

ALUMINUM PRECIPITATION IN ACIDIC PIT LAKES AT THE GIBBONS CREEK LIGNITE MINE, TEXAS, USA: FIELD OBSERVATIONS vs. LABORATORY SIMULATIONS¹

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Abstract. In April 2002, a precipitate was discovered in two acid end pit lakes that were in the process of being neutralized at Gibbons Creek lignite mine in east-central Texas. The precipitate was found in shallow water on the shoreline shelves of the ponds. It had the form of extensive mats of a light brown, finely-layered gelatinous material resting lightly on the detrital shelf material. Chemical analysis of the precipitate revealed that it was composed mostly of aluminum with subordinate iron and minor amounts of Ca and SO₄. The stoichiometry of the components and the chemical environment suggests that the aluminum is most probably in the form of a hydroxide (gibbsite) rather than an aluminosulfate. The shelves on which the precipitates were found had formed in December 2001. The precipitates had therefore accumulated over a period of 3-4 months. In this period, the pH of one pond (Pond A2P-1) had increased from pH 4.0 to 4.7 and that of the other (Pond A2P-2) from pH 4.5 to 5.0. The field observations are supported by earlier laboratory titrations of originally more acid water (as of December 1, 2000) from the same lakes. The titrations had shown a very strong buffering effect between pH 4.6 and 4.9 that had been interpreted as due to the precipitation of aluminum hydroxide. However, there are important differences between the field- and laboratory-scale reactions. It was found that the laboratory could not simulate the kinetics of field reactions, especially the effects of aging and polymerization of aluminum hydroxide, nor the openness of field systems with their virtually inexhaustible supplies of reactants.

Additional Key Words: gibbsite, aluminum hydroxide, aluminosulfate, buffering effect, aging, polymerization.

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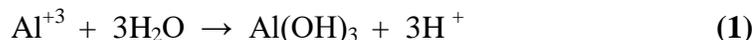
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Introduction

It is well known that neutralization of acid mine waters often results in the precipitation of metals, but it is not often that this phenomenon can be observed under relatively controlled conditions at the field scale. Such opportunities are invaluable for the testing of models derived from theory or laboratory experiments. This paper discusses the morphology and genesis of a precipitate that was monitored over a period of several months in two acid end pit lakes at the Gibbons Creek lignite mine in east-central Texas. The precipitate was first discovered by chance in the course of routine water sampling on April 1, 2002. Analysis revealed that it was very rich in Al. Observation of the precipitate over the next six months was enabled by the convergence of several favorable conditions. The water in the lakes was passing through a critical pH range, water levels in the lakes remained relatively constant, and there was relatively little wave action to disrupt the fragile deposits. Conditions changed in October 2002 with a series of rainfall events that led to a rapid rise in lake levels, and disintegration of the precipitate and its permanent submergence.

Earlier investigations at the Gibbons Creek lignite mine had established that Al was the dominant source of mineral acidity in the end lakes (Horbaczewski, 2001). This acidity may be generalized as being due to hydrolysis of the Al, as follows:



The investigations showed that hydrogen acidity (pH) would not change significantly on addition of a neutralizer, such as hydrated lime - $\text{Ca}(\text{OH})_2$ - until Fe first, and Al second, had been neutralized and removed from solution. These neutralization reactions were depicted as a series of geochemical “fences” that had to be crossed before pH would increase appreciably. Laboratory titrations of the end lake water with sodium hydroxide (NaOH) revealed strong buffering in the range pH 4.6 – 4.9, which was ascribed to the neutralization of the Al acidity. This supported the field data that showed that the pH of the end lakes did not rise above 4.9 until almost all of the Al had been removed from the water. However, there was no field confirmation of a visible Al precipitate until April 1, 2002.

Summary of Reclamation History

The end lakes are located at the Gibbons Creek lignite mine owned by the Texas Municipal Power Agency (TMPA), a municipal corporation that generates electricity for its member cities – Bryan, Denton, Garland, and Greenville. The mine used to provide fuel to TMPA’s nearby 440-megawatt Gibbons Creek Steam Electric Station. In February 1996, the mine was closed and the power plant switched to burning more economical sub-bituminous coal from the Powder River Basin in Wyoming. At the time of closure, there were four open dragline pits. Over the next three years, the pits began to fill with rainfall runoff, which steadily became more acidic, reaching pH 2.9, as pyritic material in the pit walls and in the mine spoil oxidized. In 1999, designs were finalized for the conversion of the pits into lakes. The pit walls were regraded and spillways constructed. Suitable minesoils were reconstructed to a depth of 1.22 m (4 feet) to support a pasture-land post-mining land use. This work was completed over the period November 1999 – December 2002. By the end of February 2003, all four ponds had filled with runoff and were spilling (Fig. 1). Final pond dimensions were, as follows (Table 1):

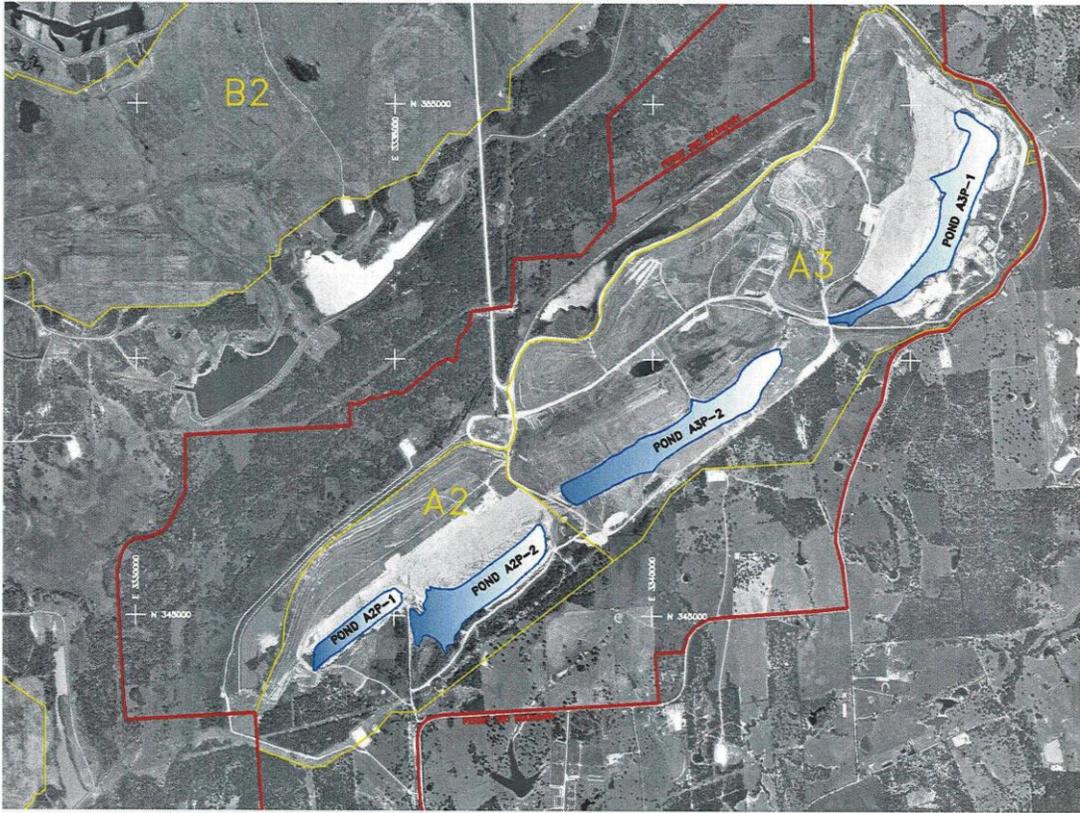


Figure 1. Location of end lakes at Gibbons Creek lignite mine, Texas.

