PRELIMINARY RESULTS OF ANOXIC LIMESTONE DRAINS IN WEST VIRGINIA

Jeff Skousen

and

Ben Faulkner

West Virginia University
Morgantown, WV 26506-6108

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Introduction

Anoxic limestone drains (ALDs) are a new technique for passively adding alkalinity to acid mine drainage (AMD). An ALD consists of high quality limestone buried in a trench, underdrain, or cell. Acid water is intercepted while it is anoxic (underground) and directed into the buried trench or cell of limestone. The limestone slowly dissolves and adds alkalinity. The major innovation of this system is that limestone coating or armoring with iron hydroxides does not or only slowly occurs when the limestone is maintained in an anoxic environment and when the incoming AMD is in a chemically-reduced state. The level of chemical reduction of the water can be estimated by the dissolved oxygen content (.~ 1 mg/1) and the oxidation state of the iron (most should be in the ferrous form). An attractive feature of this system is the use of limestone which is a cheap and readily-available source of alkalinity.

Anoxic drains were first installed as AMD pretreatment for wetland systems. ALDs pre-condition water by the addition of alkalinity which makes the wetland more efficient in oxidation and precipitation reactions.

ALDs simply raise pH and add alkalinity to water. Once the water exits the drain and becomes oxygenated, iron and manganese contained in the AMD can oxidize, hydrolyze, and precipitate. These oxidation, hydrolysis, and precipitation reactions are enhanced by the alkalinity that has been added to the water from the limestone in the drain. The alkalinity also buffers the water at around pH 6.2 because ALD-treated water contains alkalinity in the form of HCo_3-. As ferrous iron and manganese oxidize, hydrolyze, and precipitate outside the drain, the excess alkalinity in the water keeps the pH in the 6.0 to 6.5 range and allows these reactions to occur more rapidly. Since the drain maintains anoxic conditions and only attains a pH of 6.5, ferrous iron and manganese do not precipitate inside the drain or coat the limestone.

Water exiting an ALD is not completely "treated" and cannot be immediately discharged into receiving streams. The water still contains metals and acidity because H* will be produced when ferrous iron and manganese oxidize, hydrolyze, and precipitate as hydroxides. In addition to the acidity, the water exiting an ALD should also contain alkalinity due to the presence of HCO_{3-} from dissolution of limestone. Aluminum and hydrogen ions (some of the acidity in the water) have consumed some alkalinity generated from limestone and have already been neutralized inside the drain. Hydrogen ions mix with HCO_{3-} to form H_2O and CO_2, while Al reacts with $3HCO_{3-}$ to form $Al(OH)_3$ and $3CO_2$.

Ferrous iron and manganese also utilize alkalinity in the drain but they normally require a higher pH to precipitate (pH $\geq$ 8.5). Therefore, these elements must exit the drain and oxidize before they can potentially precipitate from AMD.

Other metals in AMD react similarly to aluminum and are not dependent on oxidation or high pH to precipitate as a hydroxide. For example, Cu, Pb, and Zn are metals that probably will precipitate as hydroxides inside an ALD when a pH around 6.0 and excess alkalinity are present.

Aluminum is a problem when treating coal mine drainage with chemicals. Aluminum is toxic to fish in relatively low concentrations, and is much more toxic to plants and other animals than either iron or manganese. Aluminum removal from AMD by wetlands has been variable and usually depends on whether the wetland generates alkalinity. Aluminum removal from AMD by an ALD may be more predictable and has both an advantage and disadvantage. The advantage is that aluminum precipitates and remains in the drain thereby removing it from water. But with precipitation in the drain comes the likelihood of potential clogging and failure of the drain in the future. In most (if not all) ALDs that have been constructed in West Virginia, aluminum in the influent water does not flow through the drain but is evidently precipitating in the drain.

Materials and Methods

Eleven sites where anoxic drains had been constructed to treat AMD were chosen in West Virginia. These drains were built according to a general description given in Skousen (1990), and had various amounts of limestone placed in cells or trenches. Water quantity and quality data before ALD installation are presented in Table 1. Water quality data averages since ALD installation are also presented.

Results

The ALDs constructed in West Virginia treated various flows ranging from 1 gpm to 28 gpm and most of the pre-drain AMD had pH below 4.0 (Table 1). In all cases, water pH was raised after ALD installation. Three sites showed pH values less than 5.0 after ALD treatment indicating that the drain was not fully functioning but still was adding some alkalinity to the water.

