



Modeling precipitate-dominant clogging for landfill leachate with NICA-Donnan theory



Zhenze Li*

Wuhan Institute of Rock and Soil Mechanics, China Academy of Science, Wuhan, Hubei, China

HIGHLIGHTS

- An interesting theoretical investigation into the clogging of landfill drainages.
- First time advanced modeling of precipitate-dominant clogging of DOC rich leachate.
- Up-to-date model parameters to estimate speciation of calcium and DOCs.
- Modelings calibrated with experimental results on clogging of gravel aggregates.
- NICA-Donnan theory is robust to model speciation of cation–DOC complexes.

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ABSTRACT

Bioclogging of leachate drains is ubiquitous in landfills for municipal solid wastes. Formation of calcium precipitates and biofilms in pore space is the principal reason for clogging. But the calcium speciation in leachate rich in dissolved organic matters (DOM) remains to be uncovered. In spite of its complexity, NICA-Donnan model has been used to compute the speciation of metals and the binding capacities of humic substances. This study applies NICA-Donnan theory into the simulation of calcium speciation during the formation of precipitate-dominant clogging in leachate drainage aggregates for the first time. The consideration of DOC–Ca complexation gives reasonable explanation to the speciation of calcium, which is viewed as oversaturated, in leachate with concentrated DOM. The modeling results for calcium speciation are in good agreement with a large collection of experimental observations, suggesting that NICA-Donnan theory could be used in the modelings of reactive transport and clogging of landfill leachate collection systems.

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1. Introduction

Leachate drainage system is crucial to maintaining a reasonable water head inside a landfill for compliance with environmental legislations. The granular aggregate is always designed at the interface between solid wastes body and the liner systems, performing as the drainage layer for landfill leachate. However, significant clogging of the highly permeable leachate collection system has been widely reported in the management of sanitary landfills. Intensive studies have been carried out to characterize the clogs, to evaluate the permeability reductions, to unravel the clogging mechanisms or to model the life cycle of the drainage media [1–6]. The most important mechanism for the rapid development of clogging has been recognized as the result of CaCO₃ precipitation under the

coupled cation–organic interactions [7]. Uncovering the importance of these factors is central to understanding the cause of clogging and a key element in designing sustainable leachate collection systems.

Numerical models for the prediction of the fates of volatile fatty acids and calcium as well as the service life of drainage media have been recently developed [8,9]. These studies sharpen our insight into likely important influences in the evolution of cloggings, yet there remains a big gap between speciation modeling and experimental observations. The ample organic materials normally exist in landfill leachate, though believed to be important in calcium speciation, have not been fully addressed. Baun and Christensen [10] reviewed the advances in analyzing techniques and computer models for metal speciation in landfill leachate, suggesting that colloids and organic and inorganic complexes are important for heavy metals in landfill leachate. It was also pointed out that the organic database contained in some established models on metal–organic complexation is often fairly simple to obtain a crude

* Tel.: +86 27 87199858.

E-mail address: lazyhero@live.cn

approximation of metal. A more precise determination of the metal–organic complexation appeared to be absent. Christensen et al. [11] measured and modeled the proton binding properties of fulvic acids from landfill leachate-polluted groundwater, which is likely the first study on landfill leachate using NICA–Donnan model. They tested NICA–Donnan model to simulate cadmium complexation onto the isolated fulvic acids using sets of proton binding parameters. Because the NICA–Donnan database is limited, the modeling resulted in large deviations from experimental observations. Milne et al. [12] analyzed a large collection of experimental data on the characteristics of humic acid and fulvic acid using NICA–Donnan complexation model, and statistically weighed the typical values of parameters for this model. Olsson et al. [13] calibrated the speciation calculations with the NICA–Donnan model with experimental results about Cu binding to dissolved organic carbons (DOC) from municipal solid waste incinerator bottom ash leachate and accordingly suggested new parameter values for the metal-ion and proton binding. Recent studies have confirmed the accuracy of these statistical parameters in prediction of metal speciation in humic-substance contained aqueous solution [14].

This study is aimed at modeling the mineral precipitation in the context of clogging formations in landfill leachate with NICA–Donnan theory. We first reviewed the important interactions of dissolved organic carbons with cationic metals as commonly observable in the environment. The NICA–Donnan theory was then briefly introduced along with the modeling tool. The influence of dissolved organic matter as well as the pH, CO₂ partial pressure and calcium concentration was systematically investigated. Using the most up-to-date database of model constants, a collection of reported test data on the clogging process and mineral composition of clog was modeled with various assumptions of solution properties. Good agreement between the model estimations and test data has been observed, suggesting that the NICA–Donnan theory could be applied to the modeling of the clogging processes for landfill leachate drainages.

