THE HYDROLOGY AND GEOCHEMISTRY OF ACID SEEP 1 AT GIBBONS CREEK LIGNITE MINE, TEXAS[1]

by

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Abstract

This study investigates the hydrology and geochemistry of the acid Seep 1 system at Gibbons Creek lignite mine in east-central Texas. The seep is related to the resaturation of the A2 Mine Block spoils with groundwater. Resaturation started in 1992 with the backfilling of the first dragline pit with spoil and was essentially completed in 2006 when the water table in the spoil stabilized against the level of an endlake constructed in the last dragline pit. The endlake is 36 feet higher than the seep and half a mile away. The evidence suggests that the endlake controls the water table in the intervening spoil and therefore indirectly at the seep itself. The study indicates that the spoil resaturation occurred rapidly because rainwater was able to percolate along sub-vertical pathways along the flanks of spoil ridges cast by the dragline. However, lateral movement of water through the spoil appears to have been much slower. This interpretation is based on the very distinct, yet constant, geochemical signatures of the endlake, the groundwater in two spoil wells, and the water at the seep itself.

Introduction

Purpose

This paper is an investigation of the resaturation of spoil with groundwater and the relationship with Seep 1 in the A2 Mine Block at Gibbons Creek lignite mine in east-central Texas. This surface coal mine, owned by the Texas Municipal Power Agency (TMPA), served to provide fuel to the nearby Gibbons Creek Steam Electric Station, a 470-megawatt power plant also owned by the Agency. The mine was active from 1982 until 1996 when it was permanently closed in favor of higher-grade sub-bituminous coal from the Powder River Basin in Wyoming.

The A2 Mine Block was one of six blocks at the mine. Lignite from this block was mined from 1992 to 1996. The study traces the re-establishment of groundwater in the spoil over the two decades from 1992 to the present (2012). The seep itself appeared in September 2002 and has also been intensively studied since that time.

The database used in the study includes more than 170 water level measurements made in two spoil wells and at Endlake A2P-2 and more than 250 detailed water chemistry analyses at those sites and at Seep 1 itself. All of the chemistry analyses were performed by Energy Laboratories, Inc., of College Station, Texas.

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Description of Seep 1

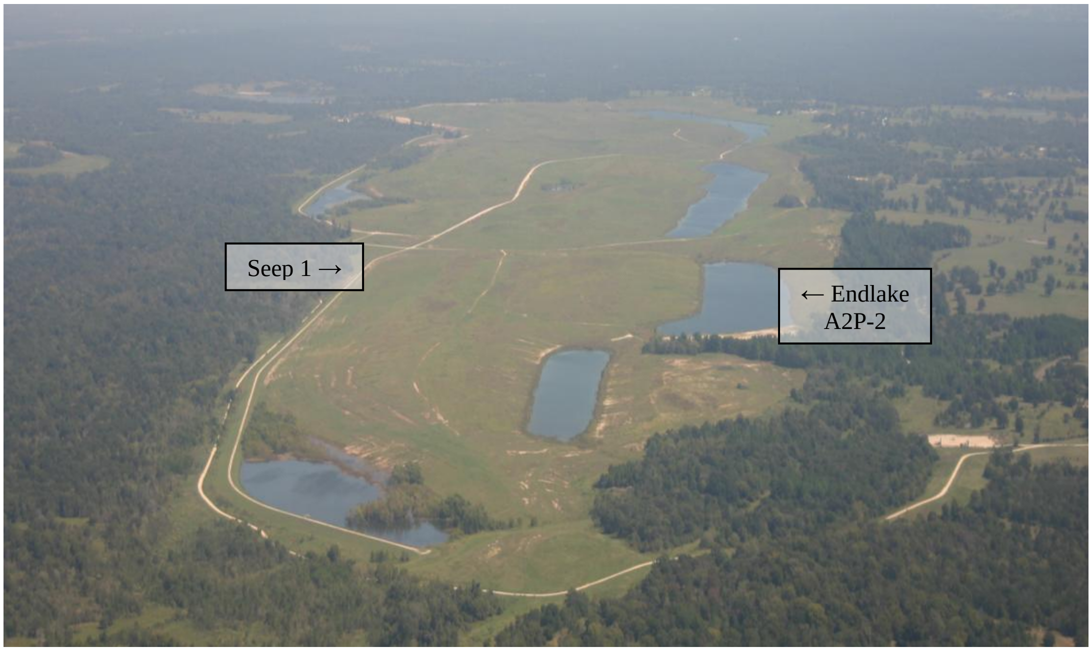
Seep 1, in its original condition before it was mitigated in 2011, occupied approximately 0.3 acres (Figure 1). The site is located at the toe of the A2 Mine Block boxcut spoil (at 3,335,785 E and 348,258 N, Texas Central State Plane coordinates, North American Datum 1927; or 30.55°N and 96.09°W, UTM). The boxcut spoil represents the location of the first dragline pits in the A2 Mine Block. The seep is at the edge of the Gibbons Creek floodplain at an elevation of approximately 200 feet above mean sea level (m.s.l.) At the time of its discovery it was flowing at about 0.5-1 gallons per minute (gpm), had a pH of 2.8-3.5, and rust-colored deposits of hydrated iron oxides.

Figure 1 – Seep 1 looking north (November 15, 2004)

Photograph: Craig Bejnar

The seep is about half a mile away from Endlake A2P-2, which is at an elevation of 236 feet above m.s.l. (Figure 2). The endlake represents the location of the last dragline pit in the A2 Mine Block.

