

## Technical Article

# Limestone Drain Design Parameters for Acid Rock Drainage Mitigation

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Submitted October 11, 2006; accepted January 18, 2007

**Abstract.** Limestone drains are an integral component of some of the most efficacious passive systems for the treatment of acid rock drainage (ARD). A critical design parameter for a limestone drain is the mass of limestone that will be required for effective treatment. This in turn depends on the flow rate, limestone dissolution rate, and associated hydraulic detention time necessary to achieve a certain effluent alkalinity for a given design life. Rates of alkalinity generation and limestone dissolution, and the quality of the limestone in terms of weight fraction of  $\text{CaCO}_3$  and percentage  $\text{CaCO}_3$  available must be known to determine the required mass of limestone. These parameters were experimentally determined for a natural and synthetic suite of ARD waters. The experimental results show that the empirical change in the alkalinity over time cannot simply be modeled as a first-order process. During the initial stage, the concentration increase is extremely fast, giving a linear and steep rise in the alkalinity. Alkalinity concentrations peaked at elapsed times of 90 to 180 minutes and then declined to a nearly constant value. The decline in alkalinity corresponds with a decline in concentrations of dissolved iron and aluminum, implying that the consumption of alkalinity by the hydrolysis of these metals is faster than the rate of alkalinity production by the dissolution of limestone, so that the reaction appears zero order in the early stage and pseudo-first order later. Because the changes in concentration were complex, considerable uncertainty exists in the rate constants for estimating alkalinity concentration. This causes problems in design equations based solely on a limestone dissolution rate that is estimated from alkalinity generation rates. A more applicable design procedure, combining the kinetics of alkalinity production and consumption with the hydraulics and chemical equilibrium of the system, is illustrated.

**Key words:** Acid rock drainage; alkalinity generation; limestone drain; limestone dissolution; Minera Los Pelambres, Chile; passive treatment system

## Introduction

A variety of passive systems have been proposed, designed, and implemented for treatment of acid rock drainage (ARD; Hedin et al. 1994; Skousen 1997). Typically, limestone is an integral component in these systems owing to its acid neutralization capacity. Often, a limestone drain (LD), in which the ARD flows through a buried trench filled with crushed limestone of uniform size, is used (Cravotta and Trahan 1999; Cravotta and Watzlaf 2002). Two types of LDs are in vogue. In the first type, called an anoxic limestone drain (ALD), an oxygen deficient condition is maintained to prevent the formation of insoluble oxides and hydroxides of Fe(III) (Hedin and Watzlaf 1994; Hedin et al. 1994). An ALD principally acts as a neutralization medium; Fe(III) precipitation is carried out separately, typically in a sedimentation pond. Preventing the formation of Fe(III) oxides and hydroxides limits limestone armoring, which would otherwise decrease the limestone's neutralization

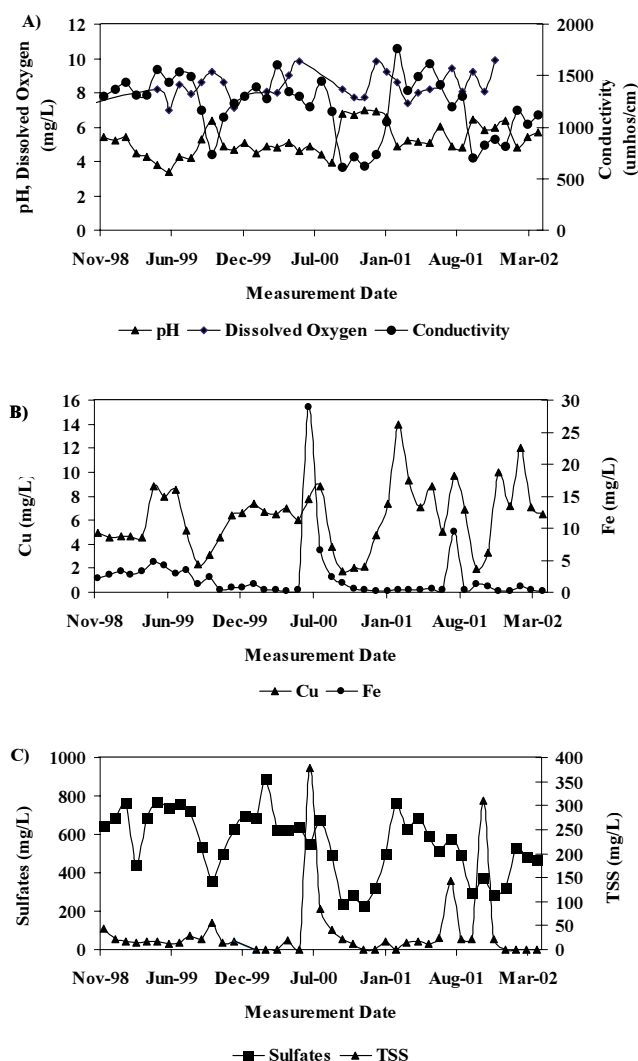
capacity and possibly reduce the porosity and permeability of the LD. Decreasing the partial pressure of oxygen ( $p\text{O}_2$ ) and consequently increasing the  $p\text{CO}_2$  potentially increases the rate of limestone dissolution compared to systems that are open to the atmosphere, such as open limestone channels or diversion wells. Most passive systems with a LD or equivalent component, such as successive alkalinity producing system (SAPS), employ anoxic conditions (Jage et al. 2001).

Stringent requirements for low concentrations of DO, Fe(III), and Al(III) in the influent ARD make ALDs inappropriate for the treatment of oxic or highly mineralized waters that are also common in mined areas (Cravotta and Trahan 1999; Cravotta and Watzlaf 2002). For this reason, oxic limestone drains (OLDs) and SAPs have also been used. Here, the interaction of the ARD and atmospheric oxygen is not prevented. Cravotta and Trahan (1999) presented data from three pilot scale OLDs that showed that OLDs are

effective for neutralization of oxic and relatively dilute ARD ( $\text{DO} > 1 \text{ mg/L}$ ; acidity  $< 90 \text{ mg/L}$ ) with low concentrations of dissolved  $\text{Al(III)}$ ,  $\text{Fe(III)}$ , and  $\text{Mn(III)}$ .

An essential design parameter of either an ALD or OLD is the rate of alkalinity generation. This in turn determines the hydraulic detention time ( $t_d$ ) necessary to attain a desired alkalinity in the effluent. Related to the rate of alkalinity generation is the rate of limestone dissolution. The volume ( $V_s$ ) or the mass ( $M$ ) of limestone required in a LD for a given flow rate depends on  $t_d$  and the rate of limestone dissolution. In theory then, the design of a LD depends on the rates of alkalinity generation and limestone dissolution.

Quantitative data on the rates of alkalinity generation and limestone dissolution due to ARD-limestone



**Figure 1.** Historical water quality of the Pelambres River immediately downstream of the Los Pelambres mine (Hydrologic Node 5)

interactions are limited. Cravotta and Watzlaf (2002) presented a set of experimental data on the rate of alkalinity generation for two ALD sites in the coal mining areas of Pennsylvania to provide qualitative and quantitative effects of variable influent compositions, detention times, and limestone purity on LD performance. These authors also obtained the limestone dissolution rate from 13 existing LDs by computing the long-term (1-11 years) mass flux of  $\text{CaCO}_3$ . From this study, they presented a method for the design of a LD based on kinetic rate constants for alkalinity production and limestone dissolution. This method differs significantly from an earlier method used by Hedin and Watzlaf (1994), who calculated design parameters for a LD based on hydraulic and equilibrium chemical factors rather than any kinetic consideration. Cravotta and Watzlaf (2002) obtained kinetic data from small-scale “cubitainer” tests, demonstrated that such data was comparable to long term data from the large long-term field tests, and suggested that this method be used to obtain kinetic parameters.

This paper presents the results of a set of carefully designed experiments aimed at determining the quantitative nature of alkalinity generation and limestone dissolution as a function of  $t_d$  during interactions of ARDs of varied compositions with a limestone bed under both atmospheric and below-atmospheric  $p\text{O}_2$ . The associated rate of rise of pH, decline in acidity, and attenuation of dissolved metals in the ARD were also investigated. The efficacy of a limestone of a given composition to treat ARD of variable compositions was studied with the objective of obtaining design parameters for a LD for mitigation of the ARD in a major copper mine, based on a combination of experimentally derived chemical equilibrium, kinetic, and hydraulic parameters.

## Materials

### ARD water

The natural ARD water used in this study was from Minera Los Pelambres (MLP), central Chile. The MLP is an open pit porphyry copper mine located on the eastern side of Andes Cordillera, close to the Chile-Argentina border at an altitude of 3,000 m above mean sea level. The mine is about 20 km to the north of Cuncumén, 70 km from the town of Salamanca and is located near an upstream portion of the Cuncumén watershed drained by the Rio Los Pelambres (Pelambres River).

In addition to the natural ARD from MLP, a set of ARD was synthesized in the laboratory by mixing the natural ARD with various proportions of metal solutions to

**Table 1.** Measured in situ values of certain water quality parameters at Hydrologic Node 5

Parameter	Sample 1	Sample 2
Sampling time	15:55	16:10
Turbidity (NTU)	6.0	6.7
Dissolved oxygen (mg/L)	8.51	8.01
Eh (mV)	293	291
pH	5.7	5.7
Conductivity ( $\mu\text{S}/\text{cm}$ )	654	648

Notes: sampling date: 12/02/2003; altitude of sampling point: 2919 m above sea level; air temperature: 18°C; water temperature: 10°C; atmospheric pressure: 721 HPa (0.712 atm); the calculated DO saturation at the elevation, pressure, and water temperature is 7.999 mg/L

simulate the types of ARD that may conceivably occur in the future at this location.

