An Assessment of the Greywater and Composting Toilet Tea Leach Field Geochemistry at the C.K. Choi Building, University of British Columbia Vancouver Campus

By

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Abstract

The geochemistry of a wetland system around the C.K. Choi Building on the University of British Columbia's Vancouver Campus was assessed. The wetland system accepts compost tea from 5 composting toilets in the building as well as greywater from the building sinks. The system was estimated to receive approximately 400L/day and has an area of $30m^2$ and a depth of approximately 1m. Dilution and geochemical processes reduce the concentrations of trace metals and nutrients in the inflowing greywater and compost tea. Removal efficiencies of 99% for ammonia were observed in the system and are attributed to nitrification and dilution. Nitrate/nitrite sees removal efficiencies of 98%, due to denitrification and dilution. Manganese(IV) and Iron (III) reduction is observed to produce soluble Mn(II) and Fe(II) which are then easily adsorbed by phosphorus and precipitated as hydroxyapatite, $MnHPO_4$, vivianite and strengite. Sulfate reduction also takes place and facilitates the precipitation of metal sulfides such as iron sulfide.

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1. Introduction

The C. K. Choi Building which contains the Institute of Asian Research on the University of British Columbia campus was selected to be a demonstration green building in 1992 as part of a half-billion dollar expansion program of the UBC campus. The building has a 3,000m^2 floor space and $4.5million budget. As part of the initiative, a greywater recycling system and composting toilets were implemented. The building contains 3,000 square meters of office space, workstations and seminar rooms. The building has 5 composting toilets. At the moment, there are approximately 200 people who consistently occupy the building and are regular toilet users.

A component of the building design is a 15 meter long rubble wetland system with an open end that processes the tea from the composting toilets as well as the greywater from the sinks. The compost tea and greywater mixture is discharged by beign pumped up to the wetland where it flows a few feet under the ground surface, in a perforated pipe. Vegetation, mainly reeds, throughout the wetland uses the effluent for moisture and nutrients, in the process removing pathogens and harmful compounds. The filtered end product finally leaves the wetland and acts as irrigation in the natural ground.

The purpose of this thesis is to assess the physical and chemical factors that influence the performance of the rubble wetlands of the C. K. Choi Building. The nutrients and trace metals concentrations of the influent and effluent of the wetland is characterized. The wetland geochemistry and physical characteristics will also be compared to other similar wetland systems in environments comparable to Vancouver's.

1.1 Wetlands

Wetlands have characteristics of both aquatic and terrestrial systems. They are a transition from one system to the next, characterized by a water table at or near the surface or by a land covered by shallow water. A wetland can function as a chemical sink, retaining more nutrients or sediments than it is releasing. This is due to a variety of properties: wetlands accumulate organics and retain nutrients and sediments; they are autotrophic systems, converting inorganic nutrients to organic biomass; they are calm, low velocity systems and so are good sedimentation basins; and they provide an excellent soil-water contact zone for biochemical processes (Mitsch & Fennesy 1991).

Wetlands are subject to seasonal changes. During the summer, the uptake of chemicals by plants and immobilization of nutrients by flora creates retention of nutrients in the system. When the flora dies, nutrients are left to decompose and leach back into the water stream. In fall and spring, there is a net release of nutrients (Mitsch & Fennesy 1991).

The following image of the C.K. Choi Building's wetland system was taken during the summer months. As can be seen, there are numerous reeds and tall grasses growing on a gravel bed.

Figure 1: C.K. Choi Wetland System (Oberlander 2008)

The next two images are, respectively, a plan and a cross-sectional view of the wetland system around the C.K. Choi Building. The wetland is approximately 15m long, 2m wide and 1m deep. The cross-sectional schematic shows that the wetland receives water from the sinks, the composting toilets and some from the building drains.
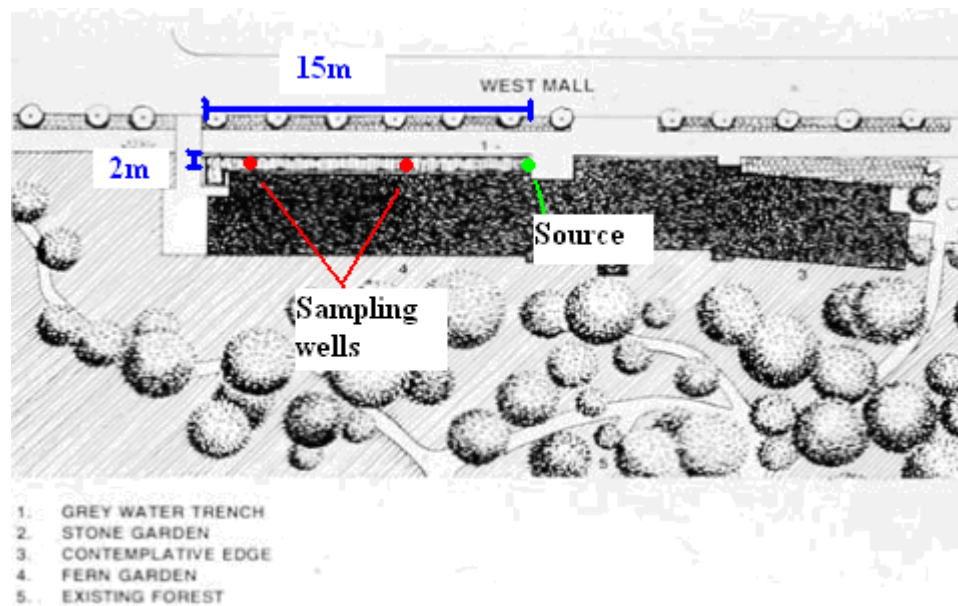
Figure 2: Plan View of C.K. Choi Wetland System (Oberlander 2008)
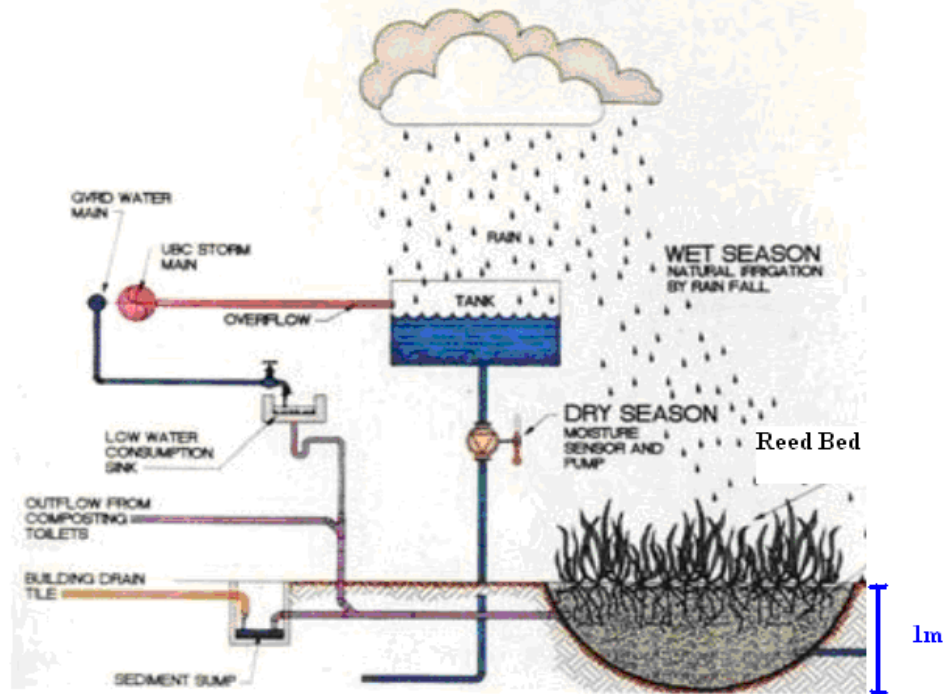
Figure 3: Cross-Sectional View of C.K. Choi Wetland System (Oberlander 2008)

1.2 Geological Surroundings

The following image shows the location of the C.K. Choi Building on the UBC campus. The C.K. Choi Building is located on the North-West side of the campus, close to the cliffs leading down to the Strait of Georgia.

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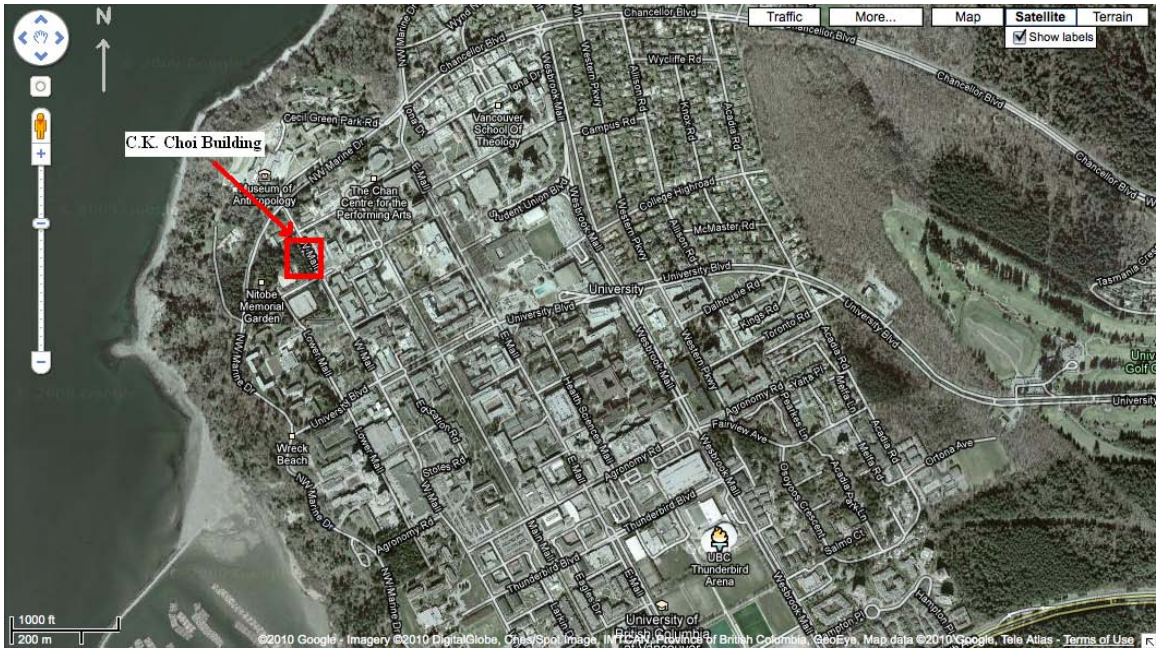
Figure 4: Map of the UBC Campus (Google Maps)

In the West Point Grey/UBC area, the stratigraphy allows for two water tables. There are two aquifers, one at sea level and another approximately 30m above that. The stratigraphy can be determined from observation of the UBC cliffs approximately 100m from the C.K. Choi building. On average, the stratigraphy of the slope consists of a 3m thick layer of glacial till, underlain by about 30m of sand and interbedded silt and clay until the upper aquifer. Under this, there is about 30m of dense silt overlying the second, lower aquifer at beach level. See Figure 5 below for reference:
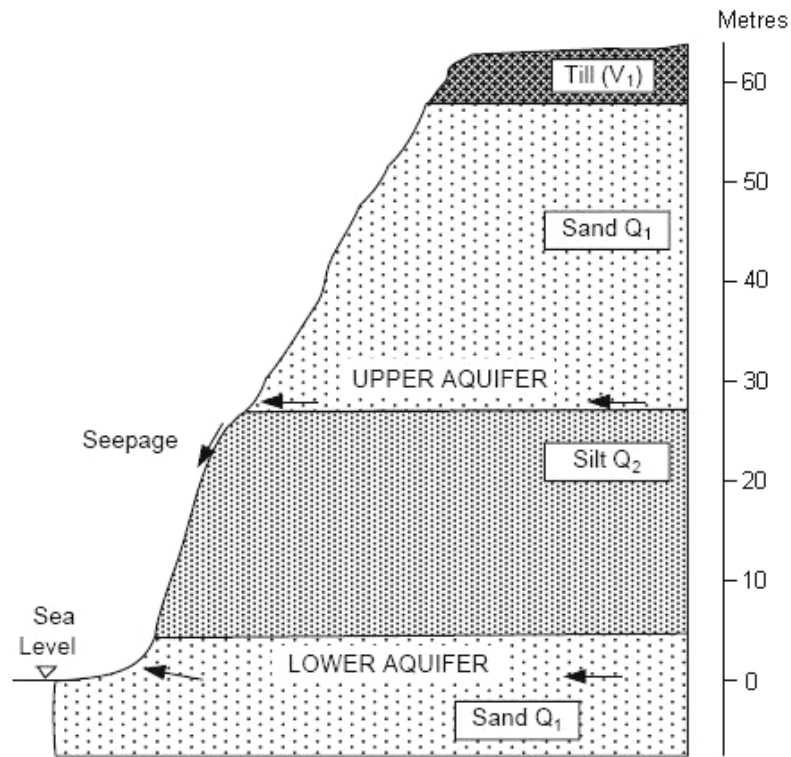
Figure 5: Cross Section of Point Grey Cliff Large Scale Stratigraphy (Dakin 2002)

