

ANOXIC LIMESTONE DRAINS TO ENHANCE PERFORMANCE OF AEROBIC ACID DRAINAGE TREATMENT WETLANDS THE TENNESSEE VALLEY AUTHORITY

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ABSTRACT

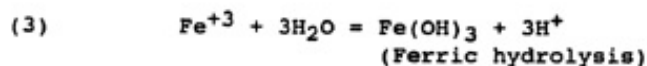
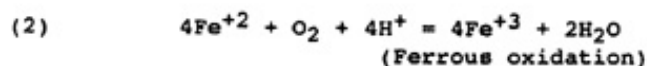
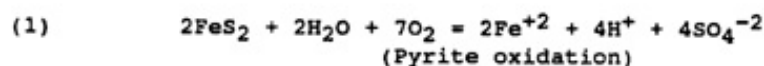
Constructed aerobic wetlands for treating acid drainage are preferred, low-cost, alternatives to conventional treatment. Drainage with high Fe (e.g., >50 mg/l) and zero alkalinity has not been amenable to treatment with wetlands alone, primarily due to Fe hydrolysis and resultant low pH. Anoxic limestone drains (ALDs) increase the alkalinity of the seep that is then routed to a constructed wetlands. Increased alkalinity buffers the aerobic wetlands system from pH decreases and enhances the effectiveness of wetlands treatment. The Tennessee Valley Authority (TVA) has modified two low-pH constructed wetlands with ALDs and has identified several "accidental" ALDs at its constructed wetlands sites, and has designed and constructed ALDs as components of recent constructed wetlands. Results indicate that ALDs can improve the capability of wetlands to meet effluent limitations without chemical treatment. ALDs

consist of an excavated seepage-interception trench backfilled with crushed limestone covered with plastic and clay soil. Most ALDs are immediately followed by deep, Fe-oxidation ponds. Dissolution rates of limestone in operational and simulated ALDs have been measured to estimate design parameters and longevity of an ALD. Potential problems with ALDs include structural and hydraulic stability, plugging due to reaction products within the ALDs, and inadequate design and installation.

INTRODUCTION

Staged aerobic constructed wetlands are an effective means of treating certain qualities and quantities of acid drainage from various mine spoils and refuse, and from coal ash disposal areas.¹ Wetlands efficiencies are related primarily to flow rates, pH, and concentrations of dissolved oxygen (DO), Fe, Mn, acidity, and alkalinity. Foremost are the relationships among influent DO, Fe speciation, alkalinity, and influent/effluent pH.

Metals removal mechanisms in wetlands are variable and numerous, but it is probable that microbially-catalyzed Fe oxidation and hydrolysis are major reactions responsible for Fe removal in aerobic wetlands systems.² These reactions may dictate the ultimate success or failure of a wetlands system because of their acidity-producing natures, summarized below.



Reactions 1-3 all occur in the backfill while reactions 2-3 occur in the wetlands. Only reaction 3 acts to increase acidity in a wetlands. If sufficient buffering capacity is not present in the acid drainage, pH will decrease in a wetlands as ferric hydrolysis proceeds. Several TVA wetlands systems, although removing substantial amounts of Fe and Mn, have had influent pH near 6.0 and effluent pHs of less than 3.0.¹ TVA's 3-cell, 2.3 acre constructed wetland at the Kingston Fossil Plant in Roane County, TN received, on average, 379 gpm of acid seepage from an ash disposal area with an influent pH of 5.5 and total Fe of 170 mg/l. Effluent from the wetlands system had a pH of 2.9 and total Fe of 83 mg/l; thus the hydrolysis of about 87 mg/l of Fe was responsible for the decreased pH.

DISCUSSION

Numerous methods, primarily chemical treatment, for treating acid drainage have been used to meet effluent standards; however these methods are expensive and require constant attention to maintain compliance with effluent limitations. Also, many chemical additives have an adverse impact on aquatic biota in receiving streams. Limestone treatment has many advantages over conventional chemical treatment including lower sludge production, lower cost, and less potential for overdosing. However, the use of limestone rock as a buffering agent was abandoned because, in an oxidizing environment, Fe hydroxides coat the limestone surface and inhibit or eliminate the dissolution of the limestone, thus preventing effective buffering. This paper discusses a passive methodology of introducing alkalinity to acid drainages in order

to buffer pH decreases in constructed wetlands due to Fe hydrolysis.

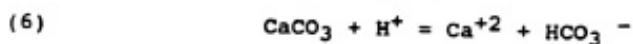
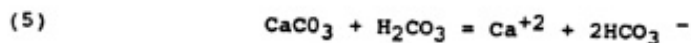
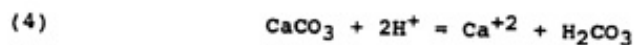
In 1988, the Tennessee Division of Water Pollution Control (TWPC) constructed and evaluated prototype passive anoxic limestone drains (ALDs) at 2 mine sites in Tennessee.³ At the same time, TVA recognized a correlation between alkalinity and DO of wetlands influent, and the relative success of TVA constructed wetlands, and conducted several relevant bench-scale studies on alkalinity enhancement to achieve NPDES compliance of acid drainage using passive aerobic wetlands systems.⁴

Results of a TVA study identified a correlation between wetlands influent alkalinity and effluent pH, Fe, and Mn. An "accidental" roadbed originated anoxic drain (AROAD) was identified at the TVA Impoundment 1 constructed wetlands, which treats high-Fe (> 100 mg/l) acid drainage emanating from a fine-coal refuse disposal area at the Fabius Coal Preparation Plant site in northeastern Alabama (Figure 1). Air photo investigations showed that a 1400-ft long, 25-foot high earth dam was constructed in 1974 over an existing coal haul road built of crushed rock that was presumably obtained from the local Monteagle formation, a high CaCO₃, oolitic limestone. Although this limestone roadbed was not intended for water quality enhancement, it was hypothesized that it was pretreating acid drainage seeping through the dike by adding alkalinity and buffering capacity so that the wetlands was producing compliance-quality discharges. TVA drilled and sampled the dike and the AROAD, and confirmed the presence of a 4-11 inch roadbed consisting of gravel-sized limestone (peloid grainstones, peloid packstones, pellet packstones/grainstones, and coarse-grained bivalved grainstone) containing 46-58% Ca.⁵ Split spoon samples of the limestone showed no evidence of mineralization or coatings on the stone. Dissolution was evidenced by the rounded edges of the recovered crushed stone. Monitoring wells were drilled and are being sampled to determine the changes in water quality as the flow passes through the earth dam. Figure 2 depicts preliminary water quality data from six monitor wells completed in the dam at various locations relative to the AROAD, the slurry lake, and the seepage.

