Cation exchange due to the diffusion of ammonium from livestock effluent through glacial clay soils

for submission to

Applied Geochemistry

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September 19, 2006

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Abstract

The objective of this study was to experimentally simulate interactions between liquid manure and soil in diffusion dominant areas beneath earthen manure storage (EMS). A previous radial diffusion cell method was modified to include an anaerobic chamber that employed a plastic glove bag supplied with inert argon gas. Anaerobic conditions were maintained during the entire run time of the experiment. Little oxidation of ammonium occurred; consequently, nitrate and nitrite concentrations were lower than the detection limit. Chloride (Cl^-) played a key role in redistribution of major cations and anions resulting from the ammonium diffusion. Linear ammonium and potassium adsorption isotherms were obtained. The resulting distribution coefficients, K_d, for ammonium ranged from 0.3 to 0.4 L/kg. Significant ammonium exchange reactions led to an average increase in hardness of 137% in the reservoirs, due to extraction of exchangeable calcium and magnesium. Geochemical mixing modeling using PHREEQC adequately simulated the linear ammonium adsorption at low dissolved ammonium concentrations (< 30mM). The predicted manure volumes to cause ammonium saturation were 1.0 to 1.4 mL/g for the glacial clay soil samples.

Keywords

Cation exchange, ammonium, glacial clays, liquid hog manure, diffusion and PHREEQC.

1. Introduction

Manure produced by intensive livestock operations has been a public concern due to the substantial volume generated. Earthen manure storage (EMS) system, constructed with local geological material, is a common means to store liquid manure in Western Canada. Old EMS systems (older than 20 years), which are scattered throughout Alberta, have no engineered liner or barrier system to prevent the seepage of liquid manure (AGDEX, 2001).

The current Alberta regulations for EMS strictly enforce the need for an engineered liner system to protect groundwater and surface water resources (AOPA, 2004). Nevertheless, the presence of nitrate and nitrite, which is commonly caused by the leakage of liquid manure from EMS, has frequently exceeded water quality guidelines. In reality, 32 to 87% of the water resources in areas of low to high intensive livestock operation regions in Alberta exceeded the Maximum Contamination Level (MCL) of nitrate for aquatic life (Alberta Agriculture, Food and Rural Development, 1998; CAESA Water Quality Study, 2004).

In order to evaluate a budget of excess nitrogen under EMS environment, the long-term diffusion effect and the interaction of liquid manure and local soils should be considered, in addition to the seepage loss of liquid manure from EMS facilities. In this study, therefore, diffusion is identified as a major transport process between liquid manure and the local soils used for the construction of EMS. The rationales for the consideration of diffusion are as follows: (1) molecular diffusion, which is the slowest contaminant transport mechanism, should be examined for long-term risk assessment and a decommissioning strategy to address unlined old EMS; and (2) EMS in the Canadian Prairies are generally located in glacial clay and/or clay tills with diffusion dominated hydrogeologic regimes.

Ammonium, which is the most abundant form of nitrogen in liquid hog manure, is regarded as the source of nitrate contamination in aquifers. According to Fonstad (2004)'s field measurement for fluid throughout EMS, low dissolved oxygen concentrations, ranging from 0.3 to 1.3 mg/L, lead to anaerobic conditions at subsurface areas of the EMS. Eh readings of less than –100 mV, and high organic carbon concentrations of approximately 6,000 mg/L, also cause nitrogen to remain in the ammonium form. Excessive ammonium can be transported to the aerobic zones of an aquifer and then be oxidized to form nitrate and/or nitrite (Kreitler, 1975, Wassenaar, 1995, Fukada et al., 2004, Hudak, 2000; Widory et al., 2004, Zebarth et al., 1999).

Fig. 1 provides a conceptual model of ammonium diffusion along fractured glacial clays and/or clay tills in the Canadian Prairies. The fractures in the glacial deposits play a key role in the long-tem redistribution of ammonium through molecular diffusion and adsorption (D'Alessandro et al., 1997; Donahue, 1999). Adsorbed and aqueous phase ammonium may prevail between the fractures. Aqueous phase-ammonium in a major facture is gradually attenuated. Significant cation exchange with the clays in contact with ammonium-rich liquid manure can be a primary cause of strong ammonium adsorption. This may lead to changes in pore fluid chemistry due to the replacement of cations present in the clays.

2. Methods

2.1. Anaerobic radial diffusion cell method

2.1.1. Cell preparation

Minimally disturbed (stainless steel Shelby tube) glacial clay soils were collected during a geotechnical site at investigation in Ponoka, Alberta (Cell UA1 to 5). The samples were extruded and trimmed to fit in the radial diffusion cell. Fig. 2-[4] shows the geometry of the PVC Teflon radial diffusion cell (RDC). To construct a reservoir hole in the soil sample in the RDC, the trimmed top surfaces of the soils were drilled along the central axis of the cylindrical RDC (O.D: 27mm, I.D.: 24mm, H: 70mm). These were not drilled down to the absolute bottom of the cells in order to allow three-dimensional radial diffusion into the porous media (Fig. 2-[3]). The typical reservoir depth was 70 mm from the top surface, and the average height of all the cells was 90 mm. A polyethylene (PE) porous liner (X-5306

Porex®-25μ fine) was inserted into the drilled hole. The intact core samples were then enclosed with O-ring seals and with the square-shaped upper-plates of the cells. The cell preparation was conducted as quickly as possible to minimize disturbance of, and moisture loss from, the soil samples.

2.1.2. Diffusive equilibrium and monitoring reservoir

After setting up the five diffusion cells, each central reservoir, which had an inner volume of 20 mL±0.08, was filled with 20mL-ultra pure water (18.2 MΩ-cm and 0.7μS/cm, Barnstead). The ultrapure water was allowed to equilibrate with the soil for 60 to 90 days, depending on the types of soil samples (Van der Kamp et al., 1996), to quantify the initial soil pore fluid chemistry. This procedure essential dilutes the original pore fluid chemistry of the soil sample by the volume of the reservoir (0.84 to 0.87 times dilution). In order to confirm diffusive equilibrium of the pore fluids had occurred, the electrical conductivity (Orion® 130A) of the reservoir solutions was measured by using a micro electrical probe and the pH change (Accumet® AR50) of the reservoirs was monitored (Van der kamp et al., 1996).

Stagnant electrical conductivity response of the reservoirs was regarded as completing diffusive equilibrium. After equilibrium was achieved, the pore fluids were sampled from the diffusion cells and filtered using syringe filtration (Waterman® nylon membrane filter paper 0.45 μm). Major cations and anions of the pore fluid were analyzed by ion chromatography

(IC), Dionex® 2500 (Applied Environmental Geochemistry Research Facility at the University of Alberta).

2.1.3. Anaerobic conditions and injection of liquid hog manure

A four hand-glove bag (Figure 2) was used to replicate the anaerobic environment beneath EMS, 2-[1]. Argon gas was added 3 or 5 times per day to maintain oxygen-limited conditions in the glove bag chamber. The anaerobic chamber was to separate the diffusion cells from the atmospheric environment of the laboratory room. It was critically important to maintain anaerobic conditions during the routine monitoring program.

After creating the anaerobic chamber, the reservoirs in the five diffusion cells were filled with 20mL±0.36-raw liquid hog manure, which was collected at the Swine Research and Technology Center (SRTC) at the University of Alberta (March, 2004). In order to measure the earlier response of the anticipated ion exchange, the effluents of about 20 mL (reservoir volume) were sampled from the reservoirs (~20 mL) after a 10-day diffusion period elapsed. A short diffusion period is required to determine effective diffusion coefficients. The effective diffusion coefficient was determined by matching the rate of change in the pore chemistry of the reservoir. If the pore fluids are allowed to completely equilibrate a diffusion coefficient cannot be determined. The analysis of effective diffusion coefficients and other transport properties is beyond the scope of this manuscript but is presented in Chang (2005).

After sampling fresh, manure effluent was immediately re-injected into the reservoirs and the samples allowed to equilibrate. During the 60-day diffusion period, a routine monitoring program assessed the effluent chemistry; this included the measurement of electrical conductivity, pH, temperature, and mass change caused by evaporation and measuring and sampling losses.

After the 60-day diffusion period, the effluent was sampled from all the cells. Conventional water chemistry analysis was conducted on the collected effluent solution, including cation and anion concentration by IC analysis, electrical conductivity, pH, temperature, dissolved oxygen (DO), hardness, alkalinity, total dissolved solids (TDS), and total organic carbon (TOC).

The final step was to investigate the potential for ammonium desorption due to the infiltration of fresh water into the clay soils. To do this, 20mL-ultra pure water was injected into each reservoir in contact with the soil samples. The desorption duration was planned to continue for a further 60 days. Routine monitoring and water chemistry analysis were carried out during the desorption-period.

2.2. Geochemical mixing models using PHREEQC

PHREEQC interactive version 2.6.0.1 (Parkhurst and Appelo, 1999), developed by the U.S. Geological Survey, was used for the geochemical mixing modeling. The simulations were divided into two modules: (1) SIMPLE MIX MODEL and (2) MIX MODEL. The SIMPLE MIX MODEL refers to the simulation of a single episode of the liquid hog manure injection. Hence, the SIMPLE MIX MODEL described the anaerobic RDC experiment with a single liquid hog manure injection. The MIX MODEL aimed to simulate the maximum number of injection episodes to achieve full ammonium saturation in soils.

3. Material characterization

3.1. Soils

The soils consisted of 31 to 34% sand and 65 to 68% clay. According to the United Soil Classification System (USCS), the sampled soils in this study were classified as sandy lean clay (CL) for Cell UA1 to 2 at 1.5 to 2.3 m depth, and sandy fat clay (CH) for Cell UA3 to 5 at 3 to 5.3 m depth. Hydrometer tests and wet sieve analysis were performed for the soil classification at the Geotechnical Laboratory at the University of Alberta. The total porosity estimated by gravimetric water content typically ranged from 0.32 to 0.42. Volumetric water contents were 32 to 33% for Cell UA1 to UA2, and 37.5 to 42% for UA3 to 5.

X-ray diffraction (XRD) and Scanning Electron Microscope (SEM) analyses were used to identify the clay mineralogy of the samples. The XRD results indicated that the soil samples were composed of smectite and illite with lesser amounts of plagioclase, chlorite, and kaolinite. Minor quantities of potassium feldspar were detected as well. The soil samples from

Ponoka consist of 60% smectite in the clay fraction within a framework sand/silt.