Figure 2 – Location of Seep 1 in relation to Endlake A2P-2 (October 1, 2010)

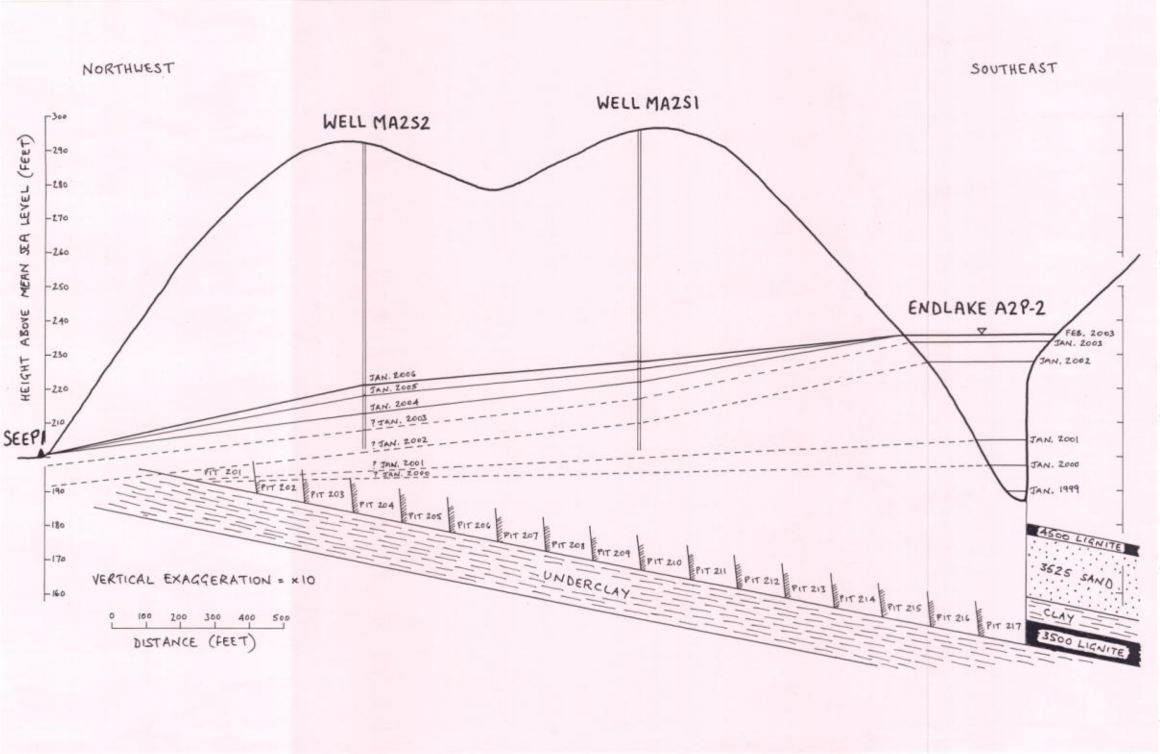


Hydrology of Seep 1 System

Cross-Section of A2 Mine Block

The geological dip section of the A2 Mine Block from northwest to southeast shows the hydrological relationships among Endlake A2P-2, groundwater monitoring Wells MA2S1 and MA2S2, and Seep 1 (Figure 3). In particular, the section shows the rise in the water table over the years 2000 to 2006. The section has been drawn with a vertical exaggeration of x10 to show the rise which would be barely visible at a true scale.

Figure 3 – Dip Section of A2 Mine Block



The groundwater wells were installed in 2003 after Seep 1 had been discovered and therefore reliable data for the elevations of the water table in the spoil are only available after that date. The elevations of the water table before that date were inferred from the levels of water in the endlake.

The section shows the down-dip progression of mine pits from northwest to southeast, starting near the outcrop of the 3500 lignite seam in Pit 201 and ending at the deepest dragline cut in Pit 217. This end pit is now occupied by Endlake A2P-2. Since the bottom of each pit was approximately 140 feet wide, the total advance over the 17 pits was about half a mile.

It should be noted that the construction of the endlake required regrading of both the highwall and spoil sides of the pit. Much of this material was pushed into the empty pit with the result that the bottom of the endlake is significantly higher than the original floor of the pit.

The extreme right-hand end of the section shows the unmined geological sequence of the A2 Mine Block, preserved in the highwall side of Pit 217. It is apparent that much of the sequence consists of the 3525 and 4525 sand units. These are predominantly sands but do contain finer-grained beds of silty clay and clay. Mining extended down to the 3500 lignite seam. Below that was the "underclay" which was left in place and is therefore shown extending across the whole section.

History of mine pit advances

The history of dragline pit advances in the A2 Mine Block is summarized in Table 1.

Table 1 – Dragline Advance in A2 Mine Block

Year	Mine Pits*
1992 (second half)	201-207
1993	207-211
1994	No mining
1995	212-215
1996 (first half)	216-217

* Navasota Mining Co. – mine production reports

Initially, the rate was fast – the pits were short and the overburden shallow. But by 1993 the rate had begun to slow. This was partly due to the geometry of the mine block which allowed the pits to become lengthened and partly due to the overburden cover becoming thicker. The geological dip meant that each pit was about three feet deeper than the previous one and the topography of the ground surface started rising because the dragline was advancing into a hill. In 1994, there was a temporary cessation of mining when the dragline was moved to assist operations in the A3 Mine Block (Figure 4).

Figure 4 – A2 and A3 Mine Blocks (April 1994)

Photograph: unknown source

The photograph shows A2 Mine Block in the foreground and A3 Mine Block in the background. The temporarily abandoned Pit 211 with two ungraded spoil ridges marking the former locations of Pits 210 and 209 is visible in the A2 Mine Block. Very little remains of Pit 208 – the ridge that marked its location has been leveled along most of its length. The regraded, gray-colored (reduced) spoil of previous mine pits is obscured by a four-foot cover of tan-colored (oxidized), non-pyritic overburden that was spread with mobile equipment. This material was then planted with permanent vegetation visible as green strips separated by erosion control terraces. At the bottom of the slope is the future location of Seep 1.

Other features of interest in the photograph include: the sedimentation pond controlling runoff from the A2 Mine Block (area of green water in the foreground); the black lignite stockpile in the middle distance; and the two draglines in the A3 Mine Block (one working from the spoil side at the far end of the chevron pit and the other working from the highwall side at the very far end of the most distant pit). Mining in the A2 Block resumed in 1995 when one of the draglines returned. Removal of coal from Pit 217 was completed a few months after both draglines were parked on February 29, 1996 and the pit was abandoned.

Physical composition of spoil

The physical composition of the spoil was determined to a large extent by the nature of the geological units that were being removed and randomly side-cast by the dragline. Since the dragline bucket in use had a capacity of approximately 75 cubic yards, there was considerable mixing of the overburden just in the process of digging and dumping. But the proportions of the geological units in the overburden were also changing as the pits progressed down-dip into deeper cover.

The average thicknesses of the geological units in A2 Block are summarized in Table 2. The two lignite seams did not contribute to the cumulative thickness since they were removed in the course of mining. The table indicates that the content of sandy units mixed into the spoil was variable falling in the approximate range of 40%-80% depending on how much of the geological column was present in the highwall.