Table 1. Dimensions of end lakes at spill elevation

Pond	Spill Elevation (m msl*)	Surface Area (hectares)	Length (m)	Width (m)	Depth (m)	Capacity (m ³)
A2P-1	68.60	9.0	610	122	17	543,000
A2P-2	71.95	19.2	854	183	23	1,333,000
A3P-1	77.10	21.8	1,524	152	19	1,936,000
A3P-2	77.13	24.3	1,524	152	21	2,294,000

* mean sea level

Preliminary Investigation of Neutralization Requirements

On December 1, 2000, as construction of the lakes or ponds was commencing, samples of water were collected for analysis of the main constituents at an outside laboratory. The results (Table 2) show a predominance of SO_4^{-2} and Ca although the Ca concentrations are not high enough to balance the SO_4^{-2} . Of particular interest is the high concentration of Al – higher than that of potassium in Pond A2P-1. Iron and Mn concentrations are relatively minor.

Table 2. Composition of water in Ponds A2P-1 and A2P-2 (as of December 1, 2000).

	A2P-1	A2P-2
pH (s.u.)	2.9	3.4
Calcium (mg/L)	438	494
Sodium (mg/L)	124	139
Magnesium (mg/L)	80	80
Potassium (mg/L)	14	23
Aluminum (mg/L)	42.1	21.9
Iron (mg/L)	11.6	4.1
Manganese (mg/L)	10.3	9.3
Sulfate (mg/L)	1,710	1,520
Chloride (mg/L)	118	152

A second set of samples was collected at the same time for titration in TMPA's laboratory to determine neutralization requirements. The samples were refrigerated and titrated four days later to pH 10.5. The results for the adjacent end lake A3P-2 demonstrated (Horbaczewski, 2001) that the titrations underestimated the actual neutralization requirements by a factor of almost 3. The conclusion from that study was that the laboratory setting was a poor simulation of field conditions primarily because it did not reproduce the slower kinetics of neutralization reactions in the field.

Methodology

Sampling of Lake Water

From December 2000 onward, unfiltered samples of water from the shores of both end lakes were collected at the beginning of each month using an 18.9-L (5-gallon) plastic pail that had been triple-rinsed with the same lake water. Care was taken to sample only water from the surface and no sediment from the shoreline shelf. Clean 1-L plastic bottles were filled by immersing them in the pail. Duplicate samples were collected – one to be stored in a refrigerator at TMPA and the other to be transported on ice to an outside laboratory within a few hours of collection using chain-of-custody protocol. No preservatives were used for these samples other

than ice. However, additional samples were collected and preserved with HNO₃ and HCl. Analyses were performed by Inter-Mountain Laboratories, Inc. (IML) of College Station, Texas, over the period 1999 to December 2002 and Energy Laboratories, Inc. (ELI) also of College Station over the period January 2003 to January 2005.

Sampling of Lake Precipitate

Samples of the precipitate were collected from shallow water with a spoon on April 3, 2002. Care was taken to sample only the gelatinous mat and to avoid detrital shelf material. The gel was collected in glass jars with screw-top lids, which were filled to the top. The jars were sealed and transported on ice to IML within a few hours of collection using chain-of-custody protocol. No preservatives were used. Back-up samples were stored in a refrigerator at TMPA.

Laboratory Procedures

The following laboratory methods were used (Table 3). The precipitates were digested using EPA solid waste (SW 846 Method 3051) procedures, including nitric acid digestion, filtration through No. 2 paper, and analysis of metals, major cations and anions using inductively coupled plasma – atomic emission spectrometry (ICP-AES). Composition was expressed on the basis of the original wet sample.

Table 3. Laboratory analysis - methods

	Water (IML)	Water (ELI)	Soils (IML)
pH	EPA 150.1	A 4500-H B	SW-846 9045C
Acidity	EPA 305.1	A2310 B	
Alkalinity	EPA 310.1	EPA 310.1	SW-846 6010B
Electrical Conductivity	EPA 120.1	EPA 120.1	
Total Dissolved Solids	EPA 160.1	EPA 160.1	
Settleable Solids	EPA 160.5	EPA 160.5	
Ca, Mg, K, Na	EPA 200.7	EPA 200.7	SW-846 6010B
Bicarbonate, Carbonate	EPA 310.1	EPA 310.1	SW-846 6010B
Chloride	EPA 300.0	EPA 300.0	SW-846 9251
Nitrogen (NO ₃ +NO ₂)	EPA 353.2	EPA 353.2	
Sulfate	EPA 300.0	EPA 300.0	SW-846 9036
Cation, Anion Sum & Balance	SM 1030F		
Al, Fe, Mn	EPA 200.7	EPA 200.7	SW-846 6010B

Sources: Water analyses: EPA (1983), EPA (1993) and SM (1995); Soil analyses: EPA (1994), and EPA (1996) (see references section).

Titration at TMPA Laboratory

The set of water samples collected on December 1, 2000, was kept refrigerated at TMPA and titrated on December 4, 2000 to an end point of pH 10.5 against a 0.01 Normal (N) solution of NaOH. The NaOH solution was added as the titrant to a 100 mL aliquot of the water sample at a rate of 1 mL per minute and the mixture stirred continuously with a magnetic stirrer. Readings of the pH were taken after each addition of titrant using an Orion Research, Inc. Model 611 pH meter equipped with an Orion ROSS® combination electrode Model 8102 that permits rapid and stable readings accurate to 0.01 pH units. The titration of the Pond A2P-1 sample was completed in 108 minutes and that of Pond A2P-2 in 75 minutes.

Interrupted Titrations at TMPA Laboratory

After completion of the initial titration, the Pond A2P-2 sample was re-titrated six times on December 4, 2000, to different pre-determined points for an analysis of the solution and of the precipitate, if any, at that point. The purpose was to track the chemical reactions and equilibria at those points. The resulting sub-samples from these “interrupted” titrations were delivered to IML on the same day for analysis of the dissolved and precipitated constituents. EPA method SW-846 6010B was used for the analysis of the precipitates. The analyses were performed on December 15, 2000.

Results and Discussion

Description of Field Precipitates

The discovery of the precipitates on April 1, 2002, in the course of routine water sampling of the end lakes was quite fortuitous. Weather conditions were very calm so that sediments in the shallow water on the shoreline shelf were easy to see in the clear water. The initial distinguishing feature of the precipitates was their structure. They consisted of irregular tan-colored masses and outcropping layers in the shelf detrital sands. The color of the precipitates was very similar to the sandy substrate so that they were difficult to distinguish when the surface of the water was not still. Closer examination revealed that the color of the precipitates in fact ranged from Munsell color 7.5YR 8/2 (pinkish white) to 7.5YR 8/4 (pink), with some 7.5YR 6/4 (light brown). Their texture in water was that of a soft, weakly coherent floc or gel. In calm water, such as at the sheltered south-west end of Pond A2P-2, they had the form of extensive near-horizontal mats arranged parallel to the shoreline, resting lightly on the detrital shelf and undulating with the motion of the waves (Fig. 2). In places on the shelf, exposures revealed inter-bedding of presumably older mats with shelf sediments. Although their bulk density was not measured directly, they were estimated to have a density of approximately 1.3 g/cm³ because they were denser than water but less dense than the underlying sand. Some of these mats had areas of up to several square meters and were up to 1-2 cm thick. They had enough coherence in water to break up under gentle wave action into sub-angular fragments (Fig. 3), which retained their coherence even when they rolled down the shelf slope under water. The mats were multi-layered as evident by color variations, but the layering was also physical because, in some cases, wave action had peeled off layers less than 1 mm thick (Fig. 4). In some cases the mats had a ripple structure suggesting that they had been deposited in sand ripples (Fig. 5). On one particularly warm, still day (April 23, 2002), a milky gel was actually observed to be forming in shallow water in the troughs of sand ripples in Pond A2P-2 (Fig. 6).

While the soft flocs had enough coherence in water to be cut with a spoon, once the material was removed from the water it flowed like a loose gel. The deposits were not cohesive enough to be picked up between finger and thumb and tended to smear out into a sticky mass, with the feel of a clayey fine silt.



