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Predicting biogeochemical calcium precipitation in landfill leachate collection systems

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Abstract

Clogging of leachate collection systems within municipal solid waste landfills can result in greater potential for contaminants to breach the landfill barrier system. The primary cause of clogging is calcium carbonate ($CaCO_{3(s)}$) precipitation from leachate and its accumulation within the pore space of the drainage medium. $CaCO_{3(s)}$ precipitation is caused by the anaerobic fermentation of volatile fatty acids (VFAs), which adds carbonate to and raises the pH of the leachate. An important relationship in modeling clogging in leachate collections systems is a yield coefficient that relates microbial fermentation of VFAs to precipitation of calcium carbonate. This paper develops a new, mechanistically based yield coefficient, called the carbonic acid yield coefficient (Y_H), which relates the carbonic acid (H_2CO_3) produced from microbial fermentation of acetate, propionate, and butyrate to calcium precipitation. The empirical values of Y_H were computed from the changes in acetate, propionate, butyrate, and calcium concentrations in leachate as it permeated through gravel-size material. The theoretical and empirical results show that the primary driver of $CaCO_{3(s)}$ precipitation is acetate fermentation. Additionally, other non-calcium cations (e.g., iron and magnesium) precipitated with carbonate (CO_3^{2-}) when present in the leachate. A common yield between total cations bound to CO_3^{2-} and H_2CO_3 produced, called the calcium carbonate yield coefficient (Y_c), can reconcile the empirical yield coefficient for synthetic and actual leachates.

Abbreviations: FSS – fixed suspended solids; KVL – Keele Valley Landfill; TSS – total suspended solids; VSS – volatile suspended solids; VFA – volatile fatty acid

Introduction

Leachate collections systems (LCS) are a key component of most modern landfills. Modern systems typically contain perforated HDPE (high density polyethylene) leachate collection pipes at a regular spacing located in a granular drainage blanket. Leachate generated by infiltration of rainwater through the waste, as well as degradation of the waste itself, is collected and removed from the landfill using this system. LCS are designed to control the head of leachate acting on the underlying landfill liner, thereby minimizing the advective flux of contaminants out of the landfill.

Field studies conducted at numerous German landfills showed that the drainage material within the LCS can become filled with incrustations, resulting in a decrease in the void volume and causing clogging (Brune et al. 1991). The chemical composition of the clog material (dry mass) averaged about 21% calcium, 34% carbonate, 16% silica, 8% iron, and 1% magnesium. After a temporary header pipe at the Keele Valley Landfill (KVL) in Maple, Ontario, Canada was exposed to leachate for about 4 years, it was exhumed, and the clog solids accumulating within the saturated zone of the drainage material were collected and analyzed (Fleming et al. 1999). The chemical composition of the clog solids was similar to that of the German landfill study: about 20% calcium, 30% carbonate, 21% silica, 2% iron, and 5% magnesium on a dry mass basis.

Cooke et al. (1999, 2001) modeled column experiments permeated with synthetic leachate (Rowe et al. 2002) and linked the reduction in medium porosity to the formation of microbial biofilms during volatile fatty acid (VFA) degradation and to calcium carbonate ($CaCO_{3(s)}$) precipitation. A key parameter used by Cooke et al. (1999, 2001) was an empirical correlation between chemical oxygen demand (COD) and calcium (Ca^{2+}) removal called the calcium yield coefficient (Y_{Ca}). Y_{Ca} can be calculated as the ratio of Ca^{2+} removed/COD removed. Rittmann et al. (2003) used a modified version of the biogeochemical model CCBATCH (VanBriesen and Rittmann 2000) to understand how microbiological, chemical, and mass transfer processes interact and control the fraction of carbonates that precipitate $CaCO_{3(s)}$ in the synthetic leachate column experiments reported by Rowe et al. (2002). Close agreement in Y_{Ca} was observed in the laboratory experiments by Rowe et al. (2002) and that deduced in the biogeochemical model by Rittmann et al. (2003).

Rowe et al. (2002) studied the role of suspended solids on the rate of clogging of gravel size material in two series of column experiments permeated with leachate. One column series used a synthetic leachate, while the other used KVL leachate. The calcium yield coefficient in the synthetic leachate experiment was $Y_{Ca} = 0.072$ mg Ca^{2+}/mg COD ($r^2 = 0.75$). A smaller value, $Y_{Ca} = 0.048$ mg Ca^{2+}/mg COD ($r^2 = 0.11$), was computed for the KVL leachate. The difference in Y_{Ca} values probably reflects differences in leachate composition and also the fraction of the clog material that is $CaCO_{3(s)}$. For example, the clog solids were 36% Ca^{2+} for the synthetic leachate, but 24% for the KVL leachate. Because the column experiments described in Rowe et al. (2002) only measured COD and Ca^{2+} concentrations before and after passing through the column, it was not known if the differences in the Y_{Ca} were due to differences in the leachates organic and inorganic contents. Additionally, it was not known if both leachates had similar acids removed. The results from the two leachates raised question about why the yield coefficient was different in the two leachates and whether there is a more unified way to represent the yield that can be used to predict $CaCO_{3(s)}$ precipitation for different types of leachates.

The objectives of this study are to develop a new yield relationship to predict calcium precipitation in landfill leachate collections systems by more comprehensively studying the changes in leachate and clog composition in well controlled laboratory column experiments. The new relationship differentiates the roles of acetate, propionate, and butyrate fermentation by microorganisms in mediating the precipitation of calcium carbonate from synthetic and actual (KVL) leachate. Additionally, the effect of leachate composition, specifically the organic and inorganic content, on the precipitation of calcium carbonate is included.

Column experiments and leachate composition

Column metodology

Two series (VS and VK) of column experiments were completed with four columns in each series, as described in detail by VanGulck (2003). Each column was constructed from PVC (poly vinyl chloride) monitoring well pipe having a 50.8-mm inner diameter, refer to Figure 1 for column schematic. Piezometers and leachate sampling ports were located along the column length. The columns were filled with 6-mm diameter glass beads. The leachate flow path length through the porous medium was 360 mm (measured directly along the length of the column). Leachate entered near the base of the column, flowed upward through the beads, and exited through a U-lock placed just above the medium. The columns operated at 21 °C, with a design flow rate of 0.5 $m^3/m^2/d$, and under anaerobic conditions. The VS and VK series were constructed and operated identically, the only difference being the type of leachate used. The VS series operated with synthetic leachate, and the VK series operated with KVL leachate. Table 1 summarizes the average composition of both leachates.

Since the synthetic leachate was generated in the laboratory, the influent concentrations were relatively

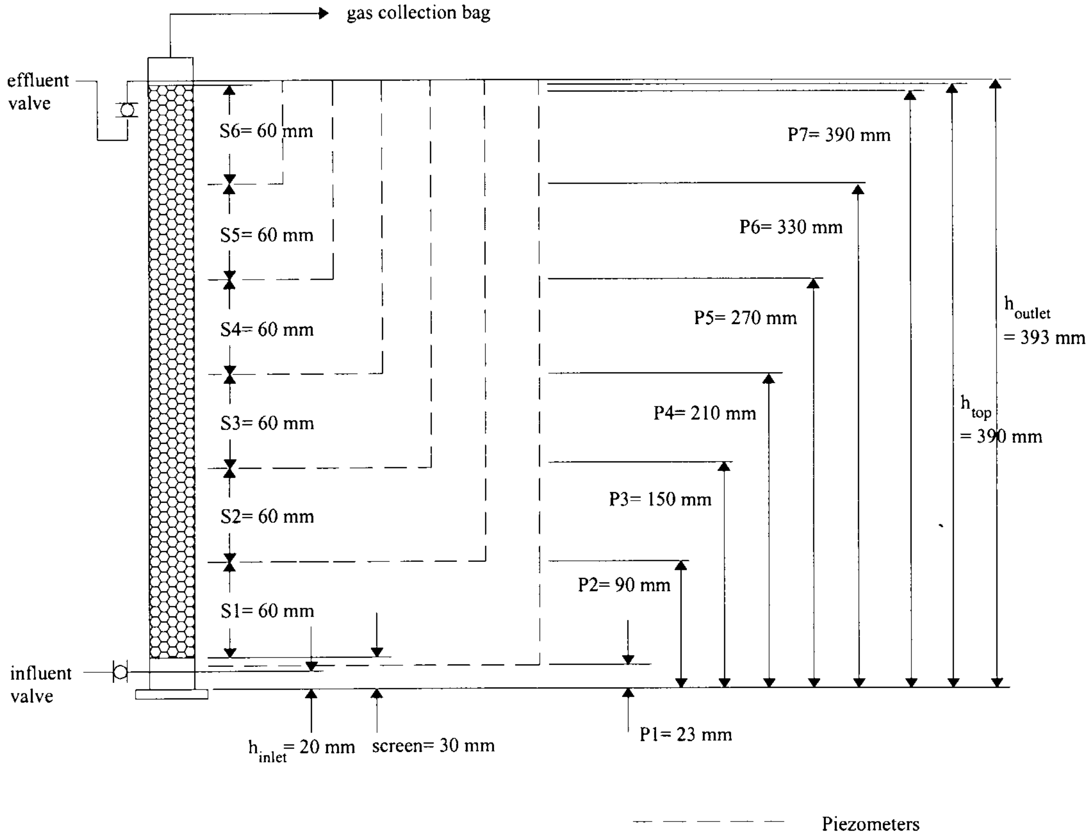

Figure 1. Column schematic (P = Piezometer, S = Section, h_{inlet} = Height of inlet, h_{top} = Top of beads, h_{outlet} = height of outlet, Length of packing = 360 mm).