2. Role of humic substance

Humic substance (HS) is a major source of DOC for landfill leachate. Wu et al. [15] reported the HS constitutes of 83% of all organics in landfill leachate. Kang et al. [16] for the first time compared humic acids from landfill leachate and standard humic acids from soils and discovered that the former is in the early stage of humification, generally possessing small molecular weights. Chai et al. [17] investigated the characterization of humic substances extracted from landfill leachate and found enhanced humidification with landfill ages. Another subsequent study further supported their conclusion [18]. It is obvious that HS and fulvic acid may not be negligible in their interactions with inorganic elements.

Extracellular polymer substance (EPS), although can vary greatly in composition depending on the microorganisms and the availability of nutrients, comprises a large proportion of biofilm mass containing proteins, and biopolymers such as humic substances [19]. Wang et al. [20] experimentally confirmed the presence of fulvic acid like substance in EPS of sewage water treatment plant. For EPS from methanogenic sludge, the main composition is carbohydrate, protein and humic substance. Protein was predominant in the methanogenic sludge (41%) while humic substance accounted for 22.8% of the extracted [21]. Floating biofilms were experimentally observed in different growth media and that the chemical composition of the medium influences the chemical composition of the biofilm matrix (EPS) [22]. The EPS of the anaerobic granular sludge investigated are predominantly composed of humic-like substances, proteins, and polysaccharides. The EPS content in each biochemical compound varies depending on the sludge type and

Table 1
Mass ratio of EPS to biofilm.

EPS/biofilm in dry mass ratio	Reference	Note
0.10–0.18	[21]	Sludge, chemical extraction
0.15–0.30	[32]	In biofilm
0.15–0.45	[33]	
0.30	[34]	In biofilm
0.39–0.42	[23]	Sludge, cation exchange extraction
0.42	[35]	Sludge, ultrasonic treatment
0.70	[22]	In biofilm
0.85	[22]	In suspension
>0.90	[19]	

extraction technique used [23]. Liu and Fang [21] reported that the extraction method they used only extract part of the overall EPS. This explains the wide deviation of reported results on EPS yield in biofilms as shown in Table 1. Ni et al. [24] also confirmed the presence of fulvic-acid-like substances in EPS. It is shown that the quantity of produced EPS increases significantly in the substrate utilization process.

Sulfate-reducing bacteria (SRB) have been recognized as key players in the precipitation of calcium carbonate by increasing the alkalinity and consuming organic acids via extracellular matrix [25,26]. The EPS of SRB are reported to exhibit three main buffering capacities, respectively corresponding to carboxylic acids ($pK_{(a)} = 3.0$), sulfur-containing groups ($pK_{(a)} = 7.0–7.1$) and amino groups ($pK_{(a)} = 8.4–9.2$). The calcium-binding capacity of these exopolymers in solution at pH 9.0 ranged from 0.12 to 0.15 g(Ca)/gEPS [25,26]. Baker et al. [27] investigated environmental factors that affect the cell's surface chemistry and reactivity. It is shown that cells without EPS possess functional groups corresponding to phosphoryl (pK_a 6.5), phosphoryl/amine (pK_a 7.9), and amine/hydroxyl (pK_a 9.9). EPS and cell both possess carboxyl groups (pK_a 5.1–5.8) in addition to phosphoryl and amine groups. The presence of EPS corresponds to an increase in the intensity and type of functional groups relative to that for EPS-free cells. EPS could form bidentate complexes with Ca²⁺ ions which inhibit precipitation [28]. The calcium binding capacities of different types of EPS extracted from bacteria have been shown to range from 50 to 180 mg Ca/g EPS [28]. Calcium carbonate saturation states in sea water have been reported to be oversaturated in a large proportion of surface water. Organics, atmospheric CO₂, thermodynamic factors have been respectively discussed in previous studies [29–31].