2. Fieldwork

Two distinct rounds of samples were collected and analyzed. Water samples were collected from two different wells along the wetland (see Figure 2), one at the end of the wetland and one in the middle of the wetland closer to where the untreated compost tea and greywater first enter. A third and fourth sample were also taken from the tanks where the tea and greywater are stored inside the building. These liquids are stored in separate tanks where they sit until their level reach a certain height and are then pumped up to the wetland. The following table lists the location of the samples collected, their volumes, methods of preservation and their use:

Table 1: Liquid Samples

Location	Date	Volume (mL)	Method of Preservation	Parameters Measured
Compost Tea Tank	Nov-08	120mL	Air tight seal and refrigerate. Acidified with HCl before using Inductively Coupled Plasma Emission Spectrometer	pH, P, Cl, N-NH4, NOx,trace metals
Greywater Tank				pH, P, Cl, N-NH4, Nox
Borehole Closest to Source				pH, P, Cl, N-NH4, NOx,trace metals
Borehole Furthest From Source				pH, P, Cl, N-NH4, NOx,trace metals
Borehole Closest to Source	Mar-09			pH, P, Cl, N-NH4, NOx,trace metals
Borehole Furthest From Source				pH, P, Cl, N-NH4, NOx,trace metals

2.1 Materials and Testing Methods

Four different analyses were conducted to assess the wetland water: pH probe analysis, nutrient analysis, Inductively Coupled Plasma Emission Spectrometry (ICP) analysis, and phreeqc simulation.

2.1.1 pH Testing

To test the pH of the samples, I used a pH probe directly on-site. Firstly, I calibrated the pH probe with standard buffers: pH 4 solution, pH 7 solution and pH 10 solution. Once the system was calibrated, I was able to measure the pH for the samples. I rinsed the pH probe with distilled water after each use to ensure that it was not contaminated.

2.1.2 Nutrient Testing

Nutrients, consisting of ammonia, chloride, nitrate/nitrite and orthophosphate were measured in the Soil Water Environment Laboratory at UBC. Samples were run

with blanks so as to detect any potential errors or contamination from sample preparation. The instrument used is called the Lachat QuickChem FIA+ (8000 series) and analyzed the concentrations automatically. A summary of the methods used by this instrument can be found in Appendix A.

2.1.3 Inductively Coupled Plasma Emission Spectrometry (ICP) Analysis

The ICP is used to determine cation and trace metal concentrations on samples acidified to pH< 1.5 with HCl. It works by injecting a nebulized mist from a liquid into the center of an argon plasma. A plasma is created by a flow of gas in a high energy field which ionizes the gas and causes intense heating, up to 10,000 K. As the mist of the sample enters the plasma, the heat dissociates most chemical compounds. The energy that the atoms absorb causes them to undergo excitation and ionization energy transitions. These transitions produce spectral emissions that are characteristic of the elements being excited. The spectrum produced by the plasma is separated into individual spectral lines by the ICP's spectrometer, which the computer can then analyze as concentrations of specified elements (Ammann, 2007).

Element concentrations are given in parts per million (ppm) on a sample volume basis, taking into account dilutions prior to testing.

2.1.4 Phreeqc Simulation

Phreeqc is a software tool for the simulation of one-dimensional unsaturated flow and solute transport. Inverse modeling was used with Phreeqc to follow the chemical changes that occur as the input water evolves along the flow path. Inverse modeling

calculates the moles of minerals and gases that enter or leave the system to account for the changes in composition along the flow path.

3. Background Literature Review

To date, researchers from around North America have conducted analyses on wetlands that process greywater, stormwater and sewage. Experiments have been conducted on sites of different scales, from industrial and commercial size wetlands to domestic wetland systems. Different experiments have emphasized their analysis on different characteristics of wetlands or different processes that occur in them, ranging from nitrogen removal to organic matter oxidation to plant uptake of nutrients. Their findings are summarized below.

3.1 Nitrogen Removal

Tuncsiper (2009) conducted a study to determine appropriate conditions for nitrogen removal. He looked at hydraulic loading rates, nitrogen loading rates, effluent recirculation, plant uptake and seasonal change on nitrogen removal efficiency.

Tuncsiper states that the most important processes that remove nitrogen from domestic sewage in small constructed wetlands are nitrification and denitrification (see Equation 2 and Table 3 respectively for equations). He quotes a study by Platzer (1997) that showed that for a constructed wetland with 250 to 630 g N/m^2/yr loading rates, the removal efficiency of total nitrogen ranges from 40% to 55%. This study also showed that horizontal constructed wetlands have a high denitrification capacity and vertical constructed wetlands have a high nitrification capacity. So by combining these two flows, higher total nitrogen removal efficiencies are optimized.

Tunciper's study found that the raw wastewater had a pH of 7, total nitrogen of 52.9mg/L, ammonium (NH_4^+(aq)) of 36.8mg/L and nitrate (NO_3^-) of 2.32mg/L. Nitrite (NO_2^-) concentrations were below 0.3mg/L. His study showed that the aerobic conditions in the vertical constructed wetland led to high nitrification rates and the anaerobic conditions in the horizontal constructed wetland led to high denitrification rates. Also, during colder months, the removal efficiencies decreased because the temperature dropped from 23 to 9 degrees Celcius.

The temperature dependent rate constant (K_T) for ammonium and nitrate were calculated by Tuncsiper using the following equation:

$$\ln\left(\frac{C_e - C^*}{C_i - C^*}\right) = -K_T \bullet t \qquad \text{(Equation 1)}$$

Where C_e is the final concentration, C_i is the initial concentration, C^* is the irreducible background concentration and t is the hydraulic residence time.

Tuncsiper quotes studies by Bavor et al (1988), Reed & Brown (1995) that calculate nitrification rate constants of 0.107L/d, 0.4107L/d respectively. He also quotes a study by Reddy & Patrick that calculates denitrification rate constants of 0.004 to 2.57L/d.

These study conditions are similar to those of the C.K. Choi wetlands in its pH conditions. However, they are dissimilar in that the nitrate/nitrite and ammonium concentrations are approximately ten times the ones found in C.K. Choi wetlands, which is expected since the C.K. Choi building does not produce as much sewage as was observed in Tuncsiper's study and its loading rate is smaller. Also, the summer and winter temperatures around UBC usually range between 11 and -5 degrees Celcius, lower than those measured for this study.

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3.2 Organic Matter Oxidation

Ptacek (1998) studied the major ion and trace metal geochemistry of a septic
plume in a shallow sand aquifer, much like the one around the C.K. Choi building. She
studied the geochemical processes linked with the movement and exchange of nutrients
with their host environment along their flow path.

Septic system effluent shows high levels of dissolved organic carbon, ammonia,
phosphorus, and pathogens. The study by Ptacek looks at an area contaminated with
blackwater (wastewater from toilets and showers). The water use in the area reaches
2500L/day and is gravity-fed from a holding tank to a tile bed. This loading rate and
consequently the nutrient concentrations in the effluent are considerably higher than
those observed in the wetland around the C.K. Choi building. Concentrations in the
holding tank were as follows:

Table 2: Composition of Septic System Effluent from Ptacek's Study (1998)

Parameter	Concentration (mg/L)
DOC	31.8
NH4	97.9
Total P	11.8
Ca	83.6
Mg	12.9
Na	42.8
K	20.6
Cl	57.0
SO4	34.1
SiO2	9.65
Fe	0.599
Mn	0.480
Cu	0.029
Zn	0.069
Al	0.10

In her study Ptacek observed the highest concentrations of dissolved organic carbon (DOC) near to the septic plume source, decreasing with distance from the bed. Removal efficiencies ranged from 60 to 80%.

The main oxidant of ammonia is oxygen. O_2 has low solubility and as a result, most oxidation takes place in the unsaturated zone. Oxidation is not, however, excluded from the saturated zone; it only occurs at much slower rates and occurs when oxidation is incomplete in the unsaturated zone. NH_4^+(aq) was found in the saturated zone, which means that oxidation in the unsaturated zone is incomplete. This could have several causes: short residence times in the unsaturated zone due to high permeability of the sands, high loading rates, and a shallow water table; or insufficient active microbes due to the sporadic discharge of wastewater.

PO_4 removal efficiencies were approximately 80%, which agrees with other sites' removal efficiencies of 50 to 80%. The main removal mechanism is through precipitation as hydroxyapatite and ferrihydrite.

Decreases in pH were observed and agree with the expected changes due to the release of CO2 from organic matter oxidation and of H^+ from NH_4^+(aq) oxidation (see following equation):

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \hspace{2cm} \text{(Equation 2)}$$

The study site contained excess carbonate minerals. The decrease in pH due to CO_2 release from organic matter oxidation and H^+ release is expected to lead to carbonate mineral dissolution, which results in an increase in alkalinity, Ca^{2+} concentrations, and other cations from the carbonate minerals. Alkalinity values ranged from 200mg/L at the effluent plume margins and 350-500mg/L in the plume core.

In Ptacek's study site, high concentrations of Mn and Fe were observed near the leachate plume, likely due to reductive dissolution of Mn(IV) oxides coupled with DOC oxidation and due to reductive dissolution of Fe(III) oxyhydroxide solids coupled with DOC oxidation respectively. Furthermore, the upper meters of sand are stained with an orange colour, indicating the presence of Fe(III) oxyhydroxide solids.

N/Cl ratios are assumed to remain relatively constant over time in the raw effluent. In Ptacek's study, given that the N/Cl ratio decreased over time, it was assumed that there was loss of N during transport from the source area. The loss of total N could be due to nitrate reduction, dilution, oxidation of NH_4^+(aq), or cation exchange reactions with NH_4^+(aq).

3.3 Plant Uptake

The performance of wetlands depends on numerous factors: influent characteristics, loading rate, storage capacity, the design of the wetland system, and environmental factors such as light and temperature. To better understand the components and mechanisms that determine the level of performance of a wetland system, Breen (1990) conducted a study using a mass balance approach to investigate individual aspects of the system. The approach intended to "describe system performance, indicate the relative size and importance of various components, suggest which removal processes are operating, and allow quantification of the removal rates" (Breen 1990).

The study wetland system consisted of washed gravel as substratum and rhizomes of *Typha Orientalis* planted in the gravel. The system had an upflow format, with influent entering at the bottom and effluent collected at the top of the system, much like the one

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around the C.K. Choi building. Results showed that the planted system removed over 80% of the chemical oxygen demand(COD), a measure of the organic compounds in the water, and 95% of the N and P. In the unplanted system, however, there as little as 7% N storage, demonstrating the plant uptake has a large effect on N absorption. Using the mass balance approach, Breen concluded that there are only two mechanisms that remove P from the system: adsorption onto the substratum and absorption by plants. Gravel has a low adsorption capacity and so adsorption did not prove useful for nutrient removal in this experiment. Plants were the major nutrient sink for N and P, absorbing 50% of the influent N and 67% of the influent P. In addition to this, denitrification was also determined to be a significant process for N removal, in both the planted and unplanted systems (Breen 1990).

4. Performance Indicators

In this analysis, I am observing a passive treatment system. Passive treatment is identified as "the deliberate improvement of water quality using only naturally-available energy sources (eg. gravity, microbial metabolic energy, photosynthesis) in systems which require only infrequent (albeit regular) maintenance in order to operate effectively over the entire system design life" (Younger et al. 2002). Therefore, I will not be looking at inputs of artificial energy or chemical reagents. With an understanding of the literature, chemistry and related experiments, the chemical and physical processes that are expected to occur in the C.K. Choi wetlands can be identified.