constant throughout the 430 days of operation. Due to the natural variability inherent in real leachate, the KVL leachate varied in its weekly concentration of acids, Ca^{2+}, and other constituents. KVL leachate had a significant biological activity and suspended solids content compared to synthetic leachate (Table 1).

Leachate was sampled from each sample port on a weekly basis and tested for COD, Ca^{2+}, acetate, propionate, and butyrate concentrations. Additionally, leachate collected from before the influent valve and after the effluent valve was tested for total (TSS) and volatile (VSS) suspended solid concentrations, as well as pH (VanGulck 2003).

Leachate testing methods

COD concentration was measured using Hach™ COD reactor with Hach™ COD reagents that heated the reagent and leachate at 150 °C for 2 hours and then analyzed with the Hach™ DR2000 Spectrophotometer. Ca^{2+} concentrations were obtained using a Philips PU9100X atomic absorption spectrometer. The pH was measured using an YSI Water Quality Monitor (Model 3400) that was equipped with the appropriate electrical probe. Total and volatile suspended solids were tested using a gravimetric measurement of the residue retained on a 0.45 μm glass fiber filter dried at 105 °C and 550 °C, respectively. VFA concentrations were obtained by gas chromatography (GC), using a Shimadzu GC-9A and Varian 3400 instruments equipped with flame ionization detectors and 15 m × 0.53 mm (or 0.25 mm) ID, 0.5 μm film NUKOL™ (Supelco, Bellfonte, PA) capillary columns. Injections to the Varian 3400 were automated (Varian 8200 auto sampler) and performed using solid phase micro phase extraction (SPME) with 10-min immersion/2-min desorption of a 75 μm Carboxen™/Polymethylsiloxane fiber (Supelco, Bellfonte, PA). All aqueous VFA samples were acidified in 1% H_3PO_4 prior to analytical separation. Isovaleric acid was used as internal calibration standard.

Table 1. Composition of synthetic and KVL leachates

Parameter	Units	Synthetic leachate		KVL leachate	
		Mean value	Standard deviation	Mean value	Standard deviation
COD (measured)	(mg/L)	14,600	860	12,200	3,470
COD (calculated)	(mg/L)	15,300[2]	3,050	8,730[2]	3,260
Acetate	(mg COD/L)	6,540	1,450	3,340	1,810
Propionate	(mg COD/L)	7,050	1,440	3,940	1,490
Butyrate	(mg COD/L)	1,700	1,410	1,610	940
Ca	(mg/L)	790	160	460	170
Total suspended solids	(mg/L)	40	40	1,000	900
Volatile suspended solids	(mg/L)	40	40	450	400
Fixed suspended solids	(mg/L)	–	–	550	550
pH	(–)	6.1	0.3	6.8	0.3
Mg	(mg/L)	404[1]		487[3]	89
Na	(mg/L)	2,840[1]		2,150[3]	570
Fe	(mg/L)	0.735[1]		171[3]	70
Al	(mg/L)	0.003[1]		1.610[3]	0.30
K	(mg/L)	319[1]		1,035[3]	240
Tot P	(mg/L)	5.34[1]		6.10[3]	4.1
TKN-N	(mg/L)	–		1,180[3]	270
Mn	(mg/L)	0.10[1]		3,660[3]	5.3
Ti	(mg/L)	–		0.183[3]	1.2
Zn	(mg/L)	0.01[1]		7.360[3]	3.5
Ba	(mg/L)	–		0.276[3]	0.1
Ni	(mg/L)	0.12[1]		0.531[3]	0.1
Cu	(mg/L)	0.01[1]		0.018[3]	0.01
V	(mg/L)	–		0.053[3]	0.003
Pb	(mg/L)	–		0.028[3]	0.04
Cr	(mg/L)	–		0.143[3]	0.03
Co	(mg/L)	0.03[1]		0.053[3]	0.01
Cl	(mg/L)	3,800[1]	3,140[3]	770	

[1] Calculated from molar mass of each constituent in synthetic leachate (Rowe et al. 2002).
[2] Calculated from the sum of acetate, propionate, and butyrate concentrations.
[3] Average of the Keele Valley leachate data published in annual reports for the period over which this study was conducted.

Influent leachate concentrations

The VS series influent synthetic leachate COD and Ca^{2+} composition averaged 14,600 (COD measured) and 790 mg/L, respectively (Table 1). The influent pH slightly increased with time from 5.9 to 6.2, with an average value of 6.1. The average influent acetate, propionate, and butyrate concentrations were 6,190, 4,660, and 930 mg/L respectively, or about 6,540, 7,050, and 1,700 mg COD/L. The total COD from the sum of the three volatile acids (15,300 mg/L) compares well with the measured average influent COD concentration of 14,600 mg COD/L, confirming that the three measured volatile acids comprise all of the total COD. Thus, the input COD concentration from acetate, propionate, and butyrate were 43, 46, and 11% of the total COD, respectively. The average influent total and volatile suspended solids concentrations were about 40 mg/L.

The VK series influent KVL leachate COD and Ca^{2+} composition averaged 12,200 (COD measured) and 460 mg/L, respectively, with an average pH of 6.8 (Table 1). Significant changes in all measured KVL leachate parameters occurred over the duration of the experiment, and the composition of the leachate changed significantly after about 150 days of operation. For example, the acetate concentration initially was about 3,500 mg COD/L, but dropped to about 2,000 mg COD/L after 150 days. Propionate had a concentration of about 2,500 mg COD/L for 60 days, then increased to about 4,500 mg COD/L by 150 days, and then fluctuated between 1,600 and 5,400 mg COD/L after 150 days. Butyrate initially was about 3,000 mg COD/L, but dropped to about 400 mg COD/L after 150 days. The average influent acetate, propionate, and butyrate concentrations were 3,340, 3,940, and 1,610 mg COD/L respectively, giving an average total COD concentration of 8,890 mg COD/L. The three measured volatile acids comprised about 73% of the total COD, indicating that other more complex organics were present in KVL leachate. Thus, the input COD concentration from acetate, propionate, and butyrate were 38, 44, and 18% of the total COD respectively. The average influent total and volatile suspended solids concentrations were 800 and 350 mg/L, respectively, each with a relatively high standard deviation of 700 and 300 mg/L, respectively.

The acetate, propionate, and butyrate concentrations were about 2.0, 1.8 and 1.1 times higher in the synthetic leachate compared to KVL. In terms of the inorganic content, the synthetic leachate had a 1.7 times larger Ca^{2+} content, similar Mg^{2+} content, about 30 times lower Mn^{2+} content, and more then 200 times lower Fe^{2+} content than KVL leachate. In addition to differences in organic and inorganic contents within synthetic and KVL leachate, KVL leachate had a large fixed suspended solids content (fixed suspended solids = total suspended solids-volatile suspended solids) of 450 mg/L; synthetic leachate did not contain any fixed suspended solids.