Hydrologic and geochemical studies have indicated that all ARDs generated from the mine area will discharge through a hydrologic node, designated as Node 5 on the Pelambres River. All points located upstream of Node 5 are affected by present-day mining activities. Thus, the water quality at Node 5 on the Pelambres River indicates the present quality of the ARD originating from MLP. Geochemical mixing models coupled with hydrologic modeling have been used to predict the water chemistry at Node 5 for two different periods of time, during the operation of the mine (years 2016 and 2031) and after the abandonment of the mine (unpublished internal reports).

Figure 1 (A-C) shows certain chemical characteristics of ARD, as historically observed, at hydrologic Node

5. These data show that the ARD water in general is oxic ( $\text{DO} > 7 \text{ mg/L}$ ). The occasional low DO concentrations under certain situations may be due to low flows during dry seasons. In general, the pH is mildly acidic, varying between 4 and 7. The long-term average concentrations of Cu, Fe, and  $\text{SO}_4^{2-}$  are  $\approx 6 \text{ mg/L}$ ,  $1.5 \text{ mg/L}$ , and  $500 \text{ mg/L}$ , respectively.

For the present investigation, 200 L of water was collected from Node 5 and designated as ARD<sub>p</sub> (acid rock drainage under present condition). During collection of the ARD<sub>p</sub>, turbidity, DO, Eh, pH, and conductivity were measured in the field (Tab. 1). Concentrations of major cations and trace metals were determined in the laboratory by an atomic absorption spectrophotometer. Hot peroxide acidity (pH end point 8.3) and alkalinity (pH end point 4.2) were determined by volumetric titration methods (ASTM 1986). The anions were determined by gravimetric methods. The results are presented in Tab. 2.

The present ARD chemistry shows that it is fully saturated with DO and net acidic (acidity – alkalinity =  $22.8 \text{ mg/L CaCO}_3$  equivalent), with a pH = 5.5 – 5.7. Due to the riffing of water flowing from a high elevation over a steep gradient, the water is naturally aerated. As a result, the DO of the water is slightly above the saturation value at this elevation and atmospheric pressure (see note with Tab. 1). Calcium is the most dominant alkaline earth metal in the dissolved state followed by magnesium and aluminum. Sodium is the most dominant dissolved alkaline metal followed by potassium. The Fe and Mn concentrations are low. The principal base metal is copper and the minor is zinc.

A series of synthetic ARD waters was prepared in the laboratory by mixing appropriate proportions of

**Table 2.** Concentrations of major cations, anions, and metals (in mg/L) in ARD from Hydrologic Node 5, as determined in the laboratory, along with pH, temperature, dissolved oxygen (DO) (mg/L), total suspended solids (TSS) (mg/L), and acidity and alkalinity (mg/L as  $\text{CaCO}_3$ )

Major cations	Ca	Mg	Na	K	Al	Si	Preservative
	90.89	6.24	14.28	5.23	2.69	9.11	$\text{HNO}_3$
	102.3	6.5	13.8	5.15	2.64	9.46	HCl
Total metals	Mn	Fe	Cu	Zn	Pb	Hg	
	0.61	0.27	8.40	0.44	<0.03	<0.001	$\text{HNO}_3$
	0.57	0.28	8.45	0.43	<0.03	<0.001	HCl
Dissolved metals	Mn	Fe	Cu	Zn	Pb	Hg	
	0.58	0.11	8.28	0.43	<0.03	<0.001	No
Major anions	$\text{SO}_4$	Cl	$\text{NO}_3$	$\text{HCO}_3$	$\text{CO}_3$		
	404	65.9	<1.50	12.2	0.0		No
Other parameters	pH/ T	DO	TDS	Alkalinity	TSS	Acidity	
	5.47/ 17.3°C	7.5	629	9.6	14	32.4	No

**Table 3.** Compositions of synthetic ARDs predicted under operational and abandonment periods of MLP; Eh is in mV, acidity (acid.) and alkalinity (alk.) are in mg/L (as CaCO<sub>3</sub>), dissolved oxygen (DO) is in mg/L, and metal concentrations are in mg/L and mmol/L (Ca, Mg, Na, and K) or  $\mu$ mol/L (other metals)

	ARD <sub>O</sub> (A)	ARD <sub>O</sub> (B)	ARD <sub>A</sub>	ARD <sub>A</sub> -Al	ARD <sub>A</sub> (II)	ARD <sub>A</sub> -Al	ARD <sub>A</sub> -Fe	ARD <sub>A</sub> -Mn
<b>pH</b>	6.02	5.32	4.08	3.08	4.18	3.14	3.01	3.01
<b>Eh</b>	-42.3	-73.5	-148.9	-154.5	-132	-207	-216	-212
<b>Acid</b>	32.8	51.0	74.9	86.6	46.8	125.7	90.7	97.1
<b>Alk.</b>	6.8	3.8	0	0	0	0	0	0
<b>DO</b>	8.13	8.01	8.37	8.40	7.94	8.17	8.18	8.20
<b>Cu</b>	2.01, 31.7	2.55, 40.1	8.08, 127	7.97, 125	10.52, 166	10.84, 170	8.25, 130	8.25, 130
<b>Zn</b>	0.76, 11.6	0.68, 10.4	1.24, 19.0	1.27, 19.4	1.94, 30	1.97, 30.1	1.20, 18.4	1.21, 18.5
<b>Ca</b>	147.05, 3.7	145.4, 4.0	144.3, 3.6	146.9, 3.7	155.4, 3.9	159.2, 4.0	147.7, 3.7	148.3, 3.7
<b>Mg</b>	24.65, 1.1	25.11, 1.0	24.96, 1.0	24.96, 1.0	29.84, 1.23	28.82, 1.19	25.3, 1.0	25.32, 1.0
<b>Na</b>	58.8, 2.5	64.0, 2.8	61.5, 2.8	73.9, 3.3	58.9, 2.6	58.0, 2.5	79.7, 3.6	60.3, 2.7
<b>K</b>	32.54, 0.83	30.72, 0.79	29.86, 0.76	29.14, 0.75	32.01, 0.82	32.44, 0.83	29.55, 0.76	31.04, 0.79
<b>Fe</b>	0.04, 0.72	0.03, 0.5	<0.03, <0.5	<0.03, <0.5	<0.05, <0.90	<0.05, <0.90	15.37, 96	<0.03, <0.5
<b>Mn</b>	0.41, 7.5	0.38, 6.9	0.39, 7.1	0.41, 7.5	0.42, 7.6	0.42, 7.6	0.40, 7.3	2.83, 51.5
<b>Al</b>	<0.50, <18.5	<0.50, <18.5	<0.50, <18.5	6.08, 225	<0.50, <18.5	5.71, 212	<0.50, 18.5	<0.50, 18.5

Source	Sample	MnO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	MgO
Tunga Sur, Illapel	A-1	0.02	1.59	0.63	5.52	51.43	0.71
	A-2	0.02	1.59	0.63	5.52	51.52	0.70
Los Vilos	B-1	0.14	7.82	4.03	13.84	47.35	0.83
	B-2	0.14	7.75	4.06	13.69	47.39	0.83
Mina Talcaruca, Coquimbo	C-1	0.01	2.68	0.74	5.03	51.14	0.53
	C-2	0.01	2.65	0.71	4.94	50.87	0.56

**Table 4.** Contents of major oxides (weight percentages) of six limestone samples

soluble salts of Na, K, Ca, Mg, Al, Fe (III), Cu, and Zn with ARD<sub>p</sub>. This set of synthetic ARD water duplicates the characteristics of the ARD that are predicted by geochemical mixing models for future periods of operation and after the abandonment of the mine. These are designated as ARD<sub>O</sub>(A), ARD<sub>O</sub>(B), and ARD<sub>A</sub>, respectively. In this designation, the subscripts “O” and “A” respectively imply operation (e.g. year

2016 and 2031) and abandonment periods. In addition, another set of ARD water was synthesized from ARD<sub>A</sub> to determine the effects of increasing Fe, Al, and Mn on rates of alkalinity generation and limestone dissolution. These ARD waters are designated as ARD<sub>A</sub>-Fe, ARD<sub>A</sub>-Al, and ARD<sub>A</sub>-Mn, respectively. These ARD compositions capture the plausible characteristics of the future ARD, predicted from geochemical and hydrologic mixing models. The compositions of the synthetic ARD waters are presented in Tab. 3.

**Table 5.** Moisture content and percent of CaCO<sub>3</sub> equivalent of three limestone samples from three different sources

Sample	Moisture Content (%)	CaCO <sub>3</sub> Equivalent (%)
A-1	0.1	90.5
A-2	0.2	93.9
A-3		97.2
B-1	0.1	84.8
B-2	0.3	86.6
B-3		82.5
C-1	0.2	93.6
C-2	0.1	94.6
C-3		90.1

#### Limestone

Limestone samples from three different sources were analyzed for their major element compositions (Tab. 4). Since the alkalinity generation potential of a limestone is directly proportional to its purity (in terms of CaCO<sub>3</sub>), limestone A was used in the experiments described below. Furthermore, the CaCO<sub>3</sub> equivalent of the limestone samples was determined according to ASTM Method C25-99-33 (ASTM 1999). These values indicate the stoichiometric capacities of the limestones for acid neutralization (Tab. 5) and do not include MgCO<sub>3</sub> as contributing toward total CaCO<sub>3</sub>.