3. Theory of NICA–Donnan model for humic substances

A detailed illustration of NICA–Donnan model has been shown by Kinniburgh et al. [36]. The main concept of this model is briefly explained in this section as it has been implemented in Visual MINTEQ [37]. Natural dissolvable organic carbon is believed to have two typical binding sites, i.e. the carboxylic site with strong affinity and the comparatively weak phenolic site. The binding affinity, or namely the dissociation constant K , determines the fraction (θ_i) of binding sites occupied by species i through the following equation,

$$\theta_i = \frac{(K_i c_i)^{n_i}}{\sum_i (K_i c_i)^{n_i}} \frac{\left(\sum_i (K_i c_i)^{n_i} \right)^p}{1 + \left(\sum_i (K_i c_i)^{n_i} \right)^p} \quad (1)$$

where c_i is the free concentration of species i in aqueous solution, n_i the component-specific non-ideality parameter reflecting the steric interaction and stoichiometry effects, and p is the

Table 2
Model parameters of DOC for Ca speciation prediction.

Parameters	Fulvic acid (soluble)	Humic acid (insoluble)
Donnan volume parameter <i>b</i>	0.57	0.49
DOM/DOC	1.65	–
Strong site (mM/g)	5.88	3.15
log(<i>k</i> ₁) (FA-H)	2.34	2.93
log(<i>k</i> ₁) (FA-Ca)	–2.13	–1.37
<i>n</i> _{H1}	0.66	0.81
<i>n</i> _{Ca1}	0.85	0.78
Width of strong site <i>p</i> ₁	0.57	0.62 _s
Weak site (mM/g)	1.86	2.55
log(<i>k</i> ₂) (FA-H)	8.60	8.0
log(<i>k</i> ₂) (FA-Ca)	–3.0	–0.43
<i>n</i> _{H2}	0.76	0.63
<i>n</i> _{Ca2}	0.80	0.75
Width of weak site <i>p</i> ₂	0.59	0.41

Note: *n* is the non-ideal binding stoichiometry for the protonation of dissolvable organic carbons.

site-specific non-ideality indicating the width of the distribution of the binding site.

Then the overall amount of bonded species (Q_i) can be predicted by

$$Q_i = \frac{n_i}{n_H} \theta_i Q_{\max,H} \quad (2)$$

where n_H and $Q_{\max,H}$ are parameters for the reference species of H^+ in terms of protonation reaction, n_H is non-ideality related to H^+ and $Q_{\max,H}$ is the maximum amount of binding capacity for H^+ .

The Donnan volume (V_D) of the humic substance is dependent on solution ionic strength in the terms of

$$\log V_D = b(1 - \log I) - 1 \quad (3)$$

where b is the model parameter that relates the volume change to the salinity.

According to the assumption of Donnan hypothesis, counterions are bonded to the extra binding sites in order to maintain the charge balance inside the Donnan volume. The equilibration equation for the electrical charge balance is written as

$$\frac{q}{V_D} + \sum_j (c_{Dj} - c_j) z_j = 0 \quad (4)$$

where q is the total charge of humic particle, V_D the Donnan volume of the humic substance, c_{Dj} the concentration of counterion j within Donnan volume, c the concentration of j in free state in aqueous solution, and z is the electric charge of component j .

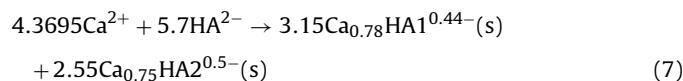
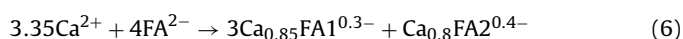
It is assumed that the bonded counterion c_{Dj} is related to the external concentration c by a linear form of equation as

$$c_{Dj} = c_j (e^{-\psi_D/kT})^{z_j} \quad (5)$$

In Visual MINTEQ, this variable is not explicitly calculated as it can be solved by determining the amount of bonded species which is of more interest for our modeling.

Ion exchange ratio $[H^+]/[M^{+2}]$ varies with cationic types and humic substances. The exchange ratio of H/Ca for fulvic acid was reported to be 0.2–0.5 [36], 0.80 [38] and 0.8–0.85 [37]. We used a moderate stoichiometric value for H/Ca as 0.8–85 in this study.

Taking into account of Milne, Kinniburgh, van Riemsdijk and Tipping's [38] statistical collection of model parameters for both fulvic acid and humic acid, we developed the necessary parameters as shown in Table 2 for the numerical simulation of Ca-HS speciation in a variety of aqueous chemical conditions. From Table 2 we can obtain the following reaction formula for humic substances.