Changes in leachate concentrations as it passed through columns

The changes in synthetic and KVL leachate COD, Ca^{2+}, and pH between the influent and effluent of the column are shown in Figures 2 and 3, respectively. Both series of experiments experienced a lag time before significant removal of COD ($>10\%$). During this time, microorganisms began to grow on the porous medium. A large removal of COD occurred after the lag phase and before steady state conditions. The steady-state phase had approximately 40% COD removal. The lag phase in the VK series was 60 days long, compared to the 280 days for the VS series. The shorter lag time in the VK series is the result of the high volatile suspended solids content in KVL leachate compared to the low volatile suspended solids content in synthetic leachate (Table 1). The higher volatile suspended solids content in KVL leachate provided a larger mass of microorganisms to inoculate the columns. The larger mass of microorganisms that entered the VK columns developed a biofilm on the porous medium that can consume VFAs at an earlier time compared to the VS columns (VanGulck 2003). The VS series was seeded with KVL leachate for 9 days to provide the column with typical landfill bacteria. The volatile suspended solids loading into the VS series columns during this period is negligible in comparison to the volatile suspended solids loading into the VK series columns.

Ca^{2+} removal also exhibited lag, transition, and steady-state phases, which occurred over similar time periods as COD removal. The precipitation of Ca^{2+} within the medium decreased the pore space (up to 60% reduction in porosity), resulting in a shorter leachate retention time. Concurrent with the decrease in COD (and Ca^{2+}), was an increase in leachate pH. Despite the lower influent pH value in the synthetic leachate compared to KVL leachate, in both cases the effluent pH approached a value of about 7.4 ± 0.2 during the steady state phase. The increase in leachate pH and decrease in Ca^{2+} concentration between the influent and effluent of the column is consistent with the leachate chemistry study by Rittmann et al. (1996), who showed that, as leachate passes through the drainage material, the loss of COD, primarily in the form of acetic acid replaces the stronger acid (acetic acid) with a weaker acid (H_2CO_3). The result is an increase in pH and carbonate concentration, both of which allow, or accelerate, the precipitation of $CaCO_{3(s)}$.

The changes in acetate, propionate, and butyrate concentrations between the influent and effluent of the column are shown in Figures 4 and 5 for the VS and VK series, respectively. In the VS series, acetate and butyrate removal occurred after about 275 and 325 days, respectively. Propionate did not experience significant removal. Ca^{2+} removal occurred at approximately the same time as acetate removal. In the VK series, acetate, butyrate, and propionate removal occurred. During the first 70 days, acetate effluent concentration increased compared to the influent, propionate concentrations did not change and butyrate decreased in concentration. The decrease in butyrate resulted in the increase in acetate, because acetate is a fermentation product from butyrate. Despite the decrease in butyrate, only a minor decrease in Ca^{2+} occurred. After 70 days, acetate and Ca^{2+} removal occurred together, substantiating that acetate ferment-

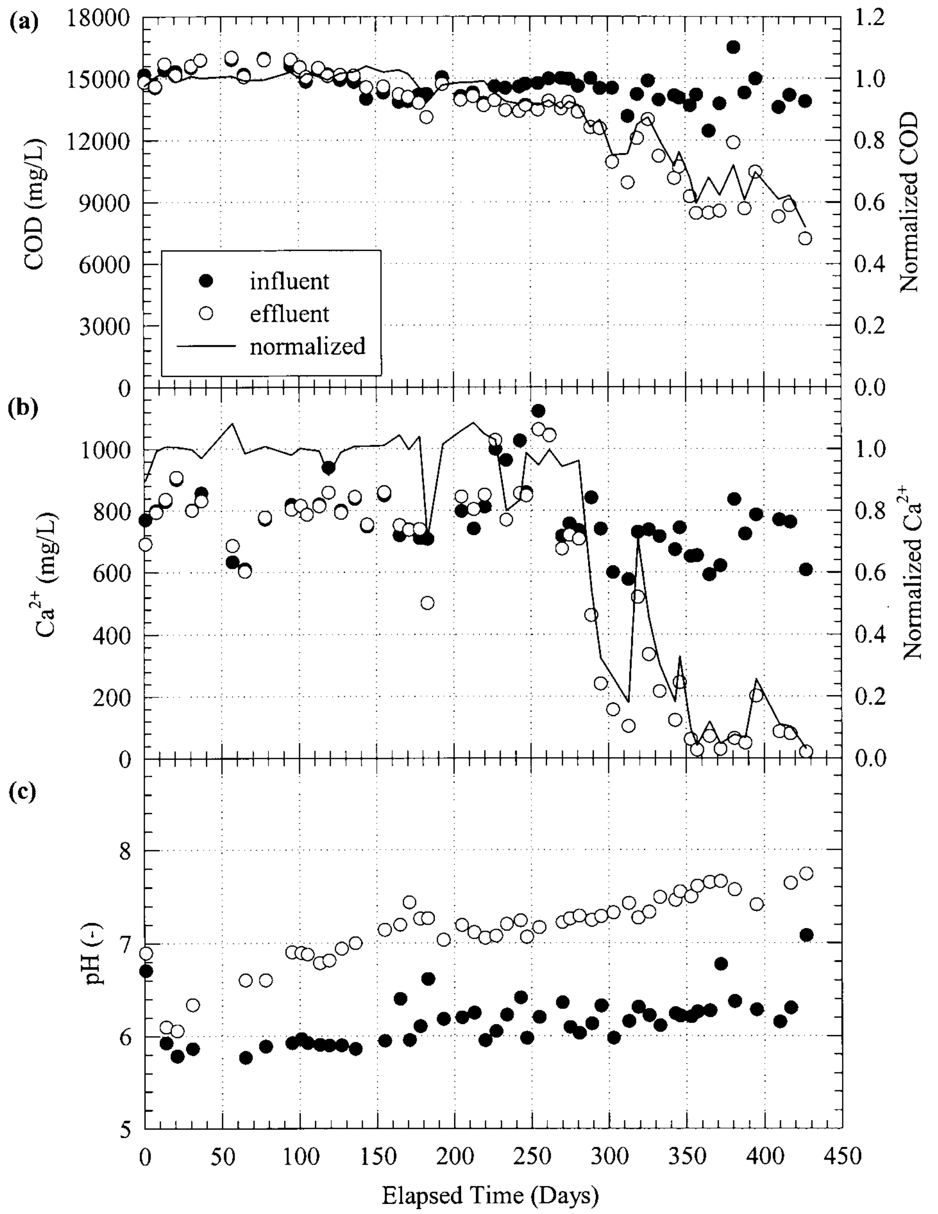

Figure 2. Variation in influent and effluent synthetic leachate characteristics with time: (a) COD (measured) versus elapsed time, (b) Ca^{2+} versus elapsed time, and (c) pH versus elapsed time.

ation primarily drives Ca^{2+} precipitation. Propionate removal began after about 150 days.

The KVL leachate contained suspended solids that were removed from the leachate as it passed through the medium (VanGulck 2003). The total, volatile, and fixed had about 60% removal in the first 50–100 days. After this time, 70-95% removal occurred. The increase in suspended solids removal is likely a result of the better straining/filtration capabilities of a partially clogged medium (primarily a result of calcium precipitation) compared with an unclogged medium. Since the fixed suspended solids in KVL leachate contain a fraction of Ca^{2+} (VanGulck 2003), straining/filtration of fixed suspended solids from leachate removed some Ca^{2+}. However, the majority of the Ca^{2+} in KVL leachate was dissolved; therefore Ca^{2+} removal through precipitation was the dominant process.

