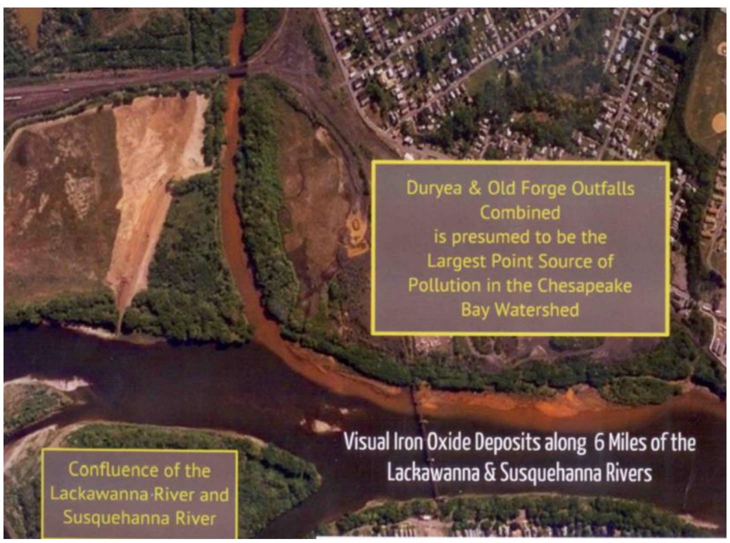
Acid Mine Water Remediation – a case study

A Toxic Legacy

During the past decade, environmental preservation and conservation issues have assumed global significance, particularly as various legislative initiatives strive to raise awareness of them. Yet, this was not always the case, Pennsylvania, with its history of coal mining has left a toxic legacy for future generations in the form of Acid Mine Drainage water.

The City of Scranton, Pennsylvania sits on top one of the largest Acid Mine Drainage (AMD) pools in the Commonwealth with approximately 130 Billion gallons of contaminated water running from Archibald in Lackawanna County in the north to Wilkes Barre in Luzerne County in the south.

Geologists refer to the Scranton Mine Pool as the Lackawanna Syncline. It is two valleys in name only. In actuality, it is one physical feature in the Ridge and Valley Physiographic Province of Eastern Pennsylvania. It appears, with some imagination, like a great "stone canoe" running 75 miles from Forest City in the northeast, to Shickshinny in the southwest. It is 5.0 miles wide at Scranton and 7.0 miles at Wilkes-Barre. Beneath its surface was found the largest and richest anthracite coal basin on the planet, the Northern Anthracite Field.



Since November 1961, when the last of the deep mine collieries closed down and turned off their pumps, the extensive system of Northern Anthracite underground mine flooded with groundwater as well as river and stream water infiltrating from the surface. What has resulted is a system of subterranean water bodies known as mine pools in a configuration somewhat like the subway system under Manhattan on steroids, 75 miles long and greater than 1,000 feet deep.

Eminating from this mine pool into the Lackawanna River is a distinct orange and yellow plume of iron (Fe) oxide laden water flowing from the Lackawanna River into the North Branch of the Susquehanna River. ***It has been anecdotally described as the largest and most visible point source of pollution in the entire Chesapeake Bay Watershed.*** The source of this Fe loading is primarily from two AMD discharges that drain several of these mine pools, the Old Forge Borehole and the Duryea Breach. These AMD points are respectively the second and sixth highest priority AMD pollution sources impacting the Susquehanna River (and ultimately the Chesapeake Bay) in the Anthracite Region.

The Old Forge Borehole discharges an average of ~60.7 million gallons per day (MGD) (~94 cubic feet per second (CFS)) with a Fe loading of ~7,700 pounds per day (lbs/day).

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The Duryea Breach discharges an average of ~14.5 MGD (~22.5 CFS) with a loading of ~2,260 lbs/day of Fe.

This legacy from the anthracite coal industry continues to give Scranton a special and not necessarily welcome distinction.

Acid Coal Mine Wastewaters

Mine drainages from coal mines are generally characterized by high level of dissolved iron and manganese at low pH levels. This type of pollution is a result of bacterial oxidation of pyrites (iron sulfides) in the mines by oxygen in the mine water. Acid is produced by the oxidation of sulfide to sulfate, ad much of the soluble iron remains in the ferrous state. Manganous compounds are leached into the mine waters and rise to fairly high levels, sometimes 20 to 100 mg/l. (Pennsylvania's DEP sets manganese levels for stream discharge at a maximum of 1.0 mg/l). Such discharges can contaminate downstream water supplies. Compositions of typical discharges from a Pennsylvania anthracite field are given below, along with analysis of a typical culm runoff from either bituminous regions of Pennsylvania.

