectiveness of this technology under field conditions, and to use data gathered during the study to better understand the hydrology of the mine. Once the ability to treat and the flow conditions in the mine are established then the cost of in situ treatment using hydrogen peroxide can be established.

T&T Mine Complex

The T&T mine complex is composed of three mines in the Freeport coal located in Preston County West Virginia. These mines are T&T #2, T&T #3, and Ruthbelle. These three operations were mined independently but eventually they were connected at two key locations. Ruthbelle was the first of the three mines, its operation was conducted beginning in the 1940's, and closed prior to 1977. In order to access additional coal reserves the T&T #2 mine drove a set of entries along the NE – SW strike just South East of the Ruthbelle mine. This corridor is two to four entries wide and about 1,800 meters in length. Plate 1. Water flows in this corridor from the T&T #2 mine to a discharge point along Muddy Creek. Along the corridor, about 600 meters from the main body of the T&T #2 mine, there is an interconnection between the Ruthbelle mine and the corridor. Plate 2. This connection allows water from Ruthbelle and from T&T #3 mines to join with the flow from T&T #2. From this point on the flow from all three mines is comingled to the discharge point along Muddy Creek. The three mines are roughly equal in size and in total represent about 1,500 acres of mining. (Miller and Skiles, 1999.) Mining ceased in 1993. In April 1994 a blowout occurred at the T&T #2 mine along Muddy Creek.

In September, 1998 a consent decree was established between Costal Coal, LLC and the West Virginia Department of Environmental Protection. Pursuant to this agreement Costal Coal has injected over 80,000 tones of limestone through a number of boreholes in an effort to neutralize the acidity in situ. A report on the effectiveness of this in situ treatment was issued in March 2002. (MWH 2002) The analysis performed in this report documented a 20 percent reduction in acidity resulting from the limestone injection. In addition to limestone injection Costal Coal, LLC took over the collection of water quality data from the WV DEP. One of the sampling sites included the T&T #2 pit mouth. Between the WV DEP and Costal Coal a water quality data set has been created that spans from February 1996 to November 2001.

The reports do not indicate points of injection or the quantities of limestone injected at each borehole except to say that some of the holes drilled during the reconnaissance portion of the study were used for limestone injection. Limestone injection took place during the field seasons of 1999, 2000, and 2001.

Water exiting the mine portal is treated by West Virginia DEP using anhydrous ammonia to raise the pH of the water. If needed, hydrogen peroxide is available on site to assist with ferrous iron oxidation, but it was not used during this field trial. Data collected in the period 1996 -2001 have been averaged by year and are presented in Table 1. For comparison, raw water data from the current study are also presented. The current data are limited to just a few samples and are not as representative of the discharge as are the earlier data.

Table 1.

Year	pH	Acidity	Sulfate	Al	Fe	Mn
1996	2.80	1324.6	1287.3	50.2	213.7	2.26
1997	2.82	952.1	1158.7	35.8	197.2	2.21
1998	2.81	642.8	1115.3	34.3	152.3	1.95
1999	3.07	670.2	1216.7	36.6	139.5	1.92
2000	2.95	865.6	1630.2	58.9	177.3	2.68
2001	3.19	509.4	1743.8	32.1	99.0	2.46
2009	2.80	453.3	1237.1	25.1	34.4	1.39

From Table 1. it is evident that although the pH and the sulfate have not changed significantly, the acidity and the metals have shown significant reduction over time.

Livengood Test Site

The mine map of T&T #2 was studied to determine the point at which flow in the mine would be concentrated into a single entry, and where conditions on the surface would allow drilling access. Parameters considered in this analysis included the elevation of the existing mine discharge, the dip of the mine, the potential influence of the mine ventilation system, and water level information from open holes left by the Costal project. A site was identified in a farmer's field which had an old well from the Costal project. This property is owned by Elvon Livengood, and permission to drill two wells was granted for this site.

The site is at the top of the hill and is nearly flat. Costal had placed stone in the field for their operation which provided a solid base for the well nearest the road. Photo 1. Shows the field overlying the targeted mine entry. The in by well was drilled adjacent to the shelter on the right hand side of the

picture. The out by well is located near the clump of trees on the left hand side of the photo. The existing Costal hole is located about half way between.



Photo 1. Livengood test site

A shelter was erected to provide shade for the hydrogen peroxide, and to provide a rain free work space for the field testing. Photo 2. shows the shelter with two 300 gallon totes of 35 percent hydrogen peroxide.



Photo 2. 35% Hydrogen Peroxide at the Livengood field site.

Electric power to the site was arranged through Allegheny energy. A transformer was set and single phase power was dropped to a pole set on the Livengood property. A meter socket and breaker box was installed. Power from this installation was distributed around the test site to operate the well sampling pump, the chemical injection pump, and other equipment. Photo 3 is aligned with the injection entry as viewed from the shelter. The white wire in the picture is provided electric power to the shelter. The Allegheny energy power pole can be seen in the background.



Photo 3. Surface alignment along mine entry

Originally, this wire was placed on the ground, but field mice found the insulation too tempting so the wire was elevated to prevent mouse executions. Keeping the peroxide injection pump operating was an added benefit.

A variable speed peristaltic metering pump, STN-85MJL5A4S Stenner Series 85, was purchased and installed at the test site. Photo 4.

Drilling

Global positioning system (GPS) coordinates were taken at the T&T #2 pit mouth and at the existing Coastal Coal borehole on the Livengood property. These data were combined with a mine map which was georeferenced to the USGS topographic map using ARC Map software. After a number of trials a best fit was obtained. GPS coordinates obtained from the georeferenced map were located on the ground and the location of the in-by well was determined. Three D Drilling of Kingwood West Virginia drilled into the mine and completed the well with two inch PVC pipe. A shale trap was placed about 20 feet above the mine and the annulus was fill with bentonite chips. The bottom ten feet of the two inch PVC pipe was drilled in the field with $\frac{3}{4}$ inch holes, and the pipe was allowed to set on the mine floor. When the drill broke through into the mine, circulation was lost consequently no material from the mine was recovered. The driller did notice that there appeared to be a soft material that flowed into the hole when the drill steel was removed. All efforts to clean this material out were unsuccessful.



Photo 4. Stenner peristaltic pump

Having encountered the mine with the first hole that hole was used along with the old Costal Coal hole to establish the entry alignment. A level transit was set up on the in-by well and a sight was taken of the Costal Well. This line was projected to the far end of the field where the out-by well was to be drilled, and the drill site was staked. Drilling on the second hole commenced, but it encountered coal at the mine horizon. This hole was backfilled and a second hole was drilled about 12 feet to the south east. The second attempt encountered the mine, and a five inch PVC casing was installed in the hole. Due to the small annulus in this hole it was determined that bentonite chips would probably bridge and prevent a proper sealing of the well. As a result the casing was left standing in an unsealed hole with a shale trap about 20 feet above the mine.

Several days later an attempt was made to bail a water sample from both of the wells. The bailer failed to go to the bottom in both holes. A borehole camera was lowered into the five inch well and the casing was observed to be crushed. The camera was too large to be lowered into the two inch well. Because the five inch casing had not been sealed in place it was possible to remove this casing and replace it with a four inch PVC casing. The five inch casing was removed without incident. Upon examination, there were no dents or scratch marks of the outside of the casing indicating that it was water pressure that crushed the pipe. The pipe collapse occurred just above the shale trap where the highest hydrostatic pressure would be expected. Photos 5 & 6 show the collapsed section of casing. The four inch casing was installed and the annulus was sealed with bentonite.



Photo 5. Collapsed 5 inch casing with shale trap.

The obstruction in the two inch well was originally observed at about 100 feet. Subsequent measurement of the obstruction found that the plug had fallen down the hole and was lodged at about 270 feet down the hole. An attempt was made to drive the plug to the bottom using a weight on a rope, this was unsuccessful. A second attempt was made to use water from the onsite pump to jet the plug out. This was also unsuccessful. Finally, a soil boring drill was brought on site and the plug was drilled out of the two inch PVC with a tri-cone bit. The drill cuttings were evaluated for evidence that the drill had perforated the casing; no ground up plastic was observed. The plug consisted of drill cutting and bentonite that were apparently dropped down the hole.

At the request of the land owner both well completions are below plow depth so that the field can be farmed. The wells are fitted with cast iron monitoring well lids so that the wells can be located with metal detectors even if they become buried.

A one half horsepower Grundfos pump was installed in the out-by well and was sampled on May 10, 2009, and was powered with a generator as AC power had not yet been installed. Initially the pump produced cloudy water with some larger particles. Upon examination these particles were determined to be limestone. The presence of fine limestone in this well explains the flowable material that the driller described when the well was drilled. Based on this observation it appears that the old Costal Coal well was not used for observation purposes as was originally thought but rather, it was used as a limestone injection well.

In order to overcome the limestone sediment in the produced water the pump was raised about one foot so that the pump intake was above the level of limestone in the well. Upon continued operation the water produce from this well lost all of its turbidity. The intake was set at 282.5 feet below surface, and the depth to water was 280.35 feet. At this depth setting the well initially produced five gallons in 1.23 minutes or slightly more than four gallons per minute. By August 28, 2009 the pump discharge rate had diminished to 0.764 gallons per minute. This reduction in flow resulted from the addition of 300 feet of pipe at the surface to convey the sample water from the out-by well to the shelter for analysis.

The flow reduction may also be due to wear cause by the limestone grit or by iron deposits on the pump resulting from the peroxide treatment. In either case the time required for water to travel from the pump to the sampling shelter was between 15 and 18 minutes.



Photo 6. Crushed 5 inch casing

Table 2 contains the results of the field testing conducted on the pumped well on May 10, 2009. Specific conductance (SC) is used to determine if the water quality from a well has stabilized prior to sampling. In a normal well, stagnate water in the well bore must be removed before the actual ground water quality can be obtained. Because this well is completed in a large pooled area that may also be flowing it is important to know how much time must be allowed so that a representative sample can be obtained. The SC rises for about 40 minutes and then fluctuates between 1033 μS and 1057 μS . At a four gallon per minute pumping rate about 160 gallons were pumped before the SC stabilized. The variability in the SC after the stabilization period is consistent with flow in the mine. Mine water is known to be variable in both space and time so short term variations in SC should be expected along with longer term seasonal trends.

Dissolved oxygen (DO) shows a similar trend decreasing from one milligram per liter to 0.48 milligrams per liter. Temperature and pH were in the stable range within nine minutes of the waters arrival at the surface. A single alkalinity test was conducted at the end of the test run. This analysis yielded an alkalinity of 120 milligrams per liter.

Table 2

Time	SC	Temp	pH	DO	Flow	Alkalinity
11:17					Pump on	
11:19	953	12.3	6.45		3.94	
11:28	1012	12.7	6.56		4.06	
11:34	1019	12.7	6.60	1.01		
11:47	1025	12.8	6.57			
11:56			6.65	0.97		
12:02	1039	12.9	6.57			
12:18	1057	13.0	6.54	0.48		
12:26	1033	13.0	6.60			
12:31	1049	12.8	6.59			
12:35						120

An initial field aeration test was also performed. An aquarium aerator was connected to a sparging stone and placed in a 500 ml graduated cylinder containing produced mine water. Table 3 contains the results of this test. Dissolved oxygen is at saturation within two minutes, and the pH has stabilized after eight minutes. The rise in pH levels is due to the exsolution of dissolved carbon dioxide. This initial test may not have been conducted for a sufficient period of time. Subsequent aeration testing on August 20 required 38 to 40 minutes for the pH to stabilize.

Table3.