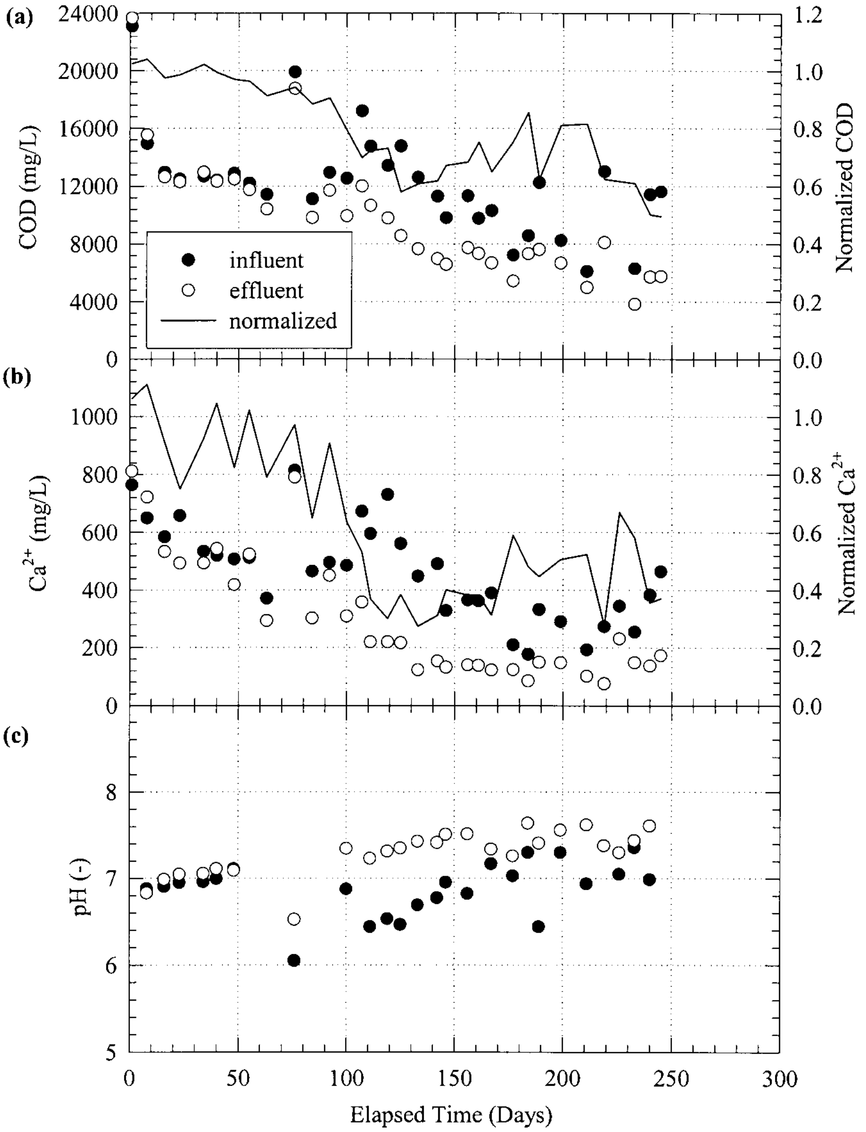

Figure 3. Variation in influent and effluent KVL leachate characteristics with time: (a) COD (measured) versus elapsed time, (b) Ca^{2+} versus elapsed time, and (c) pH versus elapsed time.

Calcium yield coefficient

In past studies (Rittmann et al. 1996; Rowe et al. 1997; Cooke 1997; Cooke et al. 1999, 2001), the calcium yield coefficient, Y_{Ca}, was obtained by plotting the removal of Ca^{2+} relative to the removal of COD and fitting the data by a linear regression analysis. The Y_{Ca} values obtained in this way for the VS and VK series were 0.141 mg Ca^{2+}/mg COD (Figure 6, $r^2 = 0.79$) and 0.064 mg Ca^{2+}/mg COD (Figure 7, $r^2 = 0.61$), respectively. Ca^{2+} and COD removed values were calculated over varying leachate treatment lengths (60, 120, 180, 240, 300 and 360 mm). Each length corresponds to the length of flow path between sample port one (P1-influent) and each successive port along the column. For example, the treatment length of 360 mm (measured directly along the length of the column) corresponds to the leachate concentration changes between P1 and P7 (influent and effluent), shown in Figures 2 and 3 for the VS and VK series respectively. Both Y_{Ca} plots show a strong correlation between COD removal and Ca^{2+} precipitation as

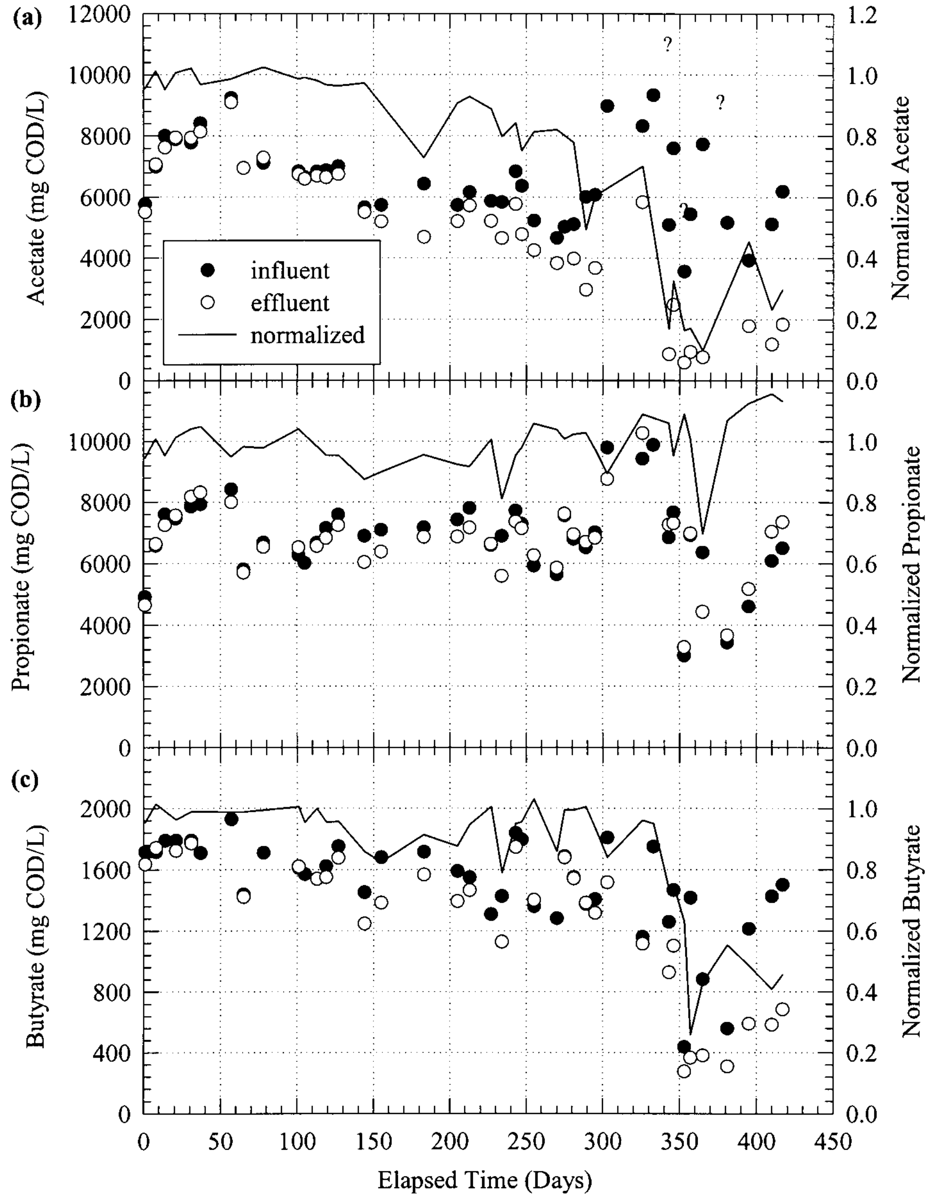

Figure 4. Variation in influent and effluent synthetic leachate characteristics with time: (a) acetate versus elapsed time, (b) propionate versus elapsed time, and (c) butyrate versus elapsed time.

$CaCO_{3(s)}$; however, the yield coefficient Y_{Ca} for the VS series was 2.3 times larger than the VK series. This difference underscores the importance of understanding why the calcium yield coefficients were so different for the two leachates and whether or not a unified approach can eliminate the difference. These issues are addressed in the following sections.

Stoichiometric link between microbial acid fermentation and calcium carbonate precipitation

Rittmann et al.'s (2003) biogeochemical modeling study showed that the primary driver for $CaCO_{3(s)}$ precipitation was acetate fermentation to methane (CH_4) and H_2CO_3. The generation of H_2CO_3 increases the total carbonate concentration, and the shift from acetic acid ($pK_a \sim 4.7$) to carbonic acid ($pK_a \sim 6.3$) increases the pH in the leachate, thereby shifting the