The cation exchange capacities of the samples were determined by conventional ammonium acetate (NH_4OAc) method (McKeague, 1981). The results were: 21.2 meq/100g for Cell UA1 to 2; 43.3 meq/100g for Cell UA3 to 4; and 34.2 meq/100g for Cell UA5 (Table 1). The high CEC values reflected the 68% smectite present in the clay fraction of the samples.

A saturated paste extraction test (Carter, 1993) was conducted to examine geochemical properties of the soil samples (Table 1). A 1:1 volume ratio of air-dried soil to deionized water was adopted to create the saturated pastes (Hogg and Henry, 1984). The saturated pastes were then centrifuged to extract the soluble salts. The background ammonium-N concentrations were 4 to 10 mg/L. The leached nitrate-N concentrations ranged from 3.4 to 8.6 mg/L. Nitrite was rarely detected because it rapidly oxidized to nitrate. The measured soil pH typically ranged from 7.9 to 8.2 for the non-saline soils.

3.2. Liquid hog manure

Table 2 shows IC analysis for the initial liquid hog manure. Notably, ammonium was a dominant species of which mole fraction is approximately 45%. Bicarbonate, potassium and chloride were 36%, 7% and 6% in mole fraction, respectively. Calcium, magnesium and sodium in the manure were extremely limited (1 to 4%).

The measured electrical conductivity and pH of the manure were 23 mS/cm (25°C), and 7.9, respectively. The dissolved oxygen (DO) reflected a very low level: 0.8 mg/L. The saturation index (SI) of calcite ($CaCO_3$), calculated by PHREEQC, was 0.2 for the liquid hog manure; consequently, calcite precipitation was expected during the experiment. Based on filed alkalinity measurements CO_2 (g) in the liquid hog manure was over saturated (SI value of 0.58) with respect to atmospheric CO_2 (SI of -3.51 for atmospheric CO_2 (g)). Degassing of CO_2 (g) from the reservoir was expected to occur during the experimental program, including the sampling and measuring of the reservoir solutions.

4. Results and discussion

4.1. Geochemical interpretation for soil-liquid manure system.

4.1.1. Initial pore fluid chemistry

Prior to sampling equilibrated reservoir solutions that were in contact with the soil samples, the required diffusive equilibrium time was predicted using ChemFlux (Fredlund and Stianson, 2003), which is a comprehensive transport-modeling tool based on the finite element method. In the 3D radial model, the conservative solute chloride diffuses from the porous media to the reservoir. The predicted equilibrium time ranged from 55 to 60 days when the equilibrium concentration for chloride reached 18 to 20 mg/L. Therefore, the reservoir solutions were sampled when the predicted 65 day period had elapsed and the pore fluid was regarded as representative of the soil samples. To confirm the diffusive equilibrium time, the electrical conductivity and pH change in the reservoir solutions were measured (Van der kamp et al., 1996). Fig. 3 shows that the determined diffusive equilibrium time ranged from 53 to 66 days for the Cell UA1, 2 and 5 samples. In the case of Cell UA3 and 4, the reservoir solution may not have completely equilibrated within the designed equilibrium time (65 days). The estimated equilibrium time for Cell UA3 and 4 ranged from 66 to 109 days. The elapsed time to reach equilibrium varied according to soil properties: particle size and clay fraction. It appeared that the soil samples with smaller particle size and more clay fraction resulted in a longer diffusive equilibrium time.

The initial pore fluid concentrations are presented in Table 3 and 4. Ammonium, nitrate, and nitrite concentrations were lower than detection limits according the IC analysis. The charge balance errors for the total dissolved major cations and anions in the pore fluids ranged from 0.60 to 1.73%.

The pH of the reservoir increased with contact time, as shown in Fig. 4. The value of log P_{CO2} ranged from -1.8 to -1.5 in cells UA1 to UA5. It is possible that developing CO_2 (g) in the pore fluids contributed to an increase in the pH of the reservoir solutions by calcite ($CaCO_3$) dissolution in the reservoirs. The saturation index (SI) of calcite ranged from -2.6 to -1.6 in the reservoir solutions, according to PHREEQC calculation. As a result of over saturation of CO_2 (g) and dissolution of $CaCO_3$, the reservoir solutions pH increased on average from 6.1

to 7.0. Therefore, the pH of 7.0 is regarded as the representative pH of the synthesized pore fluids after diffusive equilibrium periods. The value of pH 7.0 will be used for the initial pore fluid chemistry data for geochemical models.

The monitored temperatures of the reservoirs ranged from 20 to 24.5°C during the 65-day equilibrium period. The measured reservoir temperature was reasonably stable and equivalent to the temperature of the laboratory. It was assumed that a change in the reservoir temperature did not affect the initial pore fluid chemistry (Van der Kamp et al., 1996).

In order to complete water saturation, 5 to 17 mL of water was added to the soil samples in the diffusion cells. The added water volume was approximately 1.5 to 4.7% of the total volume of the soil in the cells. The effective pore fluid volume ranged from 130 to 170 mL. This estimation is based on mass balance equations that include 0.01 to 0.07% of evaporation loss and 0.38% of measurement loss. Both the initial pore fluid chemistry and the effective pore fluid volume were used for the geochemical mix models.

4.1.2. Change in pore fluid chemistry

Reservoir concentrations for the 10-day and 60-day periods of diffusion are presented in Table 3 and Table 4. During the 60-day diffusion periods, a substantial decrease of ammonium (NH_4^+) in the reservoirs occurred under the anaerobic conditions (Table 4). After a 10-day period, it was observed that approximately 53% of the initial ammonium amount (mole) in the reservoir had diffused to the soils. Ammonium diffusion, initiated by a single injection of liquid hog manure, was almost completed within 60 days (with an average 91% of the initial NH_4^+ diffused into the soil samples).

Table 5 shows the comparison between measured concentrations on diffusion-day 60 and the diluted concentrations for cations and anions. The diluted concentrations, which represent equilibrium concentrations after the diffusion and desorption processes, were calculated based on the mass balance between the diffused and remaining ions in the reservoirs and the estimated pore fluid volume (130 to 170 mL). In comparison with measured and calculated equilibrium concentrations, ammonium did not reach theoretical equilibrium. The measured ammonium concentrations in Cell UA1, 4 and 5 were about 55 to 84% lower than the expected equilibrium concentrations (See Table 5 and Fig. 5(a)). The significant concentration gradient for ammonium between background pore fluid (less than 1 mg/L, Table 3) and liquid manure (5241 mg/L) forces a dramatic decrease of effluent concentration in the reservoir. The measured concentrations of ammonium were considerably lower than the equilibrium concentrations. This reflects significant retardation of ammonium through the tortuous paths in the fine materials. (It is noteworthy that Cell UA2 data were unusual because some rock materials in the cell blocked manure transport; Cell UA2 data were thus neglected for the most part for this portion of the analysis).

During the ammonium diffusion period, chloride did not equilibrated. As shown in Table 5, the measured chloride concentrations were higher than the calculated equilibrium concentrations (i.e., 3 and 4 times higher). It is inferred that chloride would not diffuse into the porous media. Chloride (Cl^-) played a key role in achieving charge balance during the ammonium diffusion. Fig. 5-(b) and (c) show the measured and diluted concentrations of K^+ and Cl^-. Chloride preferentially exists as an ion pair with potassium in the effluent. In addition, inverse diffusion of the excess calcium and magnesium caused these elements to pair with chloride as $CaCl_2^{\bullet}$ and $MgCl_2^{\bullet}$ in the reservoir. As shown Fig. 5-(c), the charge balance error for Cl^- vs. K-Ca^{2+}-Mg^{2+} pairs ranged from 4 to 9% in the effluent solution. During the desorption process, chloride concentrations were closer to equilibrium.

Potassium and sodium diffusion was impacted by cation competition and a lower concentration gradient when compared with ammonium. The concentrations of sodium increased in the reservoir during the 60-day desorption period which indicates that exchangeable sodium diffused from the porous media to the reservoir.

Exchangeable calcium and magnesium greatly increased in the pore fluids during the ammonium diffusion period. Calcium concentrations increased up to 26 to 81% of initial concentrations in Cell UA1, 4 and 5. The inverse calcium diffusion from the porous media to the reservoir is attributable to exchange reactions. Calcite precipitation in Cell UA2 and 3 caused the decrease in calcium concentrations in the reservoirs. Significant magnesium inverse diffusion occurred due to exchange reactions during the 60-day diffusion periods. The calcium and magnesium extracted by exchange reactions led to a substantial increase in the reservoir's hardness (Fig. 6). This is because calcium (0.412 nm) and magnesium (0.428 nm) ions have a larger hydrated radius than does ammonium (0.331 nm) or potassium (0.331 nm) (Volkov, Paula et al., 1997). The larger ions cannot percolate through the collapsed interlayer of minerals where adsorbed ammonium and potassium are located and are forced back into solution (Lumbanraja and Evangelou, 1994). However in a binary system of potassium and ammonium, ammonium has the ability to expand the vermiculite interlayer by chemisorptions processes and the ammonium can exchange with the potassium (Lumbanraja and Evangelou, 1994).

According to the two-year column studies on smectite-rich clay-swine effluent, conducted by Fonstad et al., (2001), sodium, magnesium, and calcium on the exchange sites were displaced by potassium and ammonium. This caused an increase in pore fluid hardness for the long-term soil-effluent interaction. Von Breymann and Erwin (1988) discovered that magnesium was displaced by ammonium exchange in marine sediment within an anoxic environment. The extracted magnesium was approximately 40% of the total adsorbed ammonium. Clay mineralogy and CEC were similar to the soils employed in this experiment.

Accordingly, ammonium diffusion caused by chemical potential resulted in a redistribution of major cations and anions in the pore fluid. In particular, chloride, which is well known as a species of conservative transport ion, is more likely to be attenuated in the clay pore space or dispersed to the reservoir to charge balance the solutions to account for the adsorption or desorption of exchangeable ammonium, potassium, calcium and magnesium.