4.1 Chemical Indicators

With the migration of the compost tea and greywater, N and P are released from organic compounds and oxidation of DOC leads to higher concentrations of NO_3^-, PO_4, CO_2 and H^+. The principal oxidant of DOC and ammonia is oxygen. Most oxidation of the effluent takes place in the unsaturated zone. However, oxidation can occur in the saturated zone, only at much slower rates; this occurs when oxidation is incomplete in the unsaturated zone. Therefore, if products of organic matter oxidation reactions are found in the saturated zone, it is an indicator that oxidation is incomplete in the unsaturated zone. The following table lists the main oxidation reactions that take place in the effluent and their free energy. A more negative free energy means that the reaction is more likely to occur.

Table 3: Organic Matter Oxidation (Ptacek, 1998)

Process	Reaction[a]	Free energy[b] (kcal mol^{-1})
O_2 reduction	$CH_2O + 1/2\,O_2 = HCO_3^- + H^+$	-118.8
Denitrification	$CH_2O + 4/5NO_3^- = 2/5N_2(g) + HCO_3^- + 1/5H^+ + 2/5H_2O$	-112.7
Manganese(IV) reduction	$CH_2O + 2MnO_2(s) + 3H^+ = 2Mn^{2+} + HCO_3^- + 2H_2O$	-84.9
Iron(III) reduction	$CH_2O + 4Fe(OH)_3(s) + 7H^+ = 4Fe^{2+} + HCO_3^- + 10H_2O$	-26.8
Sulphate reduction	$CH_2O + 1/2SO_4^{2-} = 1/2HS^- + HCO_3^- + 1/2H^+$	-23.9
Methane fermentation	$CH_2O + 1/2H_2O = 1/2CH_4 + 1/2HCO_3^- + 1/2H^+$	-21.6

[a]Reactions from Freeze and Cherry (1979).
[b]Free energy data from Garrels and Christ (1965) and Brock et al. (1984); calculated for pH = 7.0

In the saturated zone, oxygen is not present in high enough concentrations to completely oxidize DOC and NH_4^+(aq); their oxidation depends on another electron acceptor. The expected sequence of reactions goes from denitrification, to reductive dissolution of Mn-oxides, followed by reductive dissolution of Fe-oxides (see Table 3 above). These processes are indicated by a decrease in NO_3^- concentrations and an increase in dissolved Mn^{2+} and Fe^{2+} concentrations. Other reactions, only under strongly

reducing conditions, include sulfate reduction and methanogenesis (see Table 3 above) (Ptacek 1998).

4.1.1 Total Nitrogen

The following processes were used in the model development for nitrogen removal:
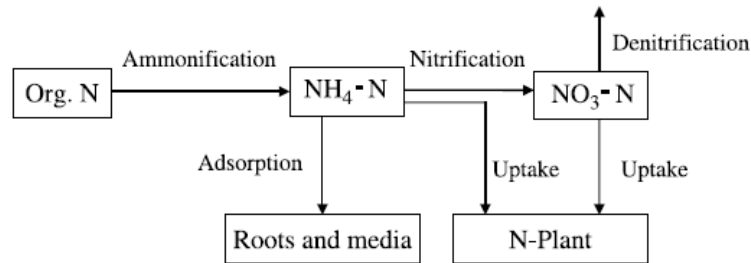
Figure 6: Model Development for Nitrogen Removal (Sonavane 2009)

Ammonification, which occurs in the composting tanks, transforms the organic nitrogen into NH_4N and nitrification transforms NH_4N into nitrates (NO_3^-). Overall the nitrogen concentration increases with nitrification and decreases with denitrification.

NH_4^+(aq) is released by aerobic degradation. It is then removed from solution by nitrification and adsorption. The process of nitrification produces nitrate (NO_3^-) (see Equation 2 on page 15), also increasing the H^+ concentration, thus decreasing the pH of the solution. So, drops in dissolved NH_4^+ concentrations are due to either dilution or due to oxidation or cation exchange reactions (Ptacek 1998).Denitrification can then occur (see Table 3 on page 18). This process uses NO_3^- to produce gaseous nitrogen (N_2(g)).

4.1.2 Manganese (IV) Reduction

Reducing conditions, as are present in the wetland system around the C.K. Choi Building, reduce manganese to its reduced state of Mn^{2+}. The reductive dissolution of

Mn-oxyhydroxides is marked by an increase in pH and DOC. Mn(IV) is more readily

reduced with organic compounds than Fe(III) and so reduction of Mn(IV) occurs before

that of Fe(III). In some instances, Mn(IV) and Fe(III) reduction can occur

simultanesouly. This is the case with unstable Fe minerals and organically complexed

Fe^{3+}. In most cases however, such as under near neutral pH conditions, organic

compounds such as oxalate, pyruvate and syringic acid reduce Mn(IV) before Fe(III) is

reduced (Grybos et al. 2009).

4.1.3 Iron(III) Reduction

Redox indicators include the redox couples NH_4^+ - NO_3^- and Mn^{4+} - Mn^{2+}, as

mentioned above, and Fe^{2+} - Fe^{3+}. Reducing conditions cause iron to be in the ferrous

oxidation state (Fe^{2+}). Between a pH of 5 to 9, Fe^{3+} concentrations are low due to the

solubility of ferric oxyhydroxide minerals such as ferrihydrite ($Fe(OH)_3$), producing Fe^{2+}

(see equation is Table 3). The presence of more than 0.1 mg/L Fe is a good indicator of

reducing conditions.

4.1.4 Sulphate Reduction

Reduction of sulphate improves water quality in several ways. Firstly, sulphate

reduction increases alkalinity and pH. Secondly, the reduction of sulfate to sulfide

induces the precipitation of metal-sulfide minerals that have low solubility. Thirdly,

sulfate reduction promotes the formation of gaseous sulfur species that diffuse into the

atmosphere. In Table 3, we can see how sulfate is reduced to produce sulfide (H_2S) in a

reducing environment such as the wetland observed. At pH values higher than 4.5, sulfate

reduction also produces bicarbonate. If Fe or other metals are present, they can combine with sulfide as is demonstrated in equation 3.

$$Fe^{2+} + H_2S \rightarrow FeS + 2H^+ \qquad \text{(Equation 3)}$$

If the sulfide gas does not react with a metal, it can diffuse upwards and escape into the atmosphere.

According to a study by Wilderman et al. (1990), sulfate reduction and precipitation of metal sulfides removes 95% of dissolved Fe, Zn, Mn, Ni and Cd.

4.1.5 Phosphorus Removal

Phosphorus concentrations (~5 – 20 mg/L) normally found in sewage effluent are much higher than the concentrations (~0.30 mg/L) observed in other aquatic environments. Phosphate is absorbed strongly by most sediments and combines with various metal cations such as iron, aluminum, manganese and calcium to form various minerals.

The main processes affecting phosphorus transport are adsorption/desorption and precipitation/dissolution. Phosphate (PO_4^{3-}) can be adsorbed by various minerals. It is a proteolytic acid with a negative 3 charge that can protonate to form HPO_4^{2-}, $H_2PO_4^-$ and H_3PO_4. Under near neutral groundwater pH conditions, HPO_4^{2-} and $H_2PO_4^-$ are the two dominant forms present. Therefore, if positively charged minerals are present such as Al, Mn(IV) and Fe(III) containing oxides and oxyhydroxides, these anions will be adsorbed (See Table 4 below).

As for precipitation and dissolution of PO_4 containing solids, the most common solids containing PO_4 are Al, Fe and Ca solids (Nriagu and Dell, 1974). At low

temperatures, the solids that control the dissolution of PO_4 include hydroxyapatite

($Ca_5(PO_4)_3OH$), variscite ($AlPO_4 \cdot 2H_2O$), strengite ($FePO_4 \cdot 2H_2O$), and vivianite

($Fe_3^{2+}(PO_4)_2 \cdot 8H_2O$) (Strumm and Morgan 1981). Groundwater that contains phosphate

and carbonate minerals is usually saturated with respect to hydroxyapatite, but its

formation is kinetically limited. Also, when both phosphate and $CaCO_3$ are present,

precipitation of Ca PO_4 is likely to occur. Siderite ($FeCO_3$) can also be a controlling

factor for the concentration of dissolved PO_4, by keeping ferrous iron concentrations low

(Ptacek 1998, Akratos 2009). The portion not sorbed to sediments is available for

phytoplanctons to uptake or it just flows out through the water stream.

Table 4: Phosphorus Removal (Spiterri et al. 2007)

Process	Reaction	Rate / Expression
Slow P adsorption/desorption into Fe oxides *	$\Sigma PO_4(aq) + Fe(OH)_3 \leftrightarrow P_{s-slow}$	$Rate = -k_{rev}(0.4^c[Fe(OH)_3] - [P_{s-slow}])\times([\Sigma PO_4(aq)] - [\Sigma PO_4(eq)])$
Slow adsorption/ desorption into calcite **	$\Sigma PO4(aq) + CaCO_3 \leftrightarrow P_{s-slow}$	$Rate = -k_{rev}(0.55^d[CaCO_3] - [P_{s-slow}])\times([\Sigma PO_4(aq)] - [\Sigma PO_4(eq)])$
Acid/base equilibria and equilibrium sorption		
Carbonate dissociation	$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^-$	$K_{eq1} = \dfrac{[H^+][HCO_3^-]}{[CO_2]}$
Carbonate dissociation	$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$	$K_{eq2} = \dfrac{[H^-][CO_3^{2-}]}{[HCO_3^-]}$
Phosphate dissociation	$H_2PO_4^- \leftrightarrow H^+ + HPO_4^{2-}$	$K_{phos1} = \dfrac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]}$
Phosphate dissociation	$HPO_4^{2-} \leftrightarrow H^+ + PO_4^{3-}$	$K_{phos2} = \dfrac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]}$
Ammonium sorption	$NH_4^+ \leftrightarrow NH_{4(ads)}$	$K_n \phi = \dfrac{[NH_{4(ads)}]}{[NH_4^+]}$
Fast P adsorption/desorption on Fe oxide *	$\Sigma PO_4(aq) \leftrightarrow P_{s-fast}$	$[P_{s-fast}] = \dfrac{K_L 0.1^c[Fe(OH)_3][\Sigma PO_4(aq)]}{1 + K_L[\Sigma PO_4(aq)]}$
Fast P adsorption/desorption on calcite **	$\Sigma PO_4(aq) \leftrightarrow P_{s-fast}$	$[P_{s-fast}] = \dfrac{K_L 0.05^d[CaCO_3][\Sigma PO_4(aq)]}{1 + K_L[\Sigma PO_4(aq)]}$

Parameter values are listed in Table 2.

* and ** Reactions NOT included in simulations of Cambridge case study (1) and Muskoka case study (2), respectively.

a CH_2O represented with an elemental composition $(CH_2O)_x(NH_3)_y(H_3PO_4)_z$, where $x=150$, $y=16$, $z=1$; Carbon is assumed to be present as DOC_1 and DOC_2.

b Ω=ion activity product/solubility product; If $\Omega>1 \rightarrow$ mineral precipitation, If $\Omega<1 \rightarrow$ mineral dissolution; h=heavy side operator to switch from precipitation to dissolution and vice versa.

c Assuming a P:Fe ratio of 0.5 (Gunnars et al., 2002) and 10% of $Fe(OH)_3$ is available for fast sorption (Slomp et al., 1996); d Assuming a P:Ca ratio of 0.6 (Freeman and Rowell, 1981) and 5% of $CaCO_3$ is available for fast sorption (Cole et al., 1953).

4.1.6 Alkalinity

Passive treatment systems, or reducing conditions, add alkalinity to wastewater. The wetland contains alkalinity producing materials such as dead plant matter (Walton-Day 2003). A study by Lorah et al (2008) observed alkalinity values of 0.5 to 1meq/L for a naturally attenuating landfill leachate. The study also showed that this value doubled during the wet season when plant growth was higher. Similar results for alkalinity (0.9 to 1.2meq/L) were observed in a natural pond setting in a study by Espinar and Serrano (2008).

4.2 Physical Indicators

4.2.1 Loading Rate

Estimated loading rates at the entrance of the wetland system and retention times were calculated. The total amount of water flowing into the wetland (Q), divided by the area of the study wetland (A), gives an estimate of the loading rate of a wetland (L).