Figure 2. Pond A2P-2 – view of shoreline, April 3, 2002



Figure 3. Pond A2P-2 – Detail of precipitate breaking up, April 3, 2002.



Figure 4. Pond A2P-2 – Detail of layering in precipitate mat, June 6, 2002



Figure 5. Pond A2P-1 – Detail of structure of precipitate mat, October 1, 2002.

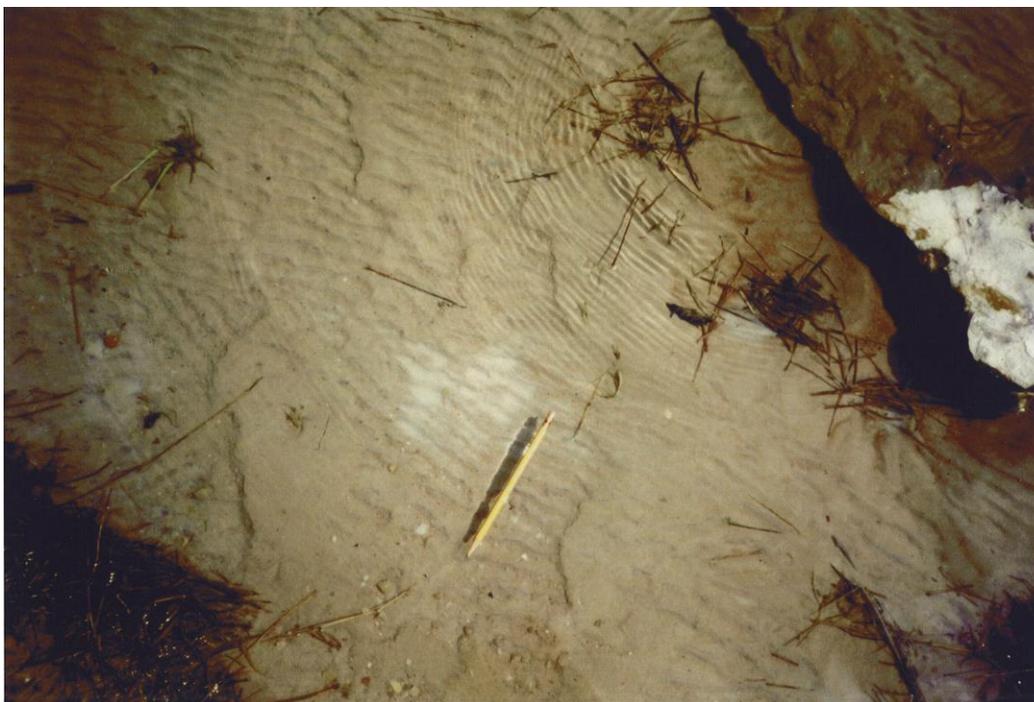


Figure 6. Pond A2P-2 - Formation of precipitate, April 23, 2002.

Ambient Conditions for Formation of Precipitates

On review, several weather-related factors were found to have converged to allow the precipitates to become observable. First, there was a protracted period from January to June 2002 in which the water levels in Pond A2P-1 and A2P-2 did not vary by more than 30 cm (1 foot). This was due to light, evenly-distributed rainfall balanced by evaporation. A stable water level allowed the formation of a stable shallow-water shelf along the shoreline. The shelf in Pond A2P-1 ranged from approximately 65.55 m (215.0 ft) to 65.73 m (215.6 ft) above mean sea level (msl), and the shelf in Pond A2P-2 from approximately 69.02 m (226.4 ft) to 69.21 m (227.0 ft) msl. These conditions encouraged the formation of extensive mats which could accumulate to an observable thickness. By the time the first observation was made on April 1, 2002, the shelf in each pond had been in place for at least three months, i.e., 90 days.

This number is not inconsistent with the number of mats observed and the number of layers in each mat. It suggests that the fine layering in the mats may be due to a diurnal process. One possibility is that diurnal temperature fluctuations, amplified in a shallow water environment, affected the solubility of the Al hydroxide. Another related possibility is that diurnal light and temperatures fluctuations caused localized daily pH fluctuations due to CO_2 from biological activity, although such activity was not investigated at the time. Yet another possibility is that energy from sunlight facilitated the polymerization of already precipitated Al hydroxide monomers – $\text{Al}(\text{OH})_3$. Precipitation rates of Fe and other heavy metals were observed by Gammons et al. (2005) to occur in daily cycles and to be correlated strongly with higher afternoon temperatures. Gammons (2005) notes that with higher water temperatures the solubility of $\text{Al}(\text{OH})_3$ will decrease, the kinetics of nucleation and growth of $\text{Al}(\text{OH})_3$ will increase, and localized evapo-concentration of Al will increase. In addition, photosynthetic

consumption of CO₂ by algae will result in a localized increase in pH during the day. All of these factors would work together to encourage precipitation during the warmer part of the day leading to diurnal precipitation cycles.

The fact that the deposits are layered may also have nothing to do with diurnal fluctuations and may be no more than a macroscopic expression of a microscopic structure. It is known that Al hydroxides have a tendency to grow in the X and Y directions rather than the Z direction due to stronger Al-OH-Al bonding within layers compared to weaker H bonding between layers (Hsu, 1989).

Evolution of Water Chemistry in Ponds A2P-1 and A2P-2

Up to September 2000, the mine pits that were to become Ponds A2P-1 and A2P-2 were joined and the chemistry of the accumulated water was the same. In September 2000, a land bridge began to be constructed between these pits for an access road and from October 2000 the chemical evolution of the two resulting water bodies began to diverge. Nevertheless, the chemistry of the water may be viewed as passing through four similar phases of evolution (Figs. 7 and 8). It should be noted that during this time, there was essentially no outflow from the pits, except for some minor pumping to lower water levels for construction, and that the pits were gradually filling with rainwater runoff.

First Phase of Chemical Evolution. Initially, the water in the common pit was at pH 2.9, as shown in September 2000 in pit A2P-2 (Fig. 8). This is where construction of a pond started. Over the period October 2000 – May 2001, overburden and spoil material was pushed from the surrounding pit walls into the water in the pit. Even though these materials did not contain any obvious neutralizing agent such as CaCO₃, the pH of the water rose to 3.4, Fe was almost completely removed, Al showed an initial strong decline and even Mn decreased slightly. The water chemistry of Pond A2P-1 followed a similar path with an increase in pH and reductions in metal concentrations. The slight time lag compared to Pond A2P-2 was due to later construction – the Pond A2P-1 pit walls were graded over the period February 2001 - November 2001. (The small dip in the pH of Pond A2P-2 in April – May 2001 may be due to the addition, through pumping, of more acid water from Pond A2P-1).

The reduction in Fe content of the water is particularly interesting. It appears that the dumping of spoil into the pit water during grading was responsible for raising the pH and drastically reducing the content of Fe. In Pond A2P-2, Fe was reduced from over 10 mg/L Fe in September 2000 to less than 1 mg/L in August 2001; in Pond A2P-1 Fe was reduced from 14 mg/L in February 2001 to 1 mg/L in October 2001. The precipitation of Fe in Pond A2P-1 was noted on May 1, 2001, when the shoreline of this pond showed strong red staining in the capillary zone (approximately 10 cm above water level). By October 2001, this staining was no longer evident.

Thus the first phase of chemical evolution of the water appears to have been the precipitation of Fe by the addition of spoil to the water. The pH of the water remained constant (at pH 3.1 in one case and pH 3.4 in the other) until virtually all of the Fe had been removed from solution.