Minutes	pH	DO
0	6.62	2.14
2	6.68	12.18
4	6.77	12.31
6	6.85	12.79
8	6.92	12.82
11	6.93	12.74
12	6.92	12.68

Based on these initial field data the water quality exiting the T&T #2 mine under the Livengood property is not the water quality that was expected. Data from the discharge showed a laboratory pH of 2.41 and an acidity of 811 mg/L. Laboratory water quality analyses for the Livengood out-by well are presented in Appendix A. Laboratory analyses for the T&T discharge are presented in Appendix B. When these data are compared it is clear that they represent two water quality evolutions. The Livengood well has 43.6 mg/L dissolved iron and it is essentially all ferrous while the mine discharge has 139.4 mg/L of dissolved iron and only 43.6 mg/l are in the ferrous oxidation state.

Hydrogen peroxide has been demonstrated for use in net alkaline conditions. The proposal had anticipated net acidic conditions based on the water quality at the mine discharge. Ammonia addition was proposed to convert the net acidic water into net alkaline water prior to oxidation with hydrogen peroxide. Because the chemistry at the Livengood site is net alkaline, the addition of ammonia was not needed.

Site Configuration and initial testing

Water from the out-by well was pumped to the surface and conveyed in a $\frac{3}{4}$ in polyethylene pipe to the in-by well adjacent to the shelter. This water was directed into the in-by well where it was available for sampling and where it could serve as dilution water for the hydrogen peroxide. Hydrogen peroxide was pumped into the in-by well and allowed to mix on the way down the hole so that the density of the 35 percent hydrogen peroxide did not result in a concentrated pool of the chemical in the bottom of the hole. Photo 7. shows the in-by well receiving pumpage from the out-by well. The $\frac{3}{4}$ inch polyethylene pipe is discharging into the beaker where the pH, DO, and ORP are measured. The overflow of the beaker goes down the well where it mixes with the peroxide which was delivered to the well from the small black tube running from the upper left to the center of the frame.



Photo 7. Mine water sampling and injection into the in-by well

On July 22, 2009, pumpage from the out-by well was measured at 2.14 gallons per minute. The peroxide metering pump was set at 0.05% of maximum flow which yielded 9 ml/min of 35 percent hydrogen peroxide. This flow was again measured on July 23 and was found to be 8.5 ml/min. After 22.5 hours no effect was observed in the mine water chemistry that could be attributed to the hydrogen peroxide addition. Table 4 contains the field data collected on the mine water produce from the out-by well.

At this time it was determined that the sampling pump in the mine was shutting off on thermal overload. Submersible pumps are cooled by the flow of water passing between the pump and the well casing. In this installation, there is no induced flow past the pump motor, and in fact the pump motor may be immersed in fine limestone particles further separating the pump from the needed cooling. In order to keep the pump from motor failure, a timer was installed that turned the pump on and off automatically at a user adjusted frequency. The initial setting on July 24 was for 30 minutes on and 30 minutes off. This frequency was changed on July 26 to 25 minutes on and 35 minutes off after the pump was found to be off as the result of thermal overload. After this adjustment the pump was able to run without any further thermal overload problems.

Table 4 Field measurement of Livengood well #3, out-by

Date	Time	pH	DO	ORP	Alk	Well
7-22-09	13:34	6.32	0.04	82		
Peroxide on 14:00 35% 18ml/2min						
7-23-09	11:52	6.47	0.05	70	119	1
7-23-09	12:06	6.48	OR	66	136	1
Peroxide 35% 17ml/2min						
Well pump on 30 min off 30 min						
7-25-09	11:44	6.42	0.23	102		1
7-25-09	11:45	6.44	0.07	102	133	1
Peroxide 12:22 35% 16ml/2min						
Increase peroxide to: 33ml/2min						
7-26-09	15:42	6.40	0.06	108	127	1
7-26-09	16:00	6.34	0.12			1
7-26-09	16:54	6.40	0.07	118		1
7-26-09	18:50	6.49	OR	123	129	1
Peroxide 35% 36ml/2min						
well pump on 25 min off 35 min						
7-27-09	18:50	6.50	OR	64	170	1
7-29-09	7:50	6.47	OR	151	132	1
7-30-09	19:50	6.5	0.05	119	127	1
Peroxide 20:10 35% 34ml/2min						
Increase peroxide to: 52ml/2min						
7-31-09	15:50	6.47	0.01	223	128	1
8-1-09	18:50	6.41	0.00	19	118	1
Peroxide 18:30 35% 48ml/2min						
8-3-09	15:50	6.48	0.03	0	130	1
Peroxide 18:30 35% 51ml/2min						
Increase peroxide to: 85ml/2min						
8-4-09	15:50	6.51	0.01	13	136	1
8-5-09	13.50	6.47	0.02	14	131	1
Peroxide off 13:25						

On July 26 the hydrogen peroxide dosing was increased to 18 ml per minute. This dosing was retested on July 30 at 17 ml/min. Over this time period there was no change in the water chemistry that could be attributed to the peroxide addition

Dosing was again increased on July 30 to 26 ml/min, it was remeasured on August 1 at 24 ml/min and again on August 3 at 25.5 ml/min. During this time period there was no change in chemistry that could be attributed to the hydrogen peroxide addition. This injection was terminated on August 5 at 13:50 hours.

The lack of connection between the in-by and the out-by wells over such a short distance required a more in depth analysis of the potential flow paths within the mine. A level survey was conducted to determine the relative elevation of the top of the three well heads and the depth to water in each of the wells. An approximate elevation of 1830 was assumed for the top of the out-by well using the mine

elevation of the out-by well as a reference point. Based on the five foot contours in the mine this estimate is believed to be within a foot of the true mine elevation. Based on this, the top of the Costal well was determined to be 1832.77 and the in-by well was determined to be 1832.19. Depth to water was measured at 280.43, 281.20 and 280.43 respectively. This yields a water elevation in the mine of 1551.79 at the in-by well; 1551.57 at the Costal well; and 1549.57 at the out-by well. Based on these elevations water flow in the mine should be in the assumed direction. Plate 2 shows that there is a parallel entry up dip of the target entry, but in order for water to flow in that entry the water level in the mine must exceed 1555 feet. Since it does not, this possibility was precluded.

The mine map also shows that there is an entry down dip of the entry in which the wells are located and that it connects to the target entry with a crosscut about 9.6 meters downstream from the in-by well. In addition, there is a stopping shown upstream of the in-by well that, if intact, would preclude flow past the in-by well. This creates an unlikely situation in which injection over an extended period of time cannot travel 30 feet to the connection with the down dip entry. This suggests that there might be an obstruction such as a roof fall that serves to isolate the in-by well. This hypothesis was tested by attempting hydrogen peroxide injection into the Costal well.

The surface plumbing was reconfigured to allow hydrogen peroxide injection into the Costal Coal well. A one inch PVC pipe was installed in the well with the bottom ten feet perforated. This pipe was needed because the Costal well is an open hole construction without a casing. Ground water flows into this well, and over the years, has deposited iron precipitates on the interior of the well bore. The discharge point of the out-by well was maintained at the shelter site and the excess water was allowed to flow into the in-by well. A new source of dilution water was obtained from a water well located on the Livengood property. This dilution water was brought to the shelter where the hydrogen peroxide was injected into the pipe and the combined flow was then directed to the top of the Costal well. Photo 8 shows water from the out-by well being measured for pH, DO and ORP. The small black pipe running from the lower right to the top of the frame contains the dilution water prior to peroxide addition.



Photo 8. measuring pH, DO, and ORP from out-by well, injection into Costal well.

Hydrogen peroxide injection was resumed on August 18. This 13 day span between injections allowed time for the influence of the prior injection to dissipate and not influence the results. Table 5 contains the results of the testing at the new injection point. From these data a rapid, definitive and proportional response was observed.

Table 5 Field measurement of Livengood well #3, out-by

Date	Time	pH	DO	ORP	Alk	Well
8-18-09	10:50	6.55	0.05	-69	116	
Peroxide on 11:10 35% @10% metering pump						2
8-19-09	8:50	5.93	5.83	250	62	2
Peroxide off 9:08						
8-20-09	8:50	6.42	0.09	3		
8-20-09	9:50	6.34	0.08	4		
Peroxide on 10:02 35% @10% metering pump						2
8-20-09	10:50	6.45	0.05	-74		2
8-20-09	11:50	5.88	3.70	13		2
8-20-09	11:51	5.87	4.16	31		2
8-20-09	11:52	5.86	4.22	41		2
8-20-09	11:53	5.85	4.34	52		2
Peroxide on 11:54 35% @05% metering pump 16.88 ml/min						
8-20-09	12:45	5.82	4.6	201		2
8-20-09	12:50	5.82	4.44	165		2
8-20-09	12:54	5.82	4.29	144		2
8-20-09	1:45	5.80	4.56	141		2
8-20-09	1:50	5.80	4.5	99		2
8-20-09	1:54	5.80	4.35	90		2
8-20-09	2:54	5.81	4.40			2
8-21-09	14:50	5.79	6.71	281		2
Peroxide on 14:40 35% @2.5% metering pump 16.88 ml/min						
8-21-09	15:50	5.79	6.48	295		2
Peroxide pump on minimum setting 8.75 ml/min @ 15:57						
8-22-09	8:50	5.73	4.59	198		2
8-22-09 *H2O2 off	9:50	5.75	3.58	178		2
8-23-09	14:50	5.75	4.76	244		2
Peroxide off 8-23-09						
8-24-09	8:54	6.21	0.73	68		
8-24-09	9:54	6.34	0.13	-39		
8-24-09	10:50	6.34	0.04	-57		
8-24-09	11:52	6.22	0.08	-42		
Peroxide on 12:00 1/3 strength 100 ml/11.58 min						
8-24-09	12:40	6:29	0.14	-79		2
8-24-09	12:45	6.31	0.10	-69		2
8-24-09	12:50	6.32	0.10	-69		2
8-24-09	12:54	6.32	0.10	-66		2
8-24-09	13:35	6.23	0.09	-87		2
8-24-09	13:40	6.27	0.06	-91		2

8-24-09	13:45	6.27	0.09	-71		2
8-24-09	13:50	6.23	0.23	-50		2
8-24-09	13:54	6.19	0.28	-41		2
8-24-09	14:35	6.07	0.27	-53		2
8-24-09	14:40	6.11	0.31	-52		2
8-24-09	14:45	6.09	0.44	-21		2
8-24-09	14:50	6.07	0.49	-20		2
8-24-09	14:54	6.07	0.52	-17		2
8-24-09	15:35	6.00	0.34	-31		2
8-24-09	15:40	6.04	0.51	-35		2
8-24-09	15:45	6.04	0.61	-5		2
8-24-09	15:50	6.03	0.61	-3		2
8-24-09	15:54	6.05	0.62	-6		2
8-25-09	10:45	6.06	0.81	13		2
8-25-09	10:50	6.07	0.75	13		2
8-25-09	10:54	6.07	0.73	12		2
Peroxide on 11:33 1/3 strength 100 ml/6 min 32.7 sec						
8-25-09	13:45	6.00	1.31	20		2
8-25-09	13:50	5.99	1.32	36		2
8-25-09	13:54	5.99	1.33	37		2
8-25-09	14:45	5.90	1.80	75		2
8-25-09	14:50	5.90	1.79	84		2
8-25-09	14:54	5.91	1.77	80		2
8-26-09	11:45	5.88	2.38	177		2
8-26-09	11:50	5.87	2.30	168	56	2
8-26-09	11:54	5.90	2.36	161		2
Peroxide on 13:12 1/3 strength 500 ml / 30 min 22.28 sec						
8-27-09	9:45	5.83	2.76	209		2
8-27-09	9:50	5.85	2.67	193	46	2
8-27-09	9:54	5.85	2.67	184		2
Peroxide off						
8-28-09	9:53	6.42	0.21	35		
8-28-09	9:54	6.41	0.15	20		
8-28-09		6.41	0.14	10		
Peroxide on 11:49 1/3 strength 500 ml / 20 min 46.88 sec						
8-28-09	11:50	6.42	0.00	-13		2
8-28-09	11:54	6.42	OR	-18		2
8-29-09	9:45	5.72	4.36	336		2
8-29-09	9:50	5.72	4.35	335	44	2
8-29-09	9:54	5.71	4.33	387		2

Once a response to injection was established, a number of tests were conducted to determine the dosage required to fully treat the mine water in situ. The data were also used to estimate travel time between the injection point and the out-by well. This analysis was complicated by intermittent nature

of the pumping from the out-by well, and the travel time that the water was in the pipe from the pump to the sampling location.