4. Modeling results and discussion

4.1. Ca precipitates in an inorganic system

Precipitation of Ca in aqueous solution was computed with a standard database of stability constants under conditions with a wide range of pH (5–9), Ca concentration (0–1000 mg/L) and CO_2 partial pressure (0–0.4 atm) using Visual MINTEQ [37]. Mineral precipitation in terms of calcite is assumed to occur when the relevant saturation index reaches 1.0,



The results are visualized in 3D contour plotting as shown in Fig. 1a and b. For solution with $[Ca] < 200$ mg/L and $p(CO_2) = 0$, calcite precipitates at pH 8.0. But for cases with $[Ca] = 1000$ mg/L and $p(CO_2) = 0.4$ atm, it precipitates at pH 6.0. Due to the difficulty to simply plot such a big dataset, we sliced the 3D plotting along different axis (Fig. 1c–e) in order to show the trend of precipitation percentage with specific variables. Precipitation is found to increase with pH and CO_2 partial pressure for a solution at certain Ca concentration (Fig. 1c). For the study range of aqueous chemical conditions, no precipitation occurs at $pH < 6.0$ (Fig. 1d). Under conditions with certain pH and $p(CO_2)$, the precipitation percentage increases with Ca concentration (Fig. 1e). The precipitation tends to take place at lower pHs with increased $p(CO_2)$.

Fig. 2 shows the precipitation of Ca^{2+} at various pHs and Ca concentrations. At neutral pHs and $[Ca] = 1000$ mg/L, 95% of Ca^{2+} would be precipitated. This number actually overestimates the formation of precipitate-dominant clogging for landfill leachate. The primary driver for $CaCO_3(s)$ precipitation in the column leaching tests was acetate fermentation to CH_4 and H_2CO_3 , which increased both the total carbonate concentration and the solution pH [39]. However, the influence of organic ligand, especially the dissolved organic material (DOM), on the speciation of Ca^{2+} was not addressed in these studies. Martin and Sayles [40] reported that a large fraction of the $CaCO_3$ dissolution that is occurring in seawater environment is attributable to the neutralization of metabolic acids produced during organic matter oxidation. Although this is different from the anaerobic condition in landfill leachate, the impact of organics appears to be a significant factor for calcium co-precipitation. It is reported that the dissolved organic matter in the form of HA inhibits the calcite precipitation rate from seawater by covering the active growth sites rather than by complexation of calcium in solution [41]. Concentrations of dissolved calcium were generally reported to be one to two orders of magnitude higher in organic acid-rich ground water than in ground water having low organic acid concentrations. Carbonate minerals were believed to be the likely sources of these elements. Similarly, concentrations of dissolved silica, derived from quartz and k-feldspar, were higher in organic acid-rich ground water than in other waters [42].

4.2. Effect of DOC on calcite precipitation

Natural dissolved organic carbon (DOC) is ample in soil and aquaculture and has a broad significance in environmental studies. Romkens and Doling [43] investigated the interaction between Ca^{2+} and DOC extracted from arable soils and it is found that DOC could be flocculated by up to 50% by addition of calcium, which is mainly the high molecular weight (HMW) organic acid. Low molecular weight (LMW) substances remained soluble even at high