Density of limestone A was measured in the laboratory. The average of 10 determinations yields a density value of 2.59 g/cm<sup>3</sup>. Note that the chemical analysis indicates that the weight fraction of CaCO<sub>3</sub> in limestone A ( $X_{\text{CaCO}_3}$ ) is 0.92 (= 51.5 wt % CaO × 100 g/mol CaCO<sub>3</sub> / 56 g/mol CaO). Of this, 93.87% ( $Y_{\text{CaCO}_3}$ ) is available for effective neutralization of an acid solution (Tab. 5).

## Experimental Methods

The general experimental set up is shown in Figure 2. Four kg of limestone with an average grain size diameter of 2 cm was loaded into the 4 L tank. The limestone column was thoroughly washed with deionized water. Subsequently, 3 L of ARD water was loaded into the column. Four columns were run in tandem. For each type of ARD, one column was run oxidic, by keeping both ports on top of the column open; the other column, designated in this experiment as anoxic (despite the initial DO concentrations), was not open to the atmosphere; nitrogen gas was bubbled through the water column standing above the limestone bed to prevent leakage of atmospheric oxygen into the system. The ARD water was circulated through the columns at a constant flow rate of 0.1 L/min; the flow rate was calibrated using deionized

water before the experiments started. Water samples were collected through the sampling port at specified time intervals. Immediately after collection of a sample, DO, pH, and Eh, were measured. The sample was filtered through a 0.45µm filter paper and alkalinity was determined. Acidity in certain samples was measured using ASTM method D 1067-82 E (ASTM 1986). An aliquot of sample (with no acid added) was decanted after 6 hours of settling in a beaker and analyzed for dissolved Ca. Another aliquot was preserved with 0.2N HNO<sub>3</sub> at pH 2 and analyzed for total metal concentrations. Frequency of sample collection was as low as 30 minutes during the first hour of the experiments and gradually increased as time lapsed. This experimental set up allowed us to determine the change in initial chemistry of an ARD water as a function of its detention time as it continued to react with a fixed initial mass of limestone. The initial hydraulic detention time and ratio of water to limestone volumes used in the experiments were calculated as follows.

For the rectangular column with a square base ( $B$ ) and height ( $h$ ), the bulk volume of limestone ( $V_B$ ), and the volumes of the water columns above ( $V_{wa}$ ) and below ( $V_{wb}$ ) the limestone column were calculated. Subsequently, the bulk density of limestone was calculated as:

$$\rho_b = 1 - \frac{M}{V_B} \quad (1)$$

Porosity ( $\Phi$ ) of the limestone bed was calculated as:

$$\Phi = 1 - \frac{\rho_b}{\rho_s} \quad (2)$$

where  $\rho_s$  is the density of the limestone as measured. The void volume was then calculated as:

$$V_v = \Phi V_B \quad (3)$$

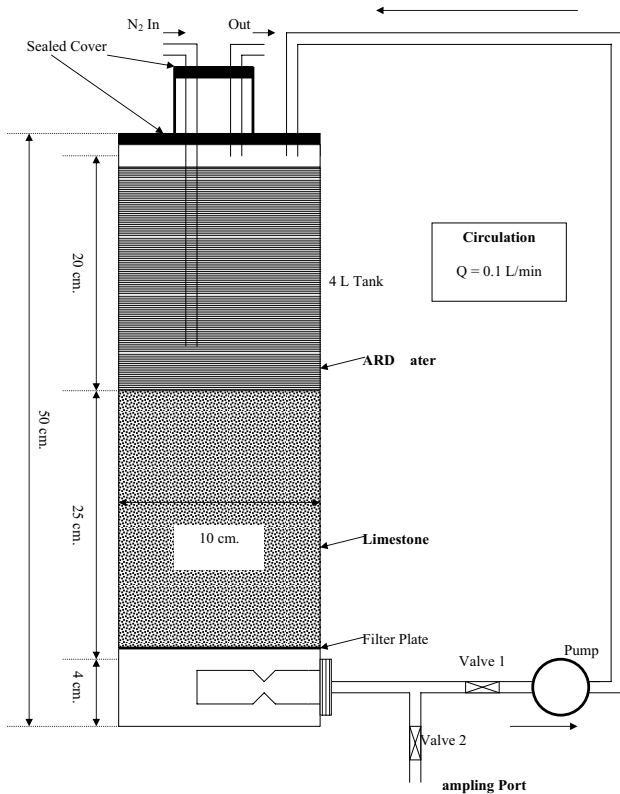
Detention time for one hydraulic cycle is then given as:

$$t_d = \frac{V_w^T}{Q} \quad (4)$$

where  $V_w^T$  is the total volume of water ( $V_w^T = V_v + V_{wa} + V_{wb}$ ) and  $Q$  is the flow rate. The water: rock ( $WR_T$ ) is calculated from Equation (5).

$$WR_T = \Phi (1 - \Phi)^{-1} \quad (5)$$

For the dimensions shown in Figure 2, with 4 kg of limestone with  $\rho_s = 2.59 \text{ g/cm}^3$ , average  $\rho_b$  and  $\Phi$



**Figure 2.** Schematic of the experimental set-up for laboratory investigation of the ARD-LD interactions



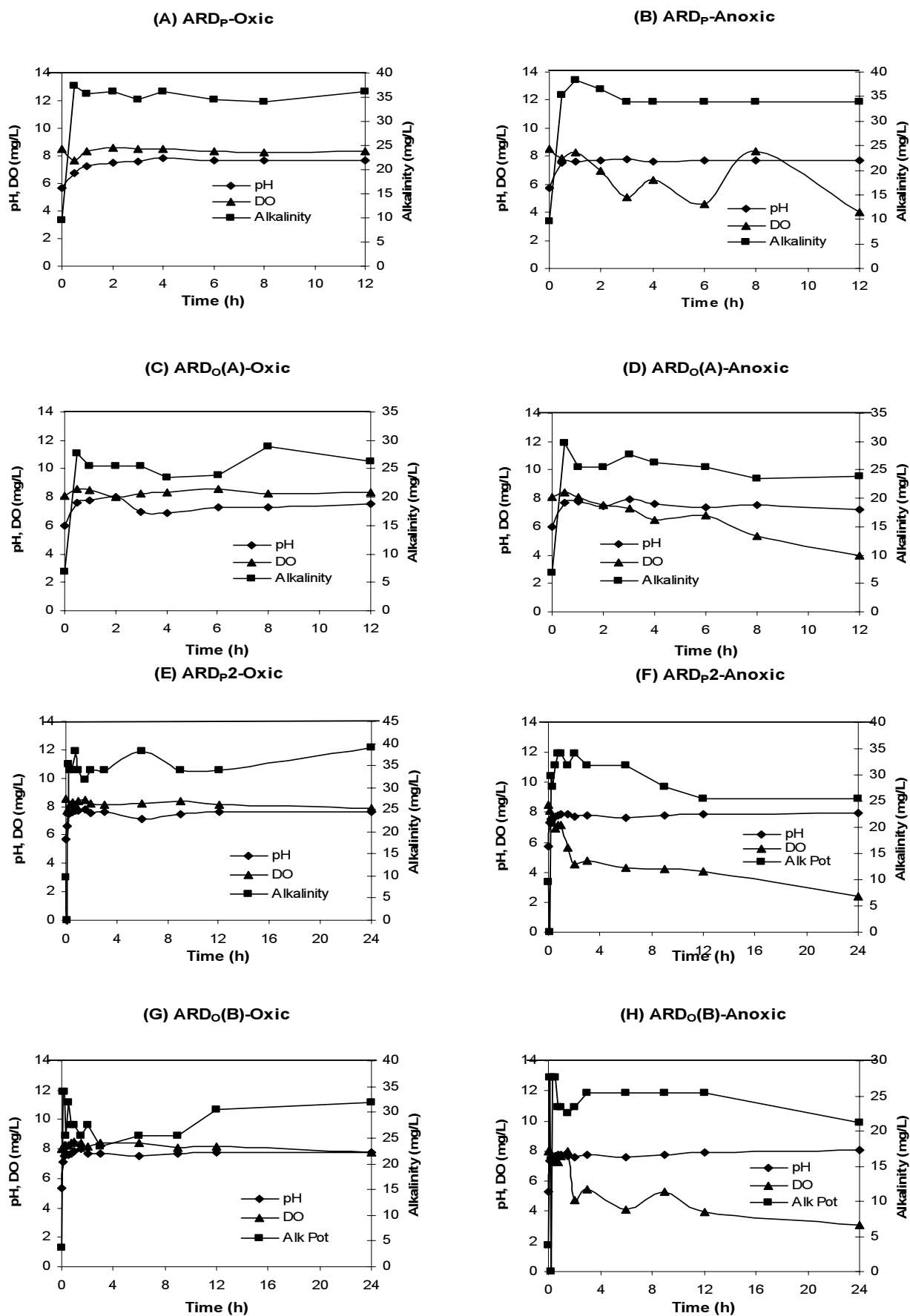


Figure 3 A–H. Effluent pH, DO, and alkalinity over time for all of the experiments presented in this study