Over 50 ALDs have now been constructed in the eastern U. S.⁶ The ALD, which consists of a shallow, limestone-filled trench excavated into the spoil and sealed from the atmosphere, passively introduces buffering capacity, as alkalinity, into the acid drainage. Changes in pH due to acid production from Fe hydrolysis in the wetlands are buffered due to the high alkalinity in the influent. Detailed design and construction guidelines have been previously published.⁷

The basic design of an ALD is shown in Figure 3. The ALD consists of an open, unlined trench or excavation backfilled with gravel-sized, crushed, high-CaCO₃ limestone. The limestone is covered with plastic to preclude oxygen infiltration and CO₂ exsolution. It is desirable to place geotechnical fabric over the plastic for protection of the plastic from puncture by equipment or manpower. A clay soil is then placed over the fabric.

It is assumed that the following reactions are applicable within the ALD:



Equation 4 reacts limestone with acidity (at pH <6.4) present in the mine drainage to form free calcium and dissolved carbon dioxide (carbonic acid). The carbonic acid further reacts with limestone in equation 5 to produce alkalinity. As reactions 4 and 5 act to increase pH above 6.4, equation 6 becomes the major reaction where bicarbonate is the dominant dissolved CO₂ species.⁸ Systems observed to date indicate that if the ALD is properly constructed, limestone in the ALD will not armour with Fe or Al precipitates and alkalinity can be significantly increased in the ALD effluent.

DESIGN

Guidelines used by TVA to determine the utility for an ALD are as follows:

- Case 1: Alkalinity > 80 mg/l, Fe > 20 mg/l; an ALD may be beneficial, but a wetlands system based on previously reported chemical loading rates is probably adequate.¹
- Case 2: Alkalinity > 80 mg/l, Fe < 20 mg/l; an ALD is not necessary, only an adequately designed wetlands.
- Case 3: Alkalinity < 80 mg/l, Fe > 20 mg/l; an ALD is recommended and probably necessary as the initial stage in a constructed wetlands system.
- Case 4: Alkalinity < 80 mg/l, Fe < 20 mg/l; an ALD is recommended, but not necessary.
- Case 5: Alkalinity ≤ 0 Mg/l, Fe < 20; an ALD will likely be necessary as Fe approaches 20 mg/l.
- Case 6: Dissolved oxygen > 2.0 mg/l or Fe oxidizing conditions exist (e.g., pH > 6.0, eH > 100 mv). An ALD should not be installed because of probable limestone armoring.

In order for an ALD to perform successfully, unaerated mine drainage must come into contact with the buried limestone. Discrete seeps or boils from embankments are generally good starting points for excavation of the ALD into the backfill. Non-point seep areas may require more innovative means of collection, such as specialized rock drains or the construction of an embankment to contain the ALD. Underground mine adits could be sealed and flooded, routing the drainage via a pipe to an ALD, or a mine adit could be backfilled with limestone and thereby delineate the boundaries of the ALD.

Maximum expected flow through the ALD should be determined to prevent hydraulic failures and disruption of the sealed nature of the ALD. Because of the relative low cost of an ALD compared to conventional treatment systems, an oversized ALD is recommended to ensure hydraulic stability and to maximize longevity. In fact, desired longevity of the ALD will likely dictate a design size far in excess of the hydraulic design requirements. A suggested crude, but conservative, method for hydraulically designing the ALD is to calculate infiltration from the contributing drainage basin at the point source of the seepage and assume an attenuation factor based on the mine fill characteristics.

Another important preliminary consideration for ALD construction is water quality. The success of an aerobic wetlands system to meet effluent limitations is directly and primarily related to influent pH, acidity, alkalinity, Fe, and Mn concentrations. Alternatively, DO and oxidation-reduction potential (ORP) are critical for the proper operation of an ALD. All waters that would be routed through an ALD should be sampled and analyzed for the above mentioned parameters. Samples should be collected directly from the seep via methodologies precluding sample aeration (e.g., peristaltic pumps, large syringes, etc.). DO and ORP must be field measurements. Fe⁺² and Fe⁺³ are good indicators of ORP (and possible armoring). If samples

are immediately acidified with HNO_3 (or another non-oxidizing acid) Fe^{+2} can be determined accurately in the lab. Ferric iron present in appreciable concentrations in the unaerated seep sample may affect the use of an ALD due to potential limestone armoring. TVA is currently investigating the effects of ferric Fe on ALDs. Al precipitation within the ALD has also been proposed as a potential plugging problem,⁹ but has not been observed at TVA systems including the IMPI AROAD where total Al is greater than 10 mg/l.

Side slopes of the excavation are not critical to the operation of the ALD and are best made near vertical to facilitate construction. High-calcium limestone (i.e., $\geq 90\%$ available CaCO_3) should be used. TVA and TWPC have used 3/4 to 1-1/2 in crushed rock in existing ALDs because of its high hydraulic conductivity, large surface area, and ready availability; however a different gradation, a well-graded mixture, or a layering of several grades of rock may be suitable. Larger rock size or more dolomitic (i.e., CaMgCO_3) stone is not recommended due to the loss of surface area in the ALD with the large rock and the lower reactivity of dolomite. The depth of limestone backfill should be determined by (1) the need to accommodate the maximum probable flow, (2) the desired longevity of the ALD, and (3) a comfortable safety factor for both (1) and (2). Desired longevity is discussed below. TVA's and TWPC's ALDs have contained limestone depths of 2 to 5 ft. Because the very lowest portion of the backfill may be rendered ineffective due to its tendency to embed in the bottom of the excavation, about 6 inches additional depth of limestone should be included to account for this loss.

A minimum of 2 ft of soil cover should be placed and compacted over the plastic and fabric covered limestone backfill. Soil should be sufficiently impermeable to oxygen migration. If available and practicable, clay soil is recommended. Alternatively, a clay, clayey-silt, or silty-clay loam should be adequate. The final cover should be slightly crowned and protected with erosion control fabric or adequately waterbarred to prevent erosion. Crowning will allow for subsidence of the ALD over the years due to limestone dissolution. Ideally, the crowned ALD should be riprapped or revegetated with species such as sericea (Leavedeza cuneata) or crownvetch (Coronilla varia), which will discourage the establishment of trees whose roots could penetrate the ALD and render it ineffective.

Prototype installations of ALDs have used 5-mil plastic and/or filter fabric covered with clay soil to seal the limestone from the atmosphere.³ More recent ALDs have used 20-mil plastic or double layers of 10-mil plastic which is significantly less expensive than 20-mil and is more readily available. Geotechnical fabric should be of quality sufficient to protect the integrity of the plastic from puncture under loads from equipment and workers.