$L = Q/A$ (Equation 3)

The turnover rate (t^{-1}) is calculated by dividing the loading rate by the average depth of the wetland (d).

$t^{-1} = L/d$ (Equation 4)

The retention time (t) is the reciprocal of the turnover rate.

The longer the retention time of the wetland, the longer the water is in contact with the biologically active soil and the greater the rate of physical processes and sedimentation.

5. Results

The following tables summarize the lab results obtained for pH and for the concentrations of ortho-phosphate, chloride, nitrate/nitrite, and ammonia in the wetland around the C.K. Choi building. These results were given from the Lachat QuickChem FIA+ (8000 series) instrument.

Table 5: pH Results

Sample ID	pH (Nov 2008)	pH (Mar 2009)
Compost Tea	7.71	
Greywater	4.72	
Effluent closest to source	6.15	7.03
Effluent furthest from source	6.04	6.92

Table 6: Ortho-phosphate Results

Sample ID	Ortho-phosphate (mg P/L) (Nov 2008)
Compost Tea	145.43
Greywater	0.58
Effluent closest to source	6.42
Effluent furthest from source	5.88

Table 7: Chloride Results

Sample ID	Chloride (mg Cl/L) (Nov 2008)
Compost Tea	3017
Greywater	36
Effluent closest to source	66
Effluent furthest from source	79

Table 8: Ammonia Results

Sample ID	Ammonia (mg N-NH4/L) (Nov 2008)
Compost Tea	692.9
Greywater	7.8
Effluent closest to source	2.6
Effluent furthest from source	5.4

Table 9: Nitrate/Nitrite Results

Sample ID	Nitrate/Nitrite (mg NOx/L) (Nov 2008)
Compost Tea	307.74
Greywater	0.12
Effluent closest to source	3.45
Effluent furthest from source	3.3

The following tables summarize the ICP results for the compost tea and liquid flowing through the C.K. Choi wetlands. The same trace metal was sometimes identified with different wavelengths, so if two different concentrations were identified, the most reasonable concentration was taken. Detection limits were set as follow: 0.1 to 100ppm for P, 10 to 500ppm for S, and 0.1 to 100ppm for all other trace metals. Therefore, if metals were present at lower concentrations than these, they should not be detected by the ICP machine. However, some of the metals were detected at lower concentrations than the standards. I chose to accept this data if concentrations for a particular metal were similar at different wavelengths. The greywater liquid was too thick to run through the ICP machine, so was not analyzed using this instrument.

Table 10: Concentrations (mg/L) of Trace Metals Retrieved in November 2008

Element	Compost Tea	Effluent Closest to Source	Effluent Further From Source
K	6067	27.9	33.81
Na	5910	38.85	38.57
S	1133	5.922	3.546
P	762.7	4.968	5.707
Ca	156.3	6.026	7.592
Fe	9.961	0.325	0.166
Mn	2.014	0.424	0.452
Zn	0.7415	0.3817	1.224
Mo	0.5117	0.02195	0.0155
Cu	0.4639	0.04734	0.1721
Ni	0.06526	0.1603	0.4537

Table 11: Concentrations (mg/L) of Trace Metals Retrieved in March 2009

Element	Effluent Closest to Source	Effluent Further From Source
Na	81.74	94.58
K	42.67	50.56
Ca	16.42	23.04
S	5.37	4.94
P	4.008	5.771
Mg	1.858	3.588
Mn	0.441	0.468
Zn	0.2287	0.218
Fe	0.211	1.025
Ni	0.1141	0.1246
Cu	0.06712	0.01969
Mo	0.01582	0.02117

6. Analysis

6.1 Dilution Effects

A graph of nutrient concentrations divided by chloride concentration was made to observe how much of the loss of nutrients was due to dilution and how much was due to the geochemical processes occurring in the wetland.
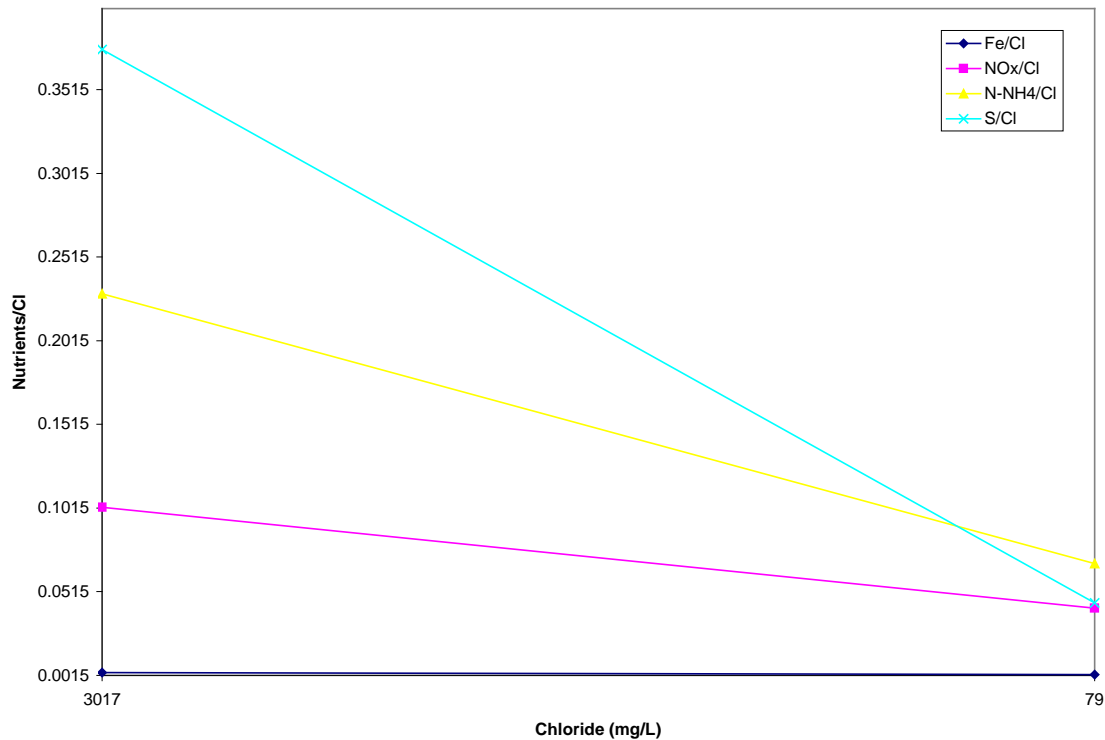
Figure 7: Dilution Test

As is observed from Figure 7 above, the lines for nutrient/Cl over Cl have a

negative slope. This means that in addition to dilution, many processes are happening to

reduce the concentrations of the nutrients present in the wastewater as it flows through

the wetland. These processes will be discussed in Section 7: Discussion.

6.2 Loading Rate

A loading rate can be estimated for the wetland system, using equations 3 and 4

(on page 24). In order to remain conservative, I assumed 200 people use the toilets and

sinks in the C.K. Choi building. Not everyone will use these washrooms all day, so I

assume each person produces 2L of greywater and compost tea per day. This totals as

400L of wastewater per day going into the wetlands. The area of the wetland was

assumed to be $20m^2$, giving the wetland a loading rate of 0.02m/day. This loading rate is

smaller than the studies observed in literature (Platzer 1997, Ptacek 1998); however it is a reasonable estimate since not many people occupy this building at this time and so the wetland does not need to support as much wastewater.

Assuming a conservative depth of 0.5m for the wetland, by taking the loading rate divided by the depth of the wetland, a hydraulic residence time can be calculated as 25 days. From the geochemistry changes observed as the wastewater flows through the system, we can confirm that 25 days residence time is sufficient to clean the effluent. From the lab results, we see that significant removal occurs early in the flow system, at the sampling well closest to the source (see Figure 2).

6.3 Rate Constant and Mass Balance

As was earlier discussed in Tuncsiper's literature review, the rate constant can be calculated using equation 1. Because of dilution, the calculated rate constants are approximate. Assuming a hydraulic residence time of 25 days and an estimated irreducible background concentration of 3mg/L for nitrate/nitrite, the rate constant for nitrification is calculated as 0.28L/d. This value is comparable to those calculated by Bavor et al (1988) and by Reed & Brown (1995) whose studies showed nitrification rate constants of 0.107L/d, 0.4107L/d respectively.

A mass balance can also be calculated. It was assumed that the compost tea flow is an eighth of the total flow, or 50L/day, and the greywater flow is seven eighths of the total flow, or 350L/day. These flows are estimates. A mass balance for nitrogen can be calculated using equation 5:

$$[NO_x] = \frac{Q_{compost}[NO_x] + Q_{greywater}[NO_x]}{Q_{compost} + Q_{greywater}} \qquad \text{(Equation 5)}$$

The brackets indicate concentrations. This equation gives a nitrate/nitrite concentration of 38.57mg/L, which is much higher than the 3.45mg/L of nitrate/nitrite observed at the sampling well closest to the source. This is an indication of both dilution and denitrification.

6.4 Removal Efficiencies

Removal efficiencies can be calculated using the load. I assumed that the flow through the system did not remain at 400L/day throughout the entire wetland system. I estimated that there was approximately 20L/d of flow lost to infiltration into the gravel. By using the following equation, removal efficiencies for various metals were calculated:

$$1 - \frac{C_2 Q_2}{C_1 Q_1} \bullet 100\% \hspace{4cm} \text{(Equation 6)}$$

Where C_2 is the concentration of the trace metal at the furthest sampling point in the wetland and Q_2 is the flow at the same place, C_1 is the concentration of the trace metal in the compost tea and Q_1 is the flow at the inlet to the wetland.

As mentioned earlier, the flow at the inlet to the wetland is estimated as 400L/day and the flow at the furthest point in the wetland is 380L/day. The following table lists the removal efficiencies for various trace metals.

Table 12: Removal Efficiencies

	P	Nitrate/Nitrite	Ammonia
C2 (mg/L)	5.707	3.3	5.4
Q2 (L/day)	400	400	400
C1 (mg/L)	762.7	307.74	692.9
Q1 (L/day)	380	380	380
Removal Efficiency (%)	99.1	98.8	99.1

These removal efficiencies are high compared to the 80% and 70% removal efficiencies observed for P and N in Tuncsiper (2009) and Ptacek's (1998) studies, but

are closer to the 95% P and N removal efficiencies observed by Breen (1990). The high

removal efficiencies observed in the wetland system around the C.K. Choi building are

likely due to the concentrations of trace metals and nutrients being low when they enter

the system and so are easily removed. Also, as observed by Breen (1990) and Walton-

Day (2003), plant uptake is a significant contribution to metal removal. Plants immobilize

metals and accumulate them in their structures, a process that takes place in the C.K.Choi

wetland system.

6.5 Phreeqc Simulation

The Phreeqc simulation was only run with the compost tea because trace metal

data was available not available for the greywater since the ICP machine could not handle

the amount of sediment in the greywater. A solution simulating the trace metal

concentrations in the compost tea was run through an environment simulating the wetland

system. Precipitates were then observed.

6.5.1 Assumptions

Assumptions were necessary while performing the Phreeqc simulation. Firstly, a

total sulfur concentration was obtained from the ICP machine. Because an input of either

sulfate or sulfide is necessary in Phreeqc, it was assumed that all the sulfur in the

compost tea was in its oxidized form as sulfate. This is an appropriate assumption since

the wetlands are a reducing environment and sulfate is also observed in wetland studies

such as Ptacek's (1998). High sulfide, instead of sulfate, is extremely toxic and is only

present in highly alkaline solutions, which is not likely the case for this wetland.

Additionally, the nitrate/nitrite concentration obtained from the Lachat QuickChem

analysis was input in the Phreeqc model as nitrate because this is the most likely species present. The model was initially run without a charge balance. The output then gave a positive imbalance to the solution. Cl was then used as a charge balance to give an electrically neutral solution. The electrically balance system allows Phreeqc to run as many processes as it can with the input given.

The input and output Phreeqc files can be found in Appendix C.

6.5.2 Results

The Phreeqc model was used to observe what reactions occurred to produce precipitate from the wastewater running through the wetland system. Looking at the output file, the minerals with positive saturation indices will precipitate out of solution. Table 13 below summarizes the minerals with positive saturation indices.