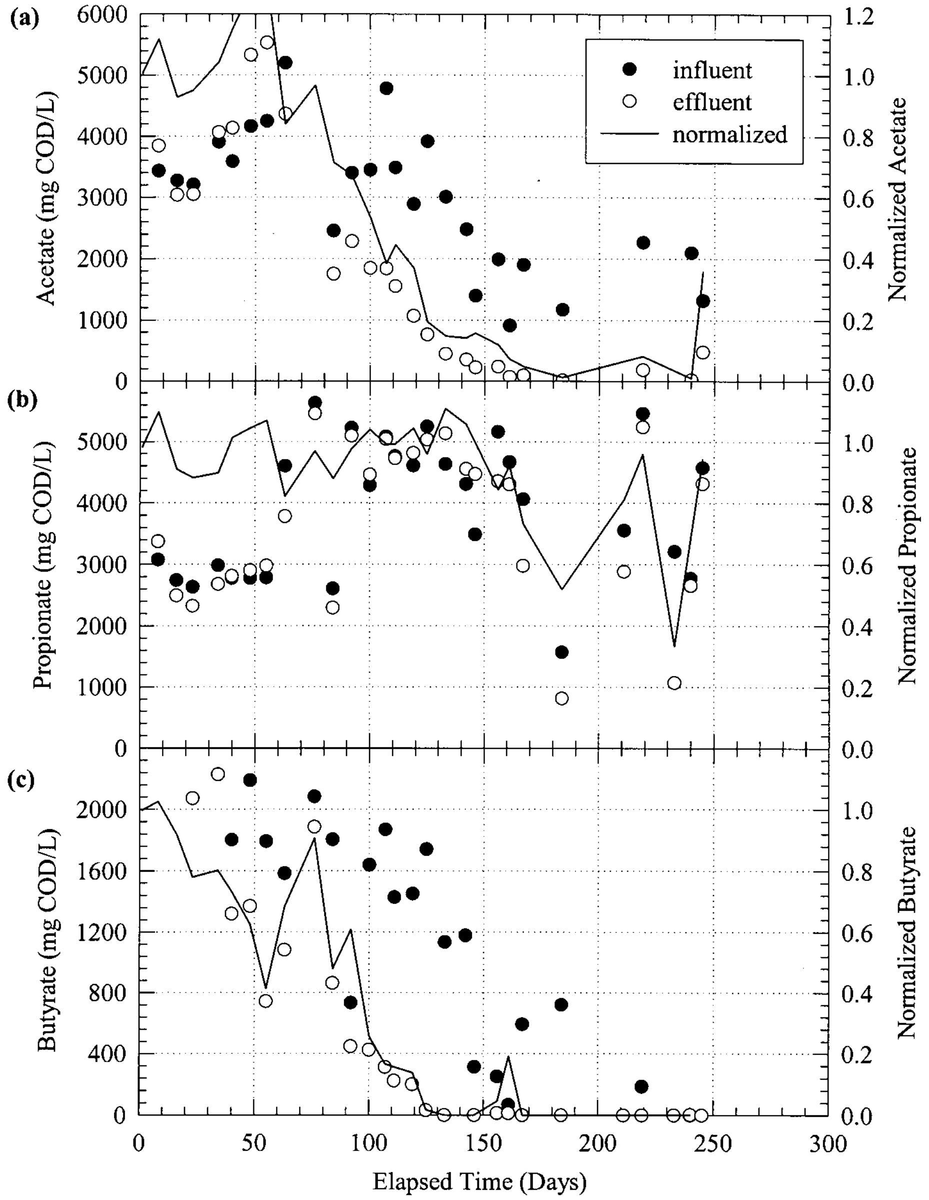

Figure 5. Variation in influent and effluent KVL leachate characteristics with time: (a) acetate versus elapsed time, (b) propionate versus elapsed time, and (c) butyrate versus elapsed time.

carbonic equilibrium toward CO_3^{2-}. Rittmann et al. (2003) and Cooke et al. (2001) modeled propionate and butyrate together as one acid (propionate), since the concentration of butyrate was much less than that of propionate and both are fermented to acetate. We adopt the approach described by Rittmann et al. (2003), but consider fermentation reactions for each of the three organic acids (butyrate, propionate, and acetate). This approach allows one to compute how the consumption of each acid affects the total carbonate concentration (by producing H_2CO_3) and the acid/base buffering (by replacing an organic acid with the weaker H_2CO_3).

Biogeochemical equations

The conversion of propionate to acetate, butyrate to acetate, and acetate to methane and H_2CO_3 are represented by the following microbiologically catalyzed reactions (Bjerg et al. 1995; Parkin & Owen 1986):

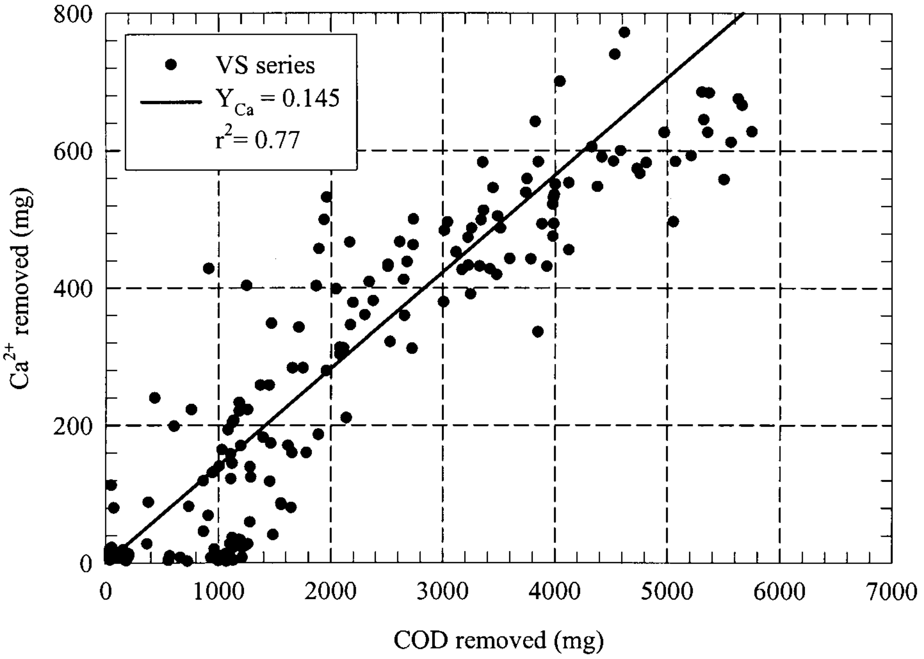

Figure 6. Measured removal of Ca^{2+} versus removal of COD and the calculation of the calcium carbonate yield coefficient (Y_{Ca}) from the linear regression of the data for the VS series. COD removed residuals minimized in regression analysis.

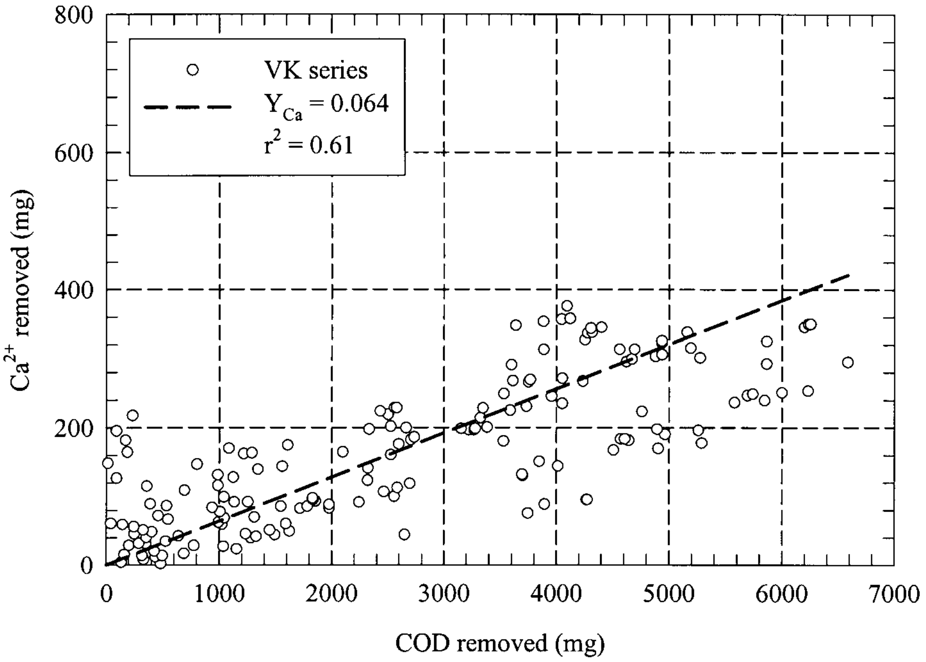

Figure 7. Measured removal of Ca^{2+} versus removal of COD and the calculation of the calcium carbonate yield coefficient (Y_{Ca}) from the linear regression of the data for the VK series. COD removed residuals minimized in regression analysis.