Measurement of the hydrogen peroxide dose is crucial to determining the dose response curve and the cost of treatment. Initial measurements during the period of injection into the in-by well were based on how much peroxide was pumped over a period of two minutes.

The Peristaltic pump, used in this application, utilized a stepping motor which operated in an on / off pattern rather than a continuous slow rotation. Consequently, the hydrogen peroxide delivery was not continuous and uniform. Variation was noted between replicates of the two minute test. In order to compensate for this variability a 100 or a 500 ml test was used.

In this test, a ring stand was used to hold the discharge tubing from the peristaltic pump. The pump was allowed to run until roughly uniform flow was obtained. After a pulse of hydrogen peroxide a volumetric flask was placed under the discharge tubing and the stopwatch was started. The test was allowed to proceed until the flask was filled to the indicated mark and at that point the elapsed time was recorded. Photos 9 & 10 show this procedure with the 500 ml volumetric flask.

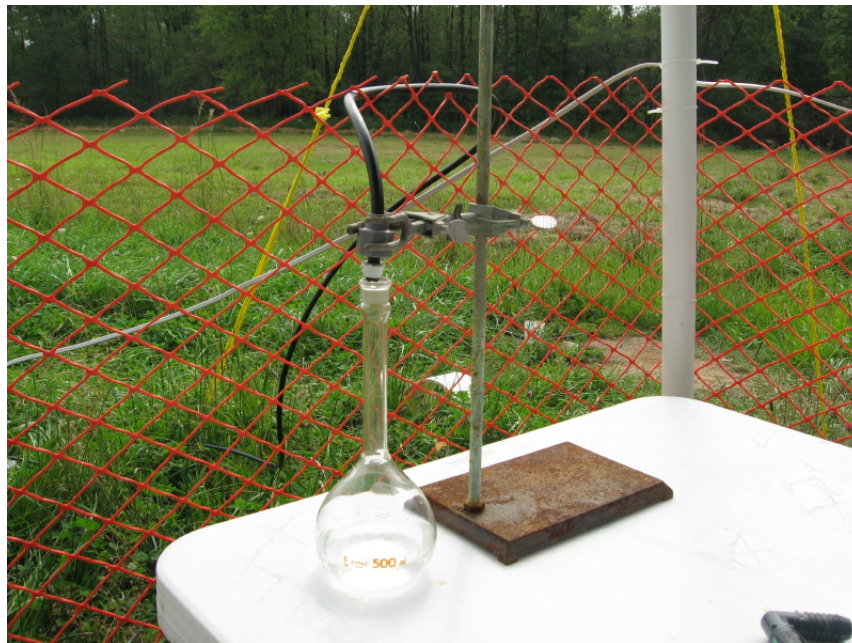


Photo 9. Determination of Hydrogen peroxide dose.



Photo 10. Hydrogen Peroxide dose measurement

Bench Tests

In order to determine when oxidation in the mine had reached completion a number of bench tests were needed to determine how the fresh mine water reacted with the peroxide and what analytic criteria provided the best assessment of full ferrous iron oxidation.

A ten liter bench test was conducted at the test site to determine the exact amount of hydrogen peroxide required to fully oxidize the ferrous iron in the T&T #2 mine. Water was pumped from the mine at well three and measured using a graduated cylinder; the water was then placed in a five gallon bucket. The bucket was placed on a stir plate and a magnet was placed in the bucket to provide continuous stirring.

Thirty five percent hydrogen peroxide was diluted using two parts water to one part hydrogen peroxide. This dilution was used to provide greater detail in the test results. An Eppendorf micro pipette was used at setting 6.0. The weight of liquid delivered at this setting was determined by adding successive doses to a beaker that was being weighed on an Ohaus Adventurer balance. These data were recorded and are presented in Table 6. The average weight of 14 pipette doses was 0.023571 grams per dose.

Diluted hydrogen peroxide was added to the ten liter mine water sample while DO, pH, and ORP were measured. These data were collected using a Hach HQ40D multi meter for pH and DO and an ExStick RE300 for ORP readings. The Hach meter determines DO using luminescence instead of a membrane. This method allows for a rapid measurement of DO. For most dosings, two replicates were measured of these three parameters to determine if additional mixing time changed the results. These data are plotted in figures 1 through 3.

Dissolved oxygen in the mine water is very low, typically about 0.05 mg/l. As a result of water volume measuring and transfer the DO content of the raw water increased to 4.91 mg/l. A plot of the DO

content of the water during the hydrogen peroxide addition shows a gradual increase in DO, but there are no changes in the graph that would indicate the completion of ferrous oxidation.

As ferrous iron is oxidized, a hydrogen ion is released for each iron atom that is oxidized. Since pH is a measure of the hydrogen ion concentration increasing that concentration is expected to lower the pH. Indeed this can be observed in Figure 2. At a dose of 0.393 grams of 35 percent hydrogen peroxide the pH of the mine water reaches its lowest point, and a break occurs in the slope of the plot. Analysis of the pH data prior to the break in slope shows an exponential relationship between peroxide addition and pH reduction. This exponential curve represents a very slight improvement of 0.001 R² over the linear model. Given that pH is a log function a linear fit should not be expected.

The best fit to the ORP data was a second order polynomial. This model improved the R² by 0.013 over the linear model. The plot of the ORP data also shows a break in slope. This break occurred at 0.385 grams of 35 percent hydrogen peroxide. This break in slope was at an ORP of 142 milli volts. The end point as determined by pH was only one pipette dose greater than the end point indicated by the ORP reading.

Either pH or ORP can be used to determine the end point of ferrous iron oxidation. This is an important consideration because the use of either of these end points will allow for the automation of dosing of the hydrogen peroxide. The use of the pH endpoint will be site specific, and it may vary seasonally depending on water chemistry. The use of the ORP endpoint is expected to be transferable site to site, and is not expected to be subject to seasonal changes or variations in the ferrous iron content. The pH data show a crisp transition in slope while the ORP transition is more gradual.

Table 6. Weight of peroxide delivered by micro pipette

Sample	Cumulative grams	Average grams
1	0.023	0.023
2	0.047	0.0235
3	0.069	0.023
4	0.092	0.023
5	0.118	0.0236
6	0.142	.023667
7	0.164	.023429
8	0.188	.0235
9	0.212	.023556
10	0.236	0.0236
11	0.259	0.023545
12	0.282	0.0235
13	0.306	0.023538
14	0.330	0.023571

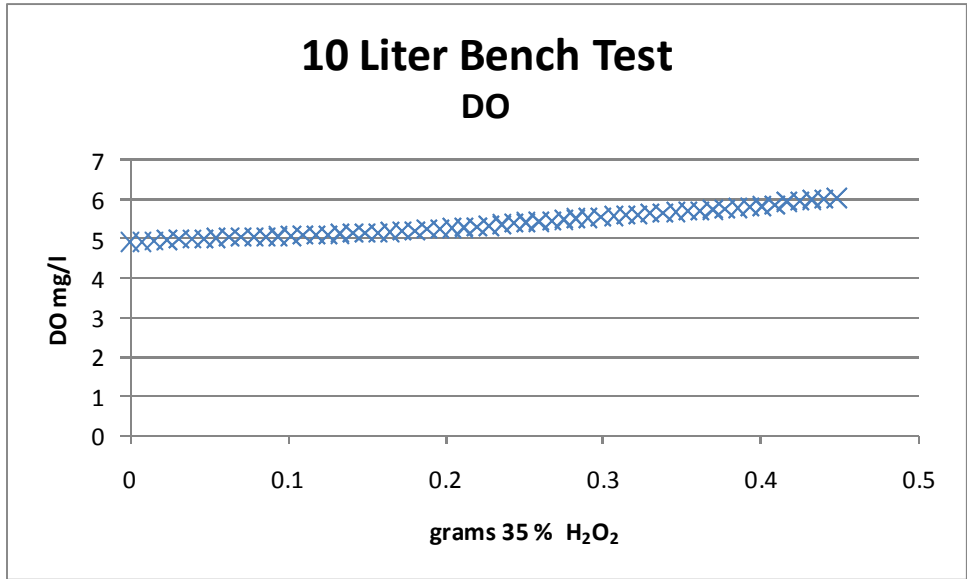


Figure 1. Change in DO with the addition of H₂O₂

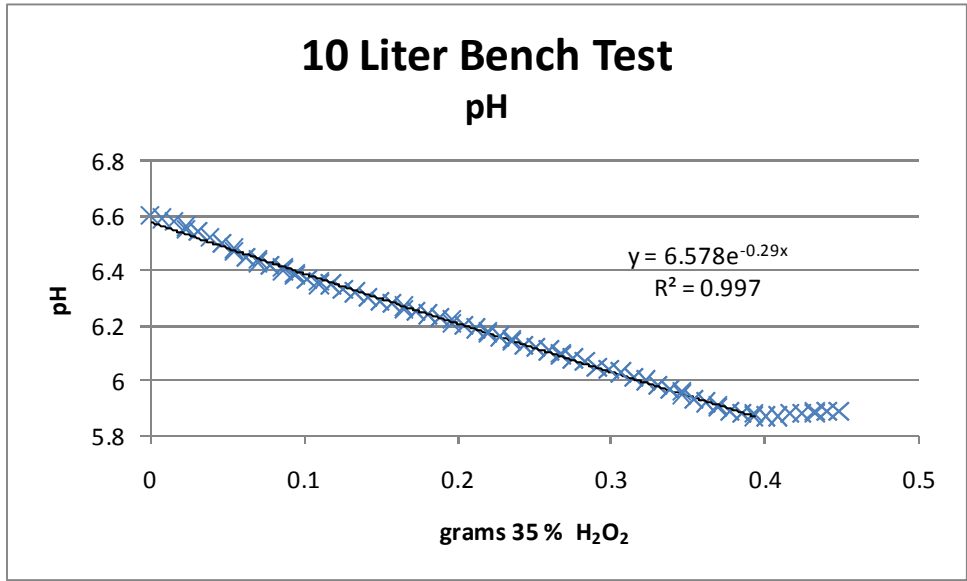


Figure 2. Change in pH with the addition of H₂O₂

Dissolved carbon dioxide is known to lower the pH of mine water, and that aeration will remove the excess carbon dioxide. Removing carbon dioxide before the addition of alkalinity reduces the amount of alkalinity required to treat the mine water. The effect of adding hydrogen peroxide on the dissolved carbon dioxide is unknown. To determine if there is an effect two aeration tests were performed: one with untreated mine water; and the other with water that had been treated with hydrogen peroxide to the pH end point (full iron oxidation).