Table 2 – Geological Units in A2 Mine Block

Geological units in stratigraphic order	Thickness of each unit* (feet)	Cumulative thickness of overburden (feet)	General content of sand units in overburden (%)
4525 Sand (Yuma)	80	141	74%
Sandy clay	30	61	41%
4500 Lignite	3	0	-
3525 Sand	25	31	81%
Overclay	6	6	0%
3500 Lignite	8	0	-
Underclay	14	-	-

* Source: Section .127 of the GCLM IV Mining Revision Application (TMPA/Morrison Knudsen, March 1991); the data are generalized – thicknesses of sand units were particularly variable.

Water levels in Mine Pit 217/Endlake A2P-2

Groundwater levels in the spoil started being measured in the two spoil wells in September 2003. Levels before that time have been inferred from correlation with water levels in Pit 217. On March 8, 1996 Pit 217 was dry and mobile equipment was still removing the last of the coal in the bottom (Figure 5). The dragline had stopped stripping overburden and can be seen parked north of the pit. By December 13, 1996 there were already several feet of water in the bottom of the pit (Figure 6), and less than two years after mining had stopped the pit had filled significantly (Figure 7).

Figure 5 – Aerial photograph of Pit 217 on March 8, 1996

Photograph: Tobin Surveys, Inc.

Figure 6 – Aerial photograph of Pit 217 on December 13, 1996

Photograph: Tobin Surveys, Inc.

Figure 7 – Mine Pit 217 on November 5, 1997 (view from southwest)

Photograph: E. Bagley

The water level in Pit 217 was first surveyed on October 29, 1998 at 186.9 feet above m.s.l. and a second survey on January 18, 1999, revealed an increase in elevation of almost five feet to 191.6 feet above m.s.l. Measurements after that are less reliable because water was pumped to and from the pit to facilitate grading of the spoil and highwall during construction of Endlake A2P-2. This began in August 2000 and was completed by May 2001.

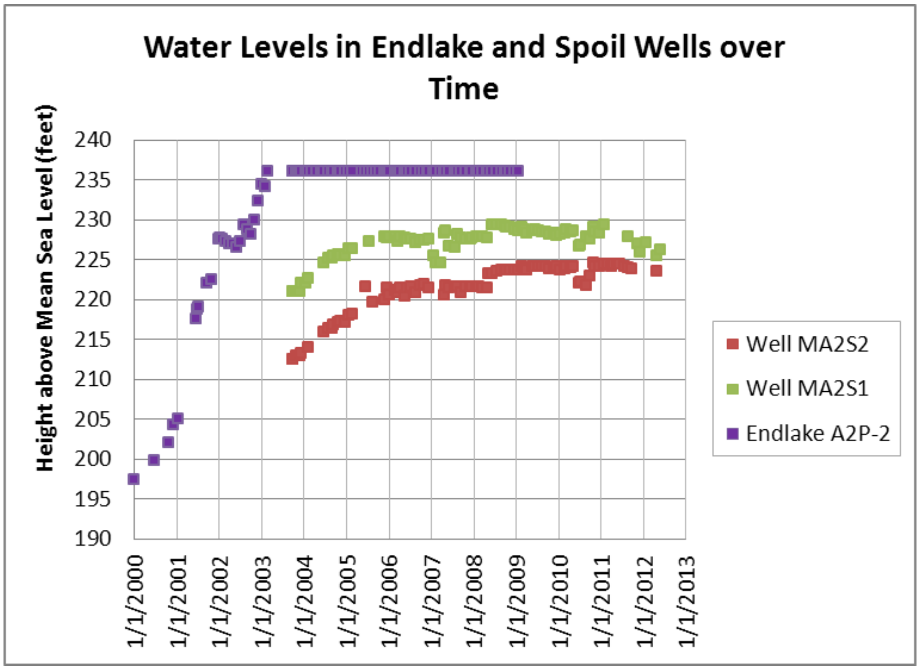
The water level in the new endlake rose particularly fast in 2001, from 205 feet above m.s.l. to 228 feet above m.s.l. This was primarily due to the displacement of water upwards in the course of dumping material pushed in from the sides of the pit. There was also a large contribution from the heavy runoff caused by Tropical Storm Allison in June 2001 and from pumping from an adjacent endlake in April-May 2001. The level continued to rise in 2002 and by February 24, 2003 the new endlake had reached its design capacity at 236 feet above m.s.l. and started spilling.

Water levels in spoil as measured in groundwater wells

By that time, Seep 1 had become active. Towards the end of July 2003, two groundwater monitoring wells were installed in the A2 Mine Block spoil between the endlake and Seep 1. The first water level measurements in these wells were made on September 26, 2003. The relationship of water levels in these wells to Endlake A2P-2 is displayed in Figure 8.

The graph shows water levels in both wells rising rapidly in 2002 and 2003 apparently reflecting the rapid rise of water level in Endlake A2P-2 in 2001. By February 2003, the endlake had reached its final elevation and spoil groundwater appears to have followed suit with levels stabilizing in the closer Well MA2S1 by early 2006 and in the more distant Well MA2S2 by late 2006.