Table 13: Phreeqc Output Saturation Indices

Mineral	Saturation Index
Chalcopyrite CuFeS2	14.5
Pyrite FeS2	11.8
Chalcocite Cu2S	9.01
Anilite Cu0.25Cu1.5S	6.43
Djurleite Cu0.066Cu1.868S	8.88
BlaubleiII Cu0.6Cu0.8S	6.85
BlaubleiI Cu0.9Cu0.2S	6.33
Covellite CuS	5.3
MnHPO4	4.78
Greigite Fe3S4	4.72
Millerite NiS	3.37
Sphalerite ZnS	1.91
N2(g)	1.79
Mackinawite FeS	0.85
FeS(ppt)	0.12
Hydroxyapatite Ca5(PO4)3OH	0
Vivianite Fe3(PO4)2:8H2O	0

It should be noted that the measured 66mg/L Cl is larger than the 13mg/L Cl computed using charge balance by Phreeqc. This charge balance discrepancy indicates either an error in the measurement of the dissolved constituents or that a significant analyte was not measured.

6.5.3 Discussion

From Table 13, as was also suggested by Strumm and Morgan (1981), we expect to see phosphate precipitate as hydroxyapatite, vivianite and $MnHPO_4$. Sulfide metals such as chalcopyrite, pyrite, chalcocite, anilite, djurleite, blaubleill, blaubeil, covellite, greigite, millerite, sphalerite, mackinawite and FeS (ppt) are expected to precipitate out of the wastewater solution flowing through the wetland. In addition to this, nitrogen gas will be produced in the system.

The expected alkalinity from the phreeqc simulation for the wastewater flowing through the wetland is 4.41meq/L. This value is the same order of magnitude as the

alkalinity values observed in ponds, marshes and sewage leachate plumes in studies by

Espinar & Serrano (2009) and by Lorah (2009). This could be explained by the fact that

testing was performed in November, a month during which vegetation is dying and

organics are collecting on the ground. In the case of the wetland around the C.K. Choi

building, most of the wetland is covered with reeds during the summer months and

starting around October, these plants begin to die and decompose on the gravel of the

wetland system.

7. Discussion

7.1 pH

As is expected, the greywater is acidic because of the soap and the compost tea

slightly basic to begin with. Standard freshwater has a pH of approximately 5.5 to 6

(Laurenzi 2010). The water flowing through the system should resemble that of standard

freshwater since it is being cleaned by the wetland, so the pH of the wastewater was

slightly acidic in March 2009, but was close to that of standard freshwater in November

2008. As the compost tea and greywater are mixed and begin to flow through the wetland

system, the pH decreases from 7.71 in the compost tea to 6.04 at the furthest point from

the building. This is as expected and is due to the oxidation of DOC increasing the

concentration of H^+ in the system. The drop in pH is also due to nitrification, consuming

$NH^{4+}(aq)$ to produce H^+. The pH observed during sample collection (pH 6.04) is also

close to the one output by the Phreeqc model (pH 6.054), which means that pH sampling

was accurate.

7.2 Ammonia

Ammonia concentrations go from 692.9mg/L in the compost tea and 7.8mg/L in the greywater to 2.6mg/L at the sample tube closest to the building outlet to 5.4mg/L at the sample tube furthest from the building. This decrease is due to nitrification, converting NH^{4+}(aq) to nitrates.

7.3 Nitrate/Nitrite

NO_x concentrations go from 307.7mg/L in the compost tea and 0.12mg/L in the greywater to 3.45mg/L at the sample tube closest to the building outlet to 3.30mg/L at the sample tube furthest from the building. This decrease is due to both dilution and denitrification. Denitrification uses NO_3^- and converts it to N_2 gas. The nitrogen gas can then escape upwards through the soil and be released into the atmosphere. Formation of nitrogen gas is also also agrees with the Phreeqc analysis performed.

7.4 Mn(IV)-Fe(III) Reduction, Sulphate Reduction and Phosphorus Removal

Looking at the ICP results, we see a decrease in Mn, Fe and S concentrations. This is due to the oxidation of DOC and the reduction of metals and S listed in Table 3 and due to precipitation of Mn, Fe and S solids.

Manganese (IV) reduction uses some of the H^+ produced from the denitrification process and converts the solid manganese dioxide, from the ground, into soluble Mn(II). Iron (III) reduction uses the solid phase iron hydroxide and H^+ to produce aqueous Fe (II). Finally, sulfate reduction uses sulfate and converts it to hydrogen sulfide. This then facilitates the precipitation of metal-sulfides such as iron sulfide and also induces the

formation of sulfur gases that migrate up through the soil and diffuse in the atmosphere. Phreeqc also shows that many other sulfide metals will precipitate with metals such as copper, nickel and zinc (see Table 13 on page 32).

Soluble Mn and Fe, in addition to Ca, are easily adsorbed by phosphorus (Strumm and Morgan 1981). Phosphorus concentrations in the compost tea are high. As the liquid flows through the system, phosphorus is removed through bacterial removal, plant uptake, adsorption by the gravel and sand, and by precipitation. HPO_4^{2-} and $H_2PO_4^-$ are the dominant forms of phosphate present at the pH conditions observed. Because of this, minerals such as hydroxyapatite, $MnHPO_4$, vivianite and strengite precipitate out of the solution.

8. Conclusion

Based upon the sampled analyzed, the wetlands processing the compost tea and greywater from the C.K. Choi building seem to be performing well. The concentrations of trace metals and minerals observed from the lab analyses agree well with the literature on wetland performance. It is expected that some trace metal concentrations will be lower than seen in other environments since the C.K. Choi building does not have many occupants, so wastewater concentrations are low to begin with. When the data from the compost tea was input in Phreeqc and simulated to run through an environment similar to that of the wetland, precipitate outputs also agreed with previous studies. Alkalinity, pH and metal concentrations are at levels that are normal and not harmful to the environment.

In further experiments, I would analyse the soil to observe what precipitates are present, so as to compare with the Phreeqc model. In this way, we could see whether some solids are present that are not available through the Phreeqc database and whether the precipitates identified with by Phreeqc are correct.

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Appendix A: Lachat QuickChem FIA+ Analysis Methods

Instrument: Lachat QuickChem FIA+ (8000 series)
Methods: Chloride, nitrate/nitrite, low ammonia, low orthophosphate
Applications: Drinking, ground and surface waters, and domestic and industrial wastes

QuickChem Methods Overview

Analyte	QuickChem Method #	Range (mg/L)	Detection Limits* (mg/L)
Ammonia (N as NH_3^+)	10-107-06-2-A	0.1 – 5.00	0.005
Chloride (Cl^-)	10-117-07-1-A	6 – 300	0.5
Nitrate / Nitrite (N as NO_3^- / NO_2^-)	12-107-04-1-B [†]	0.02 – 20.0	0.02
Orthophosphate (P as PO_4^{3-})	10-115-01-1-A	0.01 – 2.00	0.01

* blanks should always be run with a sample set to determine any potential error or contamination from sample preparation (including filtration steps).

[†] Method for 2M KCl soil extracts, but used with a straight water matrix/carrier.

Quality Control:
- Standard curves are re-run each day.
- During the run, a check standard is run every 10-15 samples to check for drift or other problems.

Method descriptions:
(taken directly from QuickChem Methods)

Ammonia: When ammonia is heated with salicylate and hypochlorite in an alkaline phosphate buffer, an emerald green colour is produced which is proportional to the ammonia concentration. The colour is intensified by the addition of sodium nitroprusside.

Chloride: Chloride reacts with mercuric thiocyanate to form a strong, covalent complex which displaces thiocyanate. The free thiocyanate reacts with aqueous iron(III) to produce ferric thiocyanate (red colour), which absorbs stongly at 480 nm.

Nitrate: Nitrate is quantitatively reduced to nitrite by passage of the sample through a copperized cadmium column. The nitrite (reduced nitrate + original nitrite) is then determined by diazotizing with sulfanilamide followed by coupling with N-(1-

naphthyl)ethylenediamine dihydrochloride. The resulting water soluble dye has a magenta colour which is read at 520 nm.

Orthophosphate: The orthophosphate ion (PO_4^{3-}) reacts with ammonium molybdate and antimony potassium tartrate under acidic conditions to form a complex. This complex is reduced with ascorbid acid to form a blue complex which absorbs light at 880 nm. The absorbance is proportional to the concentration of orthophosphate in the sample.

Potential interferences

Ammonia	1. In alkaline solution, Ca and Mg form a precipitate that scatters light (EDTA in buffer to prevent this). 2. Non-volatile amines such as cysteine, ethanolamine, and ethylenediamene cause decreased sensitivey. 3. Lauryl sulfate and some detergents can cause low recoveries.
Chloride	1. Substances that reduce iron(III) to iron(II) and mercury(III) to mercury(II) (e.g. sulfite, thiosulfate). 2. Other halides that form a strong complex with mercuric ion (e.g. Br^-, I^-).
Nitrate/Nitrite	1. Build up of suspended matter in column (pre-filter samples) 2. High concentrations of Fe, Cu, or other metals (EDTA in buffer to reduce this interference). 3. Large concentrations of oil and grease (must pre-extract sample with an organic solvent).
Orthophosphate	1. Silica forms a complex that also absorbs at 880 nm (generally an insignificant interference). 2. Concentrations of ferric iron (Fe^{3+}) > 50 mg/L cause negative error due to precipitation of orthophosphate. 3. Sample turbidity. 4. Glassware contamination.

Appendix B: ICP Data

Sampling Date	Location	Tube	Sample Labels	Mo 204.598	Cu 327.395	Cu 324.754	Mo 202.032	Zn 213.857	Zn 202.548	Zn 202.548	Cu 324.754
Nov-08	furthest from building	1 : 1	1a	0.015502	0.172134	0.219616	0.004884	1.2245	1.28063	1.28063	0.219616
Nov-08	closest to building	1 : 2	2a	0.02195	0.047343	0.096855	0.009299	0.381696	0.445887	0.445887	0.096855
Nov-08	compost tea	1 : 3	3a	0.511685	0.463857	0.72447	0.532739	0.741511	1.06938	1.06938	0.72447
Mar-09	furthest from building	1 : 4	1b	0.021174	0.019693	0.069954	0.009077	0.218021	0.277426	0.277426	0.069954
Mar-09	closest to building	1 : 5	2b	0.015817	0.067127	0.11485	0.009137	0.228709	0.286614	0.286614	0.11485

Sampling Date	Location	Tube	Sample Labels	Cr 267.716	As 193.696	As 188.980	Cr 276.653	Cr 205.560	Ni 230.299
Nov-08	furthest from building	1 : 1	1a	-0.031774	-0.005275	-0.064523	-0.012689	-0.017747	0.453686
Nov-08	closest to building	1 : 2	2a	-0.032141	0.008806	-0.074675	-0.013508	-0.019497	0.160351
Nov-08	compost tea	1 : 3	3a	-0.121301	0.17158	-0.032018	-0.047006	-0.064639	0.065269
Mar-09	furthest from building	1 : 4	1b	-0.032544	-0.002639	-0.074707	-0.013028	-0.017643	0.124578
Mar-09	closest to building	1 : 5	2b	-0.031231	0.006542	-0.062359	-0.012020	-0.018946	0.114064

Sampling Date	Location	Tube	Sample Labels	Ni 231.604	Ca 317.933	Ca 396.847	Ca 422.673	Fe 234.350	Fe 238.204	Fe 259.940	K 766.491
Nov-08	furthest from building	1 : 1	1a	0.43298	7.592	7.815	6.576	0.166	0.153	0.156	33.81
Nov-08	closest to building	1 : 2	2a	0.148449	6.026	6.225	5.115	0.325	0.318	0.319	27.9
Nov-08	compost tea	1 : 3	3a	-0.034293	156.3	145.2	145.9	9.961	10.16	10.11	6067 x
Mar-09	furthest from building	1 : 4	1b	0.114231	23.04	22.22	21.95	1.025	1.03	1.034	50.56
Mar-09	closest to building	1 : 5	2b	0.111669	16.42	16.12	15.11	0.211	0.201	0.206	42.67