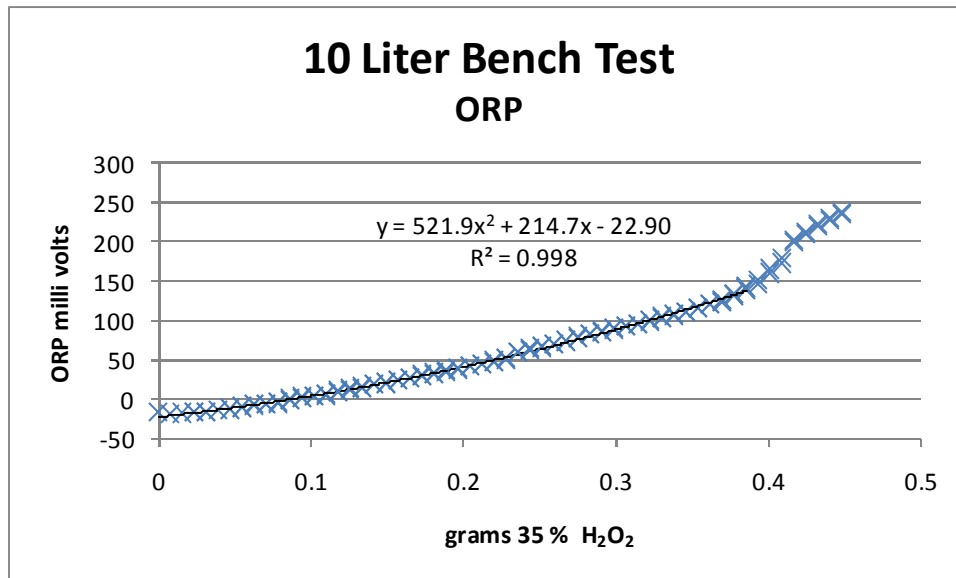


Figure 3. Change in ORP with the addition of H₂O₂



Photo 11. Aeration testing

Five hundred milliliters of mine water were measured in a graduated cylinder. A small aquarium air pump was connected with tubing to a sparging stone and the stone was placed in the bottom of the cylinder. A pH probe was placed in the top of the cylinder and the pH was recorded at one minute intervals (Photo 11). This procedure was repeated using mine water that had been treated with hydrogen peroxide. The results of this testing are contained in Figure 4 and Table 7.

After 40 minutes the pH of the untreated mine water had risen from 6.41 to 8.00. The peroxide treated mine water reacted to the aeration more quickly. After 27 minutes the pH had risen to 8.00. This indicates that if in situ peroxide addition is used, a simple aeration of the water, prior to its release,

should bring the pH of many mine discharges into compliance without the need for the addition of alkalinity. The slow response of the pH of untreated mine water to sparging is probably the result of ferrous iron oxidation caused by the aeration.

The alkalinity of the peroxide treated mine water was measured before and after aeration. Before aeration the alkalinity was 36 mg/l, after aeration the alkalinity rose to 55 mg/l due to the degassing of carbon dioxide.

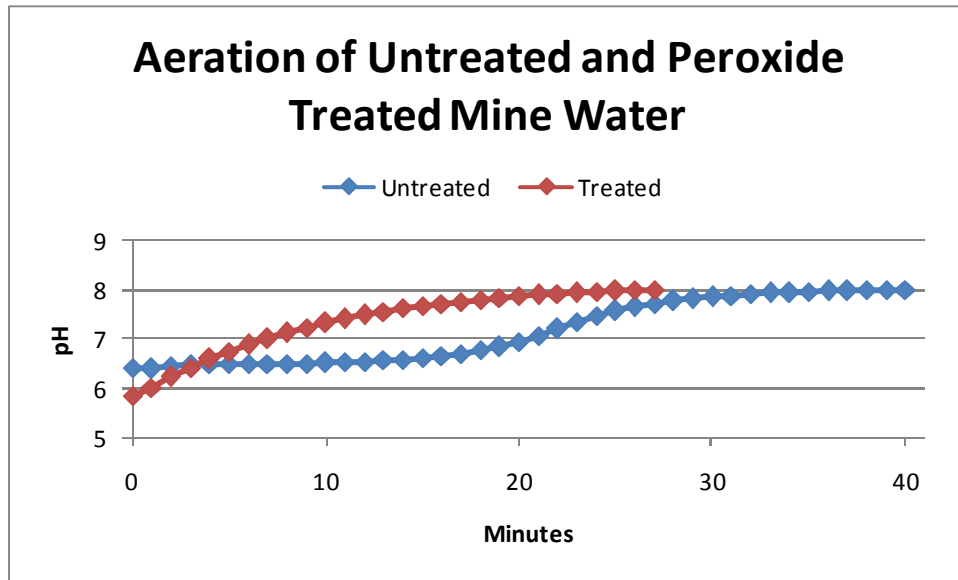


Figure 4. Comparative aeration test.

Table 7. Aeration Test Comparison: Untreated water v. peroxide treated water

Untreated		Peroxide	
Time	pH	Time	pH
0	6.41	0	5.86
1	6.40	1	6.01
2	6.46	2	6.24
3	6.49	3	6.43
4	6.50	4	6.60
5	6.50	5	6.74
6	6.50	6	6.88
7	6.50	7	7.01
8	6.50	8	7.12
9	6.51	9	7.23
10	6.52	10	7.33
11	6.53	11	7.41
12	6.54	12	7.49
13	6.57	13	7.56
14	6.59	14	7.62
15	6.62	15	7.67
16	6.66	16	7.72

17	6.71	17	7.76
18	6.77	18	7.80
19	6.84	19	7.84
20	6.94	20	7.87
21	7.07	21	7.89
22	7.21	22	7.92
23	7.35	23	7.94
24	7.48	24	7.96
25	7.57	25	7.97
26	7.65	26	7.99
27	7.72	27	8.00
28	7.78		
29	7.82		
30	7.85		
31	7.88		
32	7.91		
33	7.93		
34	7.94		
35	7.95		
36	7.97		
37	7.98		
38	7.99		
39	7.99		
40	8.00		

Flow in the Test Entry

Bench testing showed that 0.393 grams of 35 percent hydrogen peroxide was needed to fully oxidize the mine water pumped from Livengood well #3. The hydrogen peroxide dosing at Livengood #2 was adjusted to achieve, as nearly as possible, full oxidation of the ferrous iron in situ. Figure 5 is a graph of four different dosing rates. Three of these rates were less than the dose needed for complete oxidation. And one dose exceeded the amount needed for complete oxidation. The percentage of the iron that was oxidized was calculated in two ways: The first method was to take the dissolved iron value of 32.46 mg/l, prior to peroxide addition, and subtract from that number the dissolved iron value remaining after each dosing level; the difference was then divided by the original amount of dissolved iron to yield the percent of the original iron that had been oxidized. The second method is identical except that the ferrous iron data was used for the calculation. Because there could not be any iron oxidation without peroxide addition the zero-zero point was plotted and used for regression analysis.

The plot of both methods is very similar, and the R^2 values are very high. This supports the assumption that the raw dissolved and ferrous iron values were not changing significantly during the test. Based on the extrapolation of these lines the amount of 35 percent hydrogen peroxide needed to oxidize the iron present was between 6.20 and 6.32 ml/minute. When these data are combined with the data from the 10 liter bench test the flow in the mine can be calculated. That flow is 42.87 gpm or 43.70 gpm

depending on whether the dissolved or ferrous data are used. While this test was being conducted at the Livengood site the flow from the T&T #2 discharge was between 170 and 175 gpm.

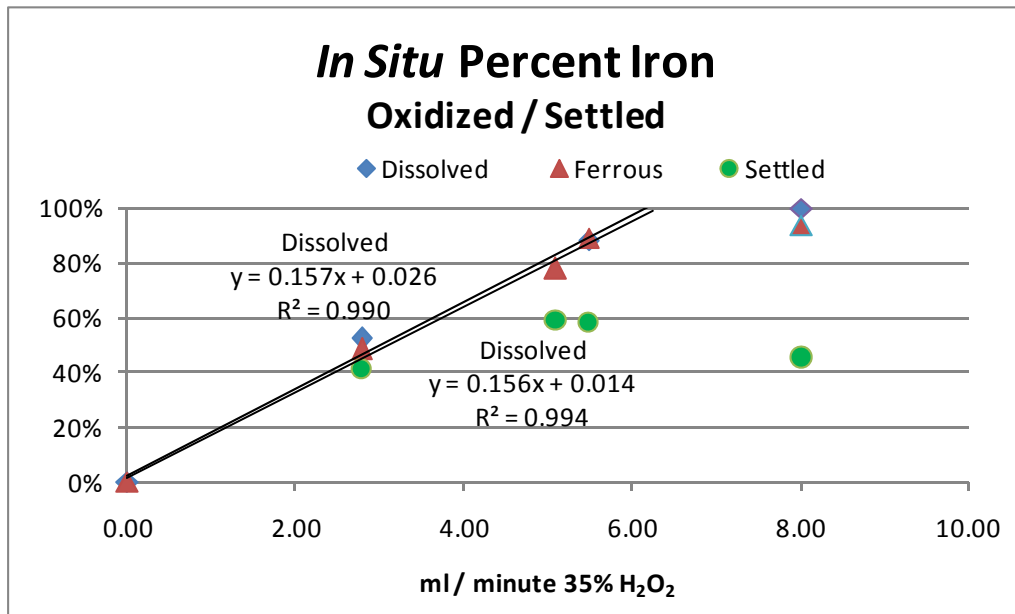


Figure 5. In Situ Iron oxidation and settlement.

Iron Settling

The amount of iron settling that occurred in situ was determined by subtracting the total iron in the mine water during the test from the total iron in the mine water before the test. The remainder was then divided by the pre test total iron to determine the percent reduction in iron as a result of that particular dosing level. In the four tests conducted, the amount of iron settled varied from 41 percent to 59 percent. Figure 5. This settling occurred in the 47.2 meters between the Costal well and the out-by well. The amount of iron that was settled appears to increase as the amount of ferrous iron oxidized increases. This is as expected. However, when hydrogen peroxide was added in excess, the settling percentage fell back to 45 percent. There are too few data points to be conclusive, but a possibility is that the excess hydrogen peroxide decomposed to oxygen and water and the oxygen adhered to the surface of the flock increasing its buoyancy and reducing its settlement.

A settling test was conducted on mine water that was reacted with hydrogen peroxide. A 500 ml graduated cylinder was filled with treated mine water and allowed to settle. Photos 12 and 13 show the amount of settling that has occurred after 50 minutes. Photos 14 and 15 show the amount of settling that occurred at 100 minutes. Photos 16 and 17 show the level of settling after 24 hours.

Substantial settling had occurred after 50 minutes, and the water was significantly clearer after 100 minutes. This degree of settling is in line with the amount of settling that occurred in the mine, despite the water being in motion. Due to the presence of the limestone sand and the limited depth of free water in this mine entry there is the possibility that impingement is responsible for a portion of the settlement that was observed.



Photo 12. Peroxide treated water 50 minute settling.



Photo 13. Peroxide treated water 50 minute settling.

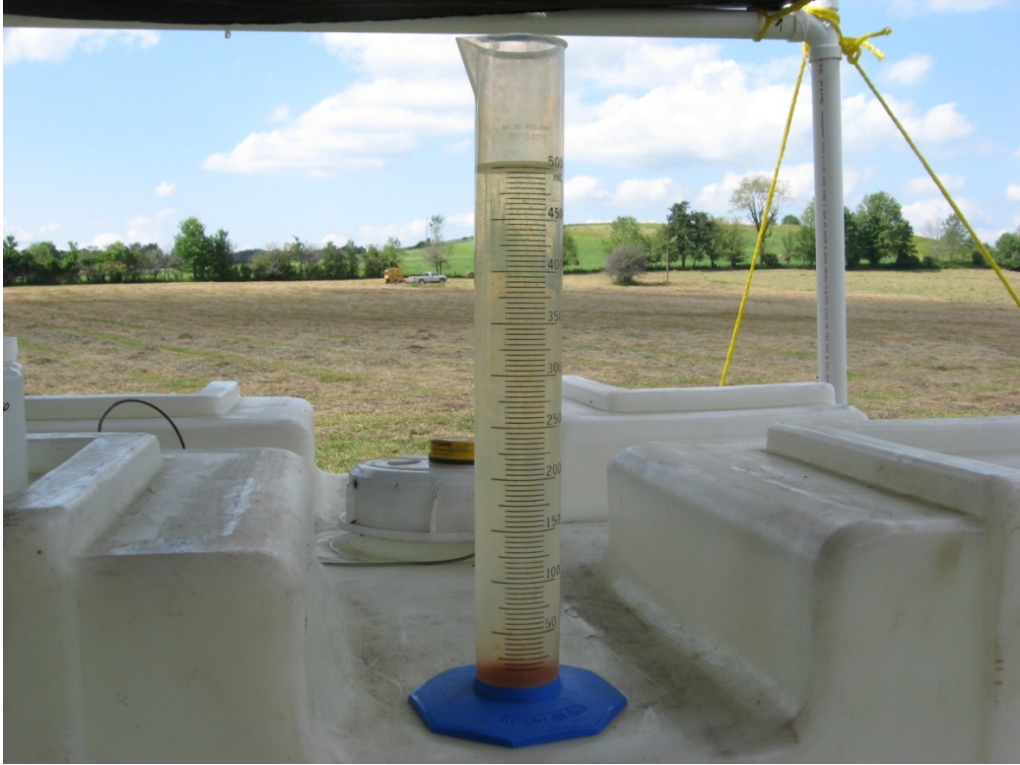


Photo 14. Peroxide treated water 100 minute settling.