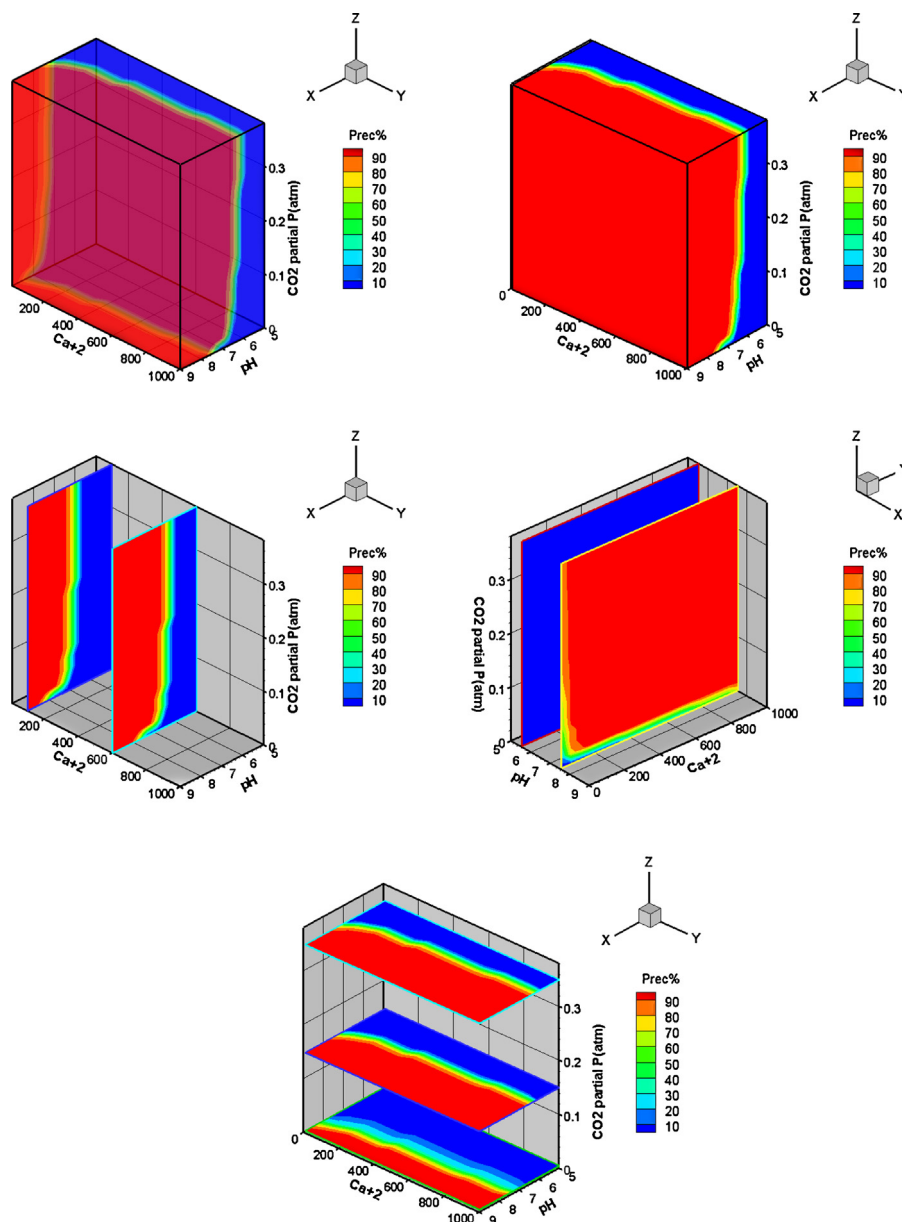


Fig. 1. 3D contour plotting of precipitation in Ca-pH-CO₂ system: (a) translucent view of the contour; (b) opaque view of the contour; (c–e) sliced profiles at different axial directions.

calcium concentration, which is believed, up to 50%, to be responsible for the DOC-facilitated solute transport [43]. As seen from Fig. 2, 90% of Ca²⁺ (initial concentration at 150 mg/L) precipitates at pH 7.5, which obviously deviates from the experimental observation of Nikolova-Kuscu, Powrie and Smallman [5]. DOC constitutes a large portion of COD of landfill leachate [44–46]. It is reported that the COD to TOC ratio tends to decrease as the landfill ages. The ratio of COD/TOC varied from 3.3 for a relatively young landfill to 1.16 for an old landfill [47].

Fig. 3 shows the relationship between dissolved Ca concentration and COD in leachate that has been previously investigated by Rowe's research group at Queens University. Two different types of leachate, i.e. the real leachate (VK) and the synthetic leachate (VS), were respectively plotted in this graph. It is shown that the Ca concentration in VS is generally higher than that in VK. The VK series of leachate has a wider distribution of COD. We predicted the change of labile Ca concentration with increasing DOC concentration, by assuming that calcite was saturated throughout the tests.

The obtained Ca concentration represents the maximum allowable concentration for a given set of parameters, e.g. $p(\text{CO}_2)$, pH and DOC, etc. From Fig. 3 it is clear that the predicted labile Ca increase linearly with the increase in COD. Respectively setting the ratio of COD/DOC at 1.3 and 3.0, we successively obtained reasonably high correlations between the modeling and test data. According to our modeling of Ca speciations, the ratio of COD/DOC for the synthetic leachate (VS) studied by VanGulck, Rowe, Rittmann and Cooke [6] was determined at 1.3, while the ratio for the real landfill leachate VK was at 3.0. VanGulck and Rowe [4] identified three major components of DOC, e.g. acetate, propionate and butyrate, which equal to 73% of the total COD. The rest 27% of COD was speculated as more complex organics, most likely the humic substances. The proportion of HS in the VK leachate is also consistent with the reported COD/DOC ratio that ranges from 1.1 to 3.1 [47]. Another interesting observation is that the synthetic leachate has a ratio of COD/DOC = 1.3. A higher value in COD/DOC is usually observed in fresh leachate compared to the aged one. In this regard, the