Maintenance of the anaerobic environment in and around the diffusion cells is a key requirement for simulating the reducing conditions of the EMS. For the entire experimental period, including the desorption process (185 days), the presence of oxygen was strictly limited by adding argon gas into the chamber. As a result, ammonium, the reduced form of nitrogen compounds, was not oxidized to nitrate or nitrite in any of the diffusion cells (See Table 4). This fact is key evidence of the importance of maintaining the anaerobic environment in the diffusion cells. In addition to nitrogen compounds, it is possible for sulfate to be reduced in the cells. Sulfate levels decreased from 46 to 80% of the initial content in all cells (Cell UA1 to 5). The author also smelled sulfide during the sampling and measuring of the raw liquid hog manure that came in contact with the glacial clay soils.

4.1.2.1 pH changes during diffusion

As shown in Fig. 7, the measured reservoir pH rapidly dropped from 7.9 to 6.2 within the first 40 days, and then increased to 6.6 over the next 20 days. It is understood that the increase in hydrogen ions in the reservoir is due to the diffusion of hydrogen ions from the pore fluid. The pH difference between pore fluid (pH 7) and effluent (pH 7.9) resulted in H^+ diffusion (Reaction 1). The predicted pH value for the effluent was between pH 7 and pH 7.8 at equilibrium; however, the final effluent pH was equilibrated at 6.2. It is possible that a cation exchange reaction between NH_4^+ and H^+ (Reaction 2) decreases the pH in the reservoir that contains effluent. When ammonium diffuses into the pore fluids, ammonium concentrations increase in that pore fluid. The ammonium with a high mole fraction is better able to occupy the exchange sites on clay minerals and thus exchange H^+. Consequently, the exchangeable H^+ diffusion maybe directly associated with the pH decrease in the reservoirs.

Reaction 3 in Fig. 7 shows that ammonium adsorption by cation exchange causes chemical regeneration when major cations exist in pore fluid (Semmens et al., 1977). As ammonium (NH_4^+) occupied the exchange sites (X^-), the major cations (M) on the clays were extracted from the sites. The cations released from the exchange sites then formed a complex with bicarbonate ($MHCO_3$) in the pore fluid. According to speciation calculations by PHREEQC, calcium, magnesium, and sodium preferably form complexes with bicarbonate. Eventually, the ammonium adsorption caused by cation exchange results in a decrease in bicarbonate in the reservoir. In reality, as shown Fig. 7, the measured alkalinity for all the cells decreased significantly, to 64 to 81% of the initial alkalinity.

The elevated Ca concentration, generated by the exchanged calcium, and the already elevated bicarbonate concentration reacted quickly enough to maintain equilibrium in the reservoir solution (Fig. 7 Reaction 4). The SI for calcite by PHREEQC speciation calculation ranged from 0.05 to 0.2; therefore, the calcite precipitation generated by the exchangeable Ca^{2+} diffusion caused a H^+ concentration increase in the effluent reservoir.

In contrast, after 40 days, an increase in pH was observed in all of the reservoirs (Fig. 7). Exsolution of CO_2 (g) occurred due to reactions between the exchanged calcium and bicarbonate in the liquid hog manure (Reaction 5). The elevated Ca and alkalinity concentration and the developing CO_2 (g) caused the increase in pH levels in the reservoir after 40 days. The measured reservoir pH increased from 6.2 to 6.6 after 40 days. The substantial decrease in TOC in the reservoirs supported the oxidation of organic compounds (e^- donor) as well as sulfate (e^- acceptor) reduction during the interaction periods (Reaction 6). The measured TOC decreased in the reservoirs, to 63 from 86% of the initially determined TOC. Sulfate (SO_4^{2-}) reduction by the oxidation of organic carbon was also indicated by the increase in pH after 40 days. Based on the measured pH levels for all reservoirs, pH ranged from 6.6 to 7.9 after 40 days. According to the Eh-pH diagram for the S-O_2-H_2O system, illustrated by Langmuir (1997), H_2S and HS^- will be the dominant sulfur forms in the anaerobic pore fluid at the measured pH levels. Furthermore, clay minerals in the cells will buffer the acidity that is generated by ammonium diffusion. It is known that clays have a mineral-controlled buffer capacity that is remarkably resistant to acidity, particularly in comparison to associated carbonates (Langmuir, 1997).

Consequently, ammonium diffusion resulted in a pH decrease in the pore fluid of all the diffusion cells in addition to a substantial increase in hardness. The initial pore fluid pH 7.0 decreased to between 6.2 and 6.6 because of H^+ diffusion resulting from the initial pH difference, the cation exchange of NH_4^+ for H^+ and Ca^{2+}, and calcite precipitation. Therefore, it is possible that changes in pH and hardness can be simple indicators of the need to investigate ammonium plumes in EMS areas.

4.1.3. Diffusion controlled adsorption

Using the anaerobic RDC method, linear ammonium and potassium adsorption isotherms (R^2= 99%) were developed in relation to the equilibrium activity of the reservoir (Fig. 8). The activities were determined by PHREEQC speciation calculation based on the Davies equation for activity coefficients. High cation exchange capacity and diffusion-controlled adsorption primarily affected the linearity of ammonium and potassium adsorption isotherms. It was assumed that the smectite-rich soil samples with high CEC values (21.2 to 43.3 meq/100g) had sufficient exchange sites to adsorb 80 to 90% of the ammonium injected into the cells. Von Breymann and Suess (1988) also showed that a linear relationship exists between adsorbed ammonium and dissolved ammonium concentration. The adsorbent were smectite-rich clay soils with high CEC (i.e., 84.2 meq/100g). The dissolved ammonium concentrations ranged from 5.3 to 36 mM. Additionally, Lumbanraja and Evangelou (1994) obtained a linear ammonium adsorption in a low dissolved ammonium level (20 mM) as well; in their experiment, ammonium competed with potassium for the exchange sites on vermiculite and smectite-type clay.

In addition to high CEC, ammonium adsorption was a function of diffusion time, a result also known as the diffusion-controlled adsorption process. The mechanism of diffusion-controlled adsorption may be divided into five steps (Kithome et al., 1998): (1) diffusion of ammonium through the pore fluid up to the smectite particle; (2) diffusion of ammonium through the smectite particles; (3) chemical exchange between ammonium and exchangeable cations on exchange sites in the interior of the smectite minerals; (4) diffusion of the displaced cations out of the interior of the mineral; and (5) diffusion of the displaced cation through the solution away from the smectite minerals. The diffusion-only process in the cells reflected both the heterogeneity and tortuosity of the intact core samples. Therefore, even when the source ammonium concentration was highly concentrated (5242 mg/L), the ammonium dissolved in pore fluid was equilibrated at low concentrations.

The clay-rich soil samples selectively adsorbed and/or desorbed major cations in pore fluid.

The competition for the limited adsorption sites depended on constituent mole fraction, ionic charge and ionic size (hydrated radius). In particular, ammonium predominated at the adsorption sites because ammonium with a high mole fraction in the source—about 45%—had more chances to occupy the sites compared to other co-existing cations. Ammonium was also preferred on adsorption site due to the presence of potassium in solution. James and Harward (1964) and Mortland (1968) showed that while NH_4^+ and K^+ have the same hydrated radius, NH_4^+ adsorption was enhanced in the presence of K^+. The adsorbed NH_4^+ tends to expand soil's inter-layer allowing it to internally diffuse onto a surface and displace trapped interlayer K^+ and structural K^+ (Lumbanraja and Evangelou, 1994). Lumbanraja and Evangelou (1994) observed that potassium adsorption, when in competition with ammonium, was suppressed, whereas ammonium adsorption was enhanced in binary (NH_4^+ - K^+) and ternary (NH_4^+ - K^+ - Ca^{2+}) systems.

4.2. Geochemical mix models for the anaerobic RDC method

The ammonium adsorption isotherm simulated by SIMPLE MIX MODEL was in agreement with the RDC experiment result (Fig. 9). The adsorption simulation had lower and upper limits that were dependent on the estimated effective pore fluid volume. The input pore fluid volume ranged from 130 to 170 mL. Notably, the lower limit simulation was in agreement with the experimental results. Fig. 9 shows the total adsorbed ammonium, both from the experiment (5.7 mmol/cell) and from the lower limit simulation (6.2 mmol/cell).

Estimated K_d ($\frac{mg/kgdrysoil}{mg/solution}$) values for ammonium ranged from 0.3 to 0.4 L/kg under anaerobic conditions and diffusion only process. It was assumed that smectite-rich clay soil samples adsorbed all the diffused ammonium because of their relatively large amount of clay soils with high CEC (21.2 to 43.3 meq/100g, dried 531 to 634 g). However, K_d from radial diffusion cells accounts for a diffusive transport characterized by heterogeneity and tortuosity of in situ soils under competition and reducing conditions. No literature that addresses the distribution coefficients, K_d, for ammonium when assessed by the anaerobic RDC method was available. However, in recent studies, Fonstad (2004) obtained 0.05 to 0.4 L/kg of K_d; Thornton et al. (2000, 2001) reported 0.06 L/kg to 0.3 L/kg values; Erskine (2000) and Ceazan et al. (1989) showed a 0.5 L/kg value and 0.34 L/kg to 0.87 L/kg values for K_d, respectively. The K_d values of these previous studies vary because of the disparate types of adsorption experiments, the CEC, clay mineralogy, initial ammonium concentration, and running time.

Fig. 10 demonstrates the simulation of the pore fluid chemistry during linear ammonium adsorption. The anaerobic condition was maintained in the simulated pore fluid. Nitrate and nitrite were not produced in this model. Potassium in competition with ammonium linearly diffused into the pore fluid. Diffusion of calcium and magnesium into the soil samples was not significant in the simulation. Sulfate reduction was also simulated by changes in pore fluid chemistry.

According to the MIX MODEL results, the predicted liquid manure volumes for ammonium saturation were 1.0 to 1.2 L/kg for sandy lean clay samples and 1.4 to 1.7 L/kg for sandy fat clay samples. (706 to 1010 mL/Cell, dilution effect was considered). Fig. 11 represents the number of mixing simulations that correspond to the required number of source injections of the initial injected ammonium concentration, at 5242 mg/L. Thus, the predicted number of injections ranged from 35 to 40 for sandy lean clays (Cell UA1 and 2) and from 43 to 51 for sandy fat clay samples. About 20 mL of liquid manure per injection was assumed. The ammonium required to saturate exchange sites using an ammonium solution concentration of 5242 mg/L ranged from 0.3 to 0.5 mol/kg (1.0 to 1.7 L/kg manure effluent), depending on the soil types.