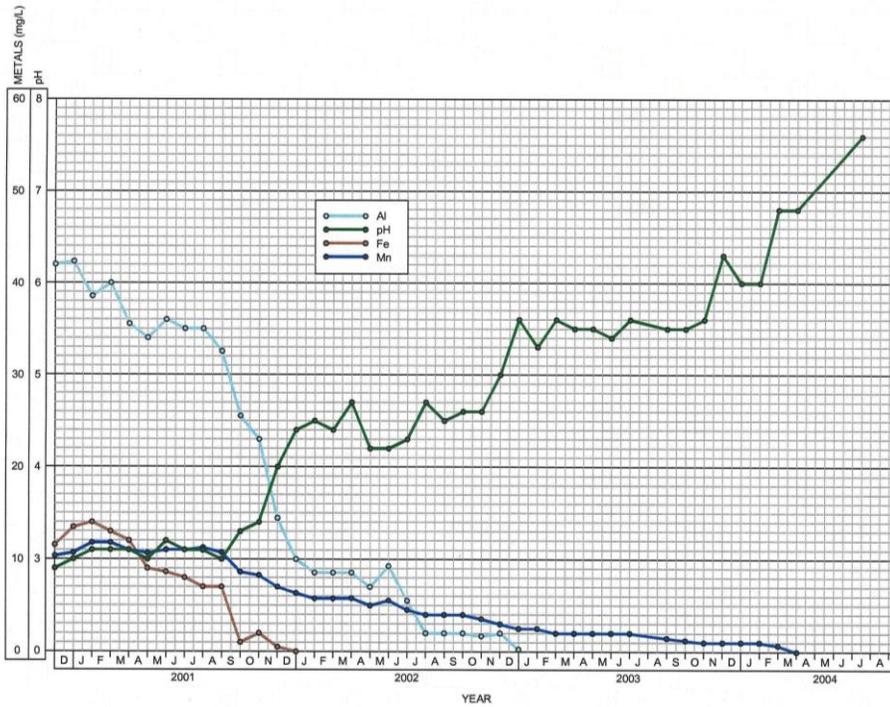


Figure 7. Chemical evolution of end lake A2P-1

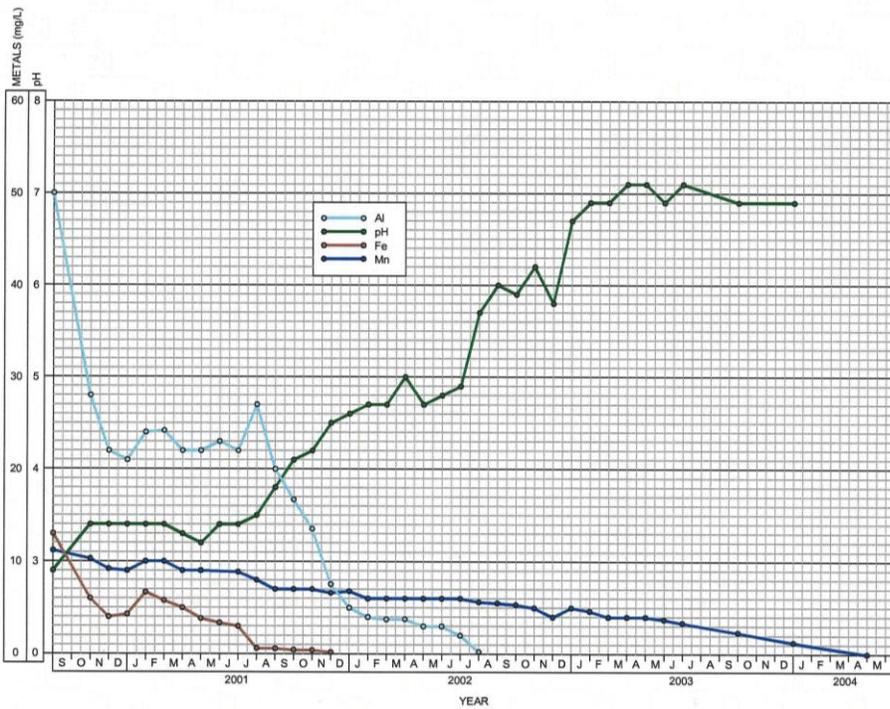


Figure 8. Chemical evolution of end lake A2P-2

Second Phase of Chemical Evolution. The reconstruction of 1.22 m (4 feet) of soil on the graded surface of the drainage area around Pond A2P-2 occurred over the period June 2001 - October 2001, and for Pond A2P-1 over the period September – November 2001. This phase introduced CaCO₃ to the system. “Superfine lime” (actually very finely crushed limestone), with an effective CaCO₃ equivalent (ECCE) of 100%, (supplied by Texas Crushed Stone, Inc., of Georgetown, Texas) was added to the minesoils as they were being built up in lifts to a full depth of 1.22 m (4 feet). The overall application rate to that depth was 224 tonnes per hectare (100 tons per acre). The reconstructed soils were planted to temporary vegetation for protection against erosion in November – December 2001, and to permanent grasses in the following spring.

The strongest pH increases and the steepest declines in Al in the pond waters occurred after this addition of limestone to the surrounding soils. In Pond A2P-2, pH began to rise from the plateau at 3.4 in August 2001 at which time Al concentrations were at 27 mg/L. As the pH shot up to 4.7 (February 2002), there was a corresponding plunge of Al in solution to 4 mg/L. For Pond A2P-1, a pH increase from 3.0 to 4.4 occurred over September 2001 – January 2002, in which time Al dropped from 32 mg/L to 10 mg/L.

Thus the second phase of chemical evolution of the water appears to be associated with the addition of limestone to the soils in the surrounding drainage areas. Periodic rain events resulted in some of this soil being eroded and washed into the ponds. The limestone introduced to the water caused rapid precipitation of Al.

Third Phase of Chemical Evolution. The third phase appears to be a period of slow but steady reduction in Al content with a correspondingly slow change in pH. In Pond A2P-2, the Al content dropped from 4 mg/L in February 2001 to 2 mg/L in July 2001, while the pH changed from 4.7 to 4.9. In Pond A2P-1, the Al content dropped from 10 mg/L in January 2002 to 2mg/L in December 2002, while the pH changed from 4.4 to 5.0. Aluminum was effectively removed from solution in Pond A2P-2 by August 2002 when the pH had risen to 5.7 and in Pond A2P-1 by January 2003 when the pH had risen to 5.6.

Fourth Phase of Chemical Evolution. The fourth phase represents the final increase in pH after the removal of Al from solution. This occurred in Pond A2P-2 after July 2002 when the pH rose from 4.9 to 6.9 by February 2003, and in Pond A2P-1 after December 2002 when the pH rose from 5.0 to 6.8 by March 2004.

Throughout these four phases, the concentration of Mn in the water followed a very gradual decline with no perturbations. It appears that Mn precipitation followed the general trend of neutralization but it did not correlate with any particular pH values in the range observed. Neither was it a component of the “acidity” parameter, which had been reduced to zero in both ponds while Mn was still present at a concentration of 4-5 mg/L. A Mn decrease simply due to dilution does not seem to be the explanation because over the period December 2000 to July 2002, the volume of water in the ponds increased by approximately 20% whereas the Mn concentrations decreased by close to 50%. Increasing pH does not seem to cause Mn precipitation until about pH 9.5 (Horbaczewski, 2001). It appears that the precipitation of Mn is controlled more by oxidation processes (Hem, 1985) and, as noted by Gammons (2005), these are slow processes, even in the presence of bacteria.

Field Precipitates - Chemical Properties

The chemical composition of the precipitates was determined on samples collected from both ponds on April 3, 2002. These data are compared to the chemistry of the overlying water in Table 4. The two sets of data are very different. In the water, SO_4^{-2} , Ca, Na and Mg ions predominate, whereas in the precipitates Al and Fe are predominant.