Photo 15. Peroxide treated water 100 minute settling.



Photo 16. Peroxide treated water after 24 hour settling.

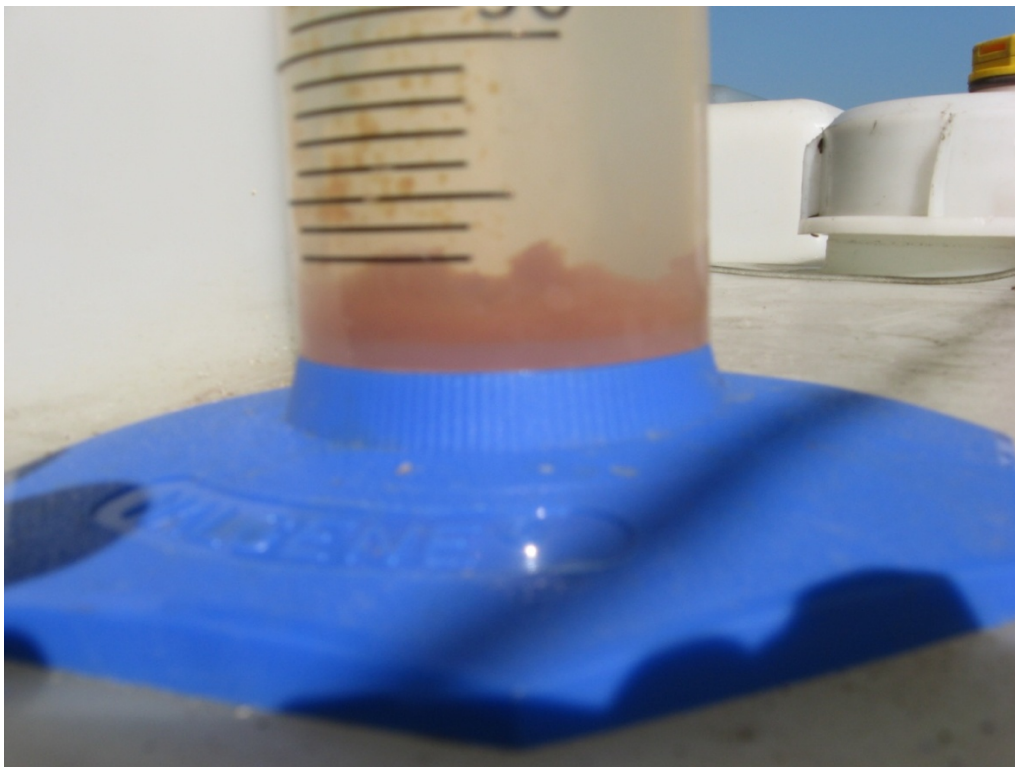


Photo 17. Peroxide treated water after 24 hour settling.

Laboratory Analysis

Periodically water samples from the out-by well on the Livengood property and from the T&T discharge were collected for laboratory analysis in addition to the field analysis. The purpose of these samples was to characterize the water and to determine the amount of ferrous iron that was present. Appendices A and B contain the laboratory results from this sampling.

Samples were analyzed at the CONSOL ENERGY research laboratory in South Park, Pennsylvania. Metals, both total and dissolved were measured using inductively coupled plasma (ICP). The initial ferrous iron analysis had a poor correlation with the dissolved metals results obtained with ICP. These data were improved by using a technique known as blank subtraction. A known blank sample was analyzed using the same technique as the ferrous iron and the resulting value was subtracted from the ferrous analysis. This method substantially improved the agreement between the ICP method and the ferrous iron results. The initial ferrous samples were reanalyzed and those results are reported in Appendices A & B. Appendix C contains the individual laboratory reports.

Raw water sampling at the T&T discharge was complicated because anhydrous ammonia was added as soon as the water entered the treatment basin. To overcome this problem, a $\frac{3}{4}$ polyethylene pipe was inserted up the left hand discharge pipe so that raw mine water could be sampled. The pipe was routed through the H-flume and shown in photo 18. Water samples were collected from the beaker at the end of the black pipe just to the left of the dispersion grate. Field measurement of pH and the clarity of the water indicated that this method of sampling effectively bypassed the anhydrous ammonia treatment. Laboratory analysis showed that ammonia in these raw water samples was 4.5 mg/l or less. The ammonia observed in the raw mine water may be the result of the disposal of the AMD treatment sludge in the T&T #3 mine, and the subsequent recycling of the transport water.



Photo 18. T&T #2 sampling point and 1.5' H-Flume



Photo19. Water samples from lt. to rt. unfiltered unacidified; filtered acidified HNO_3 ; filtered acidified HCl

Water samples for metals analysis were field filtered and acidified as required for the analytic method. Total metals were unfiltered and acidified with nitric acid. Dissolved metals were filtered through 0.45μ syringe filter, and acidified with nitric acid. Samples for ferrous iron analysis were field filtered with a 0.45μ filter and acidified with hydrochloric acid. The date and time of the sample were recorded on the sample bottle. Only new bottles were used. Photo 19 shows sample preparation of water from the out-by well taken on August 19, 2009. Note the orange color of the raw water in the beaker and on the syringe filters in the foreground. This coloration is the result of the hydrogen peroxide addition, and represents ferrous iron that has been oxidized in the mine but not yet settled.

The reaction of hydrogen peroxide with the ferrous iron present in the mine water is clearly evident. There was no apparent effect on the other metals that were analyzed. These metals are aluminum, calcium, magnesium, manganese, potassium, and sodium. While aluminum shows a difference between the total and dissolved data this difference was also present in the untreated mine water, and is not attributable to the hydrogen peroxide addition.

There was an increasing trend in the concentration of calcium, sulfate, potassium and sodium between August 24, and August 27, 2009. This increasing trend correlates with a recharge event that was recorded at the T&T discharge. This trend may also have influenced the ferrous iron concentration prior to hydrogen peroxide treatment; however there is no way to know this as treatment was in progress during this recharge event. For the purpose of this analysis the ferrous iron concentration was assumed to be stable throughout the treatment.

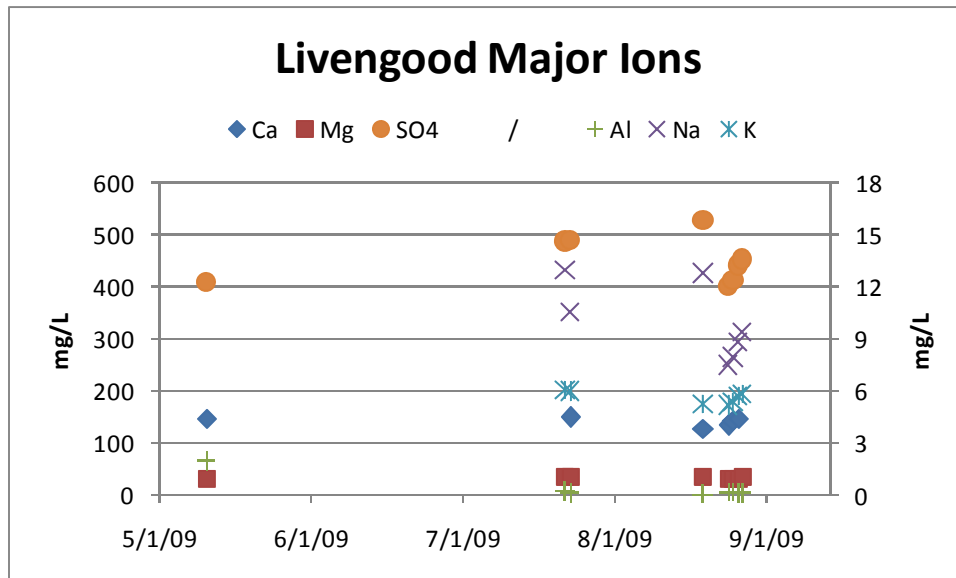


Figure 6. Major ions at the out-by well.

Effect of Hydrogen Peroxide addition on the T&T Discharge

Water from the T&T Ruthbelle mine complex exits through two entries known as: the “Pit Mouth” and the “Yellow Pipe” entries. The yellow pipe entry is slightly up-dip from the pit mouth entry and as a consequence only flows during times of high flow. During the period of hydrogen peroxide addition this discharge was not flowing. The Pit mouth entry flows all year and has two HDPE pipes that convey the water from the mine, through the mine seal, and into a small basin where anhydrous ammonia is added for neutralization. Photo 20 shows this configuration. Water from this basin flows through a 1.5 foot H-flume where the discharge flow is measured. During this field trial a pressure transducer was installed in the H-flume to record the rate of mine discharge. The transducer was set to record the water pressure in the flume on an hourly basis. Mine discharge measurement commenced on July 24 at 15:00 hours and continued through October 8 at 14:00 hours. A second transducer was set up to measure barometric pressure at the same frequency. The barometric pressure data are used to correct the pressure readings from the flume so that the height of water in the flume can be calculated. Several manual depth measurements were taken in the flume. These measurements are used initially to adjust the transducer data to a correct height of water in the flume. Subsequently these data are used to confirm that the transducer data is still representative of actual field conditions. The transducer and manual readings are presented in Figure 7.

Mine discharge during the field trial declined from about 325 gallons per minute to about 200 gallons per minute. This decline was not uniform. Periodic rises in the curve are indicative of recharge from precipitation followed by a decline after the rain fall ends. Underground mines that are poorly connected to surface show a seasonal fluctuation in discharge, but do not show a response to individual precipitation events. On the other hand mines like the T&T Ruthbelle complex that directly respond to precipitation may have zones that are highly connected to the mine allowing both air and water to enter.

Figure 7. is a plot of the mine discharge flow rate over time. Oxidation Reduction Potential readings were taken periodically and are plotted with respect to time on the right hand axis. The periods of injection and no injection are delineated so that changes in ORP can be evaluated. There is a slow rise in the ORP values during the period of the first injection into the in-by (2 inch) well. This rise seems to continue through the cessation of peroxide injection suggesting that the rise may not be related to the injection, or that the injected peroxide is being released very slowly from the point of injection. Once peroxide injection begins, in the Coastal hole, there is a rise of about 150 millivolts observed at the Pit mouth. When measured on October 8 the ORP value had returned to the levels observed prior to peroxide injection into the Coastal well.



Photo 20. T&T #2 Discharge pipe with sampling pipe inserted.

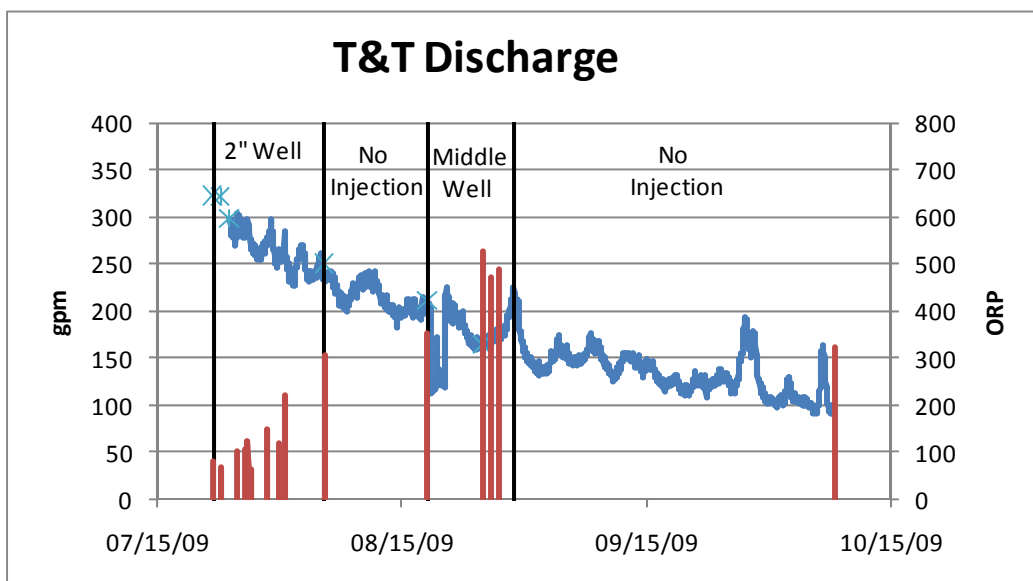


Figure 7. Discharge and ORP from T&T mine with injection periods.