5. Summary and conclusions

Maintenance of an anaerobic environment was the most critical issue in this experiment. For the entire experiment period (185 days), the oxygen level was strictly limited by means of argon gas environment. The preservation of reducing conditions during ammonium diffusion was confirmed by nitrate and nitrite concentrations lower than the detection limit .

The geochemical response of reservoir pore fluid with diffusion time was investigated by monitoring reservoir chemistry with time. Ammonium diffusion driven by a chemical gradient resulted in a redistribution of major cations and anions in the pore fluid. Chloride (Cl^-) played a key role in achieving charge balance during the ammonium diffusion. Chloride did not behave as a conservative transport species. It was hypothesized that chloride was attenuated during diffusion due to high concentration of adsorbed ammonium ion in the soils adjacent to the reservoir. Ammonium diffusion resulted in a pH decrease in the pore fluid of all the diffusion cells and more importantly the substantial increase in hardness (Ca and Mg) was observed. This increase in Ca and to a lesser extent Mg is an important indicator of an ammonium plume (Fonstad 2004)

High cation exchange capacity and diffusion-controlled adsorption primarily affected the linearity of ammonium and potassium adsorption isotherms. The distribution coefficient, K_d, determined by a radial diffusion cell method ranged from 0.3 to 0.4 L/kg under competition with co-existing cations and diffusion only mechanism.

The SIMPLE MIX MODEL adequately simulated the linear ammonium adsorption at low dissolved ammonium concentration (< 30mM) and changed pore fluid chemistry. Ammonium saturation capacity predicted by the MIX model ranged from 1.0 to 1.2 L/kg for sandy lean clay samples and 1.4 to 1.7 L/kg for sandy fat clay samples.

In conclusion, the anaerobic RDC method effectively satisfied the key requirements in characterizing the movement of ammonium through glacial clay soils; anaerobic conditions, diffusion controlled adsorption, exchange reactions and competition.

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Table 1 Geochemical properties of the soil

Geochemical index		Group 1	Group 2	Group 3
Cation exchange capacity (meq/100g)		21.2	43.3	34.2
Total nitrogen (%)		0.06	0.08	0.04
Organic matter (%)		1.5	1.5	1
Total organic carbon (%)		0.74	0.77	0.48
SPE (mg/L)	Sodium	63	60	61
	Calcium	54	52	73
	Magnesium	23	19	23
	Potassium	6	11	15
	N-Ammonium	4	7	10
	Chloride	67	31	24
	Sulfate	150	102	130
	N-Nitrate	9	3	4
	N-Nitrite	2.5	2	0.96
	pH	7.9	8	8.18
	E.C. (mS/cm)@ 25°C	0.39	0.34	0.38
	SAR	1.83	1.81	1.60
	ESR	0.03	0.03	0.02
	ESP	2.67	2.64	2.34

NOTE
(1) Group 1: Cell UA1 and UA2; Group 2: Cell UA3 and UA4 and Group 3: Cell UA5
(2) SPE denotes saturated paste extraction
(3) E.C.: Electrical Conductivity, SAR: Sodium Adsorption Ratio, ESR: Exchangeable Sodium Ratio, and ESP: Exchangeable Sodium Percent

Table 2 Geochemical property of the liquid hog manure

Analyte		Results	Unit
Cations	Calcium (Ca)	199	mg/L
	Potassium (K)	1710	mg/L
	Magnesium (Mg)	6.4	mg/L
	Sodium (Na)	611	mg/L
	Ammonium (NH_4)	5241.5	mg/L
Anions	Chloride (Cl)	1380	mg/L
	Sulphate (SO_4)	9	mg/L
	Nitrate-N	1	mg/L
	Nitrite-N	1	mg/L
	Orthophosphate (PO_4-P)	1270	mg/L
Carbonates	Bicarbonate (HCO_3)	14300	mg/L
	Carbonate (CO3)	100	mg/L
	Hydroxide (OH)	<100	mg/L
Iron	Iron (Fe)-Dissolved	4	mg/L
Organic carbon	Dissolved organic carbon (DOC)	4700	mg/L
	Total oragnic carbon (TOC)	6510	mg/L
Geochemical index	pH	7.9	pH
	Conductivity (EC)	23	mS/cm
	Hardness (as $CaCO_3$)	523	mg/L
	Alkalinity	11700	mg/L
	Dissolved oxygen (DO)	0.8	mg/L
	Density	1	g/mL
	Total dissolved solid (TDS)	10900	mg/L

Table 3 Reservoir monitoring results for major cations (unit: mg/L)

Major cations	Cell I.D.	Initial pore fluid	Initial liquid manure	Diffusion-day 10	Diffusion-day 60	Desorption- day 60
NH_4^+	UA Cell 1	< 1.0	5242	2423	508	298
	UA Cell 2	< 1.0	5242	2417	3177	59
	UA Cell 3	< 1.0	5242	1767	1067	35
	UA Cell 4	< 1.0	5242	-	136	18
	UA Cell 5	< 1.0	5242	1093	169	30
K^+	UA Cell 1	10	1710	1260	856	20
	UA Cell 2	10	1710	1340	1370	72
	UA Cell 3	6	1710	1260	854	31
	UA Cell 4	6	1710	-	408	23
	UA Cell 5	4	1710	1120	726	42
Na^+	UA Cell 1	28	611	530	460	110
	UA Cell 2	<20	611	540	600	60
	UA Cell 3	<20	611	1520	420	90
	UA Cell 4	21	611	-	320	80
	UA Cell 5	<20	611	510	460	90
Ca^{2+}	UA Cell 1	16	199	190	250	110
	UA Cell 2	<10	199	150	80	80
	UA Cell 3	13	199	180	180	120
	UA Cell 4	13	199	-	360	110
	UA Cell 5	<10	199	250	260	120
Mg^{2+}	UA Cell 1	6	6.4	15	89	45
	UA Cell 2	<2	6.4	8	17	36
	UA Cell 3	3	6.4	14	68	34
	UA Cell 4	3	6.4	-	92	29
	UA Cell 5	<2	6.4	28	106	25

Table 4 Reservoir monitoring results for major anions (unit: mg/L)

Major anions	Cell I.D.	Initial pore fluid	Initial liquid manure	Diffusion-day 10	Diffusion-day 60	Desorption- day 60
Cl^-	UA Cell 1	20	1380	1110	706	135
	UA Cell 2	<20	1380	1150	1040	69
	UA Cell 3	<20	1380	1120	684	101
	UA Cell 4	<20	1380	-	468	131
	UA Cell 5	<20	1380	1040	751	132
PO_4^{3-}	UA Cell 1	<1	1270	313	294	8
	UA Cell 2	<1	1270	282	199	47
	UA Cell 3	<1	1270	297	199	11
	UA Cell 4	<1	1270	-	41	5
	UA Cell 5	<1	1270	144	80	13
HCO_3^-	UA Cell 1	200	14300	6670	3890	751
	UA Cell 2	200	14300	8920	11500	704
	UA Cell 3	200	14300	6570	5100	801
	UA Cell 4	200	14300	-	2730	579
	UA Cell 5	100	14300	5810	3260	637
SO_4^{2-}	UA Cell 1	24	9	3	5	12
	UA Cell 2	6	9	3	2	4
	UA Cell 3	16	9	3	4	1
	UA Cell 4	16	9	-	3	2
	UA Cell 5	6	9	3	5	6
NO_2^- / NO_3^-	UA Cell 1	<0.04	1	0.4	D.L	0.3
	UA Cell 2	<0.04	1	0.4	D.L	<2
	UA Cell 3	<0.04	1	0.4	D.L	<0.2
	UA Cell 4	<0.04	1	-	D.L	<0.2
	UA Cell 5	0.05	1	0.4	D.L	<0.2

Table 5 Measured concentrations vs. diluted concentrations (equilibrium) unit: mg/L

Analyte	Cell I.D.	Diffusion-day 60		Final pore fluid after desorption	
		Measured conc.	Diluted conc.	Measured conc.	Diluted conc.
NH_4^+	Cell UA1	508	1117	29	1050
	Cell UA2	3177	1106	59	704
	Cell UA3	1067	930	35	815
	Cell UA4	136	559	18	545
	Cell UA5	169	1079	30	1058
K^+	Cell UA1	856	306	20	191
	Cell UA2	1370	291	72	117
	Cell UA3	854	237	31	145
	Cell UA4	408	187	23	148
	Cell UA5	726	269	42	190
Na^+	Cell UA1	460	119	110	57
	Cell UA2	600	109	60	33
	Cell UA3	420	extrac.	90	extrac.
	Cell UA4	320	84	80	53
	Cell UA5	460	100	90	50
Ca^{2+}	Cell UA1	250	42	110	8
	Cell UA2	80	42	80	32
	Cell UA3	180	35	120	16
	Cell UA4	360	33	110	extrac.
	Cell UA5	260	26	120	extrac.
Mg^{2+}	Cell UA1	89	5	45	extrac.
	Cell UA2	17	2	36	0.2
	Cell UA3	68	3	34	extrac.
	Cell UA4	92	3	29	extrac.
	Cell UA5	106	0.1	25	extrac.
Cl^-	Cell UA1	706	244	135	149
	Cell UA2	1040	235	69	103
	Cell UA3	684	194	101	120
	Cell UA4	468	165	131	120
	Cell UA5	751	217	132	135
SO_4^{2-}	Cell UA1	5	23	12	22
	Cell UA2	2	7	4	7
	Cell UA3	4	16	1	15
	Cell UA4	3	15	2	15
	Cell UA5	5	7	6	6

NOTE: extrac. refers to the solutes extracted from the soils to the reservoir during the diffusion