Sampling Date	Location	Tube	Sample Labels	Mg 279.553	Mg 280.270	Mn 257.610	Mn 293.931	Na 588.995	Na 589.592	Si 212.412	Si 250.690
Nov-08	furthest from building	1 : 1	1a	-2.523	-0.161	0.452	0.452	38.57	36.17	-7.615	-7.935
Nov-08	closest to building	1 : 2	2a	-2.866	-0.438	0.424	0.424	38.85	36.42	-8.271	-8.611
Nov-08	compost tea	1 : 3	3a	-1.605	7.965	2.014	2.013	5910 x	5369 x	-29.81	-30.62
Mar-09	furthest from building	1 : 4	1b	2.202	3.588	0.468	0.467	94.58	91.87	-8.451	-8.782
Mar-09	closest to building	1 : 5	2b	0.001	1.858	0.441	0.439	81.74	79.77	-8.915	-9.267

Sampling Date	Location	Tube	Sample Labels	Se 203.985	Se 185.457	S 181.972	S 182.562	P 178.222	P 213.618	P 214.914
Nov-08	furthest from building	1 : 1	1a	0.033511	2.04771	3.54607	4.1466	5.707	5.331	5.353
Nov-08	closest to building	1 : 2	2a	0.044579	-3.08811	5.92219	6.75888	4.968	5.049	5.059
Nov-08	compost tea	1 : 3	3a	0.363731	9.93926	1133.11	1194.17	762.7	762.7	758.3
Mar-09	furthest from building	1 : 4	1b	0.057906	-1.40246	4.94004	5.7107	5.771	5.719	5.779
Mar-09	closest to building	1 : 5	2b	0.026885	1.34879	5.36984	5.49449	4.008	4.165	4.217

Appendix C: Phreeqc Simulation Data

Input File:

```
SELECTED_OUTPUT
-file   thesis_trial1.xls
-water
-charge balance
-pH
-pe
-alkalinity
-percent_error
-totals      Cl S S(-2) S(6) N N(5) N(-3) N(3) N
      Ca Mg Na K
      Al Cu Fe Mn P Zn
-saturation_indices
      hydroxyapatite
      strengite
      vivianite
      hematite
      magnetite
      cupricFerrite
      Fe(OH)3(a)
      goethite
      maghemite
      MnHPO4

-equilibrium_phases
      strengite
      vivianite

PHASES
      Fix_H+
      H+ = H+
      log_k  0.0
```

```
#       Water Type
        SOLUTION    1
        pH    7.71
        Temp  25
        pe    4
        redox pe
        units mg/L
        density     1
        Cl    3017        charge
        S(6)  1133        as SO4
        N(-3) 693         as N        #NH4
        N(5)  308         as N        #NO3-
        Ca    156
        K     6067
        Na    5910
        Cu    0.4638
        Fe    9.961
        Mn    2.014
        Ni    0.0653
        P     762.7       as P
        Zn    0.7415
        -water      1           #kg
        END

        USE Solution 1
        EQUILIBRIUM_PHASES 1
        CO2(g)      -3.5  10
        siderite    0     0
        hydroxyapatite  0     0
        strengite   0     0
        vivianite   0     0
        ZnS(a)                  0     0
        Ni(OH)2     0     0
        Calcite     0     0
        SAVE EQUILIBRIUM_PHASES     2
        SAVE SOLUTION     2
        END
```