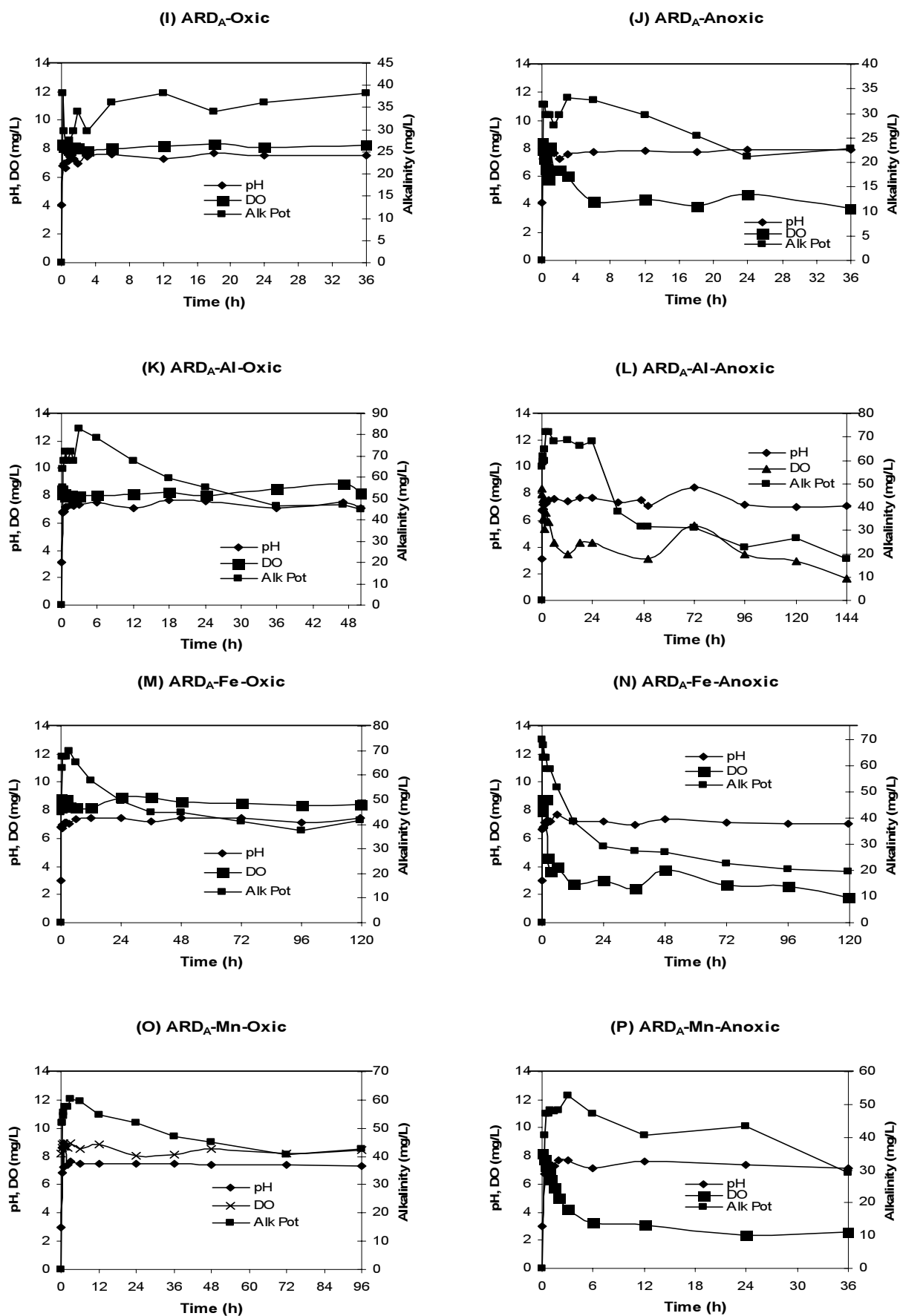
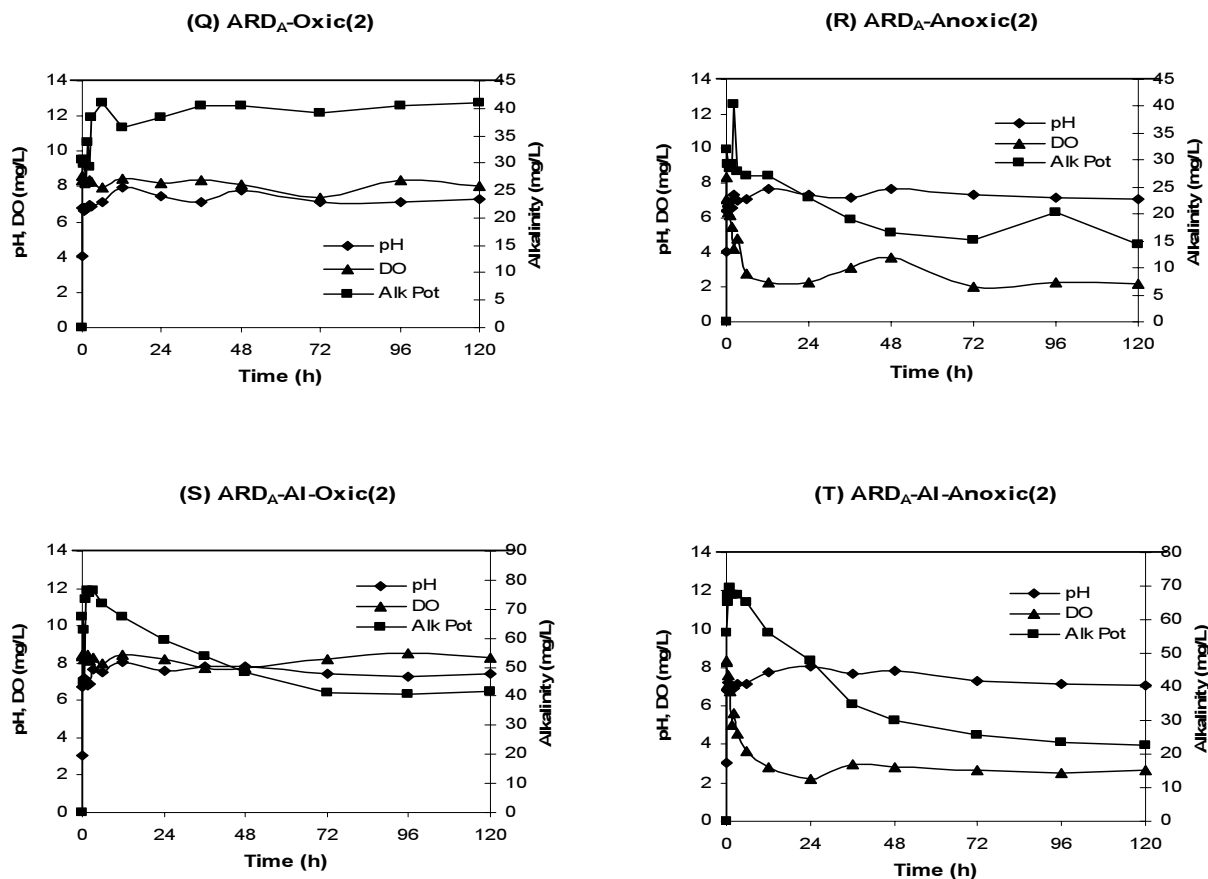


Figure 3 I-P. Effluent pH, DO, and alkalinity over time for all of the experiments presented in this study



**Figure 3 Q–T.** Effluent pH, DO, and alkalinity over time for all of the experiments presented in this study

are  $1.60 \text{ g/cm}^3$  and  $0.38$ , and  $t_d$  and  $WR_r$  are  $31.6 \text{ min}$  and  $0.62$ , respectively. The system is configured such that at any instant of reaction, the volume of limestone is greater than the volume of the ARD that is reacting with it, i.e. it is a rock-dominated system ( $WR_r > 0.5$ ).

### Experimental Results

For most compositions, the effluents attained  $\text{pH} > 7$  within 60 minutes ( $\approx 2 t_d$ ) of reaction between the limestone and the ARD water under both oxic and anoxic conditions (Figures 3 A–T). For  $ARD_A(\text{II})$ ,  $\text{pH} > 7$  was attained after 3 h of reaction under both oxic and anoxic conditions. For  $ARD_A\text{-Fe}$  (oxic), at least 90 ( $\approx 3 t_d$ ) minutes of reaction time was necessary for the pH to rise above 7.