ANALYSES OF MINE WATERS
IN WYOMING VALLEY, PENNSYLVANIA

Mine Water	pH	Fe (mg/l)	Mn (mg/l)	
Discharge I	3.4	295	22	
Discharge II	5.8	153	10.6	
Culm Bank Runoff	2.5	1044	83.2	

Source: Rozelle & Swain 1975

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Use of Ozone to Treat AMD

Ozone is a powerful oxidizing agent, far stronger than Oxygen. It is also unstable at high concentrations, decaying to ordinary diatomic oxygen. However, ozone is stable at low pH and can be used for the removal of iron and manganese. In the process, soluble ferrous and manganous ions are oxidized to ferric and manganic states, respectively, at which they hydrolyze to insoluble products which are readily removed by filtration

Fe^{+2} + O_3 $\rightarrow$ Fe^{+3} ---H_20 $\rightarrow$$Fe(OH)_3$
Mn^{+2} + O_3 $\rightarrow$$Mn^{+4}$ –H_2O $\rightarrow$$Mn(OH)_4$ $\rightarrow$ MnO_2 = $2H_2O$

Programs such as Pennsylvania DEP's AMD Treat built in conjunction with the U.S. EPA and West Virginia DEP shows the levels of oxygen needed to precipitate out metals from mine wastewaters. For complete hydrolysis using oxygen at conventional means, the pH value must be raised to a value of 10 and large settling ponds must be deployed.

Our testing has shown that ozonation in combination with an electrocatalytic process run at moderate temperatures (up to 60o C) and pressure of 1 to 2 atm was found to be effective at a pH of 3 and contains sufficient neutralizing agent at a pH of between 5 and 7 to allow for at a rapid rate the coagulation and precipitation of insoluable iron hydroxide.

Recent monitoring data indicates that the Acid Mine Drainage found in the Scranton Mine Pool is now characterized as very net alkaline, after many years being characterized as net acidic. The amount of metals, particularly Fe, in both the Old Forge Borehole and Duryea Breach discharge is also slowly declining from levels recorded in the 1970's (Table 1-1). However, the Pennsylvania DEP, acting under requirements of the Clean Water Act, found that **even with the improvement in alkalinity and Fe loading, a reduction of Fe Loading of 92 percent at the Lackawanna River mouth is still needed to meet water quality standards** (PA DEP 2005). The vast majority of this loading originates from Old Forge Borehole and Duryea Breach discharge.

Table 1-1 The change of Old Forge Borehole and Duryea Breach quality over time.

	OFB pH	OFB Net Acidity	OFB Fe	DB pH	DB Net Acidity	DB Fe
1970s	5.60	210.00	40.00	5.70	233.00	48.00
1980s	5.96	0.84	30.51	5.97	2.11	37.12
2010s	6.54	-69.80	15.18	6.53	-62.75	18.65

The Susquehanna River Basin Commission has also recently characterized anthracite mine drainage via the 2011 Anthracite Region Mine Drainage Remediation Strategy. This work recognizes the significance of Old Forge Borehole and the Duryea Breach as contributing ~25 percent of the Fe loading entering the North Branch Susquehanna and ultimately finding its way into the Chesapeake Bay. This work also ranks Old Forge Borehole and the Duryea Breach as the second and sixth highest priority discharges in the entire Susquehanna River Anthracite Region.

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The Susquehanna River Basin Commission report included the statement that, "In order to treat the AMD problem in the Lower Lackawanna River, eliminate the Fe loading needed to meet water quality standards an active AMD treatment plant is probably a necessity. Passive wetland treatment can be a component of the overall process, but due to the volumes and Fe loading of Old Forge Borehole and Duryea Breach, an active treatment plant is more than likely needed to effectively accelerate rates of precipitation to remove a majority of the precipitated metals."

Under a 1970 EPA funded and conducted an engineering design and economic study to evaluate the ozone oxidation followed by limestone neutralization of acid mine drainage. No experimental studies were performed.