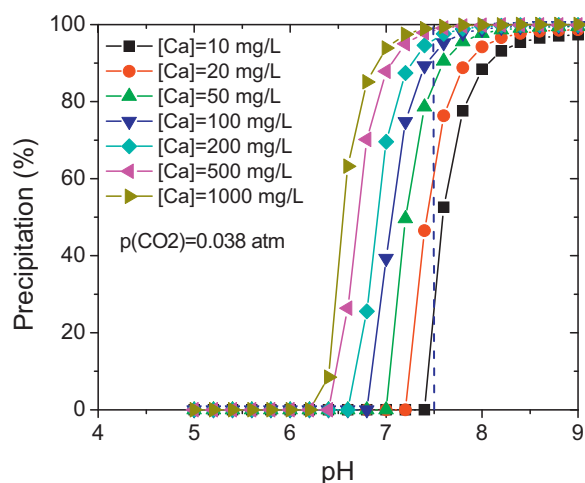


Fig. 2. Precipitation of Ca^{2+} at various pHs in presence of organic ligands.

synthetic leachate (VS) could be classified as an aged leachate, especially when the highly concentrated acetate is taken into account. The rate of clogging in leachate drainage system was faster for VK than VS, which further supports such a speculation.

Fig. 4 presents the variation of Ca precipitation with pH. The test results of Ca precipitation that are cited from the study of Nikolova-Kuscu, Powrie and Smallman [5] were plotted against the equilibrium solution pH. Three columns have been permeated with synthetic leachate representing the low-level radioactive wastes. The scattered spots below X-axis are within the experimental error range. Regarding the lack of information about the time-dependent variation of COD or DOC in leachate, it is impossible to analyze these test data using the method as we did in Fig. 3. However, this modeling considers FA as the only DOC forming ligands with Ca. By tuning the DOC concentration we obtained 3 typical curves that are consistent to the test data. The predicted DOC is >0.86 and 1.0–1.5 for less concentrated leachate (100% strength) and concentrated leachate (200%), respectively. In Table 3, we compared the ratio of the predicted DOC and the tested TOC for these columns. The mass ratio of DOC/TOC ranges from 0.75 to 1.0, which is unlikely to deviate from the fact. Due to the limited number of column tests, the coverage of the test data appears to be restricted. However, our modeling seems reasonable to explain the experimental observations.

The pH-dependent speciations of FA and calcium ligands are displayed in Fig. 5. The modeling setting is identical to the #2 case as

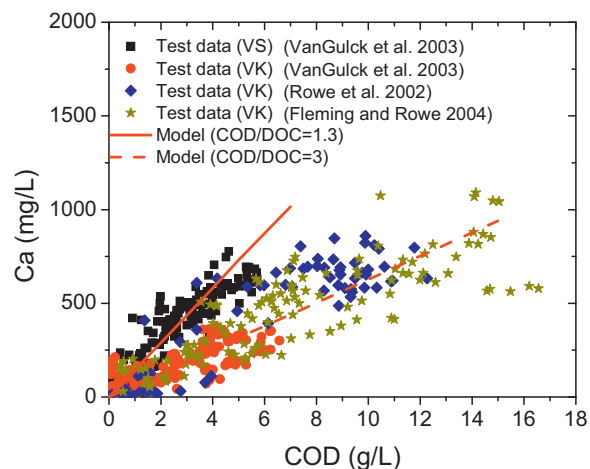


Fig. 3. Relationship between dissolved Ca concentration and COD in landfill leachate (Data are cited from refs. [1,3,6]).

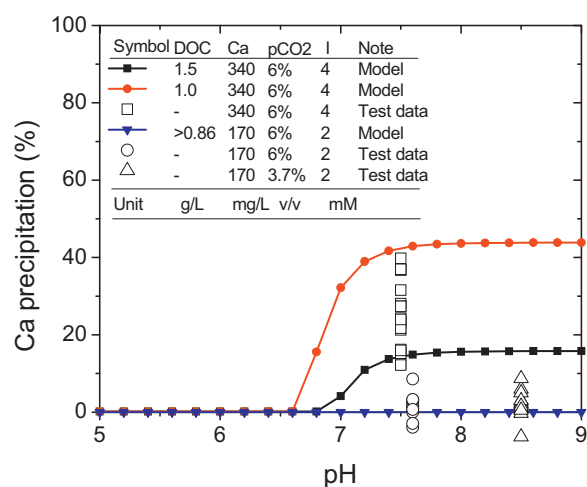


Fig. 4. Variation of Ca precipitation with solution pH as predicted with different assumption of DOC concentrations (Data is cited from ref. [5]; I indicates ionic strength (M)).