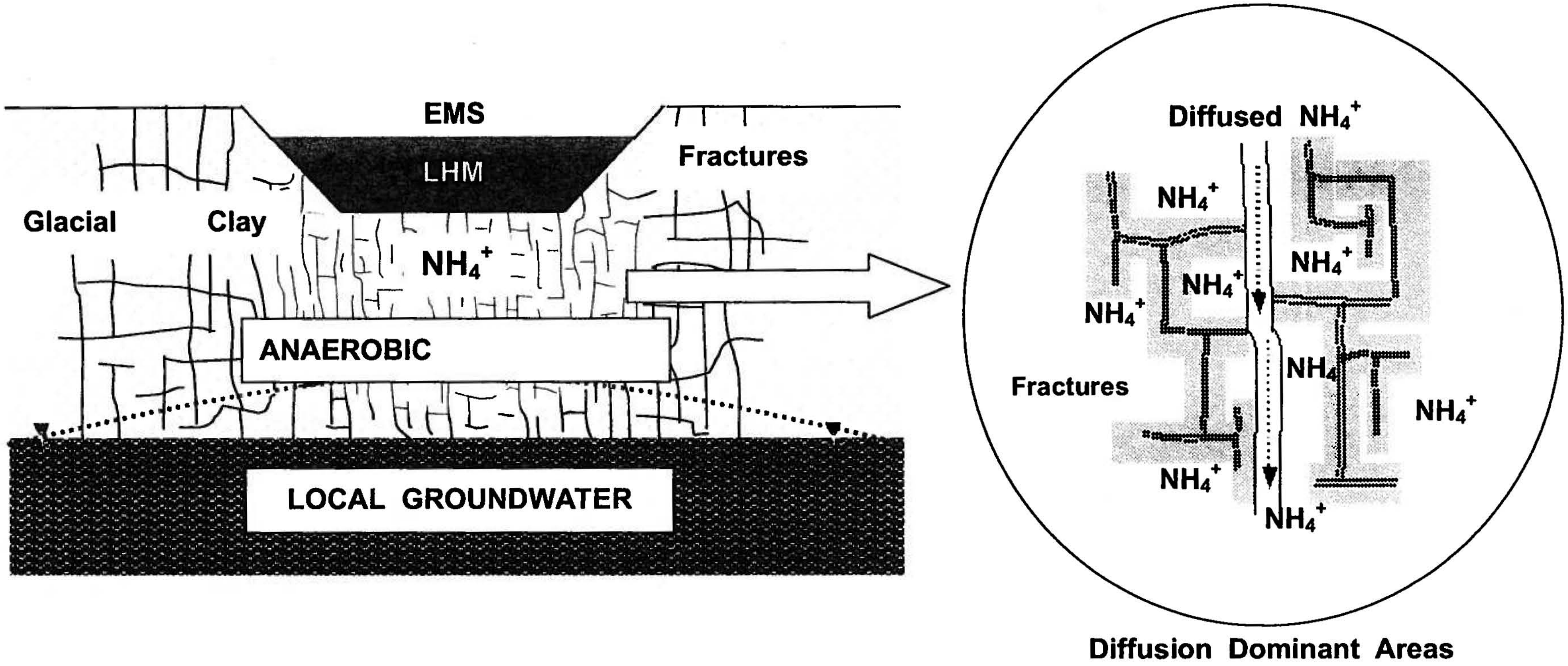


Fig.1 Conceptual model for ammonium diffusion along fractured glacial clays and/or clay tills in the Canadian Prairies

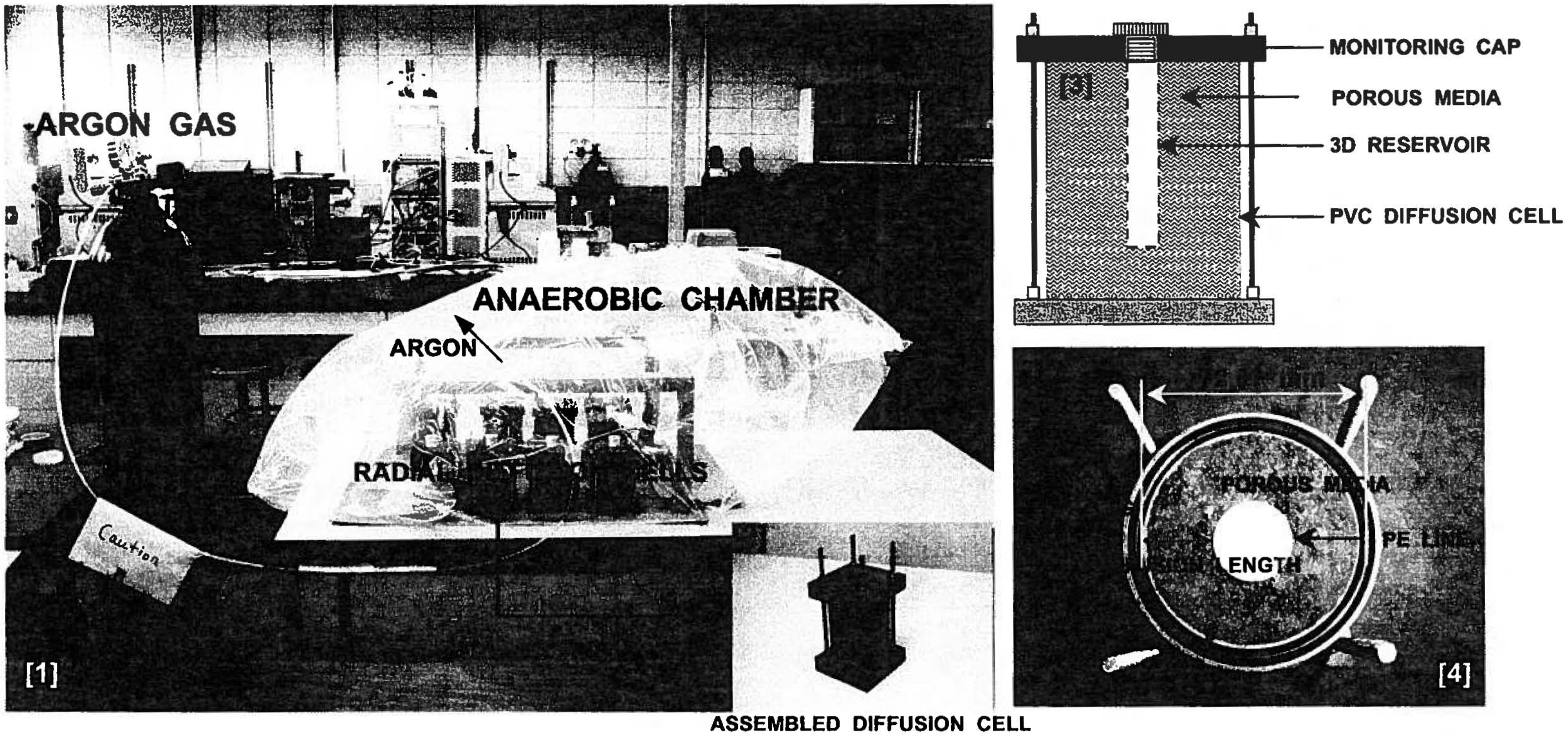


Fig. 2 Anaerobic radial diffusion cell setting and schematic of a radial diffusion cell

- NOTE: EMS denotes Earthen Manure Storage and LHM refers to Liquid Hog Manure

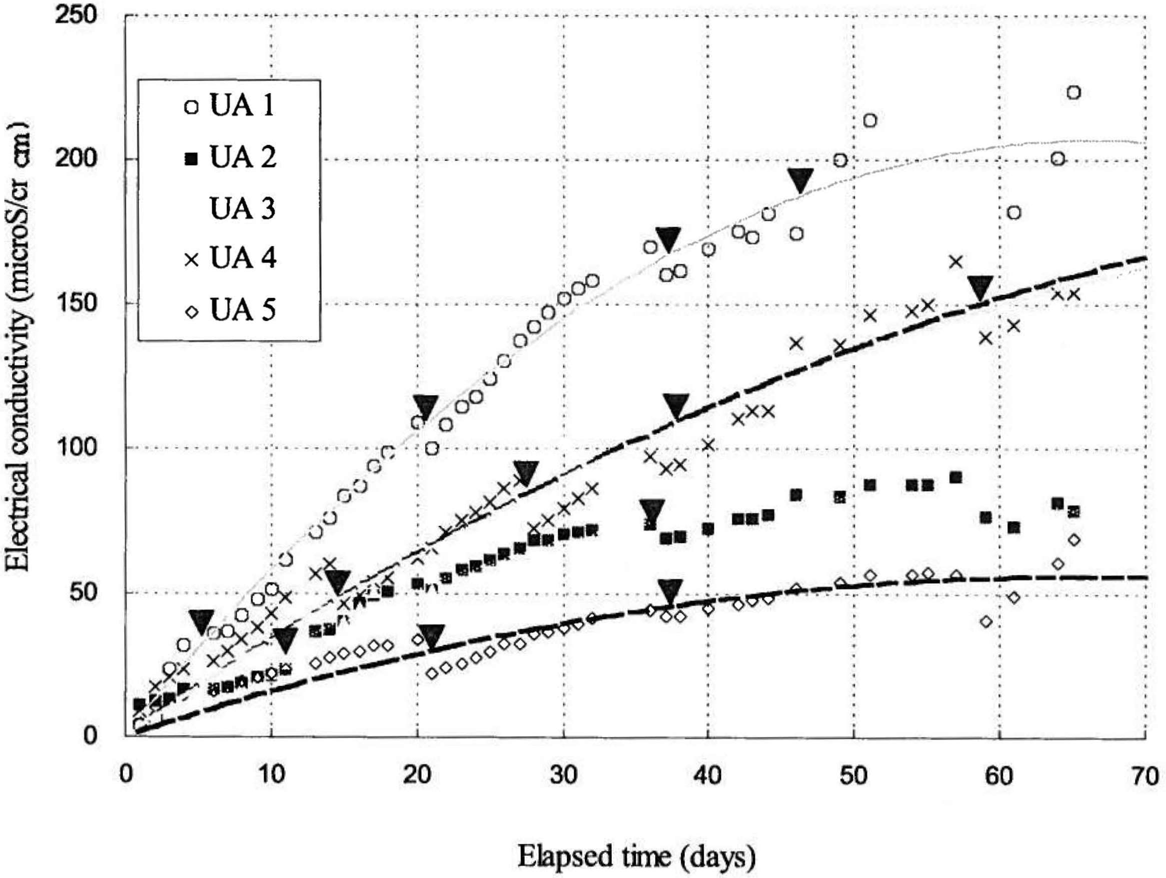


Fig. 3 Monitored electrical conductivity of the reservoirs during the diffusive equilibrium

NOTE: ▼ refers to a pure water injection for water saturation

The episode for water injection caused fluctuation of E.C. response of the reservoirs