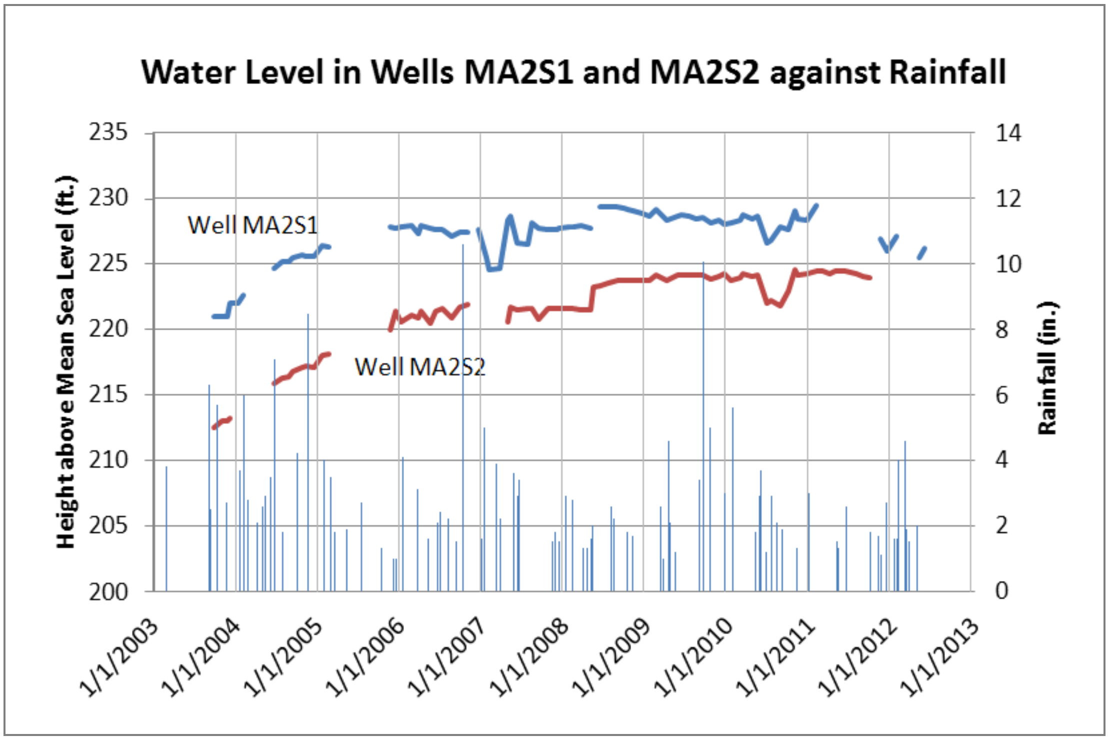
Figure 8 - Water Levels in Endlake A2P-2 and in Spoil Wells MA2S1 and MA2S2



<u>Level of spoil water table in relation to rainfall</u>

To determine if the spoil water table fluctuated in response to rain events, the spoil water levels were plotted against cumulative amounts of rain (if there were several successive days of rain) (Figure 9).

Figure 9 – Water Level in Spoil Groundwater Monitoring Wells in Relation to Rainfall



The results are inconclusive. There does not appear to be any immediate response to large rainfall events, such as the 10-inch cumulative rains in 2006 and 2009. However, by that time, the spoil areas were fully reclaimed with good covers of permanent vegetation that would have increased evapo-transpiration and reduced infiltration.

Slope of Water Table in the Spoil

The slope of the water table in the spoil over time is summarized in Table 3. Slopes of the water table were calculated for three segments of the cross-section: Well MA2S2 to Seep 1, Well MA2S1 to Well MA2S2, and Endlake A2P-2 to Well MA2S1.

Values for the first segment are negative for 2000 and 2001 suggesting that the hydraulic gradient was away from the location of the future seep and down-dip towards the location of the future Well MA2S2. By January 2002, however, the gradient was beginning to reverse suggesting an increased head towards the location of the future seep. As indicated above, Seep 1 appears to have become active a few months later and was, in fact, discovered in September 2002.

Table 3 – Slope of Water Table in Spoil over Time

Date	**Water level difference between Well MA2S2 and Seep 1** (horizontal distance = 930 feet)		**Water level difference between Well MA2S1 and Well MA2S2** (horizontal distance = 800 feet)		**Water level difference between Endlake A2P-2 and Well MA2S1** (horizontal distance = 770 feet)	
	Vertical difference (feet)	Slope	Vertical difference (feet)	Slope	Vertical difference (feet)	Slope
Jan. 2000	*-6*	*-0.6%*	*1*	*0.1%*	*2*	*0.3%*
Jan. 2001	*-4*	*-0.4%*	*4*	*0.5%*	*5*	*0.6%*
Jan. 2002	*1*	*0.1%*	*9*	*1.1%*	*18*	*2.3%*
Jan. 2003	*8*	*0.9%*	*5*	*0.6%*	*17*	*2.2%*
Jan. 2004	13	1.4%	9	1.1%	14	1.8%
Jan. 2005	17	1.8%	9	1.1%	10	1.3%
Jan. 2006	21	2.3%	7	0.9%	8	1.0%
Jan. 2007	22	2.4%	6	0.8%	8	1.0%
Jan. 2008	22	2.4%	6	0.8%	8	1.0%
Jan. 2009	24	2.6%	5	0.6%	7	0.9%
Jan. 2010	24	2.6%	4	0.5%	8	1.0%
Jan. 2011	24	2.6%	4	0.5%	8	1.0%
Jan. 2012	24	2.6%	3	0.4%	9	1.2%

Note: Italic font indicates inferred values before 2004; all vertical differences from 2004 onward were measured.

It should be noted that hydraulic gradients in two of the three segments had stopped increasing after January 2005 and had even started to decrease. Only the segment from Well MA2S2 to Seep 1 continued increasing until January 2009 after which it too stabilized. It appears therefore that the head or driving force causing the discharge of water at Seep 1 has been stable since that time.

Layering of the spoil in relation to groundwater resaturation

Several factors have affected resaturation of the spoil with groundwater in the A2 Mine Block. These are associated with how the mixed overburden material was dumped by the dragline in the first place and how it was regraded with mobile equipment afterwards.

The dragline dumped spoil in the form of long “ridges” and “valleys” parallel to the mine pit (Figure 10). As the loose spoil fell out of the dragline bucket onto the ridge, large boulders rolled down the ridge slopes to collect in a line along the interface with the previous ridge. The size of some of these boulders may be compared to the Suburban visible in the bottom right-hand corner of the photograph. As the dragline progressed along the pit, these lines coalesced to form a continuous sub-vertical plane of large boulders providing a pathway for rainfall percolation. Any rainfall trapped between the spoil ridges would be channeled along the spoil valleys to these pathways.

Figure 10 – Typical Highwall-Side Dragline Operation

Photograph: Aero Views, Mine Block B2, c. 1984 (note Suburban for scale in bottom right-hand corner).

In some digging scenarios, the dragline left additional topographic features, such as the arcuate, en echelon ridges superimposed on the main spoil ridge (see Figures 5 and 6) that further helped to trap rainfall and enhance infiltration.

Finally, as previously seen, the geological units overlying the lignite in the A2 Mine Block were in general sandy so that permeability and porosity of the spoil matrix was relatively high.

These factors conspired to facilitate initial infiltration of rainfall into the spoil and encourage downward movement. On the other hand, lateral movement through the spoil would have been impeded by the sub-vertical bedding planes created by the sliding of unconsolidated spoil material down the faces of the piles until it reached the angle of repose. Lateral movement would also have been hindered by the “ribs” of lignite left along the spoil side of the pit to hold back the toe of the spoil slope.