Output File:

```
Input file: E:\thesis\data\phreeqc trials\trial 2\Phrqc1_t1.pqi
  Output file: E:\thesis\data\phreeqc trials\trial 2\Phrqc1_t1.pqo
Database file: C:\Program Files\USGS\Phreeqc Interactive 2.15.0\wateq4f.dat

------------------
Reading data base.
------------------

        SOLUTION_MASTER_SPECIES
        SOLUTION_SPECIES
        PHASES
        EXCHANGE_MASTER_SPECIES
        EXCHANGE_SPECIES
        SURFACE_MASTER_SPECIES
        SURFACE_SPECIES
        RATES
        END
------------------------------------
Reading input data for simulation 1.
------------------------------------

        DATABASE C:\Program Files\USGS\Phreeqc Interactive 2.15.0\wateq4f.dat
            SELECTED_OUTPUT
            file  thesis_trial1.xls
            water
            charge_balance balance
            ph
            pe
            alkalinity
            percent_error
            totals      Cl S S(-2) S(6) N N(5) N(-3) N(3) N
                Ca Mg Na K
                Al Cu Fe Mn P Zn
            saturation_indices
                hydroxyapatite
```

```
        strengite
        vivianite
        hematite
        magnetite
        cupricFerrite
        Fe(OH)3(a)
        goethite
        maghemite
        MnHPO4
equilibrium_phases
        strengite
        vivianite
PHASES
        Fix_H+
        H+ = H+
        log_k   0.0
SOLUTION    1
pH      7.71
Temp    25
pe      4
redox pe
units mg/L
density      1
Cl      3017            charge
S(6)    1133            as SO4
N(-3)   693             as N         #NH4
N(5)    308             as N         #NO3-
Ca      156
K       6067
Na      5910
Cu      0.4638
Fe      9.961
Mn      2.014
Ni      0.0653
P       762.7           as P
Zn      0.7415
water 1                 #kg
END
```

```
--------------------------------------------
Beginning of initial solution calculations.
--------------------------------------------


Initial solution 1.

---------------------------Solution composition----------------------------

     Elements           Molality         Moles

     Ca                 3.964e-003    3.964e-003
     Cl                 3.828e-001    3.828e-001    Charge balance
     Cu                 7.433e-006    7.433e-006
     Fe                 1.816e-004    1.816e-004
     K                  1.580e-001    1.580e-001
     Mn                 3.733e-005    3.733e-005
     N(-3)              5.039e-002    5.039e-002
     N(5)               2.239e-002    2.239e-002
     Na                 2.618e-001    2.618e-001
     Ni                 1.133e-006    1.133e-006
     P                  2.508e-002    2.508e-002
     S(6)               1.201e-002    1.201e-002
     Zn                 1.155e-005    1.155e-005

---------------------------Description of solution---------------------------

                               pH  =    7.710
                               pe  =    4.000
                  Activity of water  =    0.985
                       Ionic strength  =  4.926e-001
                  Mass of water (kg)  =  1.000e+000
             Total alkalinity (eq/kg)  =  2.417e-002
                Total carbon (mol/kg)  =  0.000e+000
                  Total CO2 (mol/kg)  =  0.000e+000
                Temperature (deg C)  =  25.000
               Electrical balance (eq)  = -1.818e-015
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  -0.00
                          Iterations  =  16
```

```
                          Total H  = 1.112404e+002
                          Total O  = 5.572208e+001


------------------------------Redox couples--------------------------------

      Redox couple             pe  Eh (volts)

      N(-3)/N(5)            5.2077      0.3081


-------------------------Distribution of species---------------------------


                                               Log       Log       Log
     Species              Molality    Activity Molality  Activity  Gamma


     OH-                  6.894e-007  5.055e-007  -6.162    -6.296   -0.135
     H+                   2.549e-008  1.950e-008  -7.594    -7.710   -0.116
     H2O                  5.551e+001  9.846e-001   1.744    -0.007    0.000
Ca            3.964e-003
     Ca+2                 2.144e-003  5.599e-004  -2.669    -3.252   -0.583
     CaHPO4               1.379e-003  1.545e-003  -2.860    -2.811    0.049
     CaPO4-               2.557e-004  1.875e-004  -3.592    -3.727   -0.135
     CaSO4                1.542e-004  1.728e-004  -3.812    -3.763    0.049
     CaH2PO4+             3.088e-005  2.264e-005  -4.510    -4.645   -0.135
     CaOH+                6.399e-009  4.692e-009  -8.194    -8.329   -0.135
     CaHSO4+              2.692e-011  1.974e-011 -10.570   -10.705   -0.135
Cl            3.828e-001
     Cl-                  3.828e-001  2.469e-001  -0.417    -0.608   -0.190
     MnCl+                9.873e-006  7.239e-006  -5.006    -5.140   -0.135
     CuCl2-               3.660e-006  2.683e-006  -5.437    -5.571   -0.135
     CuCl3-2              3.633e-006  1.050e-006  -5.440    -5.979   -0.539
     ZnCl+                1.932e-006  1.417e-006  -5.714    -5.849   -0.135
     FeCl+                1.348e-006  9.884e-007  -5.870    -6.005   -0.135
     ZnOHCl               7.858e-007  8.802e-007  -6.105    -6.055    0.049
     MnCl2                6.964e-007  7.800e-007  -6.157    -6.108    0.049
     ZnCl2                3.270e-007  3.663e-007  -6.485    -6.436    0.049
     NiCl+                1.885e-007  1.382e-007  -6.725    -6.859   -0.135
     ZnCl3-               1.384e-007  1.015e-007  -6.859    -6.994   -0.135
     NiCl2                1.106e-007  1.239e-007  -6.956    -6.907    0.049
```

```
    MnCl3-              7.233e-008  5.304e-008   -7.141   -7.275   -0.135
    ZnCl4-2             4.343e-008  1.255e-008   -7.362   -7.901   -0.539
    CuCl+               2.404e-009  1.763e-009   -8.619   -8.754   -0.135
    CuCl2               2.086e-010  2.337e-010   -9.681   -9.631    0.049
    CuCl3-              2.792e-013  2.047e-013  -12.554  -12.689   -0.135
    FeCl+2              7.146e-014  2.065e-014  -13.146  -13.685   -0.539
    FeCl2+              3.106e-014  2.277e-014  -13.508  -13.643   -0.135
    CuCl4-2             8.763e-016  2.533e-016  -15.057  -15.596   -0.539
    FeCl3               5.019e-016  5.622e-016  -15.299  -15.250    0.049
Cu(1)          7.292e-006
    CuCl2-              3.660e-006  2.683e-006   -5.437   -5.571   -0.135
    CuCl3-2             3.633e-006  1.050e-006   -5.440   -5.979   -0.539
    Cu+                 1.899e-010  1.392e-010   -9.721   -9.856   -0.135
Cu(2)          1.406e-007
    Cu(OH)2             1.262e-007  1.413e-007   -6.899   -6.850    0.049
    Cu+2                9.180e-009  2.653e-009   -8.037   -8.576   -0.539
    CuCl+               2.404e-009  1.763e-009   -8.619   -8.754   -0.135
    CuOH+               1.827e-009  1.340e-009   -8.738   -8.873   -0.135
    CuSO4               7.480e-010  8.378e-010   -9.126   -9.077    0.049
    CuCl2               2.086e-010  2.337e-010   -9.681   -9.631    0.049
    Cu2(OH)2+2          2.717e-012  7.853e-013  -11.566  -12.105   -0.539
    Cu(OH)3-            5.865e-013  4.300e-013  -12.232  -12.366   -0.135
    CuCl3-              2.792e-013  2.047e-013  -12.554  -12.689   -0.135
    CuCl4-2             8.763e-016  2.533e-016  -15.057  -15.596   -0.539
    Cu(OH)4-2           1.499e-017  4.333e-018  -16.824  -17.363   -0.539
Fe(2)          6.718e-005
    FeHPO4              5.188e-005  5.812e-005   -4.285   -4.236    0.049
    Fe+2                1.004e-005  2.901e-006   -4.998   -5.538   -0.539
    FeH2PO4+            3.134e-006  2.298e-006   -5.504   -5.639   -0.135
    FeCl+               1.348e-006  9.884e-007   -5.870   -6.005   -0.135
    FeSO4               7.122e-007  7.978e-007   -6.147   -6.098    0.049
    FeOH+               6.317e-008  4.632e-008   -7.199   -7.334   -0.135
    Fe(OH)2             1.777e-011  1.991e-011  -10.750  -10.701    0.049
    FeHSO4+             1.395e-013  1.022e-013  -12.856  -12.990   -0.135
    Fe(OH)3-            5.094e-014  3.735e-014  -13.293  -13.428   -0.135
Fe(3)          1.145e-004
    Fe(OH)3             8.770e-005  9.823e-005   -4.057   -4.008    0.049
    Fe(OH)2+            2.060e-005  1.510e-005   -4.686   -4.821   -0.135
```

```
   Fe(OH)4-               6.170e-006   4.524e-006     -5.210     -5.345     -0.135
   FeOH+2                 3.125e-009   9.031e-010     -8.505     -9.044     -0.539
   FeHPO4+                5.118e-012   3.752e-012    -11.291    -11.426     -0.135
   FeH2PO4+2              4.078e-012   1.178e-012    -11.390    -11.929     -0.539
   FeCl+2                 7.146e-014   2.065e-014    -13.146    -13.685     -0.539
   FeSO4+                 6.407e-014   4.698e-014    -13.193    -13.328     -0.135
   Fe+3                   4.523e-014   2.770e-015    -13.345    -14.558     -1.213
   FeCl2+                 3.106e-014   2.277e-014    -13.508    -13.643     -0.135
   Fe2(OH)2+4             3.147e-015   2.195e-017    -14.502    -16.659     -2.156
   Fe(SO4)2-             2.168e-015   1.590e-015    -14.664    -14.799     -0.135
   FeCl3                  5.019e-016   5.622e-016    -15.299    -15.250      0.049
   Fe3(OH)4+5             1.621e-016   6.926e-020    -15.790    -19.160     -3.369
   FeHSO4+2               8.487e-021   2.453e-021    -20.071    -20.610     -0.539
H(0)            4.806e-027
   H2                    2.403e-027   2.692e-027    -26.619    -26.570      0.049
K              1.580e-001
   K+                    1.552e-001   1.001e-001     -0.809     -1.000     -0.190
   KSO4-                 1.483e-003   1.088e-003     -2.829     -2.963     -0.135
   KHPO4-                1.340e-003   9.822e-004     -2.873     -3.008     -0.135
Mn(2)          3.733e-005
   Mn+2                  2.491e-005   7.198e-006     -4.604     -5.143     -0.539
   MnCl+                 9.873e-006   7.239e-006     -5.006     -5.140     -0.135
   MnSO4                 1.767e-006   1.980e-006     -5.753     -5.703      0.049
   MnCl2                 6.964e-007   7.800e-007     -6.157     -6.108      0.049
   MnCl3-                7.233e-008   5.304e-008     -7.141     -7.275     -0.135
   MnOH+                 1.274e-008   9.342e-009     -7.895     -8.030     -0.135
   Mn(NO3)2              6.897e-009   7.725e-009     -8.161     -8.112      0.049
   Mn(OH)3-              2.003e-017   1.469e-017    -16.698    -16.833     -0.135
Mn(3)          3.632e-026
   Mn+3                  3.632e-026   2.224e-027    -25.440    -26.653     -1.213
Mn(6)          0.000e+000
   MnO4-2               0.000e+000   0.000e+000    -45.391    -45.930     -0.539
Mn(7)          0.000e+000
   MnO4-                0.000e+000   0.000e+000    -51.179    -51.314     -0.135
N(-3)          5.039e-002
   NH4+                  4.849e-002   3.555e-002     -1.314     -1.449     -0.135
   NH4SO4-              9.662e-004   7.084e-004     -3.015     -3.150     -0.135
   NH3                   9.277e-004   1.039e-003     -3.033     -2.983      0.049
```

```
N(5)              2.239e-002
   NO3-              2.239e-002  1.642e-002   -1.650   -1.785   -0.135
   Mn(NO3)2          6.897e-009  7.725e-009   -8.161   -8.112    0.049
Na                2.618e-001
   Na+               2.574e-001  1.826e-001   -0.589   -0.738   -0.149
   NaHPO4-           2.444e-003  1.792e-003   -2.612   -2.747   -0.135
   NaSO4-            1.931e-003  1.416e-003   -2.714   -2.849   -0.135
Ni                1.133e-006
   Ni+2              7.713e-007  2.229e-007   -6.113   -6.652   -0.539
   NiCl+             1.885e-007  1.382e-007   -6.725   -6.859   -0.135
   NiCl2             1.106e-007  1.239e-007   -6.956   -6.907    0.049
   NiSO4             6.002e-008  6.723e-008   -7.222   -7.172    0.049
   NiOH+             2.119e-009  1.554e-009   -8.674   -8.809   -0.135
   Ni(OH)2           5.075e-011  5.684e-011  -10.295  -10.245    0.049
   Ni(SO4)2-2        1.932e-011  5.584e-012  -10.714  -11.253   -0.539
   Ni(OH)3-          3.915e-014  2.870e-014  -13.407  -13.542   -0.135
O(0)              9.960e-040
   O2                4.980e-040  5.578e-040  -39.303  -39.253    0.049
P                 2.508e-002
   HPO4-2            1.741e-002  5.033e-003   -1.759   -2.298   -0.539
   NaHPO4-           2.444e-003  1.792e-003   -2.612   -2.747   -0.135
   H2PO4-            2.156e-003  1.581e-003   -2.666   -2.801   -0.135
   CaHPO4            1.379e-003  1.545e-003   -2.860   -2.811    0.049
   KHPO4-            1.340e-003  9.822e-004   -2.873   -3.008   -0.135
   CaPO4-            2.557e-004  1.875e-004   -3.592   -3.727   -0.135
   FeHPO4            5.188e-005  5.812e-005   -4.285   -4.236    0.049
   CaH2PO4+          3.088e-005  2.264e-005   -4.510   -4.645   -0.135
   FeH2PO4+          3.134e-006  2.298e-006   -5.504   -5.639   -0.135
   PO4-3             1.900e-006  1.164e-007   -5.721   -6.934   -1.213
   FeHPO4+           5.118e-012  3.752e-012  -11.291  -11.426   -0.135
   FeH2PO4+2         4.078e-012  1.178e-012  -11.390  -11.929   -0.539
S(6)              1.201e-002
   SO4-2             7.473e-003  1.547e-003   -2.127   -2.811   -0.684
   NaSO4-            1.931e-003  1.416e-003   -2.714   -2.849   -0.135
   KSO4-             1.483e-003  1.088e-003   -2.829   -2.963   -0.135
   NH4SO4-           9.662e-004  7.084e-004   -3.015   -3.150   -0.135
   CaSO4             1.542e-004  1.728e-004   -3.812   -3.763    0.049
   MnSO4             1.767e-006  1.980e-006   -5.753   -5.703    0.049
```

```
    FeSO4                 7.122e-007  7.978e-007    -6.147    -6.098    0.049
    ZnSO4                 6.903e-007  7.732e-007    -6.161    -6.112    0.049
    NiSO4                 6.002e-008  6.723e-008    -7.222    -7.172    0.049
    Zn(SO4)2-2            3.363e-008  9.720e-009    -7.473    -8.012   -0.539
    HSO4-                 3.999e-009  2.932e-009    -8.398    -8.533   -0.135
    CuSO4                 7.480e-010  8.378e-010    -9.126    -9.077    0.049
    CaHSO4+              2.692e-011  1.974e-011   -10.570   -10.705   -0.135
    Ni(SO4)2-2           1.932e-011  5.584e-012   -10.714   -11.253   -0.539
    FeHSO4+              1.395e-013  1.022e-013   -12.856   -12.990   -0.135
    FeSO4+              6.407e-014  4.698e-014   -13.193   -13.328   -0.135
    Fe(SO4)2-            2.168e-015  1.590e-015   -14.664   -14.799   -0.135
    FeHSO4+2            8.487e-021  2.453e-021   -20.071   -20.610   -0.539
Zn             1.155e-005
    Zn+2                 7.379e-006  2.132e-006    -5.132    -5.671   -0.539
    ZnCl+               1.932e-006  1.417e-006    -5.714    -5.849   -0.135
    ZnOHCl               7.858e-007  8.802e-007    -6.105    -6.055    0.049
    ZnSO4                6.903e-007  7.732e-007    -6.161    -6.112    0.049
    ZnCl2                3.270e-007  3.663e-007    -6.485    -6.436    0.049
    ZnOH+               1.610e-007  1.181e-007    -6.793    -6.928   -0.135