Figure 8. compares the dissolved iron at the T&T discharge over time. The dissolved iron values do not vary significantly whether hydrogen peroxide is being added or not added. The maximum variation is 15 percent (31 mg/l vs. 36.13 mg/l) over a period of 42 days. On August 29, with hydrogen peroxide added to excess, 100 percent of the ferrous iron was oxidized and 45 percent was settled before the water from T&T #2 mixed with the water from Ruthbelle and T&T #3. Yet despite this reduction in iron load there is no observable reduction in the iron concentration at the mine discharge. It is possible that oxidized iron from T&T #2 that did not settle in that mine may have been redissolved by the low pH water joining from the Ruthbelle mine. The pH of this water is not known, but it is expected to be lower than the 2.8 pH observed at the mine mouth due to the addition of alkaline water from T&T #2.

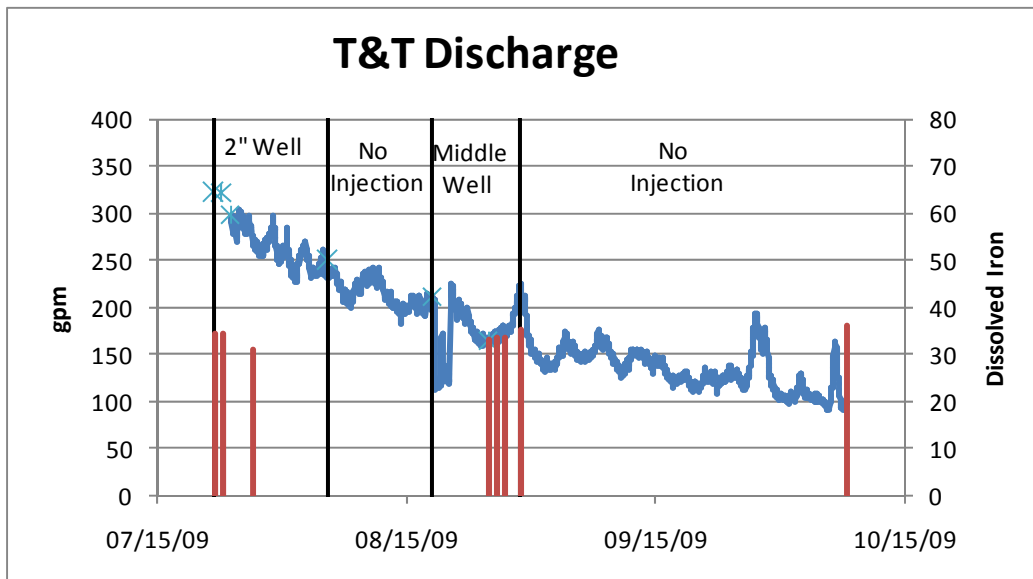


Figure 8. Dissolved iron at the T&T discharge

In Figure 9. the dissolved sulfate levels are compared over time. Within this time period there is a slight general trend toward higher sulfate concentrations as the mine discharge diminishes in volume. A short term rise in sulfate levels is also observed between August 24 and August 29. This correlates with a short term increase in the mine discharge rate due to a precipitation event. At the same time, other parameters including Ca, K, Na were rising in the out-by well in T&T #2 mine. A mine discharge sample taken on May 11, 2009, before hydrogen peroxide addition, had a sulfate concentration of 1188. mg/l which is higher than any sample that was taken during the experimental phase. Although there is variation in the sulfate concentration, the data do not indicate pyrite oxidation due to hydrogen peroxide addition.

Ferrous iron at the T&T discharge was initially measured at 43.60 mg/l on May11, 2009. This was 31.3 percent of the iron load. Eight subsequent measurements of ferrous iron averaged only 10.2 percent ferrous iron. If these eight measurements of ferrous iron are separated into two groups of four representing the effective peroxide injection period in August then ferrous iron represents 13.7 percent of the iron load during non injection periods and only 6.7 percent of the iron load during the August peroxide injection into the Coastal well. The lowest ferrous iron percentage of 4.8 percent occurred on August 29, 2009. This measurement was taken 21 hours after the peroxide dose was set to excess. Figure 10. is a plot of the percent ferrous iron compared to the dissolved iron. The sample results for

August 26, 27 and 29 seem to indicate a dose response as the peroxide dose was increasing during this time period. However, the percent ferrous iron on August 25 is anomalously low given the prior days hydrogen peroxide dosing of only 2.79 ml/min.

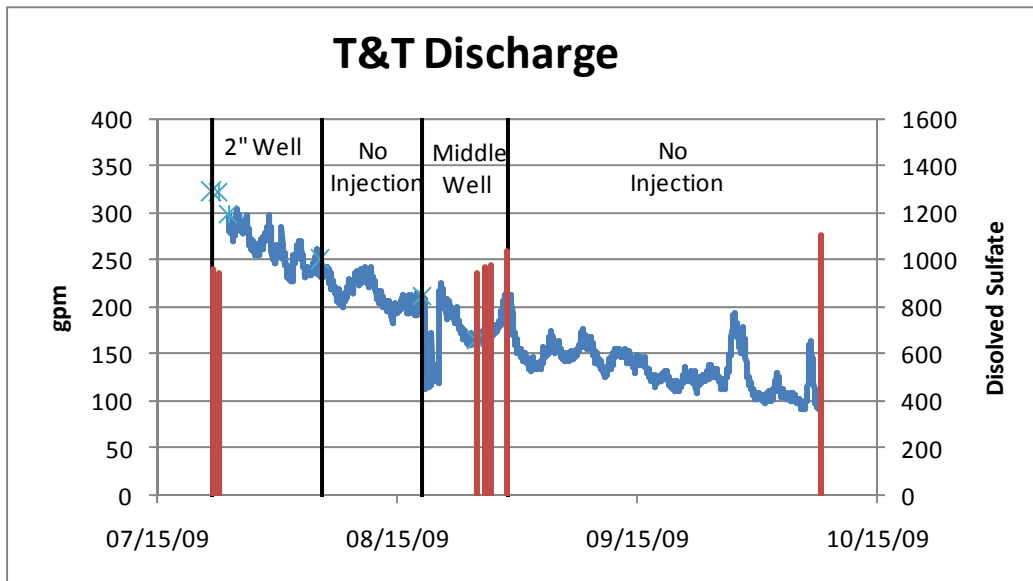


Figure 9. Dissolved Sulfate at the T&T discharge

An aeration test at the Livengood site indicated the presence of dissolved carbon dioxide. This test was repeated at the T&T #2 discharge to see if carbon dioxide continued to play a role after the convergence of the two waters. Table 8 contains the results of this testing. It is evident from these results that carbon dioxide continues to be a factor in the acidity of the T&T #2 discharge, although the effect on the acidity of the discharge is only 0.43 mg/l.

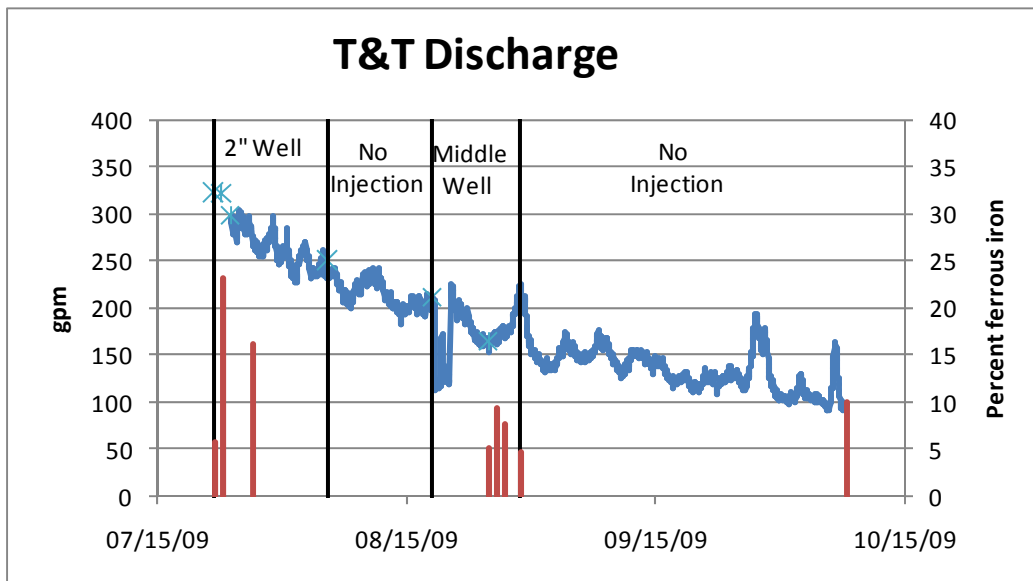


Figure 10. Ferrous iron at the T&T discharge

Table 8. Aeration test at T&T #2 discharge

Time minute	pH	Time minute	pH
0	2.89	22	2.85
0.50	2.78	23	2.85
1	2.78	24	2.86
2	2.78	25	2.86
3	2.78	26	2.86
4	2.78	27	2.87
5	2.79	28	2.87
6	2.79	29	2.87
7	2.80	30	2.87
8	2.80	31	2.88
9	2.80	32	2.88
10	2.81	33	2.88
11	2.81	34	2.89
12	2.81	35	2.89
13	2.82	36	2.89
14	2.82	37	2.90
15	2.82	38	2.90
16	2.83	39	2.90
17	2.83	40	2.90
18	2.84	41	2.90
19	2.84	42	2.91
20	2.84	43	2.91
21	2.85		

Hydrodynamics

Analysis of hydrogen peroxide dosing in the test entry indicated a flow of 43 gallons per minute. The total mine discharge at that point in time was 175 gallons per minute. Consequently, flow in the target entry is 24.6 percent of the total mine discharge. On an area basis, the T&T #2 mine represents about 33 percent of the mined area. If there is equal recharge per unit area then 8.76 percent of the flow from T&T #2 is unaccounted. A review of the mine map indicates that it is unlikely, that the missing flow for this mine is in the up dip parallel entry. This is due to the interconnection between these two entries in- by of the injection site without any ventilation stopings indicated on the mine map. At this point of interconnection, the dip of the mine would support flow to the test entry. Based on this analysis it appears that all of the flow from T&T #2 is traveling in the test entry. This also indicates that the recharge to the three mines may not be uniform. The effect of sludge disposal into the T&T #3 mine would serve to increase the apparent recharge rate to the T&T #3 / Ruthbelle complex relative to the T&T #2 mine. This increase could offset the apparent difference in recharge rates.

The raw mine water chemistry at the Livengood site is dramatically different from the raw water chemistry at the mine discharge. On July 22, 2009 water from the livengood site and from the mine discharge were analyzed for major ions. Using these analyses and the flow ratios developed on August

27, 2009 it is possible to estimate the chemistry and the flow of water coming into the corridor between the T&T #2 mine and the mine discharge point.