Also under EPA funding in 1974 laboratory studies on ozonation of actual acid mine drainage showed that at higher pH levels between both Fe and Mn could be precipitated out but that the Mn would only hydrolyze after Fe in reducing itself was hydrolyzed – a process taking time. Both chlorine and reverse osmosis were found to be ineffective in reducing Mn levels *The report concluded that while ozone was effective no design existed to produce the ozone needed to achieve results*.

The Keystone Pure Water Tech process

The AOP technology combines ozonation & electro-oxidation in the presence of catalyst freshly produced at the electrodes to break down partially the dissolved organic to form charged radicals & ions to render it insoluble when reacted with the catalyst. This breaking down of the molecules happens at quasi super critical conditions .

The Electro-catalytic AOP produces Ozone directly from water (insitu) using a patented electro-catalytic dissociation process. The resulting nascent oxygen in the presence of metal catalysts produces a mixture of powerful oxidants including oxygen radicals, ozone, hydrogen peroxide, and hydroxyl radicals. These work together to simultaneously oxidize, coagulate and eliminate organic and inorganic pollutants.

At moderate temperatures and pressures the resultant high levels of catalytic activity is comparable to those required for related methods such as supercritical water oxidation and wet air oxidation. The Keystone AOP process increases the ozone reaction rate by an order of magnitude.

In tests on the Old Forge Borehole discharge the water post processing met Pennsylvania's Chapter 93 water quality standards. Keystone was able to cost effectively treat the Acid Mine Drainage. In a large field demonstration Keystone was able to continuously process 10,000 GPD of AMD for a several week period.

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Pennsylvania's Chapter 93 of its Water Quality Standards lists the limits for chemical, physical and biological parameters that affect the suitability of Pennsylvania's surface waters in sustaining life, health, and human activities. All surface waters have designated uses which determine the standards for water quality to be met for that body of water. Protected uses group into several broad categories such as Aquatic Life, Water Supply, Recreation and Fish Consumption, and Special Protection. Within each category are specific uses; Aquatic Life includes Warm Water Fishes (WWF), Cold Water Fishes (CWF), Migratory Fishes (MF), and Trout Stocking (TSF) and Recreation and Fish Consumption includes Boating (B), Fishing (F), Water Contact Sports (WC), and Esthetics (E).

- *AMD before and after the Advanced Oxidation Process treatment*

PENNSYLVANIA CHAPTER 93 WATER QUALITY STANDARDS

Parameter	*Symbol*	*Criteria*	*Critical Use**
Alkalinity	Alk	Minimum 20 mg/l as CaCO3, except where natural conditions are less. Where discharges are to waters with 20 mg/l or less alkalinity, the discharge should not further reduce the alkalinity of the receiving waters.	CWF, WWF, TSF, MF
Ammonia Nitrogen	Am	The maximum total ammonia nitrogen concentration (in mg/L) at all times shall be the numerical value given by: un-ionized ammonia nitrogen (NH_3-N) x ($\log^{-1}[pK_T-pH] + 1$), where: un-ionized ammonia nitrogen = 0.12 x f(T)/f(pH) $f(pH) = 1 + 10^{1.03(7.32-pH)}$ f(T) = 1, T ›= 10°C $f(T) = 1 + 10^{(9.73-pH)}$, T ‹ 10°C $1 + 10(^{pK_T - pH})$	CWF, WWF, TSF, MF
		and pK_T = , the dissociation 0.090 +…constant for	