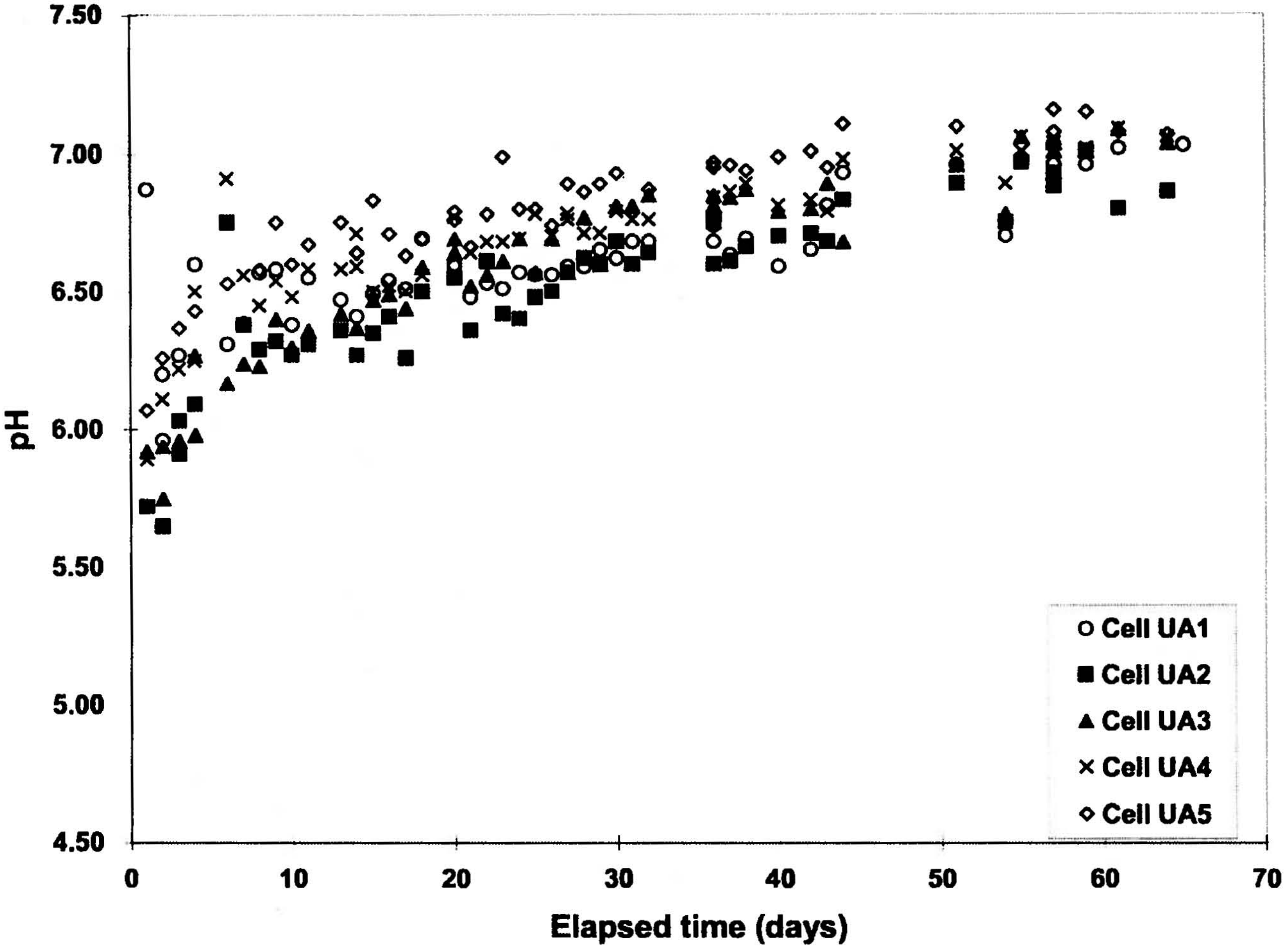


Fig. 4 Monitored reservoir pH during diffusive the equilibrium

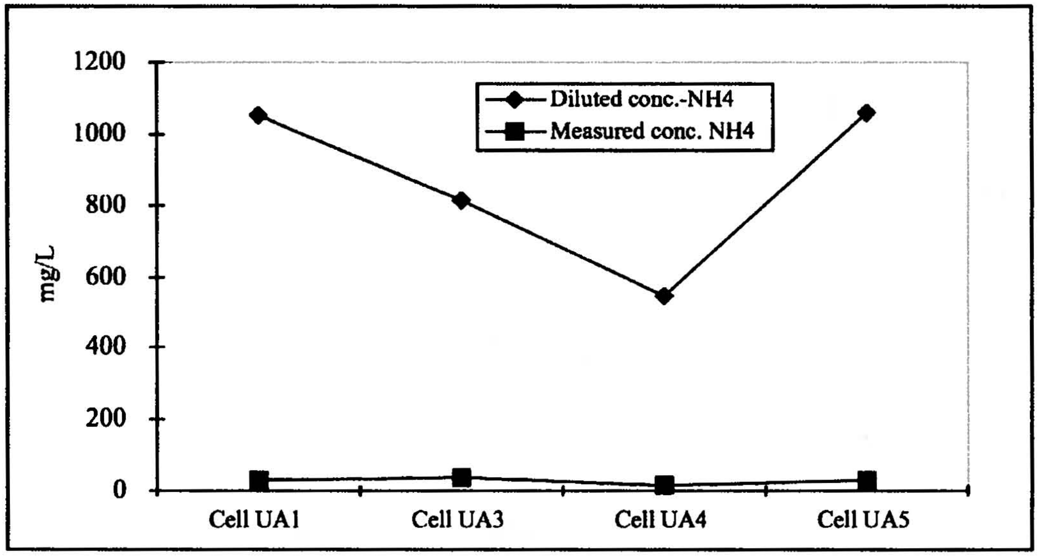


Fig. 5 (a) Measured vs. diluted ammonium concentration

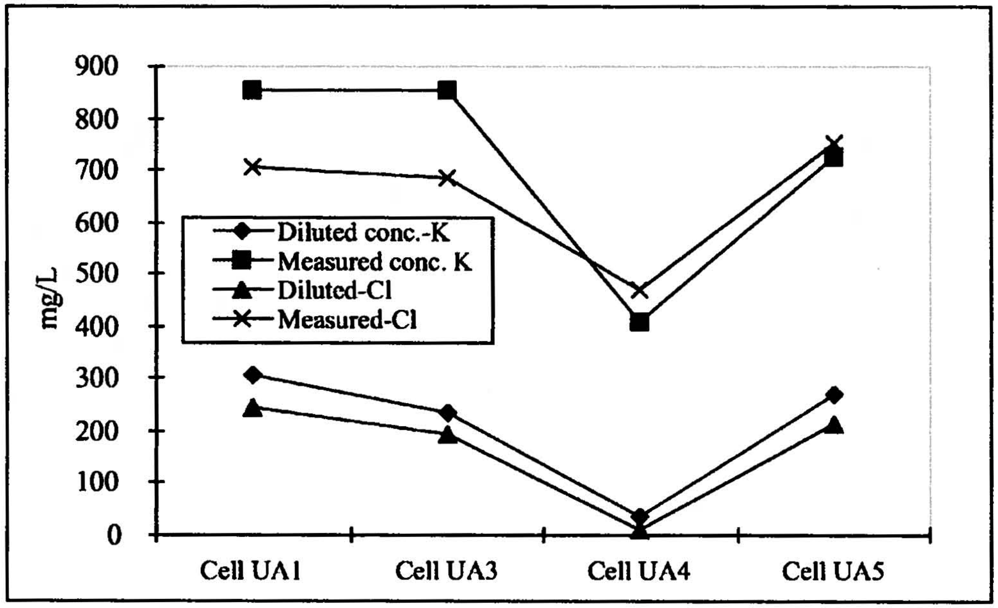


Fig. 5 (b) Measured vs. diluted potassium and chloride concentration

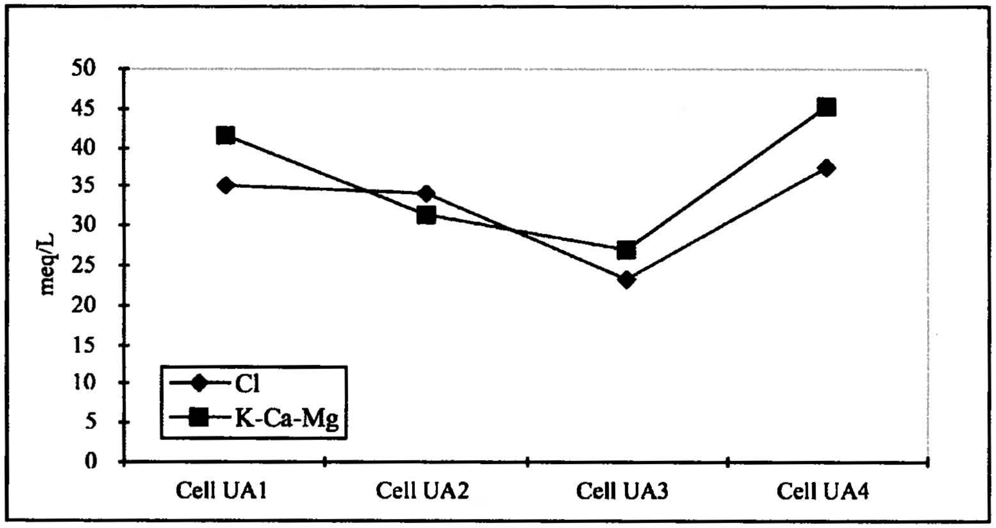


Fig. 5 (c) Milli-equivalent of Cl^- vs. K+, Ca^{2+} and Mg^{2+}

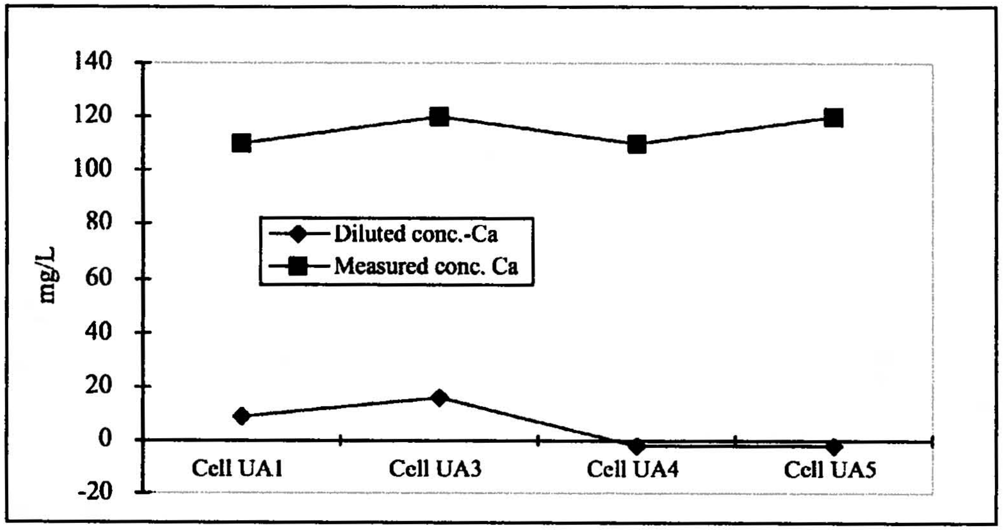


Fig. 5 (d) Measured vs. diluted calcium concentration

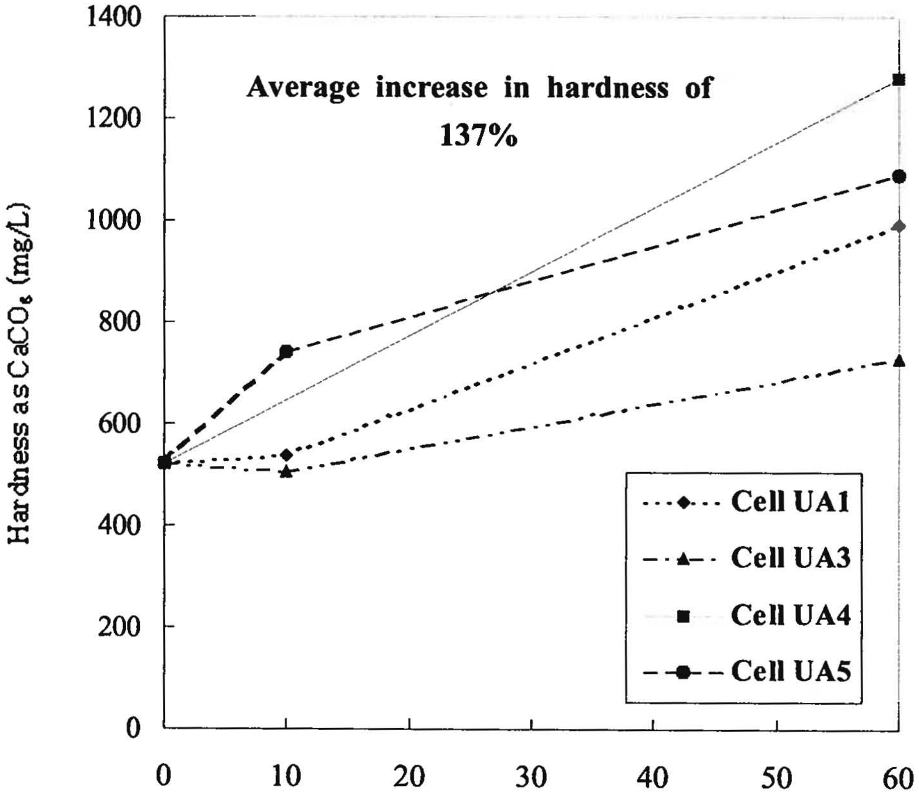
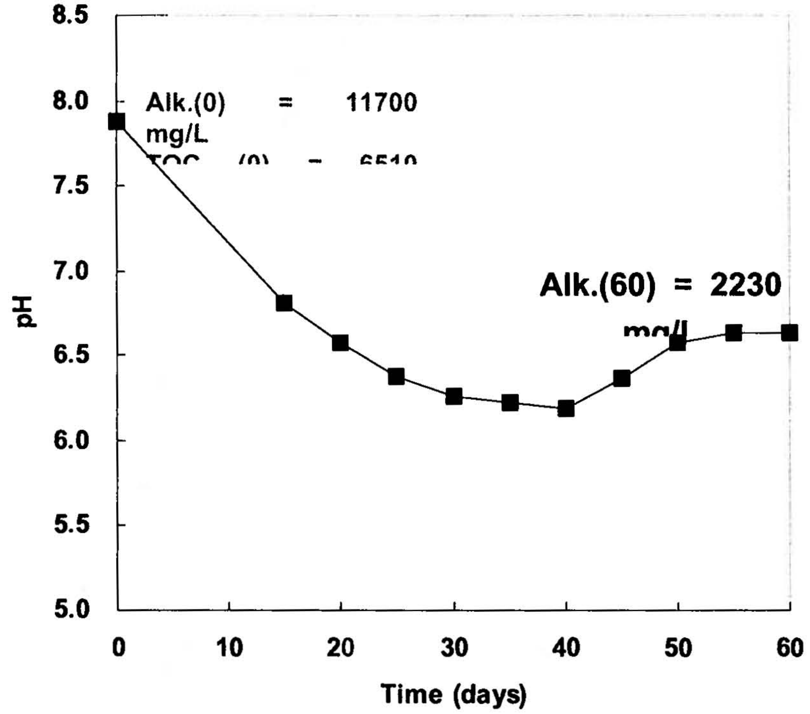


Fig. 6 Elevated hardness in all the reservoirs during the diffusion process



Decrease in pH in the reservoir:

React. [1] H^+ diffusion between pore fluid (pH 7.0) and manure (pH 7.9).

React. [2] $NH_4^+ + HX \Rightarrow NH_4X + H^+; K = \dfrac{[NH_4X][H^+]}{[NH_4^+][HX]}$