Table 9. contains the water chemistry measured on July 22, 2009 and the water flow rates established on August 27, 2009. These flows were used to generate a flow weighted average chemistry for the Ruthbelle water. The flow from Ruthbelle is calculated by subtracting the Livengood flow from the mine discharge flow. The Ruthbelle pH results from the flow weighted average of the hydrogen ion concentrations indicated by the measured pH values at the livengood site and the mine discharge. This hydrogen ion concentration was then converted back to pH and reported below. The estimated pH of 2.68 is low enough to allow for the redissolution of the iron that was precipitated, but not settled, using hydrogen peroxide in the test entry. It is possible, using standard methods to measure a negative acidity in addition to an alkalinity. For the purpose of this analysis the negative acidity of -48 mg/l reported by the laboratory was used for the flow weighted average instead of the alkalinity of 61 mg/l. Had the alkalinity value been used instead of the reported negative acidity, the indicated acidity of the Ruthbelle water would have been 375 mg/l, an increase of 4 mg/l.

Table 9. Estimated water quality from Ruthbelle mine

	Livengood	T&T Discharge	Ruthbelle est.
Flow	43	175	132
pH	6.32	2.80	2.68
Acidity	-48	268	371
Dissolved Fe	44.8	34.28	30.85
Ferrous Fe	43	2.00	0
Dissolved Al	0.02	23.29	30.87
Dissolved Mn	0.42	1.41	1.73
Dissolved Ca	147.3	198.8	215.6
Dissolved Mg	34.03	41.7	44.2
Sulfate	460.1	962.1	1125.6

Dye testing conducted by Costal Coal in 1999 indicated that the travel time between the Ruthbelle connection to the corridor and the mine pit mouth was about 32 hours. At the time of this test the flow in the mine was between 700 and 750 gallons per minute. The lower flow rates observed during this analysis, 175 gpm, may serve to lengthen this travel time.

Travel time between hydrogen peroxide injection well and the out-by sampling well was evaluated using data collected on August 24, 2009. The field values for pH and ORP are plotted in figure 11 against the number of minutes after the injection began. Two factors complicate this analysis. First, the travel time from the mine pump to the field measurement point must be removed from the raw time data, in this analysis 15 minutes were removed. Second, the intermittent nature of the sampling is less than ideal. The sampling pump was operating at 25 minutes on and 35 minutes off to prevent motor thermal overload. Despite these impediments it is evident that there was no effect during the first 41 minutes. During this time the pH increased and the ORP decreased. The ORP formed a clear bottom at 87 minutes and then began rising. The pH response was less sharp. The high value occurred at 41 minutes, but the drop in pH at 87 minutes is only 0.05 SU below the peak value. By 212 minutes the reaction to the hydrogen peroxide addition is effectively complete. These data indicate a rapid flow rate, by mine standards, of 0.54 meters per minute based on the first arrival time. These data also indicated that there is water in storage adjacent to and connected with the primary flow path. It is the dispersion and

diffusion of the primary flow through this storage water that creates the delay between the initial response and the arrival at near equilibrium conditions.

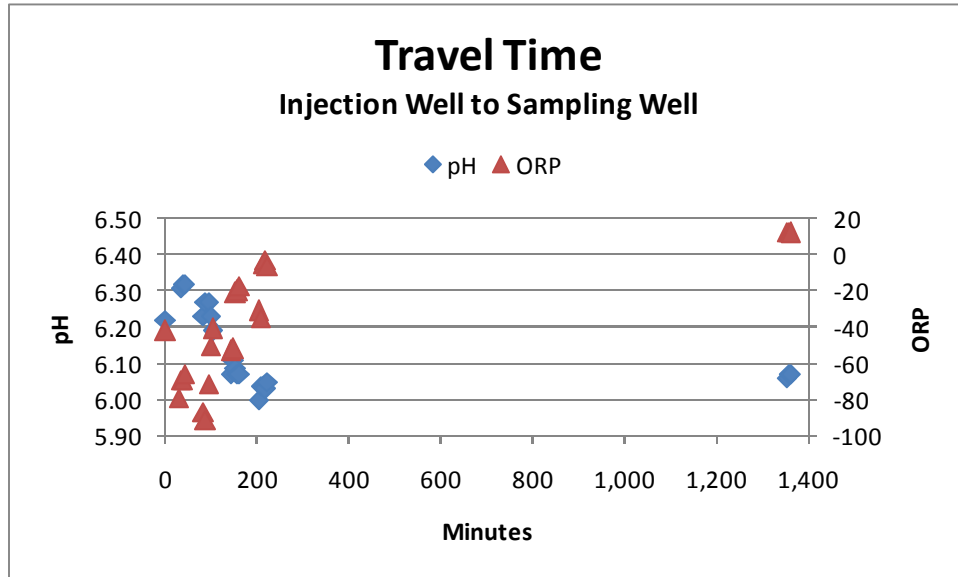


Figure 11. Travel time between the injection and sampling well.

Using a flow of 43 gallons per minute and a duration of 212 minutes to achieve near total system response then the volume of water between the two wells is estimated to be 9,116 gallons. Using the distance between the wells of 155 feet and assuming an entry width of 16 feet and the average depth of water in this entry is about 0.50 feet. This is consistent with field measurements and with the injection of limestone sand in the entry.

Cost of Treatment

Flow in the mine during the test period was between 42.87 and 43.70 gallons per minute. For the purpose of this analysis 43 gallons per minute will be used. The ferrous iron content of the water was 33.45 mg/L. Between 6.2 and 6.32 mL/min., of thirty five percent hydrogen peroxide, were needed to fully oxidize the water in the mine. Using these data, 146.51 ml are needed to oxidize 1000 gallons of mine water.

Six hundred gallons of 35 percent hydrogen peroxide were purchased and delivered for a cost of \$3,420.00. This is equal to \$ 1.505 per liter. Multiplying the cost per liter times the liters required results in the cost to treat 1,000 gallons. At 33.45 mg/l ferrous iron the cost to treat 1000 gallons is \$0.22. This can be converted to the cost per Fe mg/l per 1000 gallons which is \$0.0066.

When considering the cost of treatment, the capital cost of a project must also be included. These costs include: the cost of land, injection and monitoring wells, electric power, site security, support equipment and engineering. Table 10 includes estimates of these costs for a mine with 300 feet of cover. These costs will not vary significantly with variations in mine water chemistry; consequently they may be either large or small relative to the chemical cost. Capital cost are typically amortized over a long period of time, frequently, 20 years is used. This would reduce the annual cost to the operation of \$1,800.00 per

year. Given the amount of flow at the demonstration site the capital cost represents about \$ 0.08 per thousand gallons. If higher flows were present this cost would be significantly reduced.

Table 10. Estimate of Capital Cost

Land	1 acre	\$12,000
Well drilling	600 feet	\$ 9,000
Electric Power	100 amp service	\$ 2,500
Site facilities	Fence, shed etc.	\$ 4,000
Support equipment	ORP, PLC, pump	\$ 4,500
Engineering	40 hours	\$ 4,000
	TOTAL	\$36,000

Other operational costs may include periodic site visits and chemical analysis to check compliance. These annual costs are estimated at \$ 13,000 and \$ 2,000 respectively.

Discussion

Hydrogen peroxide oxidation of the ferrous iron in the test entry is clearly evident and effective. The data from the sampling well indicate that between 40 to 60 percent of the oxidized iron is settling in the 155 feet between the two wells. Results from the bench settling test indicate that 24 hours is needed to achieve complete settling. If half of the iron was settling in the test entry then there should be an observable reduction in the iron that is reporting to the mine discharge of about 5 mg/l. This reduction is not evident. The iron hydroxide flock initially consists of very fine particles, unless they are removed by impingement it is unlikely that they would settle in water that is moving at a maximum speed of 1.77 feet per minute. If this finely divided flock is carried into the low pH water emanating from Ruthbelle then redissolution of the iron can be expected. This condition would explain the apparent lack of response of the iron value at the pit mouth while observing an increase in ORP values during the same time period. If the sampling pump is drawing water from a pooled area, localized iron settlement in that area could affect the observed settling rate.

If settlement of the precipitate is to be achieved in situ, then a minimum 24 hour retention time is needed in the mine after the peroxide addition. At 43 gallons per minute a mine entry 16 feet wide 5 feet high and just over 100 feet long would be sufficient with sludge storage omitted. This could be accomplished at the Livengood site by drilling a new injection well in-by of the existing well along the newly identified flow path. Additional settling capacity should also be provided to accommodate the estimated high flow rate which could be 300 gallons per minute. At 43 gallons per minute the velocity of the water in a 16 foot wide by 5 foot high entry would be 0.07 feet per minute. At 300 gallons per minute the velocity would be 0.5 feet per minute.

Cost effective application of this technology will require the ability to regulate the hydrogen peroxide dose as either the flow or the ferrous iron concentration change in the mine. Either pH, or ORP can be used to delineate the ferrous iron oxidation end point. The pH end point is well defined but it is expected to vary with the amount of alkalinity present and with the amount of ferrous iron present. The ORP end point is somewhat less defined, but it should not be as dependent on the alkalinity or the amount of ferrous iron. Either technique is expected to be independent of flow. In highly variable systems a pH or ORP probe could be placed in the mine water downstream of the hydrogen peroxide

injection. The data from this probe can be used by a programmable logic controller (PLC) to regulate the hydrogen peroxide dosing rate. In more stable systems the hydrogen peroxide dose rate can be adjusted manually.

Net alkaline mine waters frequently contain dissolved carbon dioxide. This lowers the pH of the mine water and increases its acidity. Adding alkalinity to these waters results in some of the alkalinity being used to neutralize carbonic acid. Adding hydrogen peroxide to carbon dioxide rich water does not affect the dissolved carbon dioxide. This carbon dioxide can be removed after peroxide treatment resulting in a rise in the pH value.

The ferrous iron content of the water reporting to the T&T discharge appeared to show a dose response during the late August injection period, but the variation in the ferrous iron could not be directly correlated to a specific dose. This is likely due to the travel time in the corridor. Dye testing conducted by Costal had set the travel time in the corridor at 32 hours under higher flow conditions. The point of hydrogen peroxide injection is deeper into the mine and as a result additional travel time can be expected. On August 20 through 23 the hydrogen peroxide dose was in excess of that needed for full ferrous iron oxidation. The August 25 ferrous iron sample at the T&T discharge was anomalously low. This suggests a travel time from the injection well to the mine mouth of between 43.0 and 119.8 hours. This procedure was repeated for three other T&T #2 ferrous iron samples at the discharge yielding estimates of travel time between: 46.5 – 67.7 hours; 45.6 – 69.1 hours; and 47.3 – 93.6 hours. The actual travel time must comport with all of these conditions. Therefore, the estimate of travel time is placed between 43.0 hours and 67.7 hours. This is consistent with the 32 hour estimate made by Costal under higher flow conditions. While travel times shorter than 43.0 hours are possible, travel times less than 23 hours would conflict with the observed data and with the Costal travel time estimate.

Conclusions

In Situ oxidation of ferrous iron using hydrogen peroxide has been demonstrated. The reaction is rapid and proportional to dose.

Either pH, ORP, or both may be used to determine the completion of the oxidation process so that over treatment does not occur. These inputs can be used by a PLC to regulate the dose.

Hydrogen Peroxide addition does not affect the amount of carbon dioxide dissolved in the mine water. Ex-solution of that carbon dioxide will increase the pH of the raw mine water or the hydrogen peroxide treated mine water. This allows the treatment designer the ability to raise the pH at the mine discharge following *in situ* oxidation with hydrogen peroxide.

Hydrogen peroxide can be used to determine the volume of flow in an entry. Based on this calculation, it was possible to estimate the flow and water chemistry of the combined T&T #3 and Ruthbelle mines.

Injection of hydrogen peroxide into a point of concentrated flow was deemed essential during the project design, and this point was demonstrated when the designed injection well was not in the flow path. Had more reliance been placed on the indicated mine ventilation stoppings, the injection hole might have been located in a better spot.