Fermentation of propionate to acetate, carbonic acid, and hydrogen

$$CH_3CH_2COOH + 3H_2O \rightarrow CH_3COOH + H_2CO_3 + 3H_2O \quad (1)$$

Oxidation of hydrogen gas to reduce carbonic acid to methane

$$3H_2 + \tfrac{3}{4}H_2CO_3 \rightarrow \tfrac{9}{4}\,H_2O + \tfrac{3}{4}CH_4 \quad (2)$$

Reactions 1 and 2 can be combined, since insignificant H_2 accumulates in a balanced anaerobic system (Parkin & Owen 1986; Rittmann & McCarty 2001),

$$CH_3CH_2COOH + \tfrac{3}{4}H_2O \rightarrow CH_3COOH + \tfrac{3}{4}CH_4 + \frac{1}{4}H_2CO_3 \quad (3)$$

For each mole of propionate fermented, 1 mole of acetate and 0.25 mole of H_2CO_3 are produced. Thus, fermentation of propionate is replaced by an organic acid, and the carbonate is increased by a relatively small amount.

Fermentation of butyrate to acetate and hydrogen

$$CH_3CH_2CH_2COOH + 2H_2O \rightarrow 2CH_3COOH + 2H_2O \quad (4)$$

Oxidation of hydrogen gas to reduce carbonic acid to methane

$$2H_2 + \tfrac{1}{2}H_2CO_3 \rightarrow \tfrac{3}{2}\,H_2O + \tfrac{1}{2}CH_4 \quad (5)$$

Combining reactions 4 and 5 (again since insignificant H_2 accumulates in a balanced anaerobic system) gives

$$CH_3CH_2CH_2COOH + \tfrac{1}{2}H_2O + \tfrac{1}{2}H_2CO_3 \rightarrow 2CH_3COOH + \tfrac{1}{2}CH_4 \quad (6)$$

for each mole of butyrate fermented, 0.5 mole of H_2CO_3 is consumed and 2 mole of acetate are produced. In this case, the organic acid is doubled, while carbonate declines.

Conversion of acetate to methane and carbonic acid

$$CH_3COOH + H_2O \rightarrow CH_4 + H_2CO_3 \quad (7)$$

for each mole of acetate fermented, 1 mole of H_2CO_3 is produced. Thus, the organic acid is totally replaced by H_2CO_3, and the carbonate concentration is increased by a relatively large amount.

$CaCO_{3(s)}$ is precipitated by the reaction of Ca^{2+} and CO_3^{2-}.

$$CO_3 + Ca^{2+} \rightarrow CaCO_{3(s)} \quad (8)$$

The three fermentation reactions produce different amounts of H_2CO_3: 0.25 mole H_2CO_3/mole propionate, −0.5 mole H_2CO_3/mole butyrate, and 1 mole H_2CO_3/mole acetate. Thus, the fermentation of acetate generates 4 times more H_2CO_3 then propionate fermentation, while butyrate fermentation consumes H_2CO_3. Furthermore, only the fermentation of acetate destroys the organic acids, which are stronger than H_2CO_3. Fermentation of propionate replaces propionate with acetate, while fermentation of butyrate replaces butyrate with two acetate, thereby increasing the acidity of the leachate. Therefore, fermentation of acetate is the step that should drive $CaCO_{3(s)}$ precipitation by generating the greatest H_2CO_3 and removing all of the organic acids.

Past applications of Y_{Ca} in modeling $CaCO_{3(s)}$ precipitation employed a bulk measure of organic-acid removal (COD). However the stoichiometry considerations shown here demonstrate that calcium removal should be tied closely to fermentation of acetate, not propionate or butyrate fermentation. This factor is not directly accounted for in the traditional Y_{Ca} relationship. This may explain, at least in part, the difference in Y_{Ca} deduced in the VS and VK series experiments, because VS leachate had almost twice the acetate content of the VK leachate.

Carbonic acid yield coefficient

A new yield coefficient, the carbonic acid yield coefficient-Y_H, is proposed to relate the H_2CO_3 produced in reactions 3, 6, and 7 to Ca^{2+} removal.

$$Y_H = \frac{\text{Ca removed}}{\text{net } H_2CO_3 \text{ produced}} \quad (9)$$

The Ca^{2+} removed within the column was calculated as the difference in Ca^{2+} concentration measured over varying treatment lengths (60, 120, 180, 240, 300, and 360-mm) along the column. The net H_2CO_3 produced was calculated from the fermentation of each of the three carboxylic acids over the same treatment lengths. The changes in propionate, butyrate, and acetate concentrations over each treatment length were measured. Decreases in propionate and butyrate concentrations represent the amount of propionate and butyrate fermented. For each mole of propionate and butyrate fermented, 0.25 mole H_2CO_3 is produced and 0.5 mole H_2CO_3 is consumed. The changes in acetate concentration over each treatment length represent the net effect of (1) acetate produced from propionate and butyrate fermentation and (2) acetate fermented by acetate degraders. Therefore the acetate fermented within the columns was calculated by subtracting the change in acetate measured by the acetate produced from propionate and butyrate fermentation. Thus, the net H_2CO_3 produced is the product of the H_2CO_3 produced from acetate and propionate fermentation and the H_2CO_3 consumed from butyrate fermentation, giving:

$$\begin{aligned}\text{net } H_2CO_3 \text{ produced} = {} & 0.1384(\text{PA fermented}) \\ & -0.19375(\text{BA fermented}) \\ & +0.9684(\text{AA fermented})\end{aligned} \qquad (10)$$

where 0.1384 and 0.9684 are the mass ratios of H_2CO_3 produced to propionate and acetate fermented respectively (0.25 * 62 g H_2CO_3/112 g COD and 62 g H_2CO_3/64 g COD respectively), 0.19375 is the mass ratio of H_2CO_3 consumed to butyrate fermented (0.5 * 62 g H_2CO_3/160 g COD), and acetate, propionate, and butyrate fermented have units of mg COD/L. It is possible to calculate a negative value of net H_2CO_3 produced (Equation (10)) if there is a small amount of acetate and propionate fermented compared to butyrate fermented. A limitation must be set that restricts the net H_2CO_3 produced to be greater than or equal to zero; thus, calcium removal only occurs when there is a net positive H_2CO_3 produced from the fermentation of acetate, propionate, and butyrate. In deducing Y_H, data points that had a calculated net H_2CO_3 produced less than zero were not included in the regression analysis.

In a closed system with an unlimited supply of Ca^{2+}, all H_2CO_3 produced from microbial fermentation could be precipitated as $CaCO_{3(s)}$. In that limiting case, mass balance on carbonate requires that Y_H equals 0.645 g Ca^{2+}/g H_2CO_3 (40 g Ca^{2+}/62 g H_2CO_3), which places an upper limit on Y_H.

However, in both series, gas was produced and vented from the column through the piezometer ports; thus some of H_2CO_3 calculated was lost from solution through generation and removal of CO_2 gas from the system. Therefore, the Y_H calculated in the VS and VK series experiments should be less than 0.645 g Ca^{2+}/g H_2CO_3. Since the VS and VK series experiments were similar in construction and operation, the CO_2 gas transfer rates were probably similar. However, the CO_2 gas production was not measured.

The data points of H_2CO_3 produced (calculated from Equation (10)) from fermentation of acetate, propionate, and butyrate and the calcium removed (based on total calcium) within the VS and VK series are shown in Figures 8 and 9. A linear regression through the VS and VK data points yield slopes of 0.169 ($r^2 = 0.67$) and 0.116 ($r^2 = 0.67$) mg Ca^{2+}/mg H_2CO_3 respectively. Thus, a larger mass of Ca^{2+} was precipitated in the VS series compared with the VK series for a similar amount of H_2CO_3 produced, but the difference is substantially smaller than the difference in Y_{Ca} value.

Comparing the Y_H of 0.169 (VS) and 0.116 (VK) mg Ca^{2+}/mg H_2CO_3 to the theoretical value in a closed system of 0.645 mg Ca^{2+}/mg H_2CO_3 suggests that 25% (VS) and 17% (VK) of the CO_3^{2-} produced from microbial fermentation of acetate, propionate, and butyrate precipitated as $CaCO_{3(s)}$. The remaining 75% (VS) and 83% (VK) must have been incorporated into biomass, stored in the aqueous phase, evolved as CO_2 gas, or precipitated with other cations. Since biomass yields in methanogenic systems are low (Parkin & Owen 1986), biomass was not a major sink. Changes in total carbonate-$C_{T,CO3}$ (or bicarbonate) were likely small (Rittmann et al. 1996), meaning that most H_2CO_3 evolved as $CO_{2(g)}$, or precipitated with cations other than Ca^{2+}. The precipitation of cations other than Ca^{2+} requires analysis of the clog material composition and is discussed below.