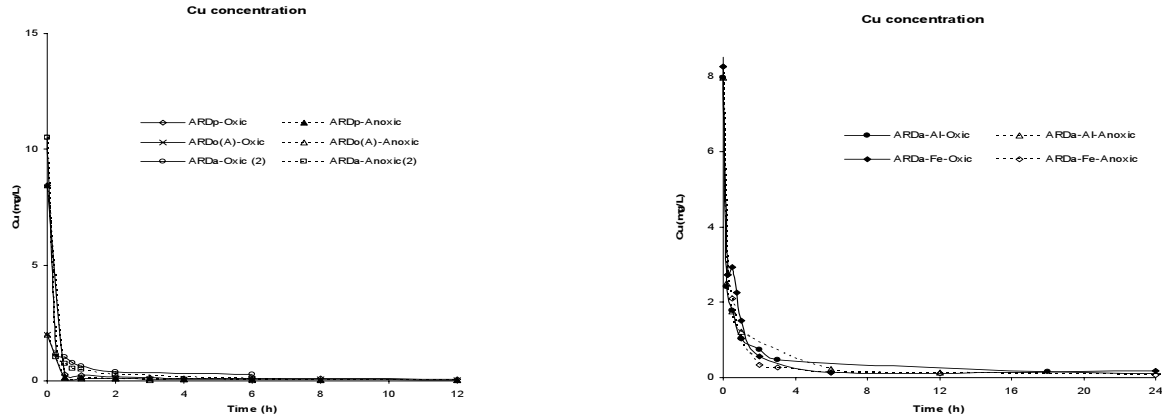
For all  $ARD_P$ ,  $ARD_O$ , and  $ARD_A$  compositions, the alkalinity of the effluents rapidly rose for the first 30 to 60 minutes of interaction of the ARD waters with the limestone, reached a maximum and then dropped and slowly attained a quasi-steady state value (Figure 3 A–L). In other words, the rate of alkalinity generation was extremely fast initially and then slowly declined with time. For most of the  $ARD_A$  (Al, Fe, Mn), the rise in

alkalinity continued for up to 3 hours (Figure 3 M–T). For two anoxic solutions, namely  $ARD_A\text{-Al}(2)$  and  $ARD_A\text{-Fe}$ , the period of increasing alkalinity was considerably shorter (Figure 3 P and R). The principal differences between the oxic and anoxic conditions was that (1) the interim and maximum values of alkalinity under oxic conditions was always higher than under anoxic conditions; and (2) the decline in alkalinity over time for all  $ARD_A$  types was more pronounced under anoxic conditions.

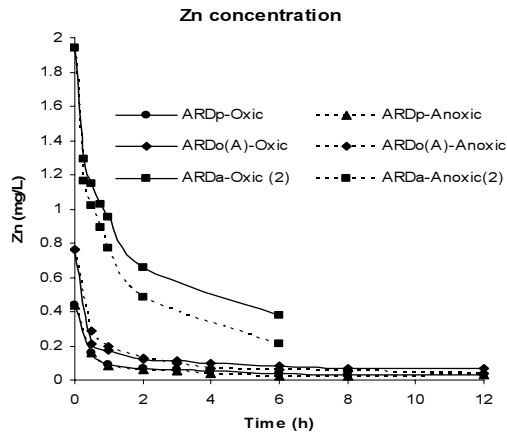
Soon after alkalinity was imparted to the ARD water by limestone dissolution, the acidity of the effluent became negative. This implies that acidity had been neutralized and that the solution had become net alkaline; computed net alkalinity (alkalinity - acidity) was less than the measured alkalinity value (pH end point 4.2).

The Ca concentrations in the effluents rose rapidly for the first 60 minutes; subsequently, the Ca concentrations in the effluents remain nearly constant (not shown). In general, the same trend was observed under both oxic and anoxic conditions and the pattern of variation of Ca concentration in the effluents followed that of alkalinity production, but was less complex.





**Figure 4.** Total Cu concentrations in the effluents for the experiments presented in this study



**Figure 5.** Total Zn concentrations in the effluents for the experiments presented in this study

Figure 4 (A-B) shows the concentration of Cu in the effluents as a function of time. The Cu concentration in the effluents fell rapidly [within the first 60 minutes ( $\approx 2 t_d$ )] after the ARD with variable initial Cu concentrations interacted with the limestone. For ARD<sub>p</sub>, ARD<sub>O</sub>, and ARD<sub>A</sub>, Cu concentration in the effluents dropped to less than 10% of the initial concentration within 30 minutes of reaction but for the ARD<sub>A</sub>-metal compositions, the drop in Cu concentration in the effluents during the same period was 25% of the initial concentration.

Figure 5 (A-B) shows the concentration of Zn in the effluents as a function of time. For the influent (ARD<sub>A</sub>) with relatively high Zn concentration, the decrease in Zn concentration in the effluent with time was gradual. For the effluents with relatively low Zn concentrations, the drop in Zn concentration was rapid. However, in both cases, more than 50% of the Zn was retained in the column within the first 60 minutes of reaction.

The Al and Fe concentrations in all of the effluents fell sharply as pH increased during the first 60 minutes.

The observed peak and decline of alkalinity corresponds with rapid decline in metals concentration. Hydrolysis reactions written with bicarbonate as a reactant and CO<sub>2</sub> as a product can account for declines in the concentrations of metals and alkalinity:

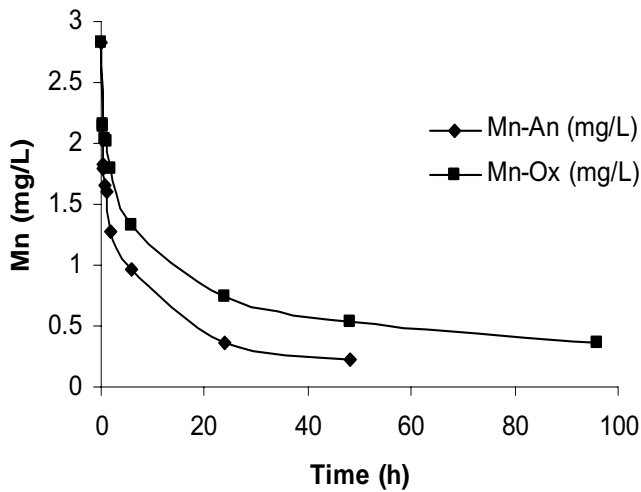


Note that hot acidity, computed net alkalinity, and Ca concentrations will not be affected by the hydrolysis reactions as written. Equal amounts of acidity and alkalinity are reacted; the change in net alkalinity is zero. For experimental conditions, the alkalinity will decrease if the limestone dissolution rate (alkalinity production) is slower than the rate of hydrolysis (alkalinity consumption). After the metals have precipitated, continued limestone dissolution will produce net-alkaline effluent. Figure 6 shows the Mn concentration in the effluents as it slowly decreased over time.

For all ARD<sub>p</sub> and ARD<sub>O</sub> compositions with initial low acidic pH and net acidity, the rise in pH above 7 occurred within 30 to 60 minutes ( $\approx 1 t_d - 2 t_d$ ). The alkalinity reached a maximum ( $C_M \approx 34.32 \text{ mg/L CaCO}_3$ ) within 60 minutes ( $\approx 2 t_d$ ).

For ARD<sub>A</sub> compositions, the pH exceeded a value of 7 at times between 45 to 180 minutes of reaction. However, the alkalinity rapidly rose to a maximum ( $C_M \approx 38.48 \text{ mg/L CaCO}_3$ ) within 10 to 15 minutes of reaction. In general, for the ARD<sub>A</sub>-metal (Al, Fe, Mn) compositions with low initial pH and high acidity, the pH exceeded 7 within 45 to 90 minutes, though the alkalinity continued to rise for up to 180 minutes ( $C_M \approx 65.98 \text{ mg/L CaCO}_3$ ).

The decline in alkalinity production with time is possibly due to a combination of factors. The primary



**Figure 6.** Total Mn concentrations in the effluents for the experiments presented in this study

factor is that the rise in pH of the solution slows down the dissolution of limestone. This is evidenced from the temporal pattern of variation of Ca concentrations in the effluents. As the pH rose from acidic to neutral values, alkalinity and Ca concentrations sharply rose in the effluents. As pH stabilized at a value lying between 7.5 and 7.8, limestone dissolution decreased, Ca concentrations in the effluents reached a quasi-steady state condition, and the rate of alkalinity production declined. The other factor is the possible armoring of the limestone with metal oxides and hydroxides. The concentrations of the metals in the effluents indicate that most of the dissolved metals are precipitated in the limestone columns. However, the experimental data presented by Ziemkiewicz et al (1997) indicate that armoring of limestone with metal hydroxides sometimes has a negligible effect on its neutralization capacity.

These observations indicate that for all compositions, a minimum hydraulic detention time of 3 hours was sufficient for effective neutralization and sufficient alkalinity production. This value of detention time is  $\frac{1}{3}$  of the typical value of detention time (15 h) recommended by previous investigators for LD (Hedin and Watzlaf 1994; Hedin et al. 1994).

Metal precipitates, presumably  $\text{Fe}(\text{OH})_3$  and  $\text{Al}(\text{OH})_3$ , were formed in the limestone column as the ARD was neutralized. The only metal that was still carried by the effluents in any significant quantity is Mn. In general, similar trends were observed under both oxic and anoxic conditions. Contrary to expectation, the anoxic effluents carried lesser amounts of metals than the oxic effluents, though this presumably is due to the fact that our water initially contained significant concentrations of DO.

## Discussion

### Rate of alkalinity production

In analyzing the rate constant for alkalinity production, Cravotta and Watzlaf (2002) assumed a first order reaction with steady state condition. Under these conditions,

$$\frac{dC}{dt} = k'(C_M - C_t) \quad (6)$$

where  $C$  is the alkalinity measured as mg/L of  $\text{CaCO}_3$ ,  $C_M$  is the maximum-obtained or steady state value of alkalinity,  $C_t$  is the alkalinity at time,  $t$  and  $k'$  is the reaction rate constant. If the above differential equation holds true, then the functional form of the alkalinity versus time curve will be given by Equation 7.