An additional design recommendation is the use of an oxidation basin immediately after the seep discharges from the ALD and prior to routing that flow into a constructed wetlands. The purpose of an oxidation basin is aimed at high Fe influents (e.g., $>50 \text{ mg/l}$). The basin allows the newly aerated and highly alkaline ALD discharge water to react and precipitate the majority of its Fe load, which can be achieved physiochemically and without the use of a constructed wetlands. The U.S. Bureau of Mines has suggested a general empirical guideline which states that about 50 mg/l Fe can be removed in an aerobic wetlands cell before reaeration is required.¹⁰ An oxidation basin will greatly enhance the efficiency and lifespan of a downstream constructed wetlands as the basin can be dredged, thus preventing excessive precipitate buildup in the wetlands. Such a pond needs simply to be designed according to existing guidelines with considerations of regulatory requirements, desired capacity, and

maintenance. Alternatively, a modified marsh-pond cell with a major portion devoted to deep (3-6 ft) water might be more applicable to acid drainage with low to moderate Fe concentrations. Figure 4 shows influent/effluent data for 3 oxidation ponds at TVA wetlands.

Longevity of an ALD has been estimated by TVA and TWPC laboratory and field investigations based on the dissolution rate of limestone.^{3,4} These studies include small-scale pilot studies and evaluations of existing ALDs and indicate that ALDs can be expected to last 20-80 years or more if properly designed and constructed.

SELECTED CASE HISTORIES

Fabius Impoundment 4

TVA's Impoundment 4 constructed wetlands (IMP 4) was built in October 1985 to treat acid drainage emanating from a fine coal refuse area at the Fabius Coal Preparation Plant in northeast Alabama.¹ The inflow water quality was characterized by pH = 5.5, total Fe = 65 mg/l, Total Mn = 17 mg/l, acidity > 200 mg/l, and alkalinity = < 30 mg/l. Flow averaged 34 gal/min. Although significant amounts of Fe and Mn were removed from the acid drainage by the 4-cell, 0.5-acre wetlands (Fe was reduced to less than 10 mg/l), the effluent pH and Mn levels required chemical treatment before final discharge to achieve permit limitations.

In April 1990, an ALD was installed upstream of IMP 4 (Figure 5). The ALD consisted of a trench 10-15 ft wide, 5 ft deep, and 260 ft long excavated into the refuse and seepage area with a swamp-tracked hydraulic excavator. Four hundred tons of 3/4" - 1 1/2" crushed limestone were backfilled into the open trench. The limestone was covered with two layers of 10-mil plastic over which was placed geofabric and 2 feet of local soil (sandy-silty loam). The surface was slightly crowned, seeded with a mixture including sericea lespedeza, mulched, and fertilized.

Figure 6 shows typical pre-ALD and post-ALD water quality for IMP 4 discharge. The ALD has successfully increased alkalinity and enabled the IMP 4 wetlands to meet pH, Fe, Mn, and suspended solids concentrations to compliance levels from the initial operation of the ALD to date; wetlands effluent pH has risen from 3.1 to 6.3, acidity has been reduced from 350 to 40 mg/l, alkalinity has increased from 0 to 100 mg/l, Fe has decreased from 6.0 to 1.0 mg/l, and Mn from 1.6 to 0.2 mg/l.

IMP 4 wetlands influent (i.e., the ALD effluent) had an average pH of 6.3 and concentrations of 85 mg/l Fe and 17 mg/l Mn before the ALD. After the ALD was installed, ALD effluent Fe and Mn concentrations decreased to very low concentrations (i.e., 0.1 mg/l). This phenomenon probably indicated oxidation and precipitation of Fe and Mn within the ALD. This was verified by a series of excavations into the ALD in May 1991. It was found that the upper portion of the limestone in the unsaturated zone of the ALD was moderately armored with Fe coatings. The stone in the saturated zone showed only traces of Fe precipitates. Two possible reasons for the armoring are hypothesized. First, the DO concentration in the ALD effluent was 1.0-2.0 mg/l with an ORP of less than zero. Although these conditions, in water, may be conducive to keeping iron in the reduced, soluble ferrous form (Fe⁺²), the atmosphere in the unsaturated zone probably had elevated oxygen levels due to several unsealed monitoring wells in the ALD. Periodic fluctuation of the water levels in this zone may have resulted in increased oxygen availability at the limestone surface for Fe oxidation/hydrolysis, resulting in armoring above the zone of saturation in the ALD.

A second hypothesis assumes that ferric hydrolysis (equation 3) is occurring in the ALD because this reaction is not affected by DO levels. The Fe^{+3} concentration in the acid drainage is probably high enough for ferric hydrolysis to occur (i.e., $\text{Fe}^{+3}/\text{Fe}^{+2} > .25$). Whether this phenomenon is occurring is under evaluation by TVA^{ll} and the U.S. Bureau of Mines.⁹

The discharge from IMP 4 remained well within compliance levels (i.e., pH 6-9, $\text{Fe} < 3.0 \text{ mg/l}$, and $\text{Mn} < 2.0 \text{ mg/l}$) during this period. It was assumed that, if ferric hydrolysis was occurring in the ALD, the system would plug and eventually fail. However, if the ALD was simply being adversely impacted by oxygen invasion, then a solution to the problem might be to induce saturated conditions throughout the majority of the ALD. In June 1991, the monitoring wells were sealed and an earth dike (Figure 7) was constructed at the discharge point of the ALD to raise the water level in the ALD approximately 3-4 feet. Measurements in the monitoring wells confirmed saturation of the ALD in its upper portion, and Fe levels have increased significantly in the ALD discharge as shown in Figure 6. Saturated conditions in the limestone appear to have ameliorated the precipitation of Fe within the ALD. Further evaluations are ongoing. Based on the above problems, it may be prudent to construct ALDs with high width /length ratio and shallower depths of limestone to ensure saturation.

The total installation cost of the IMP 4 ALD was about \$19,000. This compares to annual costs of about \$20,000 for NaOH and \$10,000 for operation and maintenance associated with conventional treatment of the IMP 4 flow from October 1985 to May 1990.

Kingston Fossil Plant

TVA's Kingston 006 constructed wetlands (KIF 006) was built in October 1987 to treat acid drainage emanating from an ash disposal embankment at the Kingston Fossil Plant in Roane County, Tennessee (Figure 8).^l Inflow water quality was characterized by pH = 5.5, total Fe = 170 mg/l, total Mn = 4.4 mg/l, alkalinity <40 mg/l, and acidity >400 mg/l with flow averaging 408 gal/min. The 2.3 acre, 3-cell wetlands system consistently removed about 50% of the Fe loading and the pH at the final cell was 2.9. The final cell was pumped to the plant's active ash pond for treatment prior to discharge.