Clog composition analysis from material within the pore space of the medium during the steady-state phase in the VS series had 37% calcium, 56% carbonate, <1% silica, <1% magnesium, and <1% iron on a dry mass basis (VanGulck 2003). Since there were negligible suspended solids within the synthetic leachate, precipitation of minerals is the dominant mechanism for Ca^{2+} and CO_3^{2-} accumulation within the clog solids. In the VK series, accumulation of Ca^{2+} and CO_3^{2-} within the pore space of the medium may occur due to the retention of fixed suspended solids (partially comprised of Ca^{2+} and CO_3^{2-}) and precipitation of minerals. During the lag phase in the VK series, there was only a small amount of acetate and Ca^{2+} removed within the column, therefore the

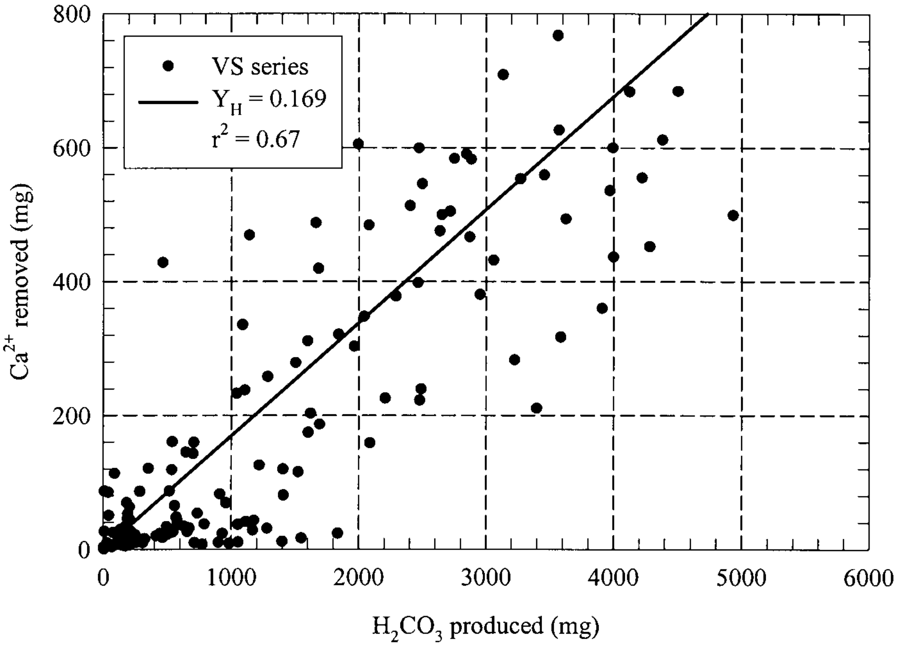

Figure 8. Measured removal of Ca^{2+} versus calculated H_2CO_3 produced and the carbonic acid yield coefficient (Y_H) from the linear regression of the data for the VS series. H_2CO_3 produced residuals minimized in regression analysis.

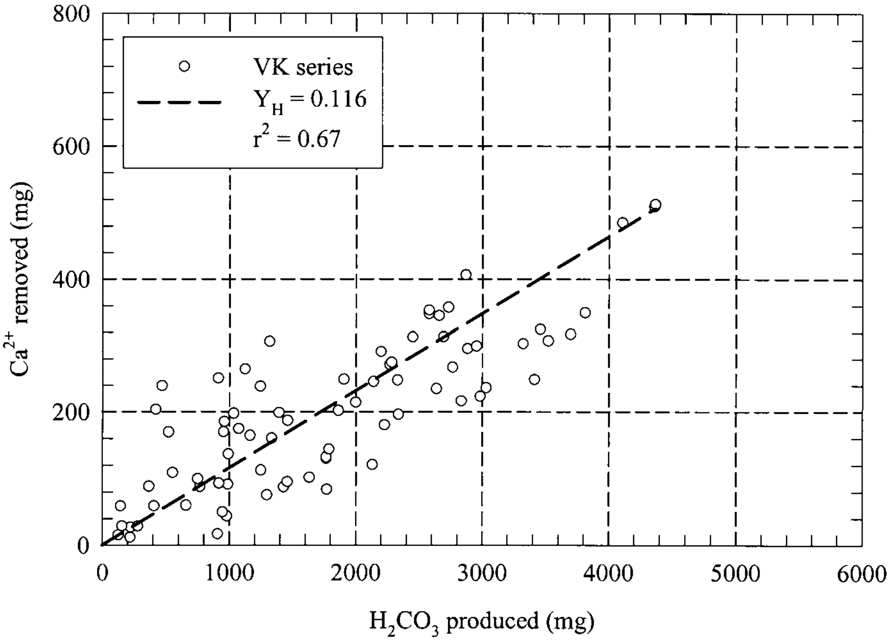

Figure 9. Measured removal of Ca^{2+} versus calculated H_2CO_3 produced and the carbonic acid yield coefficient (Y_H) from the linear regression of the data for the VK series. H_2CO_3 produced residuals minimized in regression analysis.

clog material during this time period likely is dominated by retained fixed suspended solids. The lag phase clog composition in the VK series had 9% calcium, 4% carbonate, 8% iron, and <1% magnesium (VanGulck 2003). During the steady-state phase in the VK series there were significant removals of acetate and Ca^{2+}, thus the clog material contained retained fixed suspended solids and precipitated minerals. The VK series steady-state clog had a composition of 28% calcium, 50% carbonate, <1% silica, 1% magnesium, and 3% iron on a dry mass basis (VanGulck 2003).

If precipitation were the only mechanism for Ca^{2+} accumulation within the clog material, and all Ca^{2+} within the clog material were bound to CO_3^{2-}, mass balance consideration of $CaCO_{3(s)}$ precipitation requires the $Ca^{2+}/CO^{2-}_{3(\text{theoretical})}$ ratio to be 0.666 (40 g Ca^{2+}/60 g CO_3^{2-}). Ratios less than 0.666 indicate other elements bound to CO_3^{2-}. The VS series clog material, which primarily contained precipitated Ca^{2+} and CO_3^{2-} constituents (i.e. no retained fixed suspended solids), had an average $Ca^{2+}/CO^{2-}_{3(\text{precipitated})}$ ratio of 0.660 during steady-state COD removal: thus, 99% (β = 0.99) of the CO_3^{2-} is bound to Ca^{2+} (0.660 $Ca^{2+}/CO^{2-}_{3(\text{precipitated})}$/0.666 $Ca^{2+}/CO^{2-}_{3(\text{theoretical})}$ * 100%), where β is the fraction of CO_3^{2-} bound to Ca^{2+} in the precipitated mass. During the lag phase, the VK series clog material contained Ca^{2+} and CO_3^{2-} constituents primarily from retained fixed suspended solids (i.e., only small amounts of precipitated Ca^{2+} and CO_3^{2-} mass), and had a $Ca^{2+}/CO^{2-}_{3(\text{FSS})}$ ratio of 2.26. During the steady-state phase, the clog material contained Ca^{2+} and CO_3^{2-} constituents from retained fixed suspended solids and precipitated mass, and had an average $Ca^{2+}/CO^{2-}_{3(\text{precipitated+FSS})}$ ratio of 0.56. In order to deduce β in the VK series, the ratio of $Ca^{2+}/CO^{2-}_{3(\text{precipitated})}$ was calculated through

$$Ca^{2+}/CO^{2-}_{3(\text{precipitated})} = \frac{Ca^{2+}/CO^{2-}_{3(\text{precipitated+FSS})} - (Ca^{2+}/CO^{2-}_{3(\text{FSS})}) \times \left(1 - \dfrac{CO^{2-}_{3(\text{precipitated})}}{CO^{2-}_{3(\text{precipitated+FSS})}}\right)}{\left(\dfrac{CO^{2-}_{3(\text{precipitated})}}{CO^{2-}_{3(\text{precipitated+FSS})}}\right)} \quad (11)$$

where $Ca^{2+}/CO^{2-}_{3(\text{precipitated+FSS})} = 0.56$; $Ca^{2+}/CO^{2-}_{3(\text{FSS})} = 2.26$; and

$$CO^{2-}_{3(\text{precipitated})} = CO^{2-}_{3(\text{precipitated+FSS})} - CO^{2-}_{3(\text{FSS})} \quad (12)$$

where $CO^{2-}_{3(\text{FSS})}$ mass was calculated from the division of the calcium comprised retained fixed suspended solids mass within the column at the time of the final column disassembly by the ratio of $Ca^{2+}/CO^{2-}_{3(\text{FSS})}$ of 2.26 in the lag phase clog mass; and $CO^{2-}_{3(\text{precipitated+FSS})}$ mass was calculated from the product of the steady state clog solids mass retrieved from the column during disassembly and the fraction of CO_3^{2-} (0.50) in the steady-state clog. Using Equation (11), the calculated $Ca^{2+}/CO^{2-}_{3(\text{precipitated})}$ ratio in the VK series was 0.450 (VanGulck 2003), indicating that 68% (β = 0.68) of the CO_3^{2-} is bound to Ca^{2+} (0.450 $Ca^{2+}/CO^{2-}_{3(\text{precipitated})}$/0.666 $Ca^{2+}/CO^{2-}_{3(\text{theoretical})}$ * 100%). Comparing β for the synthetic and KVL leachates shows that the fraction of CO_3^{2-} used to precipitate $CaCO_{3(s)}$ is different between the VS and VK series. Clog composition results indicate Fe^{2+} and Mg^{2+} accumulation within the VK series (VanGulck 2003); thus, the remaining CO_3^{2-} is likely bound to these cations. The larger fraction of non-Ca^{2+} cations within the VK series clog reflects the higher concentrations of these constituents in KVL leachate compared to synthetic leachate (Table 1).