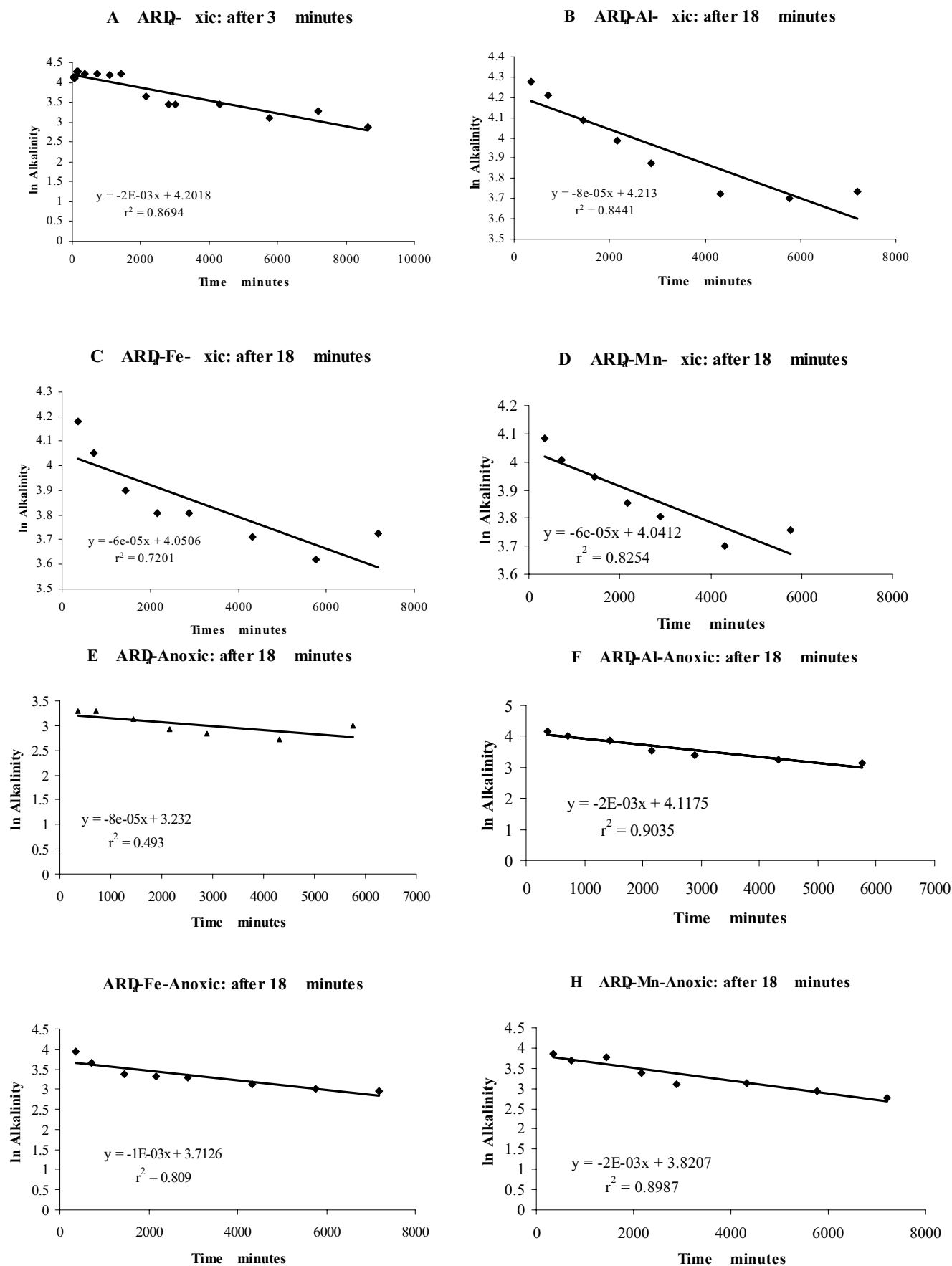
$$\int \frac{dC}{k'(C_M - C_t)} = \int dt \quad (7)$$

The constant of integration is obtained for the condition,  $C_t = C_o$  at  $t = 0$  and the functional form of the alkalinity versus time curve can be expressed as Equation 8.

$$\ln \left( \frac{C_M - C_t}{C_M - C_o} \right) = -k't \quad (8)$$

Thus, if  $\ln (C_M - C_t / C_M - C_o)$  is plotted against  $t$ , the value of  $k'$  can be determined from the best-fit line. Following this procedure, the rate constants were calculated for all of the experimental data sets. There were extreme variations in the values of the rate constants obtained in this way. Furthermore, the coefficients of determinations ( $r^2$ ) in the linear regression method were extremely low. Thus, the data needed reevaluation.

The data show that during the initial stage of reaction, the alkalinity generation rate was fast, giving the alkalinity versus time curves steep slopes. This portion of the curve is nearly linear. For  $\text{ARD}_P$ ,  $\text{ARD}_O$ , and  $\text{ARD}_A$  compositions, this portion extends up to 30 to 60 minutes of reaction. For most of the  $\text{ARD}_A$ -metal compositions, this portion extends up to 180 minutes. This portion of the curve, where there is a linear and steep rise of alkalinity with time, has an order of reaction that is possibly zero. Cravotta (2003) and Cravotta et al. (2004) suggested that second order reactions have faster initial rates than first order reactions, and may be appropriate for some conditions because pH,  $p\text{CO}_2$ , and saturation state with respect to



**Figure 7.** The natural logarithm of effluent alkalinity over time for the experiments presented in this study

calcite affect the rate of limestone dissolution and alkalinity production. Nonetheless, after the initial stage, the alkalinity versus time curve follows a first-order (or pseudo first-order) reaction. For this portion, the reaction rate can be given as Equation 9.

$$\frac{dC}{dt} = -k'C \quad (9)$$

The integrated form of Equation (9) is given by Equation 10.

$$\ln(C) = \ln(C_0) - k't \quad (10)$$

Thus, a plot of  $\ln(C)$  versus  $t$  will yield a straight line with slope  $= k'$ . Figure 7 (A-H) shows the experimental data plots. For  $ARD_A$ -oxic conditions, the rate is  $2 \cdot 10^{-4} \text{ min}^{-1}$  ( $0.012 \text{ h}^{-1}$ ), whereas for  $ARD_A$ -Al, Fe, and Mn, the rate constant varies from  $6 \cdot 10^{-5} \text{ min}^{-1}$  to  $8 \cdot 10^{-5} \text{ min}^{-1}$  with an average of  $7 \cdot 10^{-5} \text{ min}^{-1}$  ( $0.0042 \text{ h}^{-1}$ ). The values of  $k'$  obtained by Cravotta and Watzlaf (2002) for two sets of experimental data are 0.053 and  $0.058 \text{ h}^{-1}$ . This indicates that increases in concentrations of Al, Fe, and Mn in the ARD decrease the rate of decline in alkalinity (concentration). For the anoxic condition, both  $ARD_A$ -Al and  $ARD_A$ -Mn had an identical rate constant,  $k' = 2 \cdot 10^{-4} \text{ min}^{-1}$  ( $0.012 \text{ h}^{-1}$ ), which is an increase from the corresponding oxic conditions. For  $ARD_A$  the rate constant under anoxic condition,  $k' = 8 \cdot 10^{-5} \text{ min}^{-1}$  ( $0.0048 \text{ h}^{-1}$ ), which is a decrease from the corresponding value in oxic conditions. For  $ARD_A$ -Fe, the rate constant under anoxic condition,  $k' = 10^{-1} \text{ min}^{-1}$  ( $6 \text{ h}^{-1}$ ), which is significantly larger than the corresponding rate observed under oxic conditions.

This study shows that the alkalinity concentration trends are complex, both alkalinity production and consumption take place, the ARD chemistry affects these processes, and rates of limestone dissolution need to be determined for the design of a treatment system. The analysis presented above demonstrates that the rate of alkalinity production due to ARD-limestone interactions cannot be easily modeled because of competing limestone dissolution reactions that produce alkalinity and Fe(III) and Al hydrolysis reactions that consume alkalinity. Hence, fitting the alkalinity concentration data that are a function of both production and consumption processes with a first order reaction model of alkalinity production or limestone dissolution may not be valid. The alkalinity versus time plots for this experiment are complex and indicate a transition from the pseudo zero order to pseudo first order rates. The different rates for different ARD compositions but identical limestone demonstrate effects of initial values

for dissolved oxygen, pH, Al, Fe, and Mn on limestone dissolution and acidity neutralization rates.