In April 1991, a 10-acre area within the ash disposal area upgradient from KIF 006 was treated with the bactericide ProMac, and reclaimed with lime-amended soil and a grass mixture. This area had been a site where water from the plants bottom ash sluice canal had pooled and presumably contributed significantly to the KIF 006 drainage. In September 1991, an ALD was installed upstream of KIF 006 in an existing seepage collection channel along the toe of the ash embankment. The ALD consisted of a trench approximately 5 ft wide, 5-10 ft deep, and 1400 ft long. The trench was backfilled with 3,600 tons of 3/4" - 1 1/2" crushed limestone which was placed on filter fabric. The stone was covered with geotechnical fabric and 2 - 6 ft of compacted local clay loam. The ash embankment and the ALD cover was sloped approximately 3:1 and seeded with a mixture including sericea lespedeza.

The first cell of the KIF 006 wetlands was converted to an oxidation precipitation pond by dredging to a depth of about 6 - 8 ft. A shallow subsurface rise transversing the midpoint of the cell allows for reaeration of the water within the oxidation pond. It is estimated that this cell alone contains approximately 1,000,000 gallons of acid drainage.

Hard Rock Mine

TVA's Fabius HROOO constructed wetlands (Figure 9) is currently under construction and was designed to treat acid mine drainage emanating from two large seeps at the Fabius Hard Rock North and Hard Rock South reclaimed coal mines. Inflow water quality was about pH = 5.5, Fe = 40 mg/l, Mn = 17 mg/l, alkalinity <30 mg/l and acidity >200 mg/l. Flow averages 1000 -2000 gal/min with stormflows exceeding 10,000 gal/min.

The wetlands system will consist of 5 wetlands cells proceeded by 2 ALDs followed by oxidation ponds. Total area will exceed 10 acres. Currently, only one ALD has been installed. This ALD consists of a 35 ft by 350 ft trench backfilled with 1 1/2" limestone covered with geofabric and 2-3 ft of clay soil. The ALD effluent has pH = 6.6 and alkalinity of about 300 mg/l.

A hydraulic conductivity test was conducted by measuring the change in hydraulic gradient overtime in 6" diameter observation wells completed in the ALD while pumping a 10" diameter well with a suction lift centrifugal pump at 350 gpm. Separate tests were conducted with a resulting average hydraulic conductivity of 1.1×10^6 gpd/ft². Eight observation wells were used in the test. The hydraulic conductivity was calculated as if the ALD was under unconfined conditions. Equilibrium was reached within 1 hour during the test. The test was discontinued after 3 hours.

Conclusions

Anoxic limestone drains have been installed at sites in Tennessee, Alabama, West Virginia, and Pennsylvania to increase buffering capacity and alkalinity in acid mine drainage and prevent pH decreases in effluent due to Fe hydrolysis. Results to date are optimistic and in most instances alkalinity has been significantly increased to levels sufficient to buffer the flow from pH decreases. Long-term results must be evaluated to establish the stability of an ALD over the duration of acid drainage at a particular site.

Design, utility, and longevity of an ALD require further examination to develop guidelines and expectations. Particularly, stone gradation and composition, dissolution rates, reaction mechanisms and products, and the nature of ALD-enhanced Mn removal need to be researched. However, the relative simplicity and low cost of the ALD and preliminary studies indicating lifespans of several decades suggest that the system may be an effective means of renovating inefficient, existing aerobic wetlands and an important component of staged wetlands system designs, providing the capability of treating poorer quality waters with less area. To meet effluent compliance limits, TVA advocates the use of ALDs only as a staged portion of aerobic acid drainage wetlands systems, and does not recommend their use as stand alone systems, or as a stage of an anaerobic wetlands system.