Geochemistry of Seep 1 System

Ionic ratios

A useful tool in geochemical investigations is the ionic ratio. This measures the ratio of one ion to another. Unlike the use of absolute concentrations of ions, the use of a ratio eliminates the effects of concentration or dilution. Additionally, when the ionic concentrations are expressed in terms of equivalent weights, the ratio also provides information about the relative numbers of ions and therefore their chemical balance.

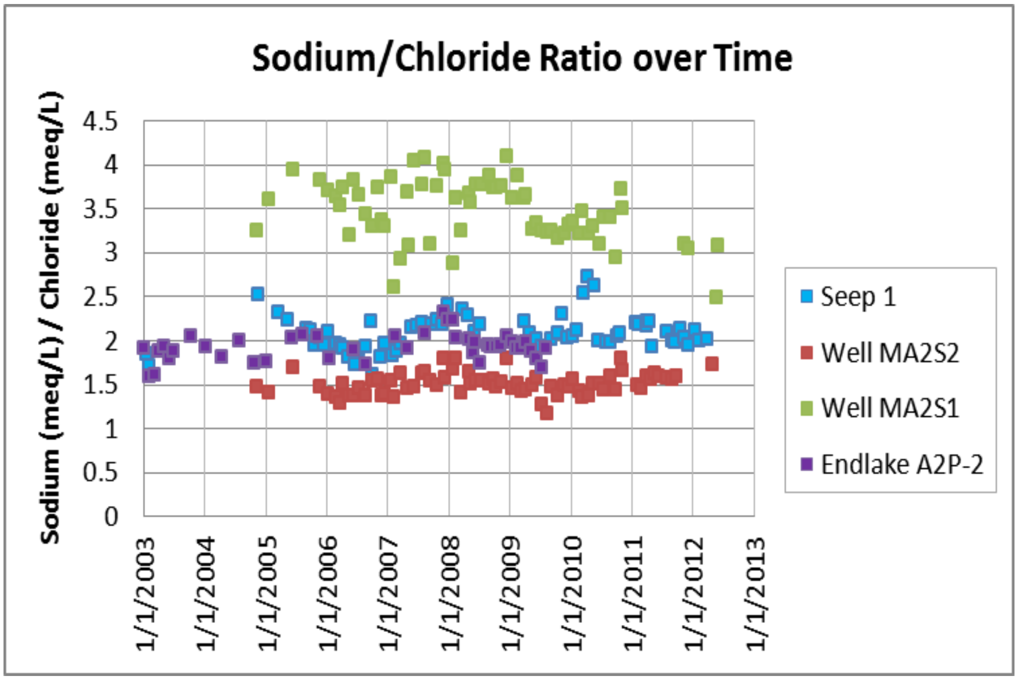
For example, a solution containing 230 milligrams per liter of sodium ions and 355 milligrams per liter of chloride ions contains 10 milliequivalents per liter of sodium ions (the equivalent weight of sodium is approximately 23) and 10 milliequivalents of chloride ions (the equivalent weight of chloride is approximately 35.5). The number of sodium and chloride ions is balanced and the Na/Cl ratio is therefore 1.0. Whether we add water to this solution (e.g., from rainfall) or lose water from this solution (e.g., through evapo-transpiration), the balance between the ions stays the same and the ratio remains constant.

The sodium-to-chloride (Na/Cl) ratio

The chloride ion actually happens to be useful in geochemical ratios because it tends to form soluble compounds and stays in solution. Also, it does not react with rock-forming minerals or any of the major cations in natural environments (Garrels and Christ, 1965, p. 9).

The chemical analyses for water at Seep 1, the two spoil wells, and Endlake A2P-2 show very different Na/Cl ratios (Figure 11). Each of these locations has its own distinct Na/Cl signature. The highest Na/Cl ratio occurs in Well MA2S1 (values of 3.0 – 4.0); the lowest occurs in Well MA2S2 (values of 1.3 – 1.8); Seep 1 is in the middle (values of 1.7 – 2.5); and Endlake A2P-2 occupies an intermediate range between Well MA2S2 and Seep 1 (values of 1.7 – 2.1).