Rate of limestone dissolution

If limestone dissolution follows a first-order reaction, then the rate equation can be expressed as Equation 11 (Cravotta and Watzlaf 2002):

$$\frac{dM}{dt} = -kM \quad (11)$$

where  $M$  is the mass of limestone and  $k$  is the reaction rate constant. The mass of limestone remaining at any time ( $M_t$ ) for a given mass of original limestone,  $M_0$ , is then given as:

$$\int \frac{1}{M} dM = -k \int dt \quad (12)$$

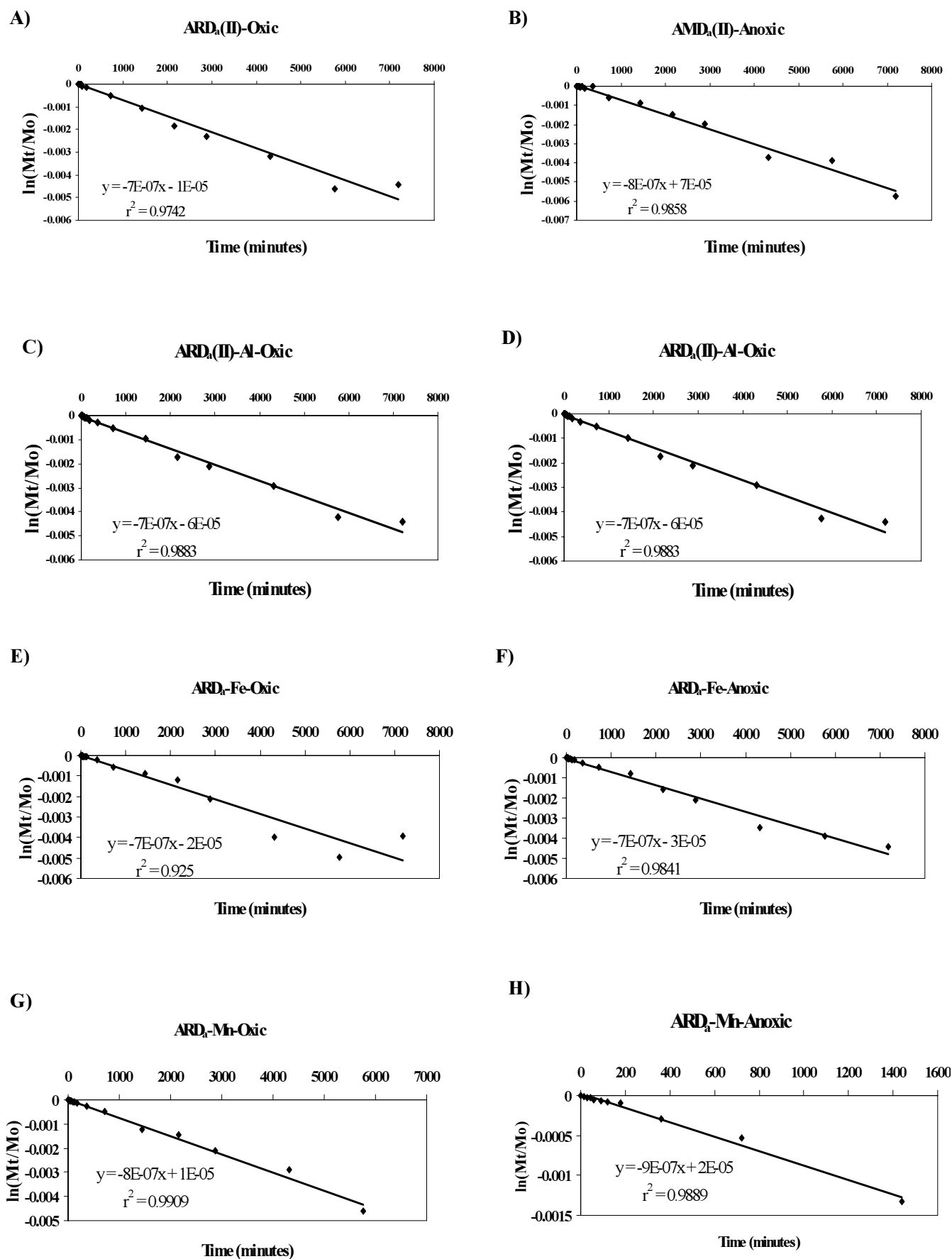
or,

$$M_t = M_0 e^{-kt} \quad (13)$$

Thus, a plot of  $\ln(M_t/M_0)$  versus  $t$  will yield a straight line with slope  $= -k$ . The mass of the remaining limestone was calculated from the experimental data using the following formula

$$M_t = M_0 - Q \cdot \Delta \text{CaCO}_3 \cdot \Delta t \quad (14)$$

where  $Q$  is the average flow rate,  $\Delta \text{CaCO}_3$  is the difference between effluent and influent concentrations of Ca expressed as  $\text{CaCO}_3$ , and  $\Delta t$  is the elapsed time since the start of the experiment. Figure 8 (A-H) shows the plots of  $\ln(M_t/M_0)$  versus  $t$ . The value of the rate constant varies from  $7 \cdot 10^{-7} \text{ min}^{-1}$  to  $9 \cdot 10^{-7} \text{ min}^{-1}$  with an average value of  $k = 0.4205$  per year. This dissolution rate constant is one to two orders of magnitude higher than the values reported by Cravotta and Watzlaf (2002). Note that this high dissolution rate is also exhibited by the anoxic experiments, where  $p\text{CO}_2 < \text{atmospheric } p\text{CO}_2$ ,  $p_{\text{CO}_2}^{\text{atm}}$ , due to purging of the water column by  $\text{N}_2$ .  $p\text{CO}_2 \gg p_{\text{CO}_2}^{\text{atm}}$  in most ALDs, a condition that is believed to facilitate limestone dissolution. The data presented above imply either that alkalinity production is faster under oxic conditions or that hydrolysis processes (which consume alkalinity) are more effective under anoxic conditions. The former is more plausible, and is consistent with Cravotta and Trahan (1999), who argued that  $\text{H}^+$  released by hydrolysis processes under oxic conditions could promote limestone dissolution. However, it is also possible that bubbling nitrogen into the anoxic columns to prevent the water from being exposed to atmospheric oxygen might have had the effect of lowering  $p\text{CO}_2$ .



**Figure 8.** Limestone dissolution rates,  $\ln(M_t/M_0)$  over time (see text for details)

## Implications for the design of a limestone drain

There are two approaches that can be taken in the design of a LD for ARD mitigation and abatement. In the first approach, equilibrium chemistry is combined with hydraulic considerations. In the second approach, introduced by Cravotta and Watzlaf (2002), the kinetics of limestone dissolution is the primary consideration. In both these approaches, the fundamental parameter that is calculated is the mass of the limestone required for a certain design period or design life of a LD.

In the first approach, the mass of limestone can be calculated using Equation (15):

$$M = \left( \frac{Q\rho_b t_d}{V_v} \right) + \left( \frac{QC_m T}{X_{\text{CaCO}_3} Y_{\text{CaCO}_3}} \right) \quad (15)$$

where  $C'$  = designed effluent alkalinity;  $T$  = design life of the drain and the other parameters are as defined before. Equation (15) is slightly modified from the one given by Hedin and Watzlaf (1994), who did not consider the  $Y_{\text{CaCO}_3}$  factor.

The first part of the right hand side of Equation (15) provides the amount of limestone necessary to meet a certain detention time for a given flow rate. This term arises simply from hydraulic considerations. The second part of the right hand side of Equation (15) arises from the chemistry, and reflects the amount of limestone that will react with a given ARD and hence will be dissolved by it over a period of time,  $T$ , to produce an effluent alkalinity,  $C$ , throughout the life of the system.

Cravotta and Watzlaf (2002) argued that there are several limitations with Equation (15). They argued that the second term on the right hand side of Equation (15) assumes linear decay of limestone due to dissolution (i.e. constant mass flux of  $\text{CaCO}_3$ ) and that this assumption is not valid, according to their short-term cubitainer tests and long-term field observations. Similarly, Equation 15 assumes that the effluent alkalinity will be at a constant maximum over the effective lifetime of the drain (longevity), after which the remaining limestone mass would be less than that required to produce the specified detention time and alkalinity.

Chemical considerations suggest that the influent acidity for  $C$  should be used in Equation 15. Use of influent acidity for  $C$  implies loading of acidity over the design life of the drain. In other words, it gives the  $\text{CaCO}_3$  equivalent of acid that will be treated over a period of  $T$ . If influent acidity for  $C$  is used in Equation 15, then the assumption is that limestone dissolution

and acid neutralization occurs in stoichiometric proportions (i.e. 1 mg/L acidity as  $\text{CaCO}_3$  will be neutralized by dissolution of 1 mg/L of pure limestone). However, such a stoichiometric relation may not really hold true due to kinetically controlled dissolution reactions and because the actual amount of required limestone may far exceed the quantity obtained from purely stoichiometric calculation. Furthermore, as discussed above, the influent acidity may vary substantially over a long period of time. For this reason, the design effluent alkalinity for  $C$  in Equation 15 is used (e.g. see Zipper and Jage 2001). In this case, the term  $Q_C$  gives the rate of alkalinity generation from the limestone bed. The usage of effluent alkalinity for  $C$  in Equation 15 implies that the rate of alkalinity generation is directly proportional to the amount of limestone dissolved. This is valid for initial conditions with near-neutral pH. However, Cravotta (2003) and Cravotta et al (2004) explained that the stoichiometry of alkalinity produced by limestone dissolution can potentially vary ( $\text{HCO}_3^-$  ranges from 0 to 2 mol per mol  $\text{CaCO}_3$  compared to constant 1 mole Ca per mol  $\text{CaCO}_3$ ) and proposed that Ca be used instead of alkalinity to estimate the limestone dissolution rate, particularly for initial conditions with low pH and no measurable alkalinity. Finally, in order to correct for limestone impurity and actual available  $\text{CaCO}_3$  for neutralization reaction, the factor  $X_{\text{CaCO}_3} Y_{\text{CaCO}_3}$  is necessary.