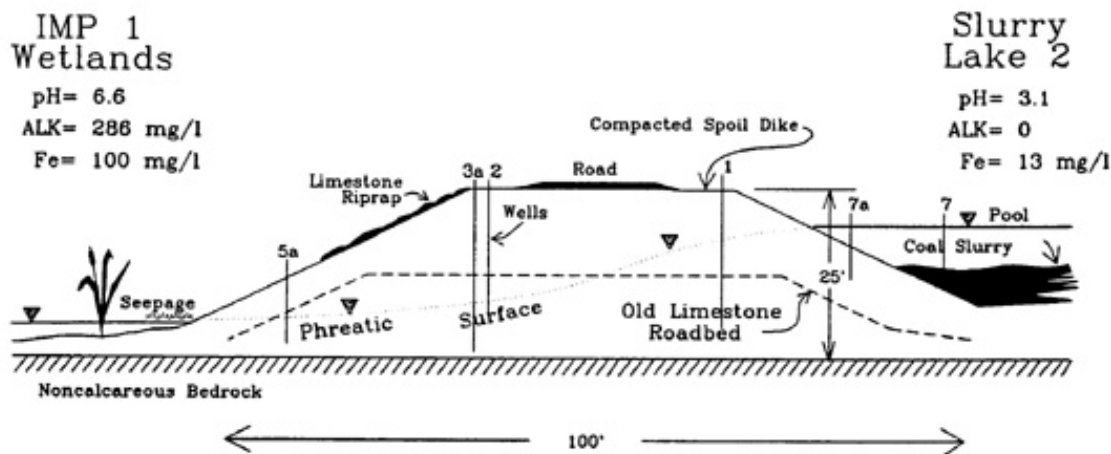
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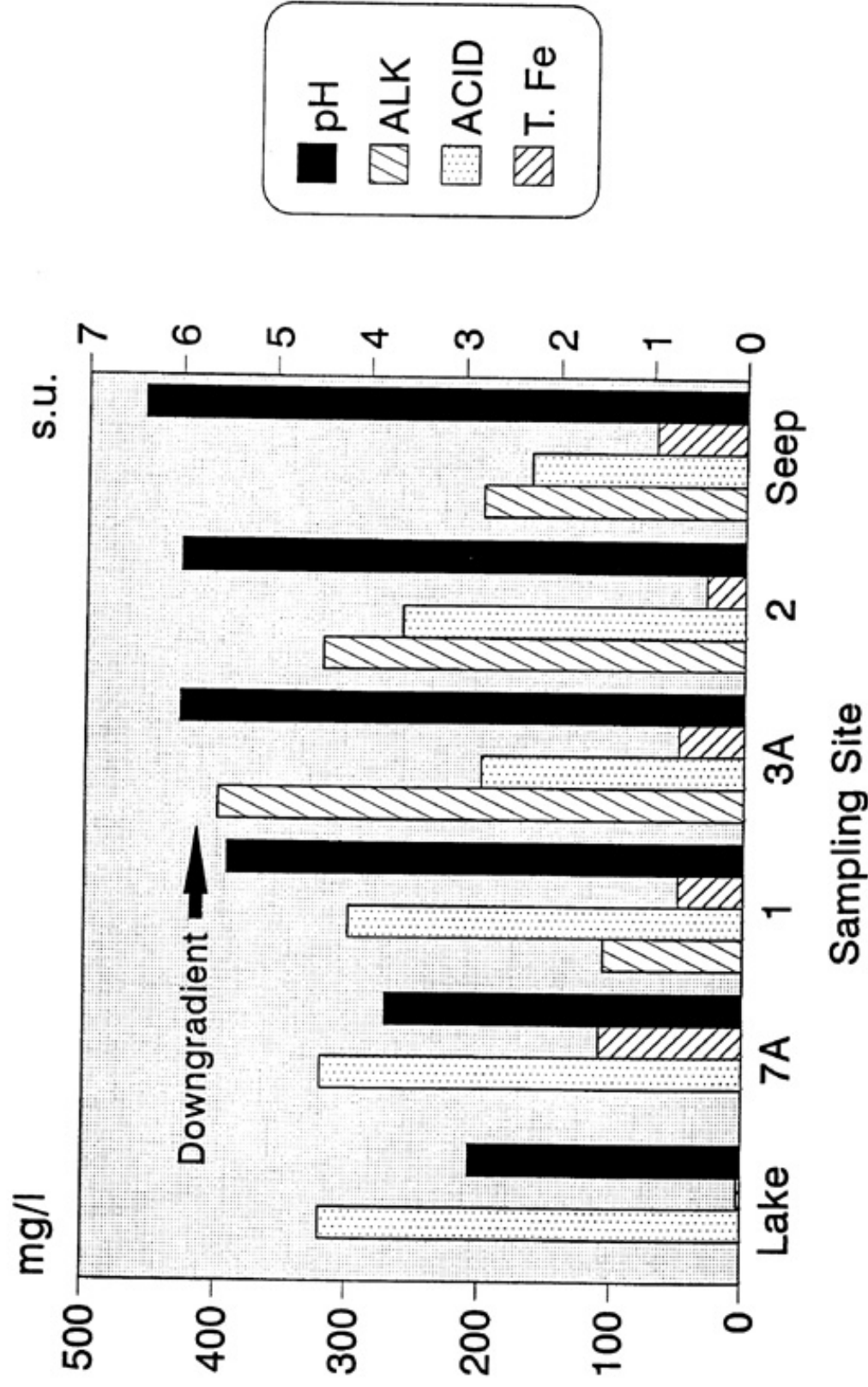
Figure 1 ACCIDENTAL ROADBED ORIGINATED ANOXIC DRAIN (AROAD)