Table 3
Fundamental parameters for the clog material.

Parameters	Values	Note
Organic clog dry weight (g)	165–337	Only for top layer above tapping #2 (5.18 L)
Porosity	0.22–0.33	The average value
Porosity change	0.06–0.17	
TOC in pore space (g/L)	115–236	
TOC in overall liquid (g/L)	0.105–0.749	
TOC in influent (g/L)	0.99–1.99	[5]
Predicted DOC (g/L)	1.0–1.50	This study
DOC/TOC	75–100%	

Note: these data are cited from ref. [5] regarding the columns of # 1–2.

shown in Fig. 4. The majority of FA-liganded Ca (48–52%) is bounded to the Donnan gel phase via the counterion accumulation effect that is governed by charge balance. Although the strong site FA1 has been mostly bound to Ca at $\text{pH} > 6.5$, adsorption merely contributes to about 3% of the overall Ca complexation. The reason for this behavior remains unclear in the current study. The calcite observed at alkaline pH conditions is mainly formed via the unbounded labile

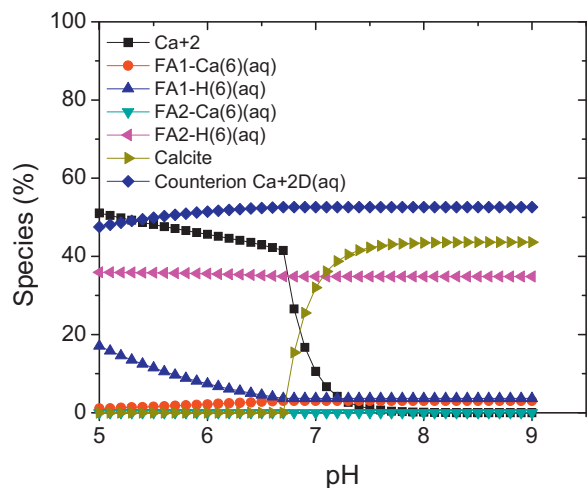


Fig. 5. Variation of calcium species with pH ($\text{pCO}_2 = 0.06$ atm, $[\text{Ca}] = 340$ mg/L, $\text{DOC} = 1.0$ g/L, 25°C).

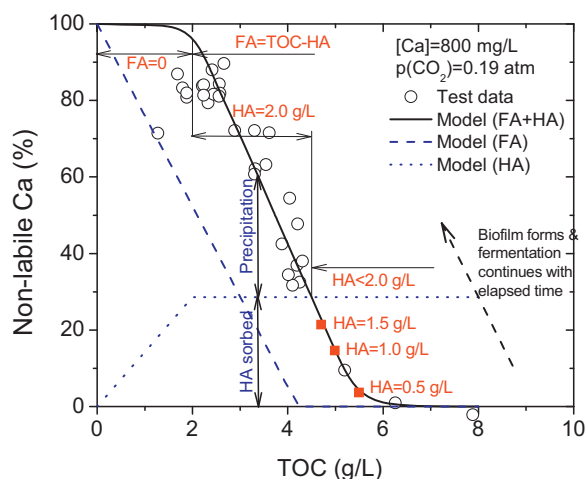


Fig. 6. Variation of non-labile Ca portions with TOC concentration (modeling conditions include $p\text{CO}_2 = 0.19$ atm, $[\text{Ca}] = 800$ mg/L, pH 7.5. Using the assumption of $\text{COD}/\text{TOC} = 3.0$ for TOC calculation. Data is about VK leachate from ref. [6]).

Ca^{2+} that is present in acidic conditions. The DOC–Ca complexes appear to be inert to precipitation reactions. Figs. 4 and 5 indicate the preferential complexation of calcium with DOC instead of precipitating out in terms of CaCO_3 . Because the total organic content tends to decrease with elapsed time as a result of bio-reactions, the DOC-liganded calcium that is labile at early stage of landfilling would become oversaturated and finally turns into calcium carbonate. Therefore, it is suggested that avoiding disposing municipal solid wastes having high organic content with wastes high in calcium could help to reduce the possibility of calcium carbonate clog [5].