Hydraulic detention time,  $t_d$ , can be obtained from an analysis of the alkalinity generation rate obtained from an experimental investigation, such as those presented above. The pattern of alkalinity production noted above suggests that a short residence time on the order of 3 h may be sufficient for alkalinity generation and neutralization of acidic pH to an above-neutral value. However, since hydraulic detention time is a critical design parameter, further exploration is necessary.

Zipper and Jage (2001) developed an empirical equation to calculate the hydraulic residence time, using Equation (16):

$$\log(t_d) = \frac{C' - 0.76[\text{Fe}] - 0.23\text{NMnA} + 58.02}{99.3} \quad (16)$$

where  $C'$  = design effluent alkalinity, NMnA = non-Mn acidity =  $C_a - 1.818[\text{Mn}]$ ,  $[\text{Fe}]$  = concentration of Fe in the influent (mg/L),  $[\text{Mn}]$  = concentration of Mn in the influent (mg/L); and  $C_a$  = influent acidity. Equation (16) is based on data collected in the field from various SAPS in the northeastern part of the USA (Jage et al. 2001). Tab. 6 provides the residence times calculated with Equation (16) for the various ARD compositions.



These calculations indicate detention times (6-14 hours) that are higher than indicated by our experiments.

The experimental data on alkalinity generation can also be used to calculate the minimum detention time necessary to achieve a desired effluent alkalinity. If Equation (8) is a valid functional form of alkalinity production, then alkalinity  $C_t$  at time  $t$  is given by Equation 17.

$$C_t = C_M - \left[ (C_M - C_0) e^{-k' t} \right] \quad (17)$$

For complete neutralization, the effluent alkalinity must exceed acidity ( $C_M > C_t$ ). Assuming the maximum alkalinity is greater than or equal to the acidity, substituting influent acidity ( $C_a$ ) for  $C_t$  in Equation (17) yields Equation (18), which gives the minimum (optimum) detention time.

$$t_d = \frac{\ln \left[ \frac{C_M - C_0}{C_M - C_a} \right]}{k'} \quad (18)$$

The experimental data presented above indicate that for various influent acidities, the quasi-steady state maximum effluent alkalinity is on the order of 66 mg/L  $\text{CaCO}_3$ . If this value is taken as the design effluent alkalinity and the rate constant  $k$  is  $0.058 \text{ h}^{-1}$ , then the calculated hydraulic detention time is 24.43 hours.

In the second approach of the design (Cravotta and Watzlaf 2002), the mass of limestone required was calculated from Equation 19:

$$M_0 = e^{kT} \cdot \left[ Q t_d \rho_s \frac{(1 - \Phi)}{\Phi} \right] \quad (19)$$

in which the terms are as defined above. In this case, a minimum value of the detention time is either assumed or calculated with the aid of Equation 18.

The application of Equation 19 requires a very good estimate of the limestone dissolution rate. As noted above, the short-term dissolution rates obtained in this study are significantly higher than the long-term dissolution rates obtained from field measurements on LDs that have been operating for some years. The implication of this is that if LDs are designed on the basis of short-term dissolution rates, then the calculated mass of limestone will be considerably more than that calculated on the basis of long-term dissolution rates. As noted with the case of alkalinity production,

which is a consequence of limestone dissolution, the rate of the reaction is indeed very fast during the initial stage ( $< 3$  hours) but slows down as time progresses.

## Conclusions and Recommendations

Limestone with high calcium to magnesium ratio ( $\text{Ca/Mg} \approx 85.5 - 87.7$ ) or a high weight fraction of  $\text{CaCO}_3$  ( $X_{\text{CaCO}_3} \approx 92\%$ ) and  $\text{CaCO}_3$  equivalent ( $Y_{\text{CaCO}_3} \approx 90.5 - 97.2$ ) is an effective agent for neutralization of ARD with varied compositions in terms of pH, acidity, and dissolved metals. Accurate information on the rate of limestone dissolution can only be obtained from long-term experiments. The short-term experiments presented in this study provide only the initial dissolution rate. But this study indicates that the rate of alkalinity generation is complex and cannot simply be modeled as a first order reaction. It appears that during the initial stage of interaction between an ARD water and limestone, the reaction is zero order with a rapid linear rise in alkalinity followed by a gradual decline in the rate of alkalinity production; the pH of the ARD rapidly rises to above-neutral values, causing a slowdown of limestone dissolution. During this later stage, the reaction is pseudo-first order. The slowdown of limestone dissolution with time is evidenced from the observed concentration of Ca in the effluent as a function of time. The Ca concentration in the effluent rapidly increases during the initial stages of the reaction and then attains a quasi steady-state value.

From these conclusions, an alternative design procedure is recommended. The detention time should be calculated based on the kinetics of long-term alkalinity production (Equation 18), along with the hydraulic requirement of the volume of limestone needed to satisfy this detention time for a given flow rate. This constitutes the bulk of the limestone requirement.

**Table 6.** Calculated detention time in hours (Equation 16) for various influent compositions used in this study

Initial solution	Oxic Conditions	Anoxic Conditions
ARD <sub>P</sub>	7.71	7.87
ARD <sub>O</sub> -A	6.32	6.45
ARD <sub>O</sub> -B	6.46	6.46
ARD <sub>A</sub>	6.61	5.42
ARD <sub>A</sub> (II)	7.75	7.68
ARD <sub>A</sub> -Al	14.31	12.24
ARD <sub>A</sub> (II)-Al	11.61	9.93
ARD <sub>A</sub> -Fe	6.14	9.13
ARD <sub>A</sub> -Mn	9.51	7.97

In order to compensate for limestone dissolution, an additional amount based on equilibrium chemical consideration must be added to the previous amount. In this case, a long design life is used to account for the uncertainties in limestone dissolution rate. A long-term monitoring program is required to assess the limestone dissolution rate, which after certain years of operation will yield a better estimate of the longevity of the limestone drain. Tab. 7 provides the results of such calculations for the ARD from MLP. In the actual field condition, where a LD is continually flushed with untreated ARD waters, limestone dissolution takes place in a continuous fashion. This loss of limestone over a period of time (design life) and availability of fresh limestone for effective reaction is calculated using Equation 15. Thus, even though our experiments were conducted by circulation of a fixed initial volume of water, the process can be easily extended to a field situation where the additional mass of limestone is calculated from the effluent alkalinity that is expected for the design life of the system, flow rate, detention time, porosity,  $X_{\text{CaCO}_3}$ , and  $Y_{\text{CaCO}_3}$ .

The experimental data indicate that the acid neutralization takes place within a short period ( $\approx 1$  h) for ARD compositions without substantial dissolved Al, Fe, and Mn. However, as the concentrations of Al, Fe, or Mn increase in the influent, then this time is increased ( $\approx 3$  h).

It is important to emphasize that the quality of the water investigated in this study differs from the high levels of Fe (II), elevated partial pressure of  $\text{CO}_2$ , and low DO usually observed in coal mine drainage ALDs, where the principal purpose of the ALD is to add high concentrations of alkalinity to the mine water. The alkalinity produced by the ARD-ALD interaction neutralizes the acidity generated during iron precipitation outside of the ALD in a sedimentation basin. However, for the type of water quality used in this study, most of the dissolved Fe(III) and Al were retained in the limestone column; both the OLDs and ALDs neutralized the acidity of the ARD but also retained most of the Fe(III) and Al as precipitates within the column. Given the initial concentration of DO, there seems to be no special advantage to an ALD, which is more expensive to construct than an OLD. Retention of the metals within the column suggests that the sedimentation basin could be made smaller, since the mass-loading rate of the metals precipitating in it will be substantially lower after the ARD passes through the LD. Finally, formation of metal precipitates may decrease the long-term performance of an OLD. However, the combination of a highly porous LD, high flow rate, and short detention time can alleviate this problem. The porosity of the LD should not be increased to the point that the system becomes

**Table 7.** Limestone mass and volume requirements calculated for a limestone drain for mitigation and abatement of acid rock drainage at Minera Los Pelambres, Chile

Design Parameters
Inflow rate: $Q = 311 \text{ L/s}$
$\text{CaCO}_3$ content of limestone <sub>3</sub> = 92%
% of $\text{CaCO}_3$ available for neutralization = 94%
Density of limestone: $\rho_{\text{ls}} = 2.59 \text{ g cm}^{-3}$
Percentage of void in the OLD: $\Phi = 0.40$
Alkalinity generation rate: $k' = 0.058 \text{ h}^{-1}$
Design Criteria
Design Life: $T = 100$ years
Influent Acidity: $C_i = 50 \text{ mg/L}$
Effluent Alkalinity: $C = 66 \text{ mg/L}$
Influent Alkalinity: $C_0 = 0$
Results
Hydraulic detention time, $t_d = 24.43$ hours
Limestone required: $2.5 \times 10^8 \text{ kg} = 252,303 \text{ t}$
Volume of limestone $\approx 97,414 \text{ m}^3$

fluid-dominated; it must remain as a rock-dominated system.

### Acknowledgements

This study was conducted under a contract with the Minera Los Pelambres mining company of Chile. The authors thank Mr. Gustavo Pössel M of Minera Los Pelambres, Santiago, Mr. Daniel Tolchinsky of Gestión Ambiental Consultores, Santiago for support, and Mr. Raul Thiers S. and Mr. Jorge Castillo G. of Aqua Calidad Del Agua Ltda, Santiago for providing laboratory facilities for the experiments presented in this study.

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