Not to Any Known Scale

Figure 2. AROAD Monitoring Well Data

Fabius Slurry Lake 2 Dam



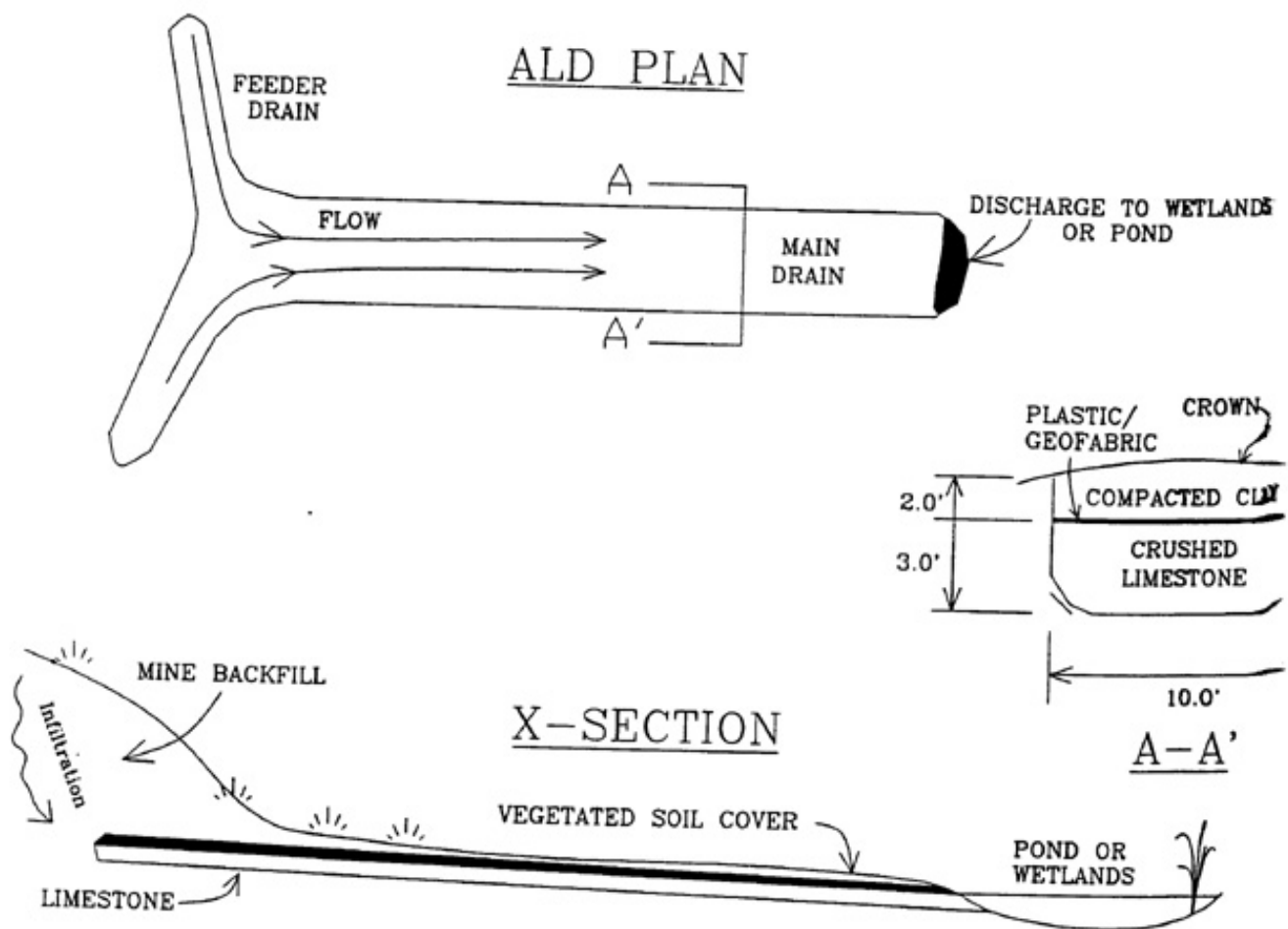
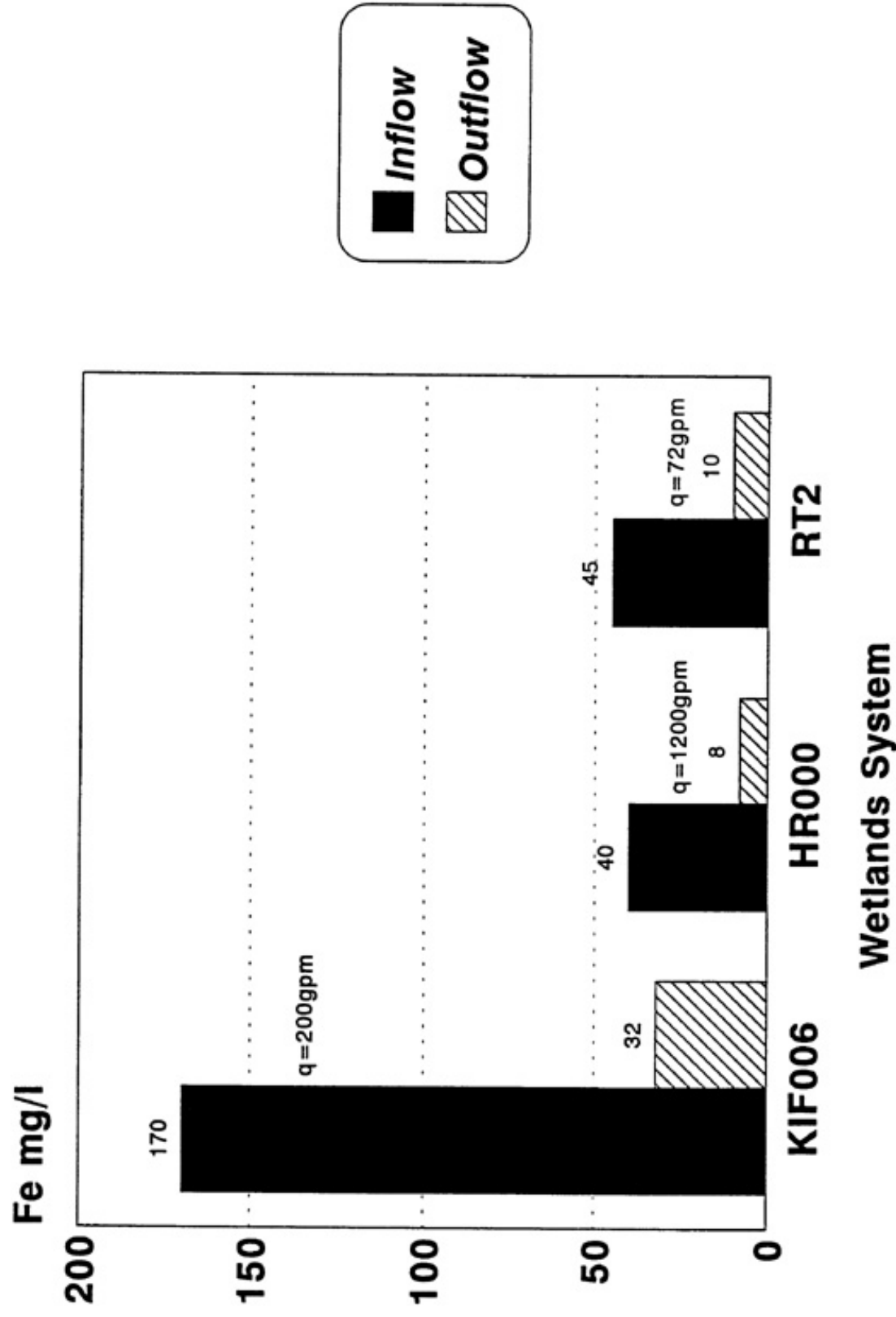