Figure 11 – Sodium/Chloride Ratio over Time

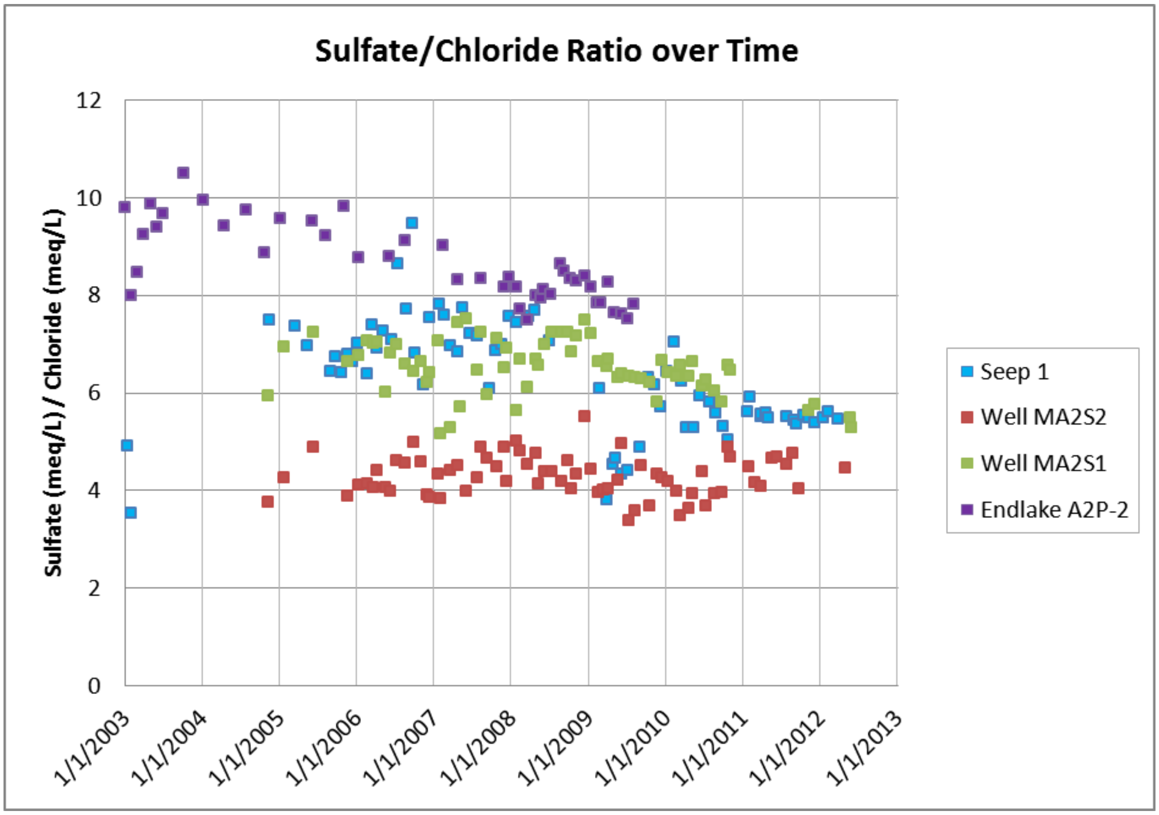


All of these values are much higher than the Na/Cl ratio encountered in seawater (0.86). At first sight, this is surprising since most of the sedimentary units at the mine were either directly deposited in seawater or were later submerged in seawater. The Na/Cl ratio in the spoil groundwater would perhaps be expected to reflect this marine origin. However, sodium is common in rock-forming minerals (such as plagioclase feldspars) which dissolve in acid environments and release the sodium thereby raising the Na/Cl ratio. Another possibility is that sodium on clay mineral cation exchange is being displaced into solution by more highly-charged calcium ions from agricultural lime applied to soils at the surface. Whatever the reason, it is evident that the Na/Cl ratio has remained remarkably constant at each site over an entire decade and that it serves as a useful "geochemical signature."

The sulfate-to-chloride (SO_4/Cl) ratio

The SO_4/Cl ratio in seawater is 0.1 but the ratios at the four study sites are considerably higher (Figure 12).

Figure 12 – Sulfate/Chloride Ratio over Time



There are two probable reasons for this. One is the presence of sulfate ions from naturally occurring gypsum (calcium sulfate) which is somewhat soluble and can therefore contribute the additional sulfate ions. The other is the formation of sulfate from the oxidation of pyrite that is commonly present in the reduced part of the overburden.

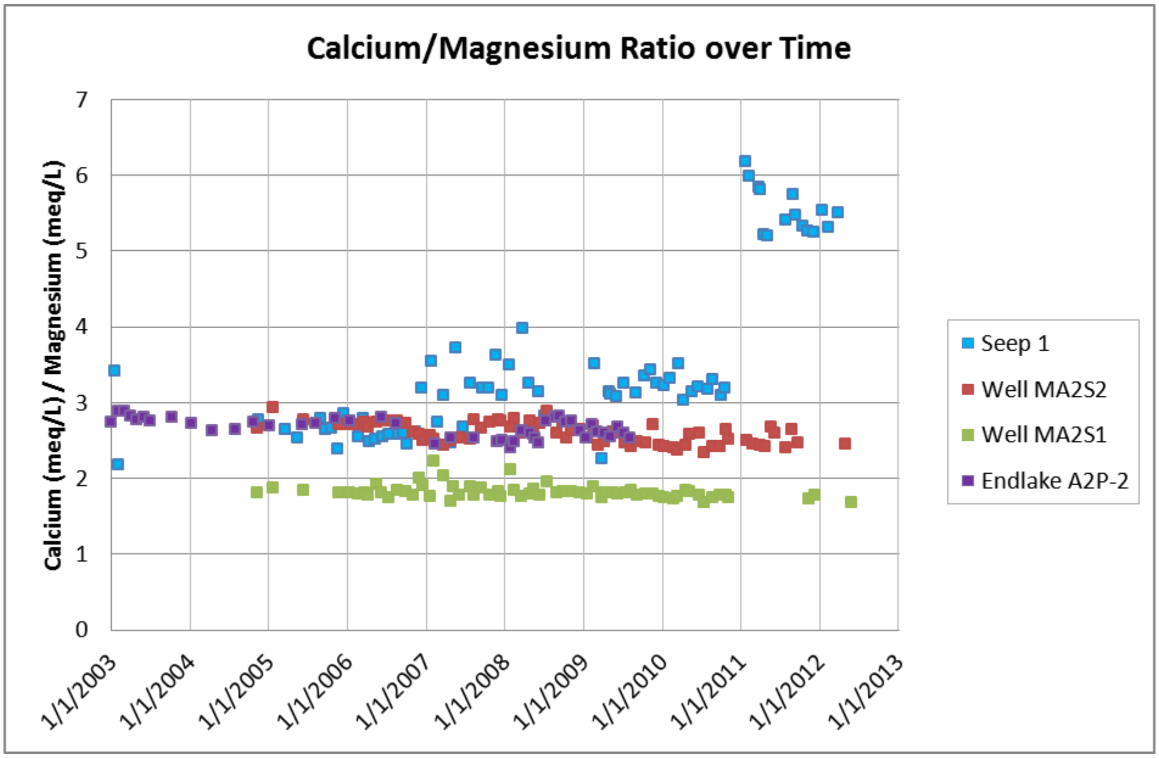
It is interesting to note that the SO_4/Cl ratio shows a decreasing trend at three of the four sites. If pyrite were still actively oxidizing, the sulfate contents would be rising in relation to the constant chloride contents and the ratios would be showing an increasing trend. The decreasing trend is consistent with an interpretation that the oxidation reactions are declining and producing less sulfate. The exception appears to be Well MA2S2 which shows the lowest ratio and no change since 2005. This may indicate that this well, which is in older spoil than Well MA2S1, has exhausted its pyrite reserves and is at a background level. Well MA2S1 appears to be trending towards this level.

The calcium-to-magnesium (Ca/Mg) ratio

The Ca/Mg ratio is generally very constant in natural waters because the two cations are chemically very similar. The two spoil wells and Endlake A2P-2 support this observation (Figure 13). They show very constant yet distinct values over many years.

Seep 1 is different because it displays a steep increase in the Ca/Mg ratio at the beginning of 2011. This reflects the influx of calcium from the wetland mitigation structure that was built at the site. This structure was designed with limestone beds, the source of the calcium, for the treatment of the seep's acidity.