Table 4. Chemical properties of water and associated precipitates* in Ponds A2P-1 and A2P-2

Parameter	Pond A2P-1		Pond A2P-2	
	Water Sampled April 1, 2002	Precipitate Sampled April 3, 2002	Water Sampled April 1, 2002	Precipitate Sampled April 3, 2002
pH	4.7 s.u.	4.7	5.0 s.u.	5.0
Acidity	55 mg/L	Not analyzed	24 mg/L	Not analyzed
Total Dissolved Solids	2,160 mg/L	Not analyzed	2,530 mg/L	Not analyzed
Sodium	107 mg/L	41 mg/Kg	133 mg/L	66 mg/Kg
Potassium	17 mg/L	9 mg/Kg	18 mg/L	11 mg/Kg
Calcium	349 mg/L	96 mg/Kg	447 mg/L	173 mg/Kg
Magnesium	88 mg/L	26 mg/Kg	86 mg/L	38 mg/Kg
Bicarbonate	2 mg/L	Not detected	4 mg/L	Not detected
Chloride	57 mg/L	20 mg/Kg	113 mg/L	60 mg/Kg
Sulfate	1,420 mg/L	405 mg/Kg	1,630 mg/L	659 mg/Kg
Aluminum	8.3 mg/L	4,090 mg/Kg	3.7 mg/L	5,020 mg/Kg
Iron	0.09 mg/L	2,720 mg/Kg	0.06 mg/L	4,170 mg/Kg
Manganese	5.69 mg/L	20 mg/Kg	6.19 mg/L	38 mg/Kg

* All analyses of precipitates expressed on the basis of as-received, moist material.

The analytical data show a close balance between total cations and total anions for the water, but a large imbalance for the precipitates. It is inferred that the balancing anions in the precipitates are OH^{-1} ions although there may also be some silicate, aluminate or aluminosilicate complexes acting as anions. The data also show a marked difference in the ratio of Al to Fe between the water and the precipitate. Iron is essentially non-existent in the water and yet makes up a large percentage of the metal content of the precipitate. This probably accounts for the pinkish to light brown color of the precipitate. All metals, other than Al and iron, show very low concentrations in the precipitate. Even Mn is very low.

The only other minor co-precipitate appears to be CaSO₄. In the water, the ratio of Ca to SO₄²⁻ ions is less than 1.0, but in the precipitate it is higher (just over 1.0) suggesting the presence of CaSO₄ (gypsum).

When the mole ratios of SO₄ to Al and of K to Al are plotted against each other, the compositions of the precipitates from both ponds plot directly in the gibbsite field. This is not exactly in agreement with the findings of Nordstrom (1982). His investigation of the stability fields of various aluminosulfate minerals indicated that, at a SO₄²⁻ ion activity of 10⁻² M (similar to the concentration in Ponds A2P-1 and A2P-2), jurbanite should control the solubility of Al between pH 0 and 4.00, alunite from pH 4.00 to 5.71, and gibbsite only at pH values above 5.71 (Table 5). Since the pH of the supernatant water at the time of sampling of the precipitate was 4.7 in Pond A2P-1 and 5.0 in Pond A2P-2, the composition of the precipitate would be expected to be alunite (the Al analog of jarosite) and not gibbsite. However, as indicated by Evangelou (1995, p. 73), Al-hydroxy-sulfate complexes are metastable and may take months to form stable precipitates. Even if such minerals do get precipitated, they may partially (incongruently) re-dissolve selectively releasing SO₄²⁻ ions into solution leaving gibbsite as the precipitate. Theoretically, this should not occur until the pH is at 5.7 but this threshold may easily be affected by kinetics or other ionic species such as Mg²⁺, which would draw SO₄²⁻ ions into solution since MgSO₄ is highly soluble (Evangelou, 1995, p. 75).

Table 5. Solubilities and stability fields of various aluminosulfate minerals (Nordstrom, 1982)

Name	Formula	Solubility Product (K _{sp})	pH Range for Precipitation	
			(SO ₄) ²⁻ activity of 10 ⁻⁴ M	(SO ₄) ²⁻ activity of 10 ⁻² M
Alunogen	Al ₂ (SO ₄) ₃ .17H ₂ O	10 ⁻⁷		
Jurbanite	Al(SO ₄)(OH).5H ₂ O	10 ^{-17.8}	0 – 3.3	0 – 4.00
Alunite	KAl ₃ (SO ₄) ₂ (OH) ₆	10 ^{-85.4}	3.33 – 4.47	4.00 – 5.71
Basaluminite	Al ₄ (SO ₄)(OH) ₁₀ .5H ₂ O	10 ^{-117.7}		
Gibbsite	Al(OH) ₃	10 ⁻⁷	> 4.47	> 5.7

Laboratory Titrations of End Lake Samples

As previously mentioned, laboratory were used in the early stages of reclamation to predict neutralization requirements. Samples of water had been collected on December 1, 2000 and had been titrated four days later against a 0.01N NaOH solution. The results of the Pond A2P-1 and A2P-2 titrations are depicted on Fig. 9, which shows a characteristic plateau due to buffering in the following pH ranges: Pond A2P-1 (pH 4.5 to 4.9); and Pond A2P-2 (pH 4.6 to 5.1).

The plateau also corresponds to the pH range in which a milky white precipitate was observed to form during the titrations. The precipitation of Al hydroxide depends on the ratio of hydroxide to Al (Al hydroxide requires three OH⁻ ions for every Al⁺³ ion). It is therefore more helpful to plot the titration curves of pH against the molar ratio NaOH/Al, instead of against just NaOH (Hsu, 1989). For both titrations, the plateau of buffering remains in the range pH 4.5 – 4.9, but for Pond A2P-2 it occupies the NaOH/Al range 1.3 – 3.0 and in the case of Pond A2P-1 it is in the 1.8 – 3.8 range. The first visible signs of precipitation in the laboratory titrations were at a NaOH/Al ratio of 2.8 for the A2P-2 water sample and 2.1 for the A2P-1 sample (Table 6).

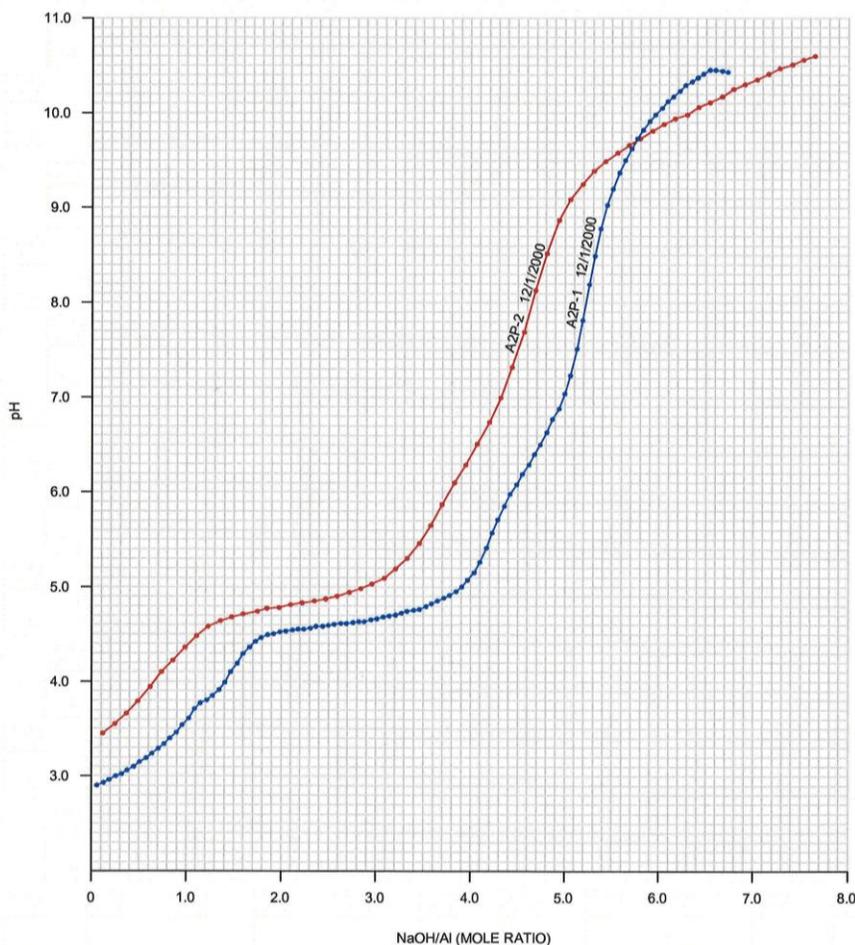


Figure 9. Gibbons Creek lignite mine - laboratory titration of acid end lake water (standardized)