4.3. Effect of insoluble humic acid on calcium precipitation

Ca fraction in the clog material is reported to be 0.20 in field and 0.25–0.31 in column experiments [4]. VanGulck, Rowe, Rittmann and Cooke [6] determined the Ca fraction to be 0.36 and 0.24 for VS and VK leachate, respectively. For calcite the theoretical Ca fraction is 0.40 according to the molecular weight. Lower values in Ca fraction indicate occurrence of compounds other than calcite in the clogging stage. Fleming and Rowe [1] reported the fraction of calcite in clog material as 0.30–0.40. Rowe, VanGulck and Millward [3] questioned the source of Ca precipitation in clogging is not totally resulted from carbonate precipitation. It has been hypothesized that Ca may be bound up with other chemicals. The following part will be devoted to the discussion of the impact of insoluble organic material on Ca precipitation.

Fig. 6 presents a series of test data about the clogging of drainage layer permeated with landfill leachate (VK, from VanGulck, Rowe, Rittmann and Cooke [6]). Our modeling shows that neither FA nor HA would be sufficient to best-fit the test data. By adding up HA and FA together as TOC, we obtained modeling results that are consistent with the experiments. The HA content is calculated as 2.0 g/L. The clogging starts from the right hand side of the curve (FA + HA) where TOC is at its peak value. The red squares mark the growth in HA as TOC keeps reducing, implying the gradual accumulation of biofilm or bacteria, until TOC is about 4.5 g/L. After this point, the content of humic acid stabilizes at 2.0 g/L, indicating the equilibrium phase, or steady-state phase has been reached. Rowe, VanGulck and Millward [3] characterized the “lag phase” as (1) COD reduces less than 10%; (2) the effluent pH increases from 6.3 to 7.5–7.9; (3) biofilm grows to cause obvious reduction in drainable porosity. The steady-state phase is characterized as (1) COD and Ca reduce significantly; (2) effluent pH stabilizes; (3) drainable

porosity keeps decreasing due to calcium precipitation [6]. The early reduction in the porosity at lag phase is hypothesized to be caused primarily by biofilm growth with negligible calcium precipitation compared with the steady-state phase at which the calcium precipitates control the amount of clogging [3]. Our modeling results coincide very well with these previous observations.

From Fig. 6 we can calculate the mass ratio of calcite to the total clog material. Since the initial Ca concentration is 800 mg/L, and the TOC stabilized at 2.0 g/L at the end of the column test, therefore the precipitated calcite consists of 1.0 g/L in solution. Assuming the clog is composed of both calcite and HA, then the mass percentage of calcite is 33% ($=1.0/(1.0+2.0)$). This is located right in the range of the reported value of 0.3–0.4 by Fleming and Rowe [1] who experimentally examined the mineral constituents of the clog material. Accordingly, the Ca content in the clog could be calculated. The humic acid–calcium ligand has a Ca % at 17.4% in case of saturated sorption. Calcite has 40% of Ca due to the molecular weight. The averaged mass proportion of Ca in the clog is thus at 24.9% ($= (0.4 + 0.348)/3$), which in turn agrees well with the reported 24% for the clog of VK leachate [6].

5. Conclusion

In this study, the speciation of calcium in clogging of landfill drainage media was modeled with NICA–Donnan theory for the first time. Comparison has been made between the predicted and observed behavior for the clogging of column leaching tests. The model parameters for humic substances from various sources of DOC that were selected from literatures proved to be representative of landfill leachate. Simulation results confirmed that calcium in landfill leachate is oversaturated in view of the inorganic chemical reactions. The consideration of DOC–Ca complexation gives reasonable explanation to the speciation of calcium in leachate with very high organic content. The modeling results about calcium precipitation are in good agreement with a large collection of experimental observations. For leachate containing low-level of DOC it is sufficient to predict calcium speciation by consideration of fulvic acid. But for leachate containing high-level of DOC it is necessary to take into account of both fulvic acid and insoluble humic acid. The modeling in this study indicates that complexation of calcium with fulvic acid gives rise to the labile Ca concentration, while the complexation of calcium with humic acid contributes to the formation of cloggings. Biological fermentation gradually reduces DOC concentration, leading to consecutive cloggings. The work described in this paper has shown that the NICA–Donnan model could be applied into the numerical simulation of bioclogging in order to provide a much more substantial understanding of the fate and speciation of inorganic elements in landfill leachate.

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