		ammonia in water. 2730 (T + 273.2) []	
		The average total ammonia nitrogen concentration over any 30 consecutive days shall be less than or equal to the numerical value given by: un-ionized ammonia nitrogen (NH_3-N) x ($\log^{-1}$[pK_T-pH] + 1), where: un-ionized ammonia nitrogen = 0.025 x f(T)/f(pH) f(pH) = 1, pH ›= 7.7 f(pH) = $10^{0.74(7.7-pH)}$, pH ‹ 7.7 f(T) = 1, T ›= 10°C f(T) = 1 + $10^{(9.73-pH)}$, T ‹ 10°C 1 + 10($^{pK_T-pH}$)	
		The pH and temperature used to derive the appropriate ammonia criteria shall be determined by one of the following methods:	
		1) Instream measurements, representative of median pH and temperature—July through September.	
		2) Estimates of median pH and temperature—July through September—based upon available data or values determined by the Department. For purposes of calculating effluent limitations based on this value the accepted design stream flow shall be the actual or estimated lowest 30-consecutive-day average flow that occurs once in 10 years.	
Bacteria	Bac_1	(Fecal coliforms/ 100 ml)—During the swimming season (May 1 through September 30), the maximum fecal coliform level shall be a geometric mean of 200 per 100 milliliters (ml) based on a minimum of five consecutive samples each sample collected on different days during a 30-day period. No more than 10% of the total samples taken during a 30-day period may exceed 400 per 100 ml. For the remainder of the year, the maximum fecal coliform level shall be a geometric mean of 2,000 per 100 milliliters (ml) based on a minimum of five consecutive samples collected on different days during a 30-day period.	WC
	Bac_2	(Coliforms/100 ml)—Maximum of 5,000/100 ml as a monthly average value, no more than this number in more than 20 of the samples collected during a month, nor more than 20,000/100 ml in more than 5% of the samples.	PWS
Chloride	Ch	Maximum 250 mg/l.	PWS
Color	Col	Maximum 75 units on the platinum-cobalt scale; no other colors perceptible to the human eye.	PWS
Dissolved Oxygen		The following specific dissolved oxygen criteria recognize the natural process of stratification in lakes, ponds and impoundments.	

		These criteria apply to flowing freshwater and to the epilimnion of a naturally stratified lake, pond or impoundment. The hypolimnion in a naturally stratified lake, pond or impoundment is protected by the narrative water quality criteria in § 93.6 (relating to general water quality criteria). For nonstratified lakes, ponds or impoundments, the dissolved oxygen criteria apply throughout the lake, pond or impoundment to protect the critical uses.	
	DO_1	For flowing waters, 7-day average 6.0 mg/l; minimum 5.0 mg/l. For naturally reproducing salmonid early life stages, applied in accordance with subsection (b), 7-day average 9.0 mg/l; minimum 8.0 mg/l. For lakes, ponds and impoundments, minimum 5.0 mg/l.	CWF
	DO_2	7-day average 5.5 mg/l; minimum 5.0 mg/l.	WWF
	DO_3	For the period February 15 to July 31 of any year, 7-day average 6.0 mg/l; minimum 5.0 mg/l. For the remainder of the year, 7-day average 5.5 mg/l; minimum 5.0 mg/l.	TSF
Fluoride	F	Daily average 2.0 mg/l.	PWS
Iron	Fe_1	30-day average 1.5 mg/l as total recoverable.	CWF, WWF, TSF, MF
	Fe_2	Maximum 0.3 mg/l as dissolved.	PWS
Manganese	Mn	Maximum 1.0 mg/l, as total recoverable.	PWS
Nitrite plus Nitrate	N	Maximum 10 mg/l as nitrogen.	PWS
Osmotic Pressure	OP	Maximum 50 milliosmoles per kilogram.	CWF, WWF, TSF, MF
pH	pH	From 6.0 to 9.0 inclusive.	CWF, WWF, TSF, MF
Phenolics (except § 307(a)(1) (33 U.S.C.A. § 1317(a)(1)), Priority Pollutants)	Phen	Maximum 0.005 mg/l.	PWS
Sulfate	Sul	Maximum 250 mg/l.	PWS
Temperature		Maximum temperatures in the receiving water body resulting from heated waste sources regulated under Chapters 92a, 96 and other sources where temperature limits are necessary to protect designated and existing uses.	See the following table.

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Conclusions

Acid Mine Drainage from Pennsylvania's abandoned coal mines continues to be a major source of pollution impacting the Susquehanna River and ultimately the Chesapeake Bay.

While the US Environmental Protection Agency and others conducted bench scale experiments no previous group has conducted significant large scale trials of new technology.

The Susquehanna River Basin Commission concluded that an active treatment plant would be necessary to treat the Fe loading resulting from the discharges from the Old Forge Borehole and Duryea Breach discharge.

Keystone Pure Water Tech using its AOP process has shown through large scale field trials that it is able to precipitate out iron and manganese cost effectively and efficiently especially when compared to traditional active treatment plants.

The Keystone AOP solution provides a means to solve Pennsylvania's toxic coal legacy, meeting Chapter 93 Water Quality Standards and eliminating a major source of pollution for the Chesapeake Bay.