In theory, precipitates should start appearing at a NaOH/Al ratio of 3.0. Experiments performed by Hsu et al., (1989) confirm this and show that at ratios greater than 3.0, crystalline Al(OH)₃ forms within a few hours especially in the presence of Cl⁻ and SO₄⁻² ions. However, precipitates may appear at lower ratios, such as 2.7 and even 2.4 if the NaOH is added quickly. Barnhisel and Bertsch (1989, p. 768), in their review of montmorillonite synthesis, noted that free gibbsite was generally detected at OH/Al ratios of 2.4, 2.5, and 2.7, after aging for up to 34

weeks. The observations presented in Fig. 9 and Table 6 are consistent with these earlier findings

It appears that in these partially neutralized solutions (i.e., at less than NaOH/Al = 3.0), there are positively-charged poly-nuclear OH-Al complexes (Hsu, 1989). Up to a NaOH/Al ratio of approximately 2.0, these OH-Al polymers are probably limited in size and may be no larger than double or triple rings; beyond that they form larger polymers. The key point is that these polymers need to dissociate into monomeric species (a relatively slow process) for the formation of gibbsite (Hsu, 1989). Thus partially neutralized solutions are metastable and may form a precipitate of crystalline Al(OH)₃ on aging. The situation is also complicated by the fact that the Al-OH polymers actually form a continuous series with no clear distinguishing breaks between true solutes, colloidal particles and precipitates (Hsu, 1989).

Table 6. Precipitates formed during titration of December 1, 2000 water samples

Sample	pH	NaOH/Al Ratio	Description of Precipitate
A2P-1	3.34	0.77	Solution clear and colorless – no precipitate.
	3.80	1.22	Solution slightly turbid – pale yellowish.
	4.54	2.12	Abundant fine flocs; solution still pale yellowish.
A2P-2	4.98	2.84	Initial white flocs.
	6.51	4.07	Abundant white flocs.
	9.25	5.19	Yellowish hue.

Analysis of Solid and Dissolved Phases from Titrations

To determine the chemical equilibria occurring at different stages of the Pond A2P-2 titration, the titration was repeated to six pre-selected points corresponding to the following amounts of NaOH titrant: 10 mL, 24 mL, 30 mL, 40 mL, 50 mL, and 60 mL. The selection of these points was arbitrary except for the 24 mL point, which represented the first appearance of a precipitate (at the theoretically predicted NaOH/Al ratio of 3.0). At the time of the titrations (December 4, 2000), precipitates were also observed in the next four sub-samples with higher NaOH/Al ratios. All six sub-samples were submitted to IML for analysis of the solutions and precipitates.

IML performed the analyses on December 15, 2000. The results for the solutions are summarized in Table 7 (which also shows the composition of the raw un-titrated water). All six sub-samples from the titrations showed changes in pH from those measured during the titrations 11 days earlier. This will be discussed further under the next sub-heading. As would be expected, the major cations (Ca, Mg, and K) and the major anions (SO₄⁻² and Cl⁻¹) were not precipitated and just showed gradual declines due to dilution. Sodium, of course, showed a gradual increase due to addition from the titrant, NaOH. The minor metals (Al, Fe, and Mn) did not show significant reductions in solution until the last two sub-samples, i.e., above pH 6.5 (as measured on December 15, 2000).

The analytical results for the precipitates are summarized in Table 8. Only the last two sub-samples (with the highest NaOH/Al ratios) were analyzed because the precipitates in the other two sub-samples had disappeared. The two precipitates were dominated by Al but the pH was high enough by that time to also precipitate Mn and even Mg in the last sub-sample.

Table 7. Analysis of Pond A2P-2 water sampled on December 1, 2000, titrated to six pre-determined points with NaOH solution on December 4, 2000, and analyzed by IML on December 15, 2000

	Untitrated water	10 mL	24 mL	30 mL	40 mL	50 mL	60 mL
NaOH/Al Ratio	-	1.2	3.0	3.7	5.0	6.1	7.4
pH (12/4/00)	3.4	4.6	5.0	5.9	8.9	9.9	10.5
pH (12/15/00)	-	4.4	4.8	5.3	6.5	9.0	9.7
Ca (mg/L)	494	407	380	388	348	320	293
Mg (mg/L)	80	72	64	66	58	53	46
K (mg/L)	23	20	19	20	17	16	15
Na (mg/L)	139	148	153	172	164	172	177
SO ₄ (mg/L)	1,520	1,560	1,380	1,320	1,240	1,150	1,080
Cl (mg/L)	152	123	110	107	100	94	88
Al (mg/L)	21.9	19.8	17.6	16.6	15.0	ND	ND
Fe (mg/L)	4.1	3.6	3.2	3.0	2.7	ND	ND
Mn (mg/L)	9.3	8.7	7.6	7.2	6.6	0.3	0.0

It is known that at pH 9, the silicate ion begins to exert a strong effect on the precipitation of Al(OH)₃ (Hsu, 1989) and this may explain the continued presence of the precipitates. However, this high pH is beyond that encountered in the end lakes and is therefore not representative of field conditions and is not discussed further.

Effects of Aging on Titration Curves

The changes in pH that occurred between December 4 and December 15 were subjected to further verification by re-testing the pH of the same six sub-samples by IML this time on January 19, 2001 (i.e., 46 days after the titration on December 4, 2000). With one exception, the pH values had dropped even further (Fig. 10).

This observation is consistent with the phenomenon of “aging”, which is interpreted as a consequence of polymerization (Hsu, 1989). As Al-OH polymers form, positively-charged OH⁻¹ ions are released resulting in additional acidity. The polymerization reaction is slow so that the accompanying drop in pH will also take time to become evident. As the pH drops, the additional acidity would be expected to re-dissolve some of the Al that had initially been precipitated in the titration. This would explain the disappearance of precipitates that had been observed at the time of the original titration on December 4, 2000.

Table 8. Chemical properties of solution and associated precipitate* at 50 mL and 60 mL titration points (expressed as mg/L and mg/Kg). (Original water sample taken from Pond A2P-2 on December 1, 2000).

Parameter	50 mL Titration Point		60 mL Titration Point	
	Solution	Precipitate	Solution	Precipitate
pH	9.0 s.u.	Not Applicable	9.7 s.u.	Not Applicable
Sodium	172 mg/L	Not Detected	177 mg/L	Not Detected
Potassium	16 mg/L	3,900 mg/Kg	15 mg/L	3,430 mg/Kg
Calcium	320 mg/L	8,100 mg/Kg	293 mg/L	10,200 mg/Kg
Magnesium	53 mg/L	2,100 mg/Kg	46 mg/L	6,280 mg/Kg
Chloride	94 mg/L	Not Analyzed	88 mg/L	Not Analyzed
Sulfate	1,150 mg/L	Not Analyzed	1,080 mg/L	Not Analyzed
Aluminum	Not Detected	21,800 mg/Kg	Not Detected	15,200 mg/Kg
Iron	Not Detected	4,420 mg/Kg	Not Detected	3,060 mg/Kg
Manganese	0.3 mg/L	9,800 mg/Kg	0.0 mg/L	7,140 mg/Kg

* All analyses of precipitates expressed on the basis of as-received, moist material.

Water Chemistry in Relation to Aluminosulfate Mineral Stability Fields

An interpretation of the water chemistry data in terms of mineral equilibria is presented below, although it should be viewed as tentative given the significance of kinetics in precipitation reactions of Al. The original chemistry of the water in the end lakes (as of December 1, 2000) is summarized in the inset box (Fig. 11). The evolution of the water chemistry as the pH increased is depicted on the graph by the series of points.