The β values can be used to relate all the cations in leachate bound to CO_3^{2-} to Ca^{2+} removed:

$$\text{total cations removed with } CO_3 = \frac{\text{Ca removed}}{\beta} \quad (13)$$

Figure 10 plots Ca^{2+} removed/β versus H_2CO_3 produced for the VS and VK series. Fitting each series with a linear regression analysis yields slopes of 0.170 (r^2 = 0.67) and 0.171 (r^2 = 0.67) mg cations removed with CO_3^{2-}/mg H_2CO_3, respectively. The similarity of the two slopes suggests similar amounts of carbonate precipitated in the synthetic and KVL leachate for a similar amount of H_2CO_3 produced. Thus, a common yield between carbonates precipitated and H_2CO_3 produced, called the calcium carbonate yield coefficient (Y_c = 0.17 mg cations as Ca^{2+} removed with CO_3^{2-}/mg H_2CO_3), can be used to relate the mass of calcium precipitated to the total mass of cations (as Ca^{2+}) precipitated.

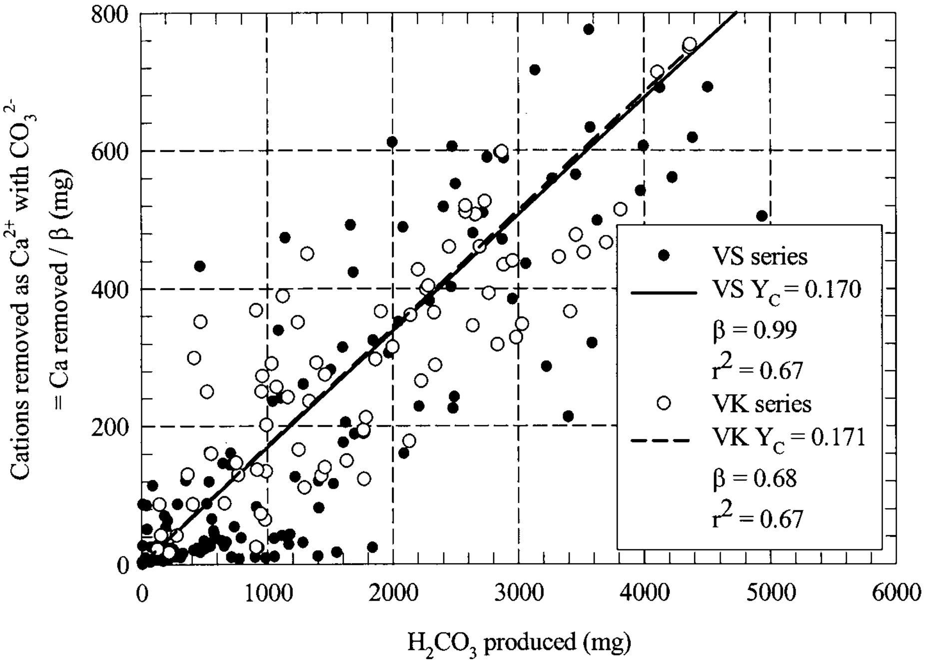

Figure 10. Calculated cations removed as Ca^{2+} with CO_3^{2-} versus calculated H_2CO_3 produced and the carbonate yield coefficient (Y_c) from the linear regression of the data for the VS and VK series. VS Yc and VK Yc regression lines visually coincide. VS series $\beta = 0.99$, VK series $\beta = 0.68$. H_2CO_3 produced residuals minimized in regression analysis.

Summary

If the amount of acetate, propionate, and butyrate fermentation can be modeled as leachate passes through drainage layer within a collection system (Cooke et al. 1999, 2001), the mass of calcium deposited within the void spaces of the medium can be calculated by completing the following three steps.

Step 1: Calculate the net acetate, propionate, and butyrate fermented in leachate due to active biofilms and suspended degraders as leachate passes through porous medium. Cooke et al. (1999, 2001) modeled the drainage layer as an anaerobic fixed film reactor using a modified version of the procedure proposed by Rittmann & McCarty (1981).

Step 2: Calculate the net H_2CO_3 produced from acetate, propionate and butyrate degradation through Equation (10), where the amount of acetate, propionate and butyrate fermented must have units of mg COD/L.

$$\begin{aligned}\text{net } H_2CO_3 \text{ produced} &= 0.1384(\text{PA fermented}) \\ &\quad -0.19375(\text{BA fermented}) \\ &\quad +0.9684(\text{AA fermented})\end{aligned} \tag{10}$$

Only positive values of net H_2CO_3 produced are used in Step 3.

Step 3: Calculate the calcium concentration and the total cation mass (as Ca^{2+}) removed using the calcium carbonate acid yield coefficient by rearranging Equations (9) and (13) as follows.

$$\text{Ca removed} = Y_C \beta \times (\text{net } H_2CO_3 \text{ produced}) \tag{14}$$

$$\text{Total cations removed} = Y_C \times (\text{net } H_2CO_3 \text{ produced}) \tag{15}$$

where Y_C was deduced as the slope of total cations removed with CO_3^{2-} versus H_2CO_3 produced and has value of 0.17 mg cations (as Ca^{2+}) removed with CO_3^{2-}/mg H_2CO_3, and β has a value of 0.99 for synthetic leachate and 0.68 for KVL leachate. Since it is possible to calculate Ca^{2+} removal that is larger than the Ca^{2+} (or total cations) concentration, a limitation must be set that restricts Ca^{2+} (or total cations) removal to be less than or equal to Ca^{2+} (or total cations) availability.

Conclusions

An important parameter in modeling clogging within leachate collection systems is a yield coefficient relating microbial fermentation of volatile fatty acids to precipitation of $CaCO_{3(s)}$. The development of a refined yield coefficient called the carbonic acid yield coefficient (Y_H), which relates the H_2CO_3 produced from microbial fermentation of acetate, propionate, and butyrate to Ca^{2+} removal, was presented. The Y_H can be used in clogging models to predict the precipitation of $CaCO_{3(s)}$ precipitation due to individual volatile fatty acid fermentation. Fermentation of acetate generates 4 times more H_2CO_3 then propionate fermentation, while butyrate fermentation consumed H_2CO_3. Additionally, fermentation of acetate destroys the organic acid, whereas fermentation of propionate replaces propionate with acetate and fermentation of butyrate replaces butyrate with two acetate. Thus, fermentation of acetate to form H_2CO_3 is what drives the $CaCO_{3(s)}$ precipitation, provided a precipitating cation is available. The Y_H deduced in a column experiment permeated with synthetic leachate ($Y_H = 0.169$ mg Ca^{2+}/mg H_2CO_3) was larger than that obtained in a similar column experiment permeated with KVL leachate ($Y_H = 0.116$ mg Ca^{2+}/mg H_2CO_3).

Analysis of clog material accumulated within the pore space of the medium show that a greater percentage of the CO_3^{2-} bound to Ca^{2+} in the VS series (99%) compared to the VK series (68%). This reflects the higher concentrations of non-Ca^{2+} cations (e.g., Fe^{2+} and Mg^{2+}) in KVL leachate than in synthetic leachate. Accounting for all the cations in the clog that are bound to CO_3^{2-}, not just Ca^{2+}, leads to a unified single yield, the calcium carbonate yield coefficient ($Y_c = 0.17$ mg cations (as Ca^{2+}) removed with CO_3^{2-}/mg H_2CO_3), that can be used to predict precipitation of $CaCO_{3(s)}$ and other cation-carbonate solids in leachate collection systems.

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