Figure 13 – Calcium/Magnesium Ratio over Time

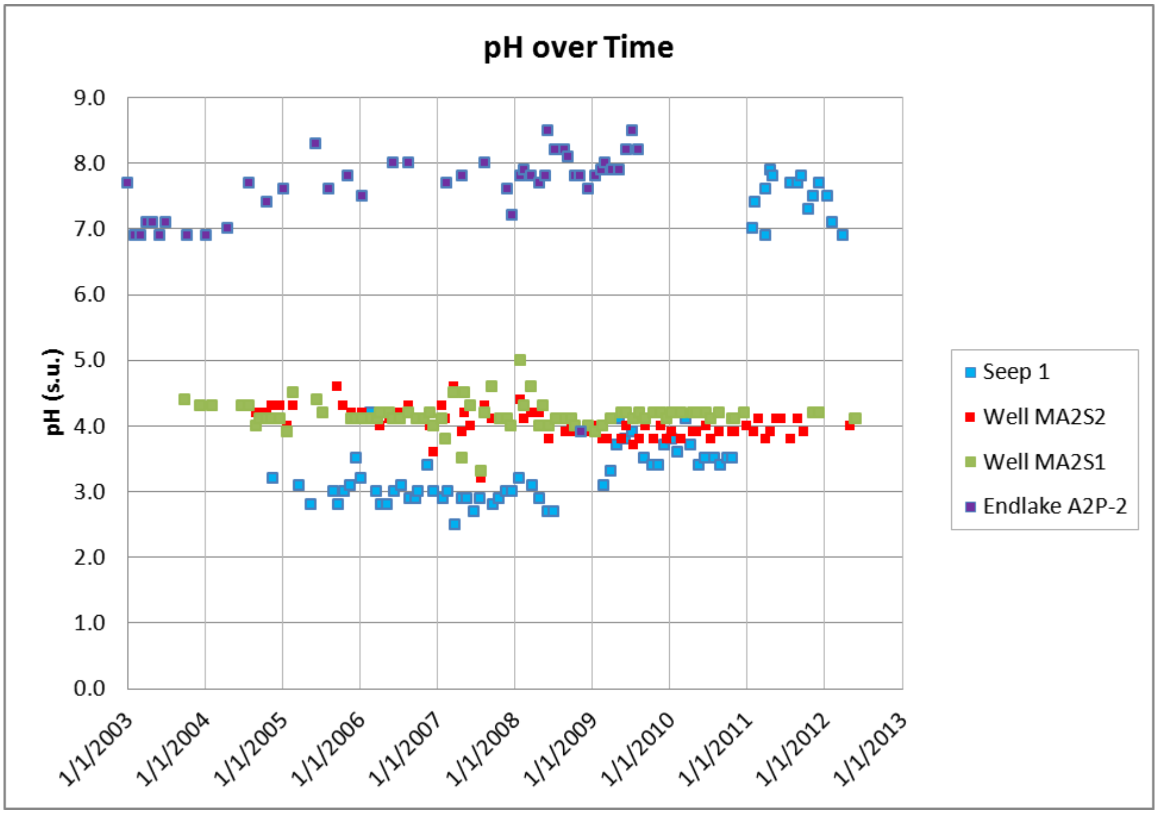


pH over time

Some further corroboration of the trends in the ionic ratios may be found in the variation of pH over time (Figure 14). There are three trends of particular interest.

The first is that shown by the two spoil wells. The pH at these locations was somewhat variable in the first few years but since 2008 it has settled into a narrow range between pH 3.8 and 4.2. In addition, the pH values of the two wells are very similar and even overlapping unlike the very different geochemical ratios for Na/Cl, SO_4/Cl, and Ca/Mg. This suggests that the pH is the result of similar chemical reactions. This, combined with the fact that the pH has remained very constant for more than the last five years suggests that the pH is being buffered, perhaps by an aluminum oxyhydroxide system or an alumino-silicate system, as had been observed earlier in Endlake A3P-2 (Horbaczewski, 2001).

Figure 14 – pH over Time



The second trend relates to Endlake A2P-2. Here it is evident that the pH has increased over time to reach equilibrium with a system controlled by limestone (from the inwash of limestone treated minesoils). The maximum pH normally attained with limestone is about 7.9; the excursions to higher pH values in the summer months are probably attributable to increased photosynthesis and growth of algae (Stumm and Morgan, 1996, p. 173).

The third trend relates to Seep 1. First, there is the increase in pH from approximately 3.0 up to pH 3.5 – 4.0 that started in 2009. It should be noted that this was not associated with an increase in the Ca/Mg ratio (see Figure 13). Thus, it was not due to an addition of calcium to the system, as would have happened if limestone had been added. Instead, it seems to correlate with the drop in the SO_4/Cl ratio at that time (see Figure 12). It would seem that the increase in pH and the decrease in the SO_4/Cl ratio reflect a slowing down in the rate of pyrite oxidation perhaps indicating that the supply of pyrite is running out. This would be consistent with previous observations of rapid disintegration and decomposition of pyrite in minesoils at Gibbons Creek (Horbaczewski, 2007).

It should be added that once the pH starts increasing from 3.0 the role of the ferric ion as a rapid oxidizing agent of pyrite decreases. Ferric iron can no longer remain in solution and is precipitated as the familiar rust-colored oxyhydroxide that is observed at Seep 1. Oxidation of pyrite, if any is still available, can then only proceed through slower bacterially-mediated processes.

The other observation concerning Seep 1 is the immediate jump in pH from 3.5 in October 2010 to pH 7.0 in January 2011. This is due to the construction of the mitigation structure that consists of a limestone screen and a wetland. The addition of calcium to the system is corroborated by the simultaneous, steep increase in the Ca/Mg ratio (see Figure 13).

Interpretation

The following interpretation is offered as a possible account of how groundwater resaturation occurred in the spoils of the A2 Mine Block and how that has influenced Seep 1.

Groundwater resaturation of the spoil began as soon as the first spoil ridges were cast by the dragline in 1992. Infiltration and deep percolation of rainfall was facilitated by:

- The topography of the spoil, which prevented surface runoff.
- Sub-vertical pathways of large boulders along the flanks of spoil ridges.
- Minimal evapo-transpiration due to rapid infiltration and lack of vegetation.
- High infiltration and permeability of the spoil due to its sandy matrix.