The plot suggests that, given the high SO₄⁻² activities in the water, the initial precipitates in end lakes A2P-1 and A2P-2, at pH levels below approximately 3.8 should have been jurbanite and/or alunite. Jurbanite and alunite have SO₄⁻² in their structure, and alunite also has K (Table 5). Above pH 3.8, the trend line crosses over into the gibbsite stability field; gibbsite contains

neither SO_4^{-2} nor K. However, as noted by Gammons (2005), gibbsite does not replace jurbanite and alunite as the least soluble mineral until it crosses their stability lines at approximately pH 4.6.

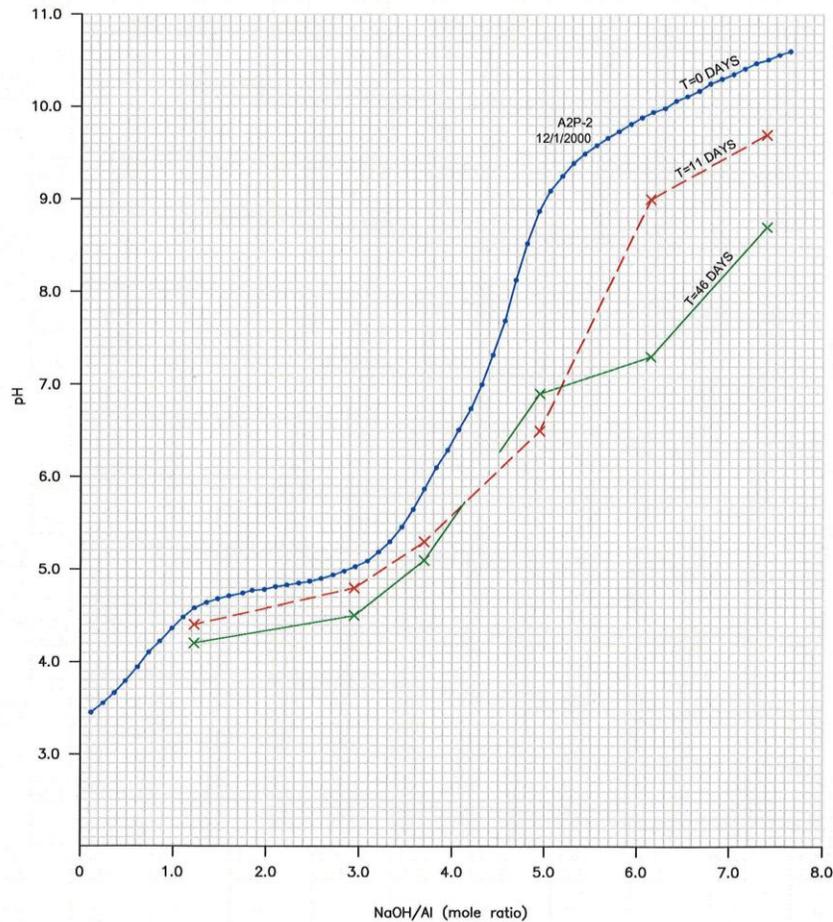


Figure 10. Gibbons Creek lignite mine – effects of aging on pH of titrated Pond A2P-2 water

It is possible that the early (presumed, because they were not observed) precipitates that formed when the pH of the water was still less than 4.6, were in fact composed of aluminosulfates, in the same way that jarosite (the Fe analog of alunite) has been observed in low pH spoil areas at the mine. This may account for the steep decrease in Al concentrations before the “Al hydroxide sink” and its associated near-constant pH was attained (Figs. 7 and 8). The precipitates sampled on April 3, 2002, were associated with water of pH 4.7 (Pond A2P-1) and pH 5.0 (Pond A2P-2) and appear to correspond to the “Al hydroxide sink”. They did not show stoichiometric contents of SO_4^{-2} corresponding to either alunite or jurbanite. As previously discussed, they may have formed either directly as gibbsite or were initially formed as aluminosulfates which subsequently gave up their SO_4^{-2} through partial re-dissolution.

As a final comment, it should be noted that the data plotted in Fig. 9 relate not to the activity of Al^{+3} but to the total Al concentration. It is probable (Gammons, 2005) that the fraction of Al present as Al^{+3} was significantly less than 50% given the high SO_4 concentrations and probable predominance of Al- SO_4 pairs, resulting in a reduced thermodynamic concentration of Al^{+3} which would tend to cause the points to plot lower on the graph. This reinforces the supposition that the early lakes were close to saturation with jurbanite or another hydroxy aluminosulfate rather than gibbsite.

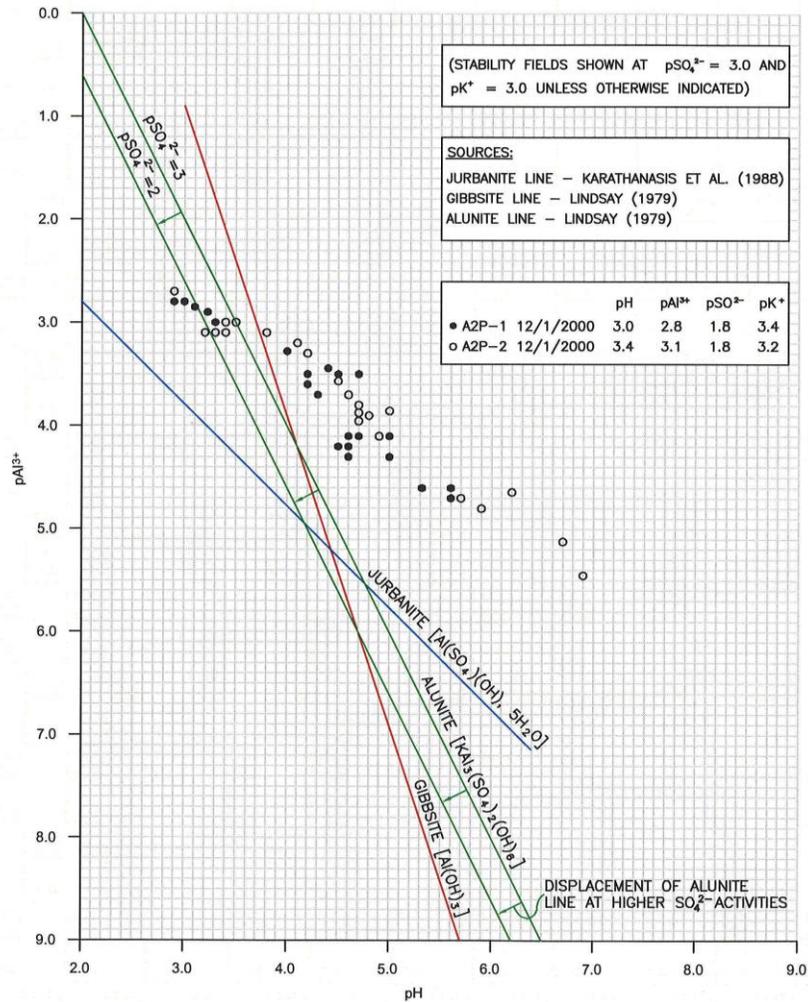


Figure 11. Gibbons Creek lignite mine – chemistry of end lake water in relation to mineral stability fields.

Reconstruction of Formation of Aluminum Precipitate

The following is offered as an interpretation of the sequence of geochemical events in the end lakes at the Gibbons Creek lignite mine.

After closure of the mine in February 1996, the exposed pyritic material began reacting with rainfall runoff. The oxidation reaction was probably mediated by mesophilic bacteria (bacteria whose optimum temperature range is 25° - 40°C) such as *Acidithiobacillus* (formerly *Thiobacillus*) *ferrooxidans* and *Acidithiobacillus thiooxidans*, and the ferric ion (Fe⁺³) through the following reactions (Brown and Jurinak, 1989; Evangelou, 1995, p. 80; and Olson and Clark, 2004):



As outlined by Olson and Clark (2004), oxidation of pyrite probably occurred through the electron-accepting behavior of the Fe⁺³ ion, which can form a surface complex on the surface of pyrite more readily than O₂ can. Bacteria mediate the process by producing extra-cellular polymeric substances which allow them to attach themselves to pyrite surfaces and these substances form complexes with Fe⁺³. Although the O₂ in the above reactions comes from water, atmospheric O₂ is still needed for bacterial growth. As much as one tonne of O₂ is estimated to be required to oxidize one tonne of pyrite in industrial applications and oxidation may be achieved in as little as 9 months (Brierley, 2000). At Gibbons Creek mine the acidity of the end lakes fell to about pH 3.0 in less than 3 years.