From the data, pre-drain water acidity was generally higher than post-drain water acidity. The decrease in acidity generally ranged from 50 to 80%. Only two exceptions were found. The Greendale 1 6/61 site showed an increase of acidity, while the Greendale 5 272 site showed only a 20% reduction in acidity. As mentioned, decreases in acidity were expected since limestone dissolution neutralized hydrogen and aluminum, two components of acidity, inside the ALD.

Post-drain iron concentrations, unfortunately like acidity, were always less than pre-drain iron contents except for the Greendale 1 6/61 site. The lower iron concentrations in post-drain samples may be due to small amounts of ferric iron being retained in the drain (some oxidation, hydrolysis, and precipitation inside the drain). In some cases, the amount of iron retained in the drain was 50%. If iron was precipitating in the drain, these drains with high iron concentrations may experience limestone coating and eventual clogging. Manganese concentrations were generally more similar when comparing pre-drain vs. post-drain water samples and, as such, appeared less likely to be precipitating in the drain.

The majority of aluminum in pre-drain AMD, in all but two cases, was not found in water coming out of ALDs. The aluminum apparently precipitated inside the drain as predicted. In water coming out of most ALDs, aluminum concentrations were less than 1, but 7 or 8 months after installation of some ALDs, aluminum concentrations slowly rose to 3 or 4 mg/l.

Sulfate, a common anion in AMD, has also been discussed as a possible precipitate in ALDs as gypsum when calcium is abundant. In most of these drains, sulfate appeared to be lower in post-drain water compared to pre-drain water and this precipitation reaction may have occurred. However, calcium concentrations were not measured and more research is needed to answer this question.

Based on preliminary results from Table 1, the ALDs installed at Greendale sites 5 271 and 272, and 10 296, and Lobo Capital site 13/18 were not functioning at full capacity. These drains decreased acidity and raised pH, but excess alkalinity was not found. The reason for poor performance and low alkalinity generation has not been determined. The problem may have been due to faulty construction or improper placement of materials. Several of the drains are currently being dug up and problems may be explained.

Discussion

Several questions on ALD treatment of AMD still remain but practical questions relate to sizing and construction of the drain. For example, if a drain is built larger with more limestone in the cell or trench, will the drain with the extra limestone actually produce more alkalinity? Based on observation, the alkalinity generated in a drain is a function of the amount and quality of the AMD. If more acid water moves through the drain, more limestone will dissolve creating more alkalinity. So for the same amount and quality of water, a certain amount of alkalinity will be generated.

Second, if a drain is built larger with more limestone, will the drain actually last longer? Having such limited experience with these ALDs, this question is difficult to answer. However, these drains will probably experience mechanical problems through clogging or plugging before the limestone in the drain completely dissolves.

References

Skousen, J. 1991. Anoxic limestone drains for acid mine drainage treatment. Green Lands

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Table 1. Preliminary results of 11 anoxic limestone drains built in West Virginia and Pennsylvania. The values represent averages over several sampling periods and should only be used for comparative purposes.

Site	Flow	pH	Acid	Alk	Fe	Mn	Al	SO4	pH	Acid	Alk	Fe	Mn	Al	SO4
		Pre-Drain AMD							Post-Drain Water						
	gpm		mg/l	mg/l	mg/l	mg/l	mg/l	mg/l		mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
Greendale															
1 6/61	17.4	4.1	87	2	27	13	3	150	5.9	150	55	100	20	0	690
2 5/71	3.3	3.4	640	0	204	92	26	1500	6.0	175	146	160	77	1	2200
3 421/422	5.8	3.0	355	0	176	62	40	1030	6.1	140	60	75	72	2	1210
5 271	1.0	3.2	1000	0	139	202	98	2410	4.5	470	0	110	168	65	1900
272	1.0	3.0	550	0	120	168	55	1820	3.5	450	0	70	125	50	1480
10 293	1.5	2.8	372	0	78	105	9	1300	5.8	80	75	40	90	0	1220
296	4.8	2.8	546	0	178	114	5	1700	5.9	131	0	110	80	1	1540
13 351	1.0	3.1	460	0	25	140	50	2500	6.0	70	50	20	135	4	2100
Preston	1.0	2.8	2100	0	650	17	45	3500	6.7	143	214	500	14	0	2040
Lobo Capital															
13/18	28.0	3.2	432	0	159	2	14	1335	3.6	121	0	127	2	0	900
1/21	23.0	2.9	470	0	96	3	18	780	6.2	9	131	58	4	0	575