Figure 3. Basic Design of Anoxic Limestone Drain

Figure 4. Fe Removal in Oxidation Ponds



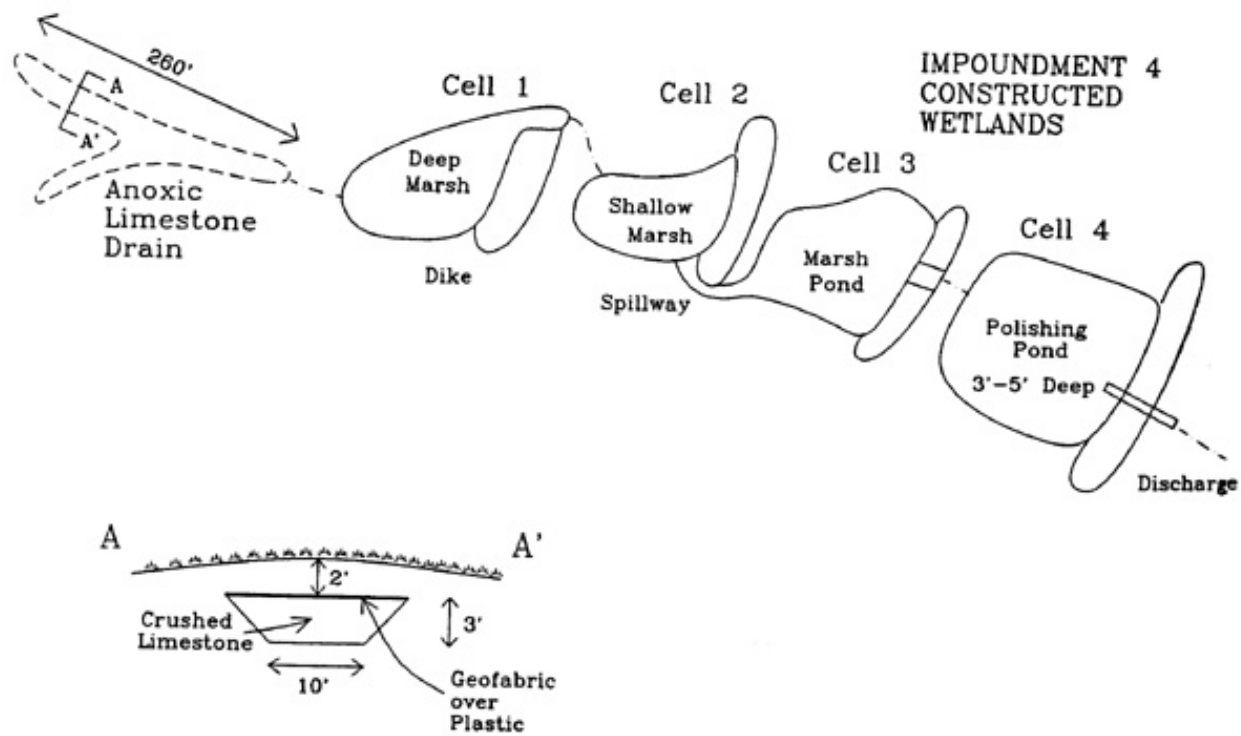


Figure 5. Schematic of Fabius Impoundment 4 Constructed Wetlands

Figure 6. IMP4 Data Before & After ALD

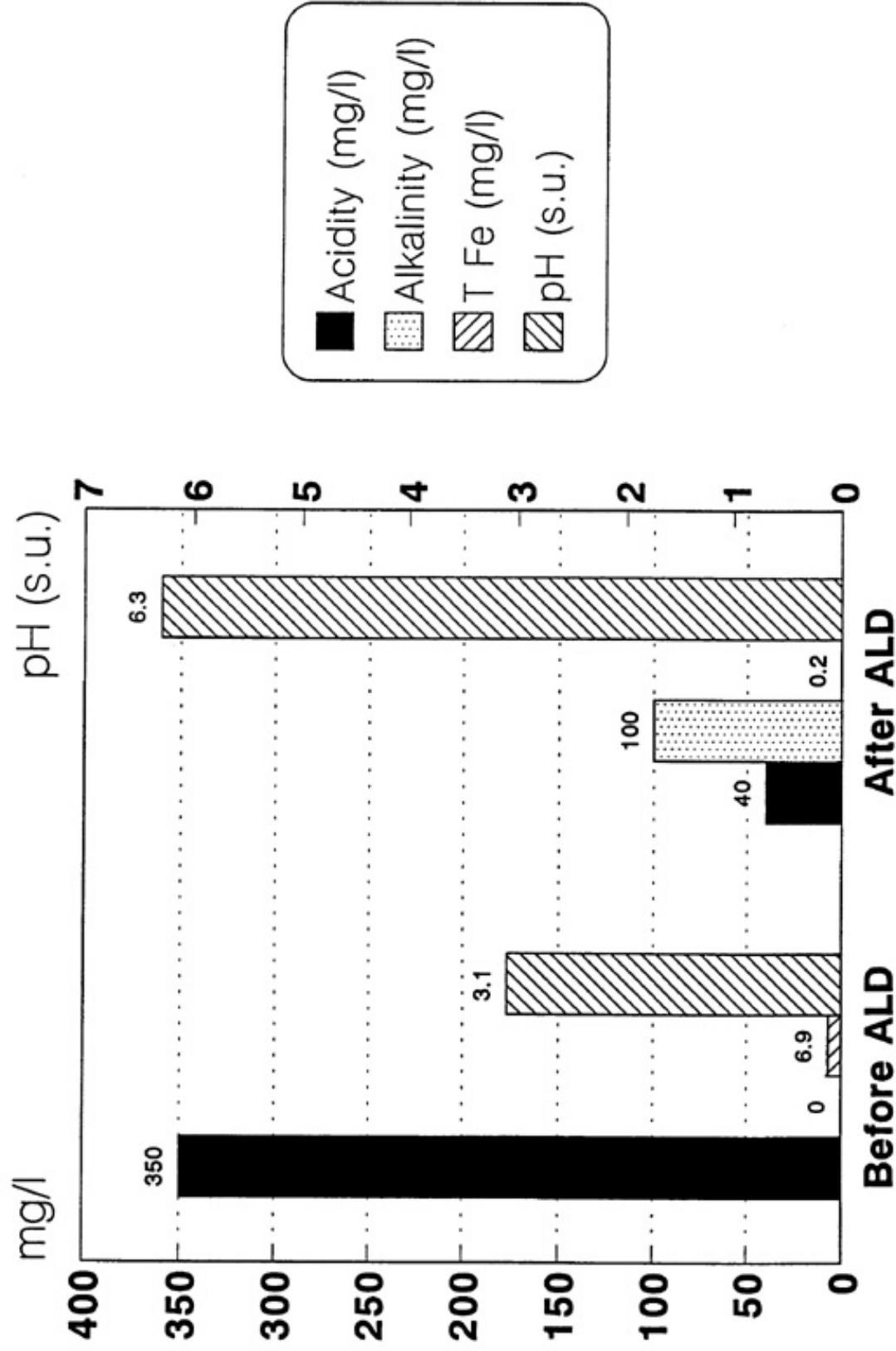
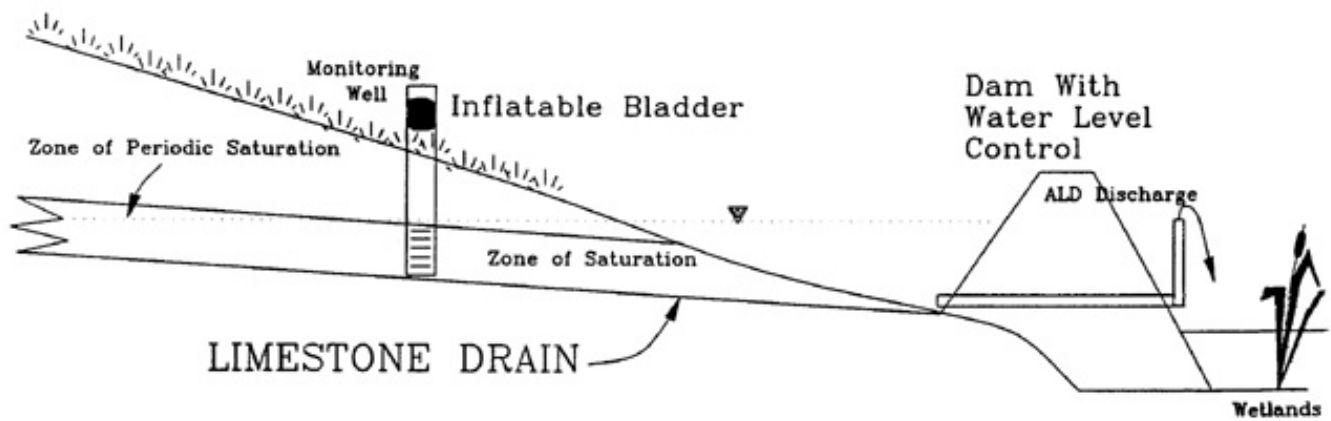