As the pH of the water dropped, the clay minerals in the pit walls began to decompose. The stratigraphic setting of the mine is in the late Eocene, dated at approximately 34.5 Ma (Yancey, 1997). This period was one of intense leaching resulting in the formation of aluminous lateritic deposits, including bauxite (key mineral constituent gibbsite) and kaolin (key mineral constituent kaolinite) (Austin, 1998). Kaolinite may be thought of as gibbsite to which silica (SiO₂) has been added – gibbsite sheets interlayered with silica sheets. Montmorillonite may be thought of as a gibbsite sheet sandwiched between two silica sheets with cations such as Ca and Mg added between the sandwiches. Such cations could have been derived from marine transgressions, which appear to have occurred frequently at the time the Gibbons Creek lignites were being deposited (Yancey, 1997). Regardless of origin, the main clay minerals in the soils and overburden currently at the mine are montmorillonite and kaolinite. Both of these minerals are rich in Al – the generic formula for the montmorillonite half unit cell is Si₄Al_{1.5}Mg_{0.5}O₁₀(OH)₂Ca_{0.25} (Borchardt, 1989) and the formula for kaolinite is Al₂Si₂O₅(OH)₄ (Dixon, 1989); Fe may be present in these minerals but in subordinate amounts. Of significance to this discussion is the fact that montmorillonite readily decomposes at pH values below 3.6 through hydrolysis (Borchardt, 1989).

When the clay minerals began to decompose, the dominant cations that passed into solution in the end pit water came to be Ca, Mg, Na, and Al (Table 2). The predominant anion was SO₄ with very subordinate chloride. The overall concentration (total dissolved solids) of salts eventually reached 3,000 mg/L – almost one-tenth the salinity of sea-water. The high Ca content apparently came from the overburden since this occurred well before any agricultural limestone had been added to the soils. The predominant source of the Ca was probably gypsum (CaSO₄.2H₂O), which is common and which also probably derived from the marine transgressions. Limestone (CaCO₃) was originally present in the geological formation as

evidenced by shell fossils, but was leached out of the overburden over geological time – it has not been observed in the field or in laboratory analyses.

The trend of increasing acidification of the pit water began to be reversed with the commencement of reclamation operations. The dumping of overburden and spoil materials in the course of reclamation was sufficient to raise the pH enough to precipitate most of the Fe from solution as evidenced by the water analyses and the red staining in the capillary fringe at the shore-line. Since there were no free carbonates in the overburden, the neutralizing agents were probably soluble and exchangeable cations, which are commonly concentrated below the redox boundary (O'Shay, 1982). The basic cations passed into solution and the much smaller hydrogen ion (or more accurately, hydrated proton) was taken up from the pond water and became adsorbed onto clay mineral exchange sites. It should be noted that the pH of the water remained steady while the Fe was being precipitated and did not start rising significantly until limestone could assist as a neutralizer.

The addition of finely crushed limestone in the next stage of reclamation had a pronounced effect on reducing acidity. The limestone was washed into the ponds with rainfall events and completed the removal of Fe from solution. This allowed the pH to rise out of the “Fe hydroxide sink” at about pH 3.1 (Pond A2P-1) and pH 3.4 (Pond A2P-2) and increase rapidly to about pH 4.5. Aluminum concentrations in the water fell as this was happening and it is speculated that this was a time of precipitation of some form of hydrated aluminosulfate, such as jurbanite, alunite or “alunogen”. Then, from pH 4.7 to 4.9 (Pond A2P-2) and from pH 4.4 to 5.0 (Pond A2P-1) there was a protracted period in which the pH changed very little while gibbsite began to be precipitated. This is thought to correspond to the “Al hydroxide sink” seen in the titrations and observed earlier in an adjacent lake that was being treated with hydrated lime – $\text{Ca}(\text{OH})_2$ (Horbaczewski, 2001). The Al hydroxide precipitation occurred in a period in which there happened to be a fortuitous interlude of calm weather between January and July 2002, allowing the accumulation of the precipitate to be observed. In July 2002, heavy rains washed in a lot more limestone which rapidly completed the elimination of Al from solution. At about pH 5.0, the pH was able to start rising out of the Al hydroxide sink increasing rapidly to pH 7.0.

A final comment needs to be made on the apparent precipitation of a small amount of CaSO_4 (gypsum). Analysis of the field precipitates (Table 4) indicated a close stoichiometric balance between Ca and SO_4^{-2} unlike the ratio in the overlying water. Theory indicates that metals, such as Fe, Al, and Mn form ion-pairs with SO_4^{-2} ions. The formation of such ion-pairs encourages the gypsum in the overburden to dissolve to replace the SO_4^{-2} ions in solution. This sets up a “cascade effect” and results in an increasing content of Ca and SO_4^{-2} in solution. The reverse is thought to occur as Fe, Al, and Mn are precipitated from solution (Evangelou, 1995, p.71). The liberated SO_4^{-2} ions react with the excess Ca provided by limestone to form gypsum which precipitates as its solubility product becomes exceeded.

The simulation of acid water neutralization in the field with laboratory titrations was of limited use beyond showing where buffering activity due to Al could be expected. The primary problem concerned reaction kinetics. Reactions that occurred in nature over a period of 3½ years were compressed down to a few hours, or even less, in the laboratory. The six “interrupted” titrations of Pond A2P-2 were each completed in minutes (less than 15 minutes for the last titration in which 60 mL of titrant was used). This allowed no time for time-dependent processes to occur – such as those associated with biologically-mediated oxidation, ion exchange and sorption, silicate decomposition and oxy-hydroxide polymerization (aging). The titrations also

suffered from localized pH extremes as the relatively strong alkali (NaOH) dropped into the sample. In the field, pH changes were very gradual both because of the scale of the water bodies and because the neutralizer was CaCO_3 and not NaOH. Other factors that clearly could not be reproduced in a laboratory setting included: the “open-system” conditions of a virtually inexhaustible supply of reactants in the minerals in the pit walls, and daily cycles of solar radiation and warming.

Conclusions

The following conclusions were drawn from this study:

- The precipitates discovered in the end pit lakes at Gibbons Creek mine on April 1, 2002, were primarily aluminous with subordinate Fe and minor amounts of CaSO_4 (gypsum).
- These precipitates appeared to form in the same pH ranges previously identified as an “Al hydroxide sink” – in the range pH 4.6 – 4.9.
- The precipitate mats were composed of fine layers, or laminae less than a millimeter in thickness, physically separable by gentle wave action.
- There were noticeable color variations among layers, attributed to slight variations in Fe content.
- Each layer, or lamina, was interpreted as representing a day’s deposition.
- The formation of layers was attributed to diurnal environmental cycles in the micro-environment of deposition on the shoreline shelves and, in particular, in the sand ripple troughs on the shelves.
- The cycles could have been caused by fluctuations in temperature, solar radiation, or carbon dioxide causing localized pH cycles superimposed on the overall pH trend.
- On one occasion, the formation of a milky suspension was observed in the troughs of sand ripples in very still water near the shore.
- A purely chemical reaction is postulated for the precipitation for the Al.
- However, it is not possible at this stage to discount the mediation of organic materials derived from the lignite deposits, algae or microbiological agents.
- Stoichiometric considerations suggest that the Al is in the form of gibbsite, although this has not been verified mineralogically.
- Theoretical considerations suggest that initial unobserved precipitates were probably aluminosulfates but that gibbsite was probably the stable phase by the time the precipitates described in this paper were identified.

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