React. [3] $[X]M^+ + NH_4^+ + HCO_3^- \Rightarrow [X][NH_4^+ + MHCO_3$

React. [3] $[X]M^{+2} + NH_4^+ + 2HCO_3^- \Rightarrow [X]NH_4^+ + M(HCO_3)_2$

React. [4] $Ca^{+2} + HCO_3^- \Rightarrow CaCO_3 + H^+$

Increase in pH in the reservoir:

React. [5] $Ca^{+2} + 2HCO_3^- \Rightarrow CaCO_3 + CO_2(g) \uparrow + H_2O$

React. [6] $2CH_3O + SO_4^{-2} \Rightarrow 2HCO_3^- + H_2S$

Cf. Eh-pH diagram for S-O- H-O system (Langmuir, 1997)

NOTE

X^-: exchange site with monovalent
M: major cations (Ca, Mg, K, Na)
Alk. (0) and (60): measured alkalinity on day 0 and day 60
TOC (0) and (60): measured TOC on day 0 and day 60.

Fig. 7 Change in pH during the diffusion periods and related geochemical reactions in the diffusion

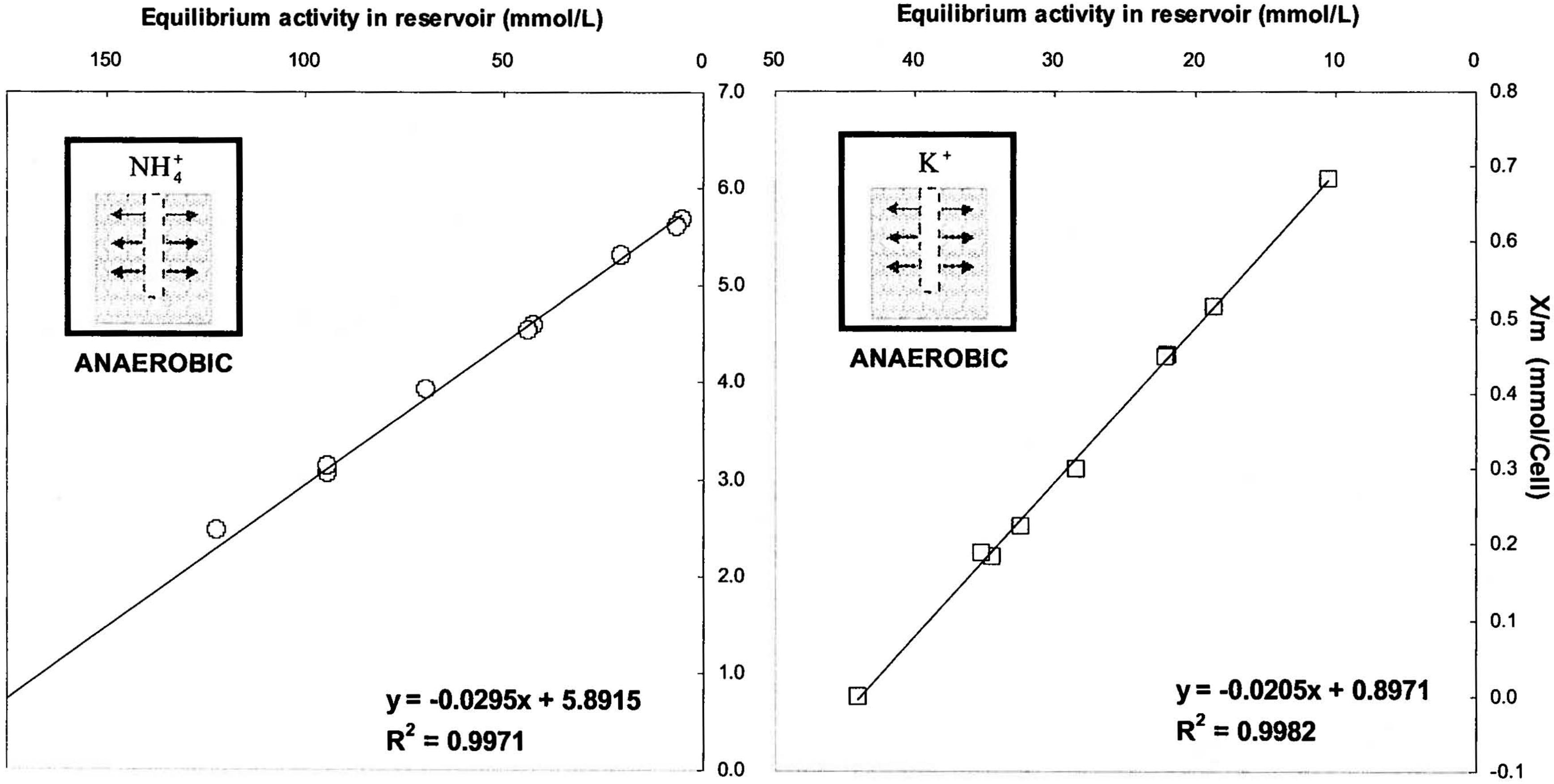


Fig. 8 Linear ammonium and potassium adsorption isotherms under anaerobic conditions using the RDC method