Figure 7
PREVENTING O_2 INVASION OF ALD



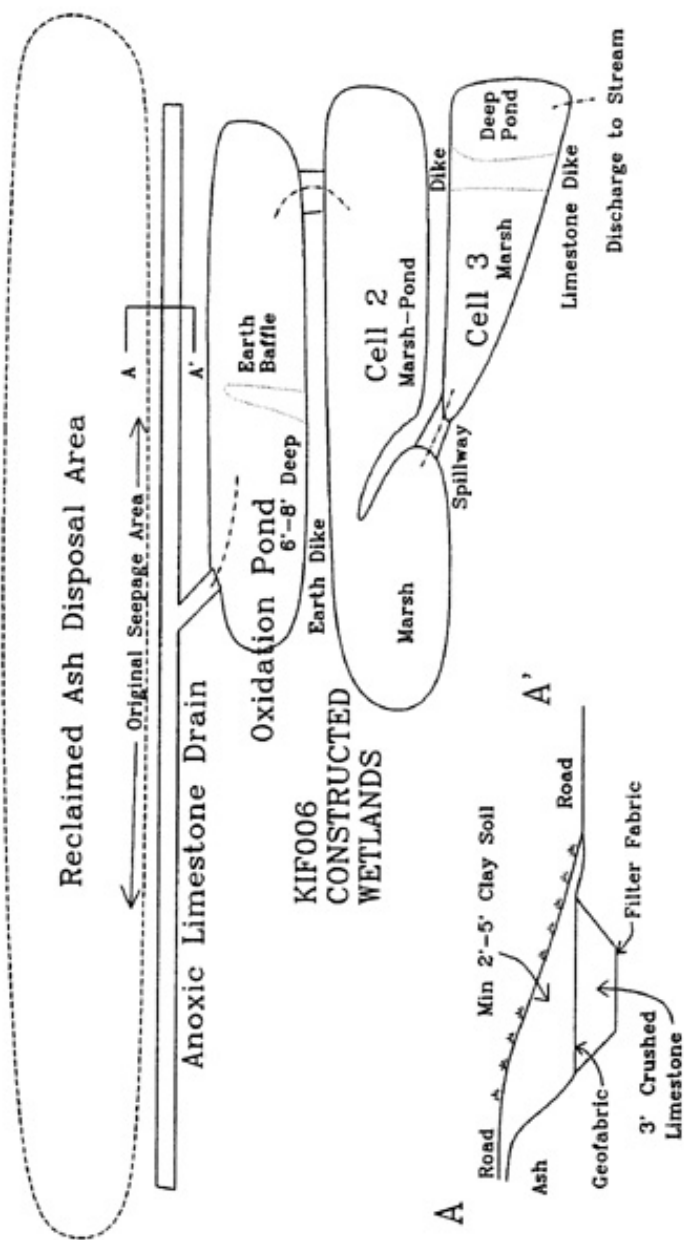


Figure 8. Schematic of Kingston (KIF006) Constructed Wetlands

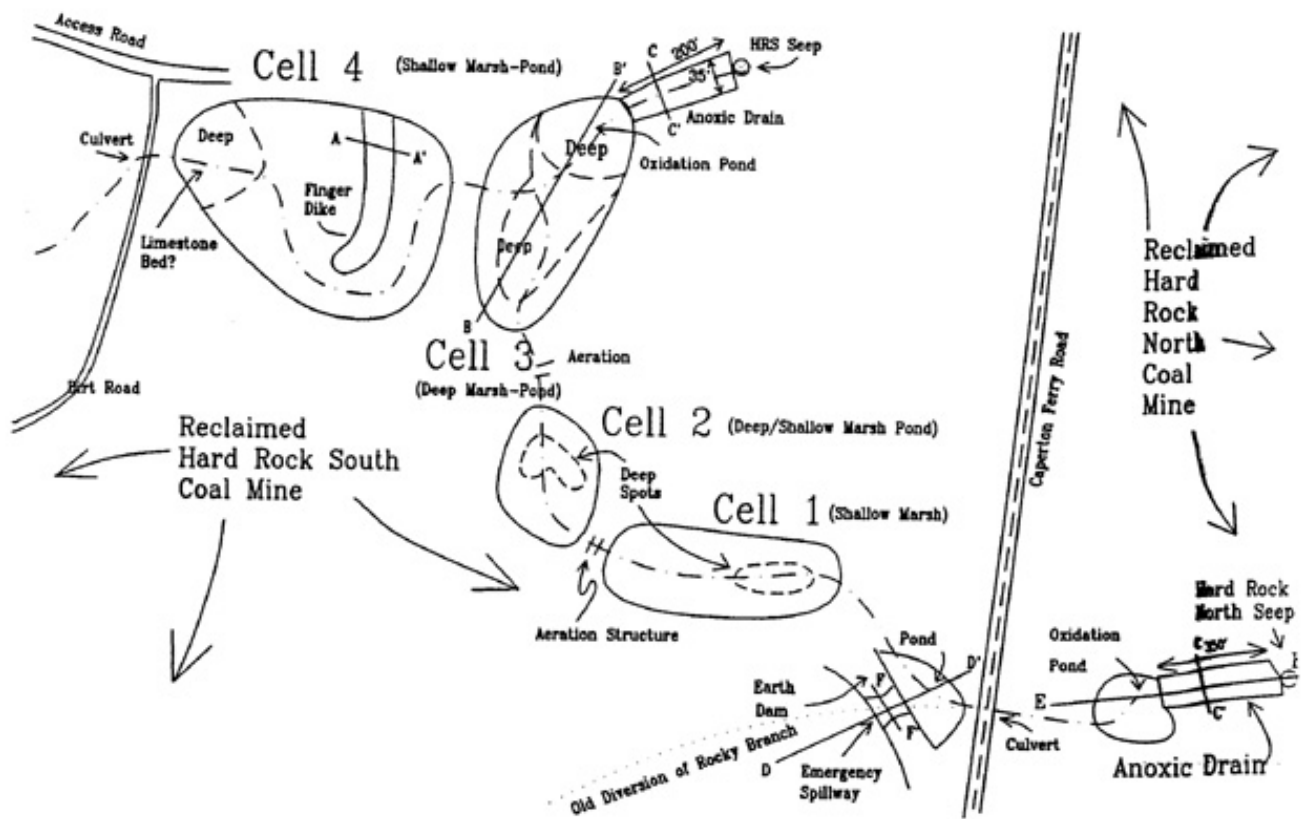


Figure 9. Schematic of Hard Rock (HR000) Constructed Wetlands