Rainwater percolated downwards until it reached the thick “underclay” that formed the floor of the original mine pits. The water collected in the spoil but did not move laterally to any significant extent. This is borne out by the very distinct and constant geochemical “signatures” (ionic ratios) of water at each of the four sites – Endlake A2P-2, the two spoil wells, and Seep 1. In fact, the water that collected in the mine pits came predominantly from surface rainfall runoff, with some seepage from the highwall side of the pit. Seepage from the spoil side of the pit was very minor probably because it was impeded by the sub-vertical orientation of “bedding planes” along the spoil ridges. Another obstacle to lateral movement may have been the “ribs” of lignite that were often left on the spoil side of the pit to hold back the toes of the loose spoil.

Within a few years enough groundwater had collected in the spoil to establish a potentiometric surface, or water table, in the unconfined spoil aquifer. Initially, the water table probably followed the dip of the underclay towards the deepest open pit. Once mining stopped, the last pit (Pit 217) began to fill rapidly with surface runoff. Construction of Endlake A2P-2 in this pit accelerated the rise of the water level because material pushed from both sides of the pit displaced the water already present. As a result, the floor of the endlake is estimated to be about 35 feet higher than the original floor of the pit. The steep rise in the water level was also due to heavy runoff from Tropical Storm Allison in June 2001, and to a lesser extent from pumped additions of water from adjacent pits. Endlake A2P-2 reached its final operating level in early 2003 and the water table in the spoil stabilized to this new level three years later. Since then, the slope of the water table in the spoil has remained constant and the elevation of the water table has fluctuated by less than three feet.

Rainwater percolating through the spoil has participated in a number of geochemical processes, the most important of which involved the oxidation of pyrite (iron disulfide – FeS_2). The first phase, termed the “initiation phase” (Nordstrom, 1982), occurred when the pH was near-neutral (7.0) and when atmospheric oxygen was the primary oxidizing agent of the pyrite. This involved the decomposition of pyrite to ferrous iron and elemental sulfur and the subsequent slow oxidation of sulfur to sulfate. Once sulfate anions had formed, there were two possible chemical pathways. Where a neutralizer, such as calcium was available, the sulfate anions reacted with the calcium cations to form calcium sulfate (gypsum). This is a neutral product and the reaction proceeded no further. Where there was a deficit of neutralizing cations, the sulfate paired with hydrogen from water to form hydrogen sulfate (sulfuric acid).

As more sulfuric acid formed in the second pathway, the pH continued to drop and enabled sulfur-oxidizing bacteria to assist in the oxidation process, which now entered the “acid-generation phase” (Nordstrom, 1982). At this stage, with the pH below 5.5, the acid water began to interact with clay minerals in the spoil. Initially, this involved the release of “exchangeable” aluminum and iron ions, but as the pH approached 4.5, the clay minerals began to decompose releasing “structural” aluminum and iron ions.

By pH 4.5, the acid water also began to decompose plagioclase feldspars (calcium-sodium alumino-silicates) releasing calcium and sodium into solution. As before, the calcium combined with sulfate to form gypsum while the sodium ions remained in solution balancing remaining sulfate anions. The additional sodium probably accounts for the high Na/Cl ratio in the spoil compared to seawater. Another potential source of calcium was the reactive “Superfine” limestone (Texas Crushed Stone of Georgetown, Texas) applied to the top four feet of surface minesoil.

The third and final stage of pyrite oxidation is called the “catalytic phase” (Nordstrom, 1982). In this phase, the ferric ion replaces oxygen as the oxidizing agent. It starts at about pH 4.5 and by pH 3.0 it is the only important oxidizer of pyrite. This stage was only reached at Seep 1. However, by January 2009, the reactions at Seep 1 were insufficient to maintain the low pH and it began to increase. The decreasing SO_4/Cl ratio suggests that the formation of sulfate was slowing down because the pyrite reserves near the seep were becoming exhausted. This interpretation is consistent with other observations on the high rate of weathering of pyrite in Gibbons Creek minesoils (Horbaczewski, 2007). Of course, at Seep 1, these reactions have been superseded by the installation of a limestone-and-wetland mitigation structure in 2011 which has rapidly brought pH values to neutrality.

The pH of the two spoil wells has never fallen to less than about 3.8 and now these wells appear to be stabilizing at about pH 4.1, suggesting that the pH is being buffered. A similar buffering reaction was observed in Endlake A2P-2 in 2002 (Horbaczewski, 2006). In that situation the buffering was thought to be controlled by aluminum oxyhydroxides. In the spoil situation, alumino-silicates may also be at play. The buffering is expected to continue until eventually enough cations are leached into this zone to restore the balance with the sulfate anions and allow the pH to rise towards neutrality.

Conclusions

The following conclusions may be drawn from this study:

- Resaturation of spoil with groundwater started as soon as rain fell on raw dragline-cast spoil.
- The ridge-and-valley topography of the spoil trapped rainwater and prevented runoff.
- Rainwater percolated deep into the spoil along pathways of coarser material on the spoil slopes.
- Rapid infiltration, lack of vegetation, and deep percolation minimized evapo-transpiration losses.
- This changed when the spoil peaks and valleys were regraded and planted to permanent vegetation.
- From that time on, infiltration and deep percolation decreased significantly.
- Endlake A2P-2, the two spoil wells and Seep 1 have very different geochemical signatures.
- Yet these geochemical signatures have been very constant at each site for at least a decade.
- Lateral mass movement of water through the spoil would have blurred these signatures.
- Lateral movement of water may be slowed by the sub-vertical “bedding” of the spoil ridges.
- Remnant lignite “ribs” left in each pit may also have impeded lateral water movement.
- However, there is a potentiometric surface in the spoil that controls the height of the water table.
- This surface appears to be linked to the level of water in the endlake.
- The discharge of groundwater at Seep 1 is driven by the local gradient of the water table.
- This has remained constant since 2006 and is unlikely to change significantly.
- The SO_4/Cl ratio at Seep 1 is declining and suggests that pyrite sources are becoming exhausted.
- The pH at Seep 1 had started rising even before the construction of the mitigation structure.
- The constant Ca/Mg ratio indicates that this was not caused by the addition of limestone.
- But the construction of the limestone mitigation structure did significantly raise the Ca/Mg ratio.
- The pH of the water in the spoil wells is buffered and is unlikely to change significantly.
- The buffering may be due to reactions with aluminum oxyhydroxides or alumino-silicate minerals.
- The water table in the spoil stabilized three years after the water level stabilized in the endlake.
- The seep became active sooner than that because it was driven by the local hydraulic gradient.
- The hydrological and geochemical systems stabilized within fourteen years after the start of mining.
- The systems would have stabilized faster had there not been a one-year break in mining.

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