The chemical cost of Hydrogen Peroxide treatment has been calculated to be \$0.0066 per mg/l ferrous per 1000 gallons. The estimated capital cost for a single site is \$36,000 although this number will vary with site specific conditions.

The travel time in the corridor from the Coastal injection well to the pit mouth is between 43.0 and 67.7 hours.

Settling of the iron hydroxide precipitate has been demonstrated at bench scale, is indicated by laboratory analysis at the Livengood sampling well, but could not be confirmed at the T&T pit mouth. This is believed to be attributable to the high velocity in the test entry combined with the low pH of the Ruthbelle flow which resulted in the re-dissolution of the iron precipitate.

The effect of hydrogen peroxide addition on the ORP and the ferrous iron data at the pit mouth was observable.

Recommendations

The water quality from the T&T #2 mine is net alkaline and low in aluminum, as a result it will not benefit greatly from additional alkalinity addition. On the other hand, the water joining the corridor from Ruthbelle would benefit greatly from additional alkalinity. The potential addition of alkalinity to the sludge disposal water in T&T #3 should be investigated.

In Situ settlement of iron should be achievable if the location of the injection well is located further in-by the current location. This would provide fully flooded entries with slow water velocity to promote settling, it would provide storage volume for the sludge, and It should also be possible to avoid the complications associated with the limestone sand injection.

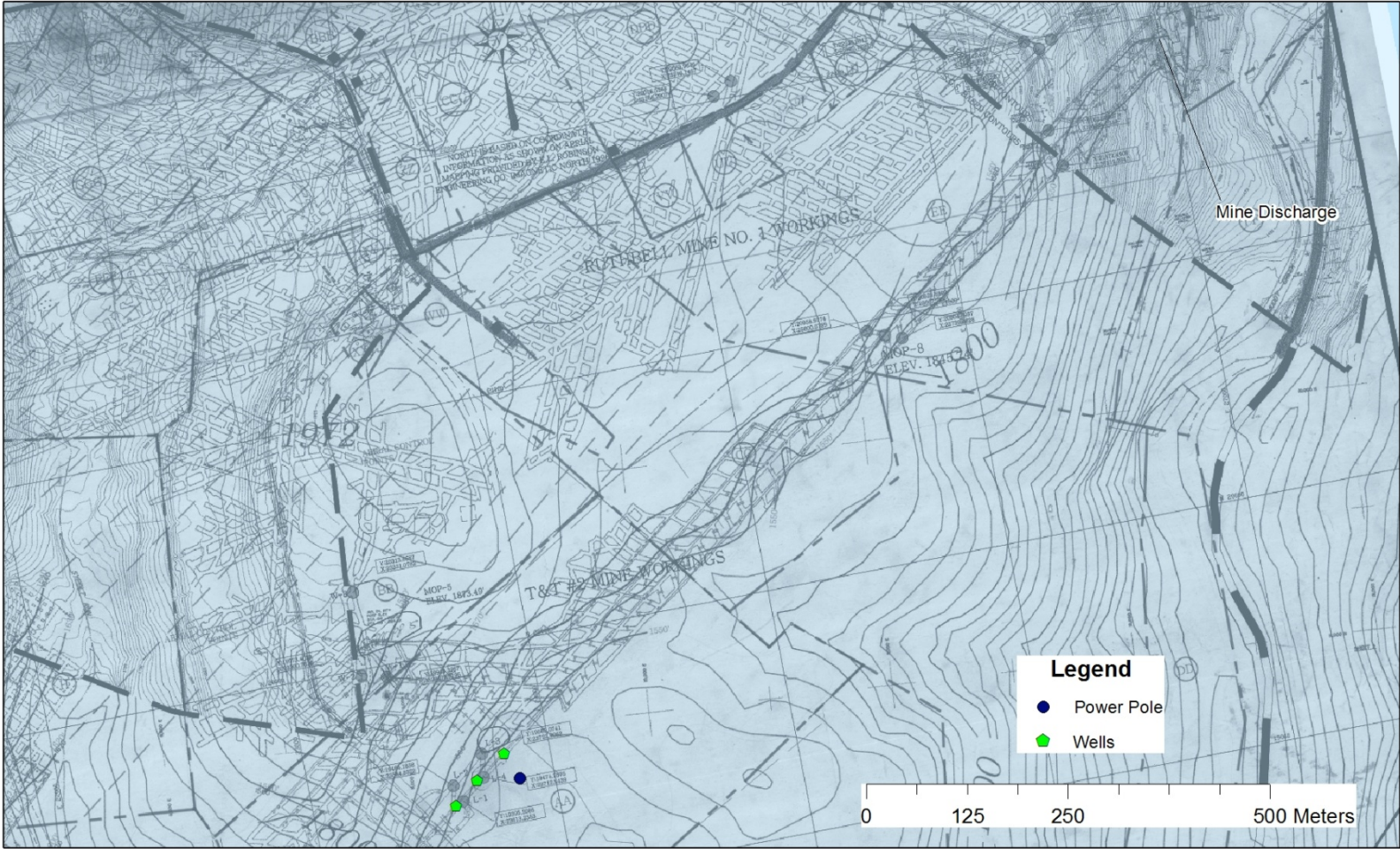
References

Miller, C. N. and Skiles K. D., 1999, T&T Environmental Restoration Project Feasibility Study, Report of Findings, June 1999, Coastal Coal – West Virginia, LLC

MWH, March 2002, T&T Environmental Restoration Project, Results and Conclusions from a two-year Review of Alkaline Injection at the T&T Mine.

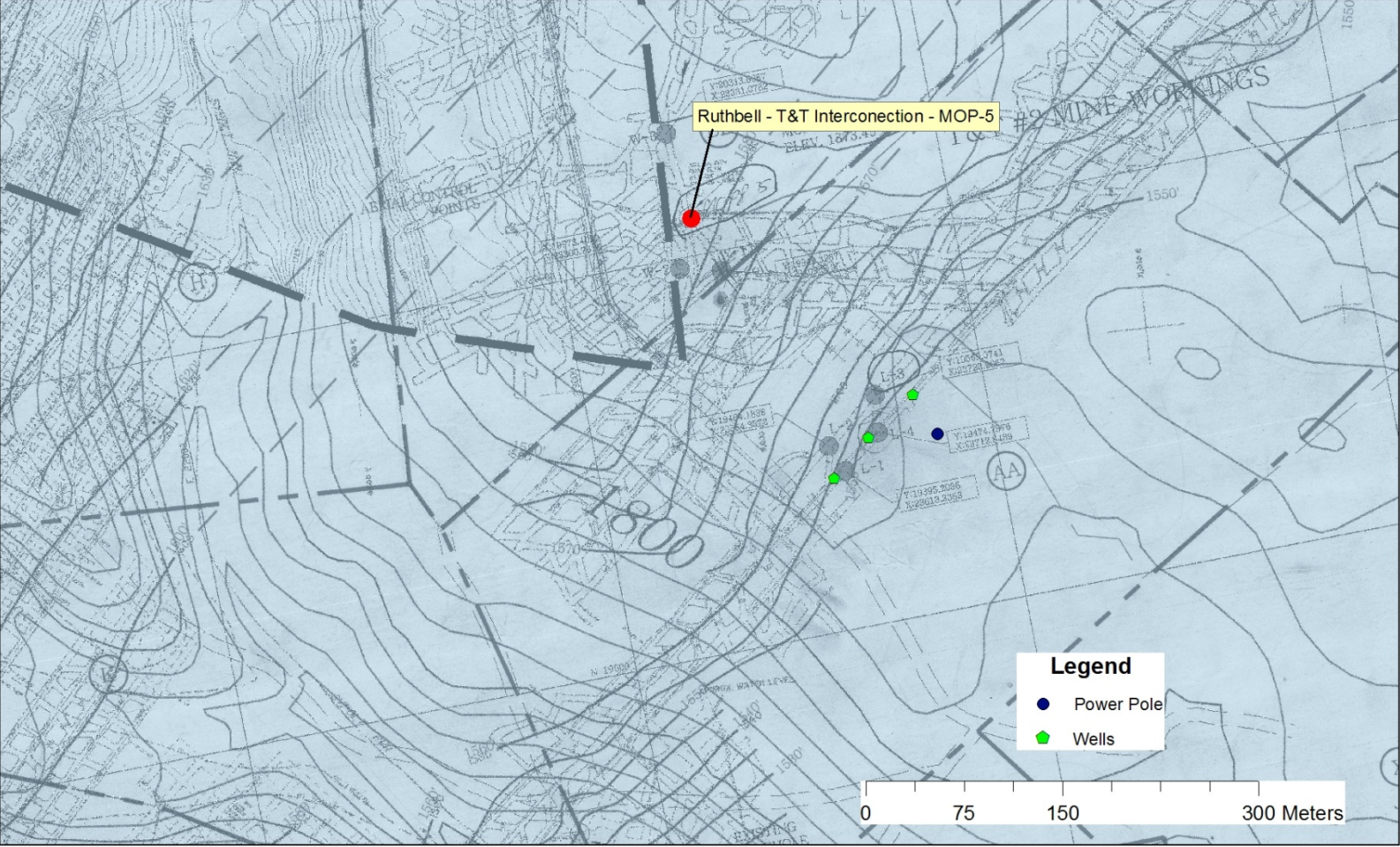
Ziemkiewicz, P. F. et. al. February 2001 WV173 Phase II Monongahela Basin Mine Pool Project Final Report. National Mine Land Reclamation Center, West Virginia University, Morgantown, West Virginia. 385 p.

T & T #2 Injection Well Location



Hydrogen Peroxide injection point is located inby the Ruthbell connection

T & T #2 Injection Well Location



Hydrogen Peroxide injection point is located inby the Ruthbell connection

Appendix B
T&T Chemical Analysis

Date	pH	Acidity	Alkalinity	Iron			Al		Ca		Mg		Mn		SO4		NH4	Cl	K		Na	
				Total	Dissolved	ferrous	Total	Dissolved	Total	Dissolved	Total	Dissolved	Total	Dissolved	Total	Dissolved			Total	Dissolved	Total	Dissolved
5/11/09	2.41	811.00	0.00	137.60	139.40	43.60	49.39		128.90		33.10		1.31		1188.00		3.30	6.00				
7/22/09 11:44																						
7/22/09 11:53	2.88	281.00	0.00	70.55	34.28	2.00	47.67	23.29	392.00	198.80	82.15	41.70	2.79	1.41	1982.00	962.10	4.50	<6	6.71	3.16	25.73	2.74
7/23/09 22:17	2.94	268.00	0.00	69.53	34.57	8.00	46.04	23.09	377.60	197.90	79.67	41.93	2.67	1.39	1917.00	946.50	4.00	<6	6.68	3.18	14.75	2.74
7/24/09																						
7/25/09 12:44																						
7/25/09 12:51																						
7/27/09 7:14																						
7/27/09 7:51				30.41	31.00	5.00																
7/29/09 6:52																						
7/31/09 15:07																						
8/25/09 9:50				33.32	32.44	1.70	23.86	23.79	199.20	195.20	42.07	41.48	1.33	1.33	906.00	942.10			3.40	3.32	4.22	5.07
8/26/09 10:30				33.43	33.24	3.10	23.72	24.33	196.10	197.60	41.44	41.62	1.34	1.36	895.00	965.00			3.21	3.27	4.61	5.21
8/27/09 9:10				33.54	33.10	2.50	24.37	24.63	199.90	200.20	42.43	42.16	1.38	1.39	917.20	977.10			3.20	3.20	4.09	5.30
8/29/09 9:10				35.35	35.22	1.70	25.54	26.63	208.40	216.30	44.41	45.36	1.41	1.43	1015.00	1033.00			3.16	3.22	4.77	3.93
10/8/09 15:00				36.14	36.13	3.63	28.07	28.38	223.70	230.10	46.98	48.13	1.47	1.50	1077.00	1104.00			3.02	3.06	5.33	4.24

Note: Total metals and sulfate analyses and for 7/22 and 7/23 contain a 2 to 1 dilution error