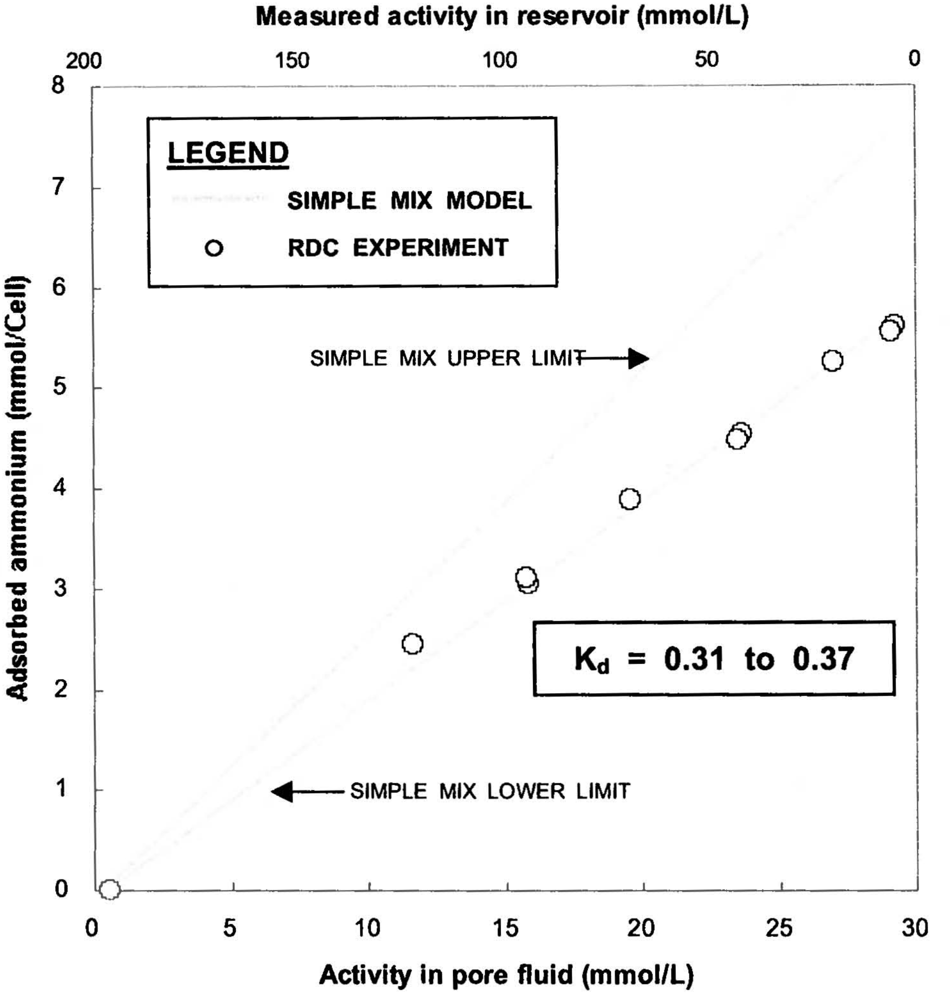


Fig. 9 Ammonium adsorption determined by the RDC experiment and SIMPLE MIX MODEL

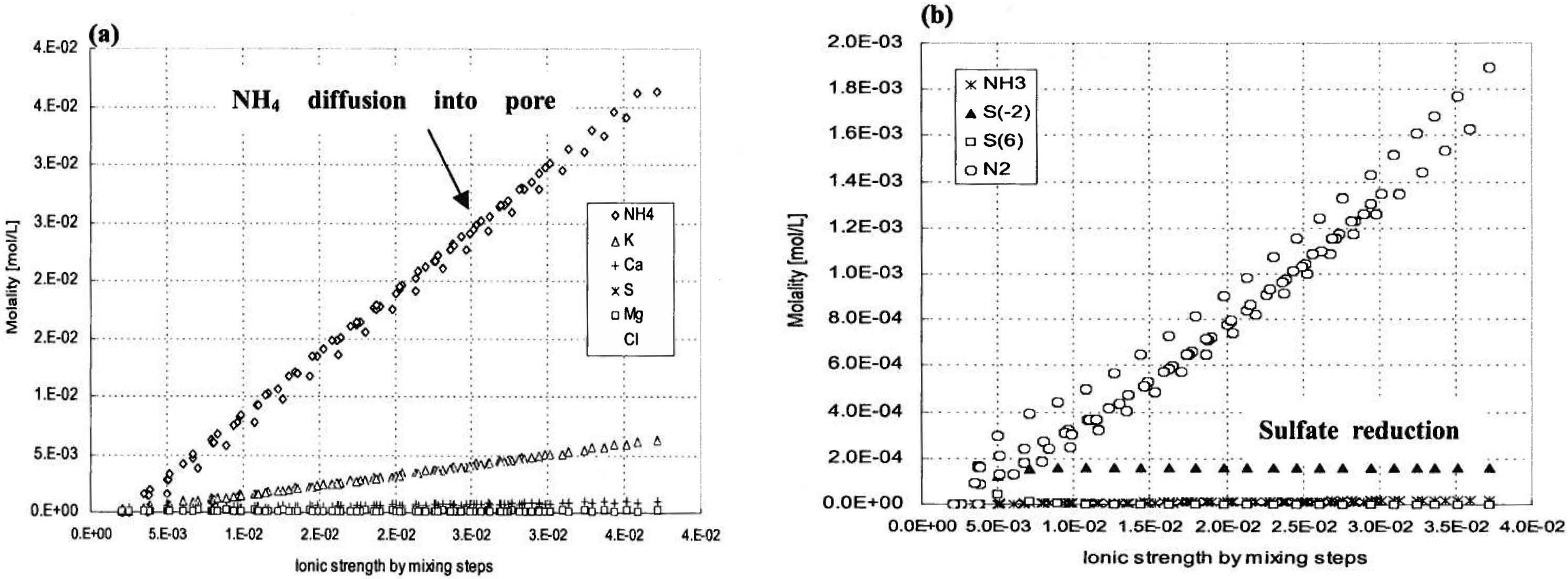
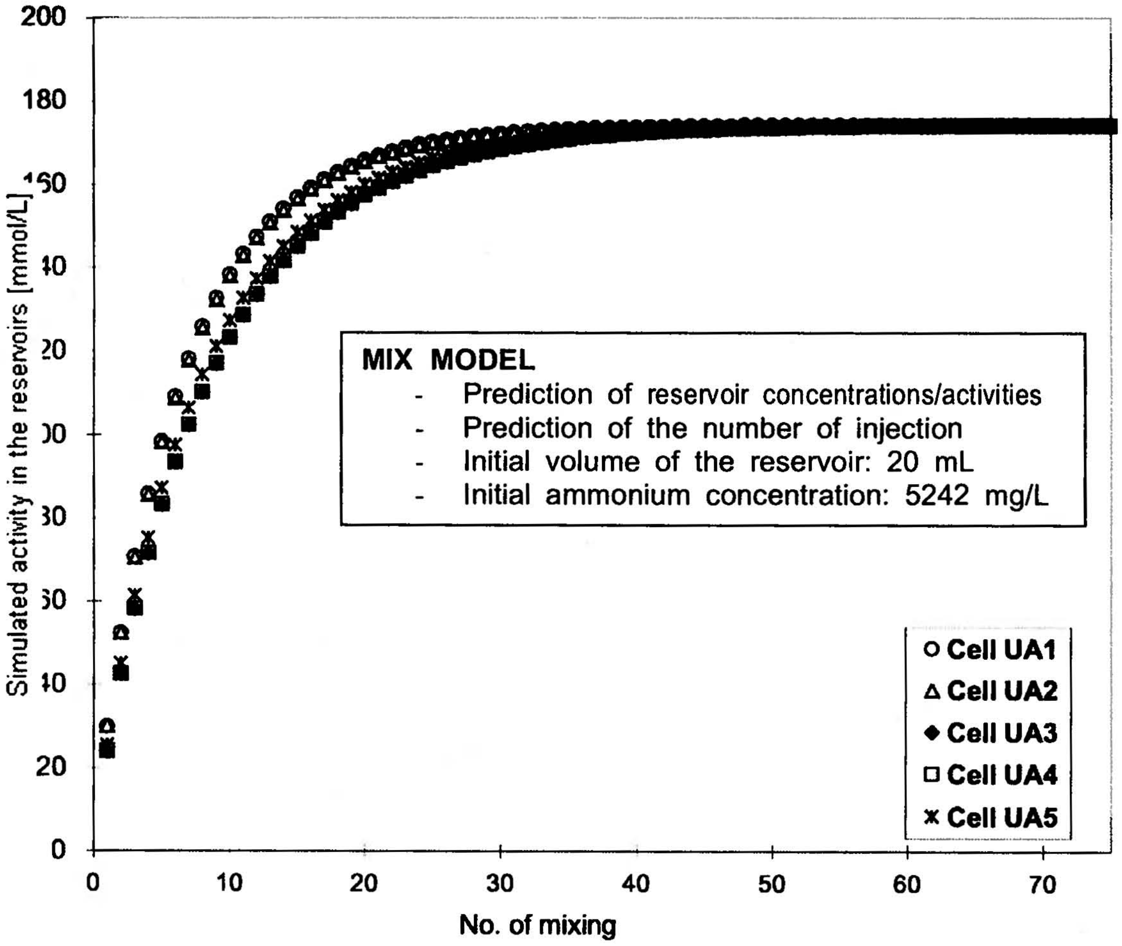


Fig.10 change in pore fluid chemistry simulated by SIMPLE MIX



MIX MODEL

- Prediction of reservoir concentrations/activities
- Prediction of the number of injection
- Initial volume of the reservoir: 20 mL
- Initial ammonium concentration: 5242 mg/L

Fig.11 Result of the MIX MODEL simulation