    ZnCl3-               1.384e-007  1.015e-007    -6.859    -6.994   -0.135
    Zn(OH)2              6.111e-008  6.845e-008    -7.214    -7.165    0.049
    ZnCl4-2              4.343e-008  1.255e-008    -7.362    -7.901   -0.539
    Zn(SO4)2-2           3.363e-008  9.720e-009    -7.473    -8.012   -0.539
    Zn(OH)3-             1.491e-011  1.093e-011   -10.827   -10.961   -0.135
    Zn(OH)4-2            3.027e-016  8.748e-017   -15.519   -16.058   -0.539

----------------------------Saturation indices----------------------------

    Phase              SI log IAP  log KT

    Anhydrite         -1.70    -6.06    -4.36  CaSO4
    Antlerite         -6.02     2.27     8.29  Cu3(OH)4SO4
    Atacamite         -1.99     5.35     7.34  Cu2(OH)3Cl
    Bianchite         -6.76    -8.52    -1.76  ZnSO4:6H2O
    Birnessite        -9.92    33.68    43.60  MnO2
    Bixbyite          -6.45    -7.07    -0.61  Mn2O3
    Brochantite       -6.24     9.10    15.34  Cu4(OH)6SO4
    Bunsenite         -3.69     8.76    12.45  NiO
```

```
Chalcanthite      -8.78  -11.42   -2.64   CuSO4:5H2O
Cu(OH)2           -1.81    6.83    8.64   Cu(OH)2
Cu2(OH)3NO3       -5.07    4.17    9.24   Cu2(OH)3NO3
Cu2SO4           -20.57  -22.52   -1.95   Cu2SO4
Cu3(PO4)2         -2.75  -39.60  -36.85   Cu3(PO4)2
Cu3(PO4)2:3H2O    -4.50  -39.62  -35.12   Cu3(PO4)2:3H2O
CuMetal           -5.10  -13.86   -8.76   Cu
CuOCuSO4         -16.08   -4.55   11.53   CuO:CuSO4
CupricFerrite     18.08   23.96    5.88   CuFe2O4
Cuprite           -2.75   -4.30   -1.55   Cu2O
CuprousFerrite    15.33    6.41   -8.92   CuFeO2
CuSO4            -14.40  -11.39    3.01   CuSO4
Fe(OH)2.7Cl.3      9.10    6.06   -3.04   Fe(OH)2.7Cl0.3
Fe(OH)3(a)         3.66    8.55    4.89   Fe(OH)3
Fe3(OH)8           6.75   26.97   20.22   Fe3(OH)8
Fix_H+            -7.71   -7.71    0.00   H+
Goethite           9.56    8.56   -1.00   FeOOH
Goslarite         -6.57   -8.53   -1.96   ZnSO4:7H2O
Gypsum            -1.50   -6.08   -4.58   CaSO4:2H2O
H2(g)            -23.42  -26.57   -3.15   H2
H2O(g)            -1.52   -0.01    1.51   H2O
Halite            -2.93   -1.35    1.58   NaCl
Hausmannite       -6.81   54.22   61.03   Mn3O4
Hematite          21.13   17.12   -4.01   Fe2O3
Hydroxyapatite    11.10    7.68   -3.42   Ca5(PO4)3OH
Jarosite(ss)       4.42   -5.41   -9.83   (K0.77Na0.03H0.2)Fe3(SO4)2(OH)6
Jarosite-K         5.14   -4.07   -9.21   KFe3(SO4)2(OH)6
Jarosite-Na        1.47   -3.81   -5.28   NaFe3(SO4)2(OH)6
JarositeH         -5.40  -10.79   -5.39   (H3O)Fe3(SO4)2(OH)6
Langite           -7.69    9.10   16.79   Cu4(OH)6SO4:H2O
Maghemite         10.74   17.12    6.39   Fe2O3
Magnetite         23.26   27.00    3.74   Fe3O4
Manganite         -3.37   21.97   25.34   MnOOH
Melanothallite   -13.52   -9.79    3.73   CuCl2
Melanterite       -6.19   -8.40   -2.21   FeSO4:7H2O
Mirabilite        -3.24   -4.35   -1.11   Na2SO4:10H2O
Mn2(SO4)3        -56.03  -61.74   -5.71   Mn2(SO4)3
Mn3(PO4)2         -5.47  -29.30  -23.83   Mn3(PO4)2
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MnCl2:4H2O        -9.09    -6.38     2.71   MnCl2:4H2O
MnHPO4             5.51    -7.44   -12.95   MnHPO4
MnSO4            -10.62    -7.95     2.67   MnSO4
Morenosite        -7.15    -9.51    -2.36   NiSO4:7H2O
Nantokite         -3.70   -10.46    -6.76   CuCl
NH3(g)            -4.75    -2.98     1.77   NH3
Ni(OH)2           -2.05     8.75    10.80   Ni(OH)2
Ni3(PO4)2         -2.52   -33.82   -31.30   Ni3(PO4)2
Ni4(OH)6SO4      -15.20    16.80    32.00   Ni4(OH)6SO4
Nsutite           -8.88    33.68    42.56   MnO2
O2(g)            -36.36   -39.25    -2.89   O2
Portlandite      -10.65    12.15    22.80   Ca(OH)2
Pyrochroite       -4.94    10.26    15.20   Mn(OH)2
Pyrolusite        -7.70    33.68    41.38   MnO2
Retgersite        -7.46    -9.50    -2.04   NiSO4:6H2O
Strengite          4.89   -21.51   -26.40   FePO4:2H2O
Tenorite          -0.78     6.84     7.62   CuO
Thenardite        -4.11    -4.29    -0.18   Na2SO4
Vivianite          5.47   -30.53   -36.00   Fe3(PO4)2:8H2O
Zincite(c)        -1.40     9.74    11.14   ZnO
Zincosite        -11.49    -8.48     3.01   ZnSO4
Zn(NO3)2:6H2O    -12.72    -9.28     3.44   Zn(NO3)2:6H2O
Zn(OH)2-a         -2.71     9.74    12.45   Zn(OH)2
Zn(OH)2-b         -2.01     9.74    11.75   Zn(OH)2
Zn(OH)2-c         -2.46     9.74    12.20   Zn(OH)2
Zn(OH)2-e         -1.76     9.74    11.50   Zn(OH)2
Zn(OH)2-g         -1.97     9.74    11.71   Zn(OH)2
Zn2(OH)2SO4       -6.25     1.25     7.50   Zn2(OH)2SO4
Zn2(OH)3Cl        -4.04    11.16    15.20   Zn2(OH)3Cl
Zn3(PO4)2:4w       1.13   -30.91   -32.04   Zn3(PO4)2:4H2O
Zn3O(SO4)2       -26.24    -7.22    19.02   ZnO:2ZnSO4
Zn4(OH)6SO4       -7.68    20.72    28.40   Zn4(OH)6SO4
Zn5(OH)8Cl2       -6.44    32.06    38.50   Zn5(OH)8Cl2
ZnCl2            -13.92    -6.89     7.03   ZnCl2
ZnMetal          -39.43   -13.67    25.76   Zn
ZnO(a)            -1.57     9.74    11.31   ZnO
ZnSO4:H2O         -7.92    -8.49    -0.57   ZnSO4:H2O
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End of simulation.
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Reading input data for simulation 2.
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          USE Solution 1
          EQUILIBRIUM_PHASES 1
          CO2(g)      -3.5  10
          siderite    0      0
          hydroxyapatite   0      0
          strengite   0      0
          vivianite   0      0
          ZnS(a)                   0      0
          Ni(OH)2     0      0
          Calcite     0      0
          SAVE EQUILIBRIUM_PHASES      2
          SAVE SOLUTION      2
          END
-----------------------------------------
Beginning of batch-reaction calculations.
-----------------------------------------


Reaction step 1.


Using solution 1.
Using pure phase assemblage 1.

----------------------------Phase assemblage----------------------------


                                        Moles in assemblage
Phase                SI log IAP  log KT     Initial        Final        Delta

Calcite             -4.78  -13.26   -8.48  0.000e+000            0  0.000e+000
CO2(g)              -3.50   -4.97   -1.47  1.000e+001  1.000e+001 -1.791e-005
Hydroxyapatite      -0.00   -3.42   -3.42  0.000e+000  6.008e-004  6.008e-004
```

```
Ni(OH)2                      -5.36     5.44   10.80   0.000e+000              0   0.000e+000
Siderite                     -4.44   -15.33  -10.89   0.000e+000              0   0.000e+000
Strengite                    -4.15   -30.55  -26.40   0.000e+000              0   0.000e+000
Vivianite                     0.00   -36.00  -36.00   0.000e+000   4.774e-005   4.774e-005
ZnS(a)                       -0.66    -9.71   -9.05   0.000e+000              0   0.000e+000


--------------------------Solution composition--------------------------


        Elements              Molality        Moles


        C                    1.789e-005   1.791e-005
        Ca                   9.588e-004   9.600e-004
        Cl                   3.823e-001   3.828e-001
        Cu                   7.424e-006   7.433e-006
        Fe                   3.838e-005   3.843e-005
        K                    1.578e-001   1.580e-001
        Mn                   3.729e-005   3.733e-005
        N                    7.269e-002   7.278e-002
        Na                   2.615e-001   2.618e-001
        Ni                   1.131e-006   1.133e-006
        P                    2.315e-002   2.318e-002
        S                    1.200e-002   1.201e-002
        Zn                   1.154e-005   1.155e-005


--------------------------Description of solution--------------------------


                            pH  =   6.054      Charge balance
                            pe  =  -2.435      Adjusted to redox equilibrium
               Activity of water  =   0.985
                  Ionic strength  =   4.388e-001
              Mass of water (kg)  =   1.001e+000
           Total alkalinity (eq/kg) =   4.412e-003
               Total CO2 (mol/kg)  =   1.789e-005
              Temperature (deg C)  =  25.000
            Electrical balance (eq) =  -1.536e-015
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =   -0.00
                      Iterations  =  25
                         Total H  = 1.112390e+002
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                        Total O  = 5.571354e+001

--------------------------Distribution of species--------------------------

                                          Log       Log       Log
     Species              Molality   Activity  Molality  Activity    Gamma

     H+                  1.149e-006  8.834e-007   -5.940    -6.054   -0.114
     OH-                 1.527e-008  1.116e-008   -7.816    -7.952   -0.136
     H2O                 5.551e+001  9.851e-001    1.744    -0.007    0.000
C(-4)          2.775e-010
     CH4                 2.775e-010  3.070e-010   -9.557    -9.513    0.044
C(4)           1.789e-005
     CO2                 9.732e-006  1.077e-005   -5.012    -4.968    0.044
     HCO3-               7.633e-006  5.340e-006   -5.117    -5.272   -0.155
     NaHCO3              5.005e-007  5.537e-007   -6.301    -6.257    0.044
     CaHCO3+             1.785e-008  1.306e-008   -7.748    -7.884   -0.136
     MnHCO3+             4.618e-009  3.377e-009   -8.336    -8.471   -0.136
     NaCO3-              1.331e-009  9.734e-010   -8.876    -9.012   -0.136
     FeHCO3+             1.217e-009  8.897e-010   -8.915    -9.051   -0.136
     CO3-2               1.184e-009  2.835e-010   -8.927    -9.547   -0.621
     NiCO3               4.171e-010  4.614e-010   -9.380    -9.336    0.044
     NiHCO3+             2.213e-010  1.618e-010   -9.655    -9.791   -0.136
     MnCO3               1.444e-010  1.598e-010   -9.840    -9.796    0.044
     CaCO3               8.230e-011  9.105e-011  -10.085   -10.041    0.044
     FeCO3               1.024e-011  1.133e-011  -10.990   -10.946    0.044
     ZnHCO3+             1.862e-015  1.362e-015  -14.730   -14.866   -0.136
     Ni(CO3)2-2          7.948e-016  2.273e-016  -15.100   -15.643   -0.544
     ZnCO3               1.036e-016  1.146e-016  -15.985   -15.941    0.044
     Zn(CO3)2-2          2.428e-021  6.946e-022  -20.615   -21.158   -0.544
     CuHCO3+             4.077e-022  2.981e-022  -21.390   -21.526   -0.136
     CuCO3               1.533e-022  1.696e-022  -21.814   -21.771    0.044
     Cu(CO3)2-2          2.116e-028  6.053e-029  -27.674   -28.218   -0.544
Ca             9.588e-004
     Ca+2                7.190e-004  1.917e-004   -3.143    -3.717   -0.574
     CaH2PO4+            9.232e-005  6.752e-005   -4.035    -4.171   -0.136
     CaHPO4              9.192e-005  1.017e-004   -4.037    -3.993    0.044
     CaSO4               5.518e-005  6.105e-005   -4.258    -4.214    0.044
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    CaPO4-                  3.724e-007  2.724e-007    -6.429    -6.565    -0.136
    CaHCO3+                 1.785e-008  1.306e-008    -7.748    -7.884    -0.136
    CaHSO4+                 4.320e-010  3.159e-010    -9.365    -9.500    -0.136
    CaCO3                   8.230e-011  9.105e-011   -10.085   -10.041     0.044
    CaOH+                   4.851e-011  3.548e-011   -10.314   -10.450    -0.136
Cl             3.823e-001
    Cl-                     3.823e-001  2.497e-001    -0.418    -0.603    -0.185
    MnCl+                   9.870e-006  7.218e-006    -5.006    -5.142    -0.136
    FeCl+                   7.853e-007  5.743e-007    -6.105    -6.241    -0.136
    MnCl2                   7.112e-007  7.868e-007    -6.148    -6.104     0.044
    NiCl+                   1.883e-007  1.377e-007    -6.725    -6.861    -0.136
    NiCl2                   1.129e-007  1.249e-007    -6.947    -6.904     0.044
    MnCl3-                  7.400e-008  5.412e-008    -7.131    -7.267    -0.136
    CuCl3-2                 4.346e-010  1.243e-010    -9.362    -9.905    -0.544
    CuCl2-                  4.295e-010  3.141e-010    -9.367    -9.503    -0.136
    ZnCl+                   1.862e-012  1.362e-012   -11.730   -11.866    -0.136
    ZnCl2                   3.218e-013  3.561e-013   -12.492   -12.448     0.044
    ZnCl3-                  1.364e-013  9.976e-014   -12.865   -13.001    -0.136
    ZnCl4-2                 4.365e-014  1.249e-014   -13.360   -13.904    -0.544
    ZnOHCl                  1.689e-014  1.868e-014   -13.772   -13.729     0.044
    CuCl+                   1.024e-019  7.487e-020   -18.990   -19.126    -0.136
    FeCl+2                  1.540e-020  4.404e-021   -19.813   -20.356    -0.544
    CuCl2                   9.075e-021  1.004e-020   -20.042   -19.998     0.044
    FeCl2+                  6.717e-021  4.912e-021   -20.173   -20.309    -0.136
    FeCl3                   1.109e-022  1.227e-022   -21.955   -21.911     0.044
    CuCl3-                  1.216e-023  8.896e-024   -22.915   -23.051    -0.136
    CuCl4-2                 3.892e-026  1.113e-026   -25.410   -25.953    -0.544
Cu(1)          8.641e-010
    CuCl3-2                 4.346e-010  1.243e-010    -9.362    -9.905    -0.544
    CuCl2-                  4.295e-010  3.141e-010    -9.367    -9.503    -0.136
    Cu+                     2.178e-014  1.593e-014   -13.662   -13.798    -0.136
Cu(2)          7.423e-006
    Cu(HS)3-                7.423e-006  5.428e-006    -5.129    -5.265    -0.136
    Cu+2                    3.894e-019  1.114e-019   -18.410   -18.953    -0.544
    CuCl+                   1.024e-019  7.487e-020   -18.990   -19.126    -0.136
    CuSO4                   3.281e-020  3.630e-020   -19.484   -19.440     0.044
    CuCl2                   9.075e-021  1.004e-020   -20.042   -19.998     0.044
    Cu(OH)2                 2.616e-021  2.894e-021   -20.582   -20.538     0.044
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   CuOH+                      1.699e-021  1.242e-021   -20.770   -20.906   -0.136
   CuHCO3+                    4.077e-022  2.981e-022   -21.390   -21.526   -0.136
   CuCO3                      1.533e-022  1.696e-022   -21.814   -21.771    0.044
   CuCl3-                     1.216e-023  8.896e-024   -22.915   -23.051   -0.136
   CuCl4-2                    3.892e-026  1.113e-026   -25.410   -25.953   -0.544
   Cu(OH)3-                   2.659e-028  1.945e-028   -27.575   -27.711   -0.136
   Cu(CO3)2-2                 2.116e-028  6.053e-029   -27.674   -28.218   -0.544
   Cu(OH)4-2                  1.513e-034  4.328e-035   -33.820   -34.364   -0.544
   Cu2(OH)2+2                 2.361e-036  6.752e-037   -35.627   -36.171   -0.544
Fe(2)          3.838e-005
   FeH2PO4+                   1.572e-005  1.149e-005    -4.804    -4.940   -0.136
   Fe(HS)2                    9.690e-006  1.072e-005    -5.014    -4.970    0.044
   Fe+2                       5.825e-006  1.666e-006    -5.235    -5.778   -0.544
   FeHPO4                     5.800e-006  6.417e-006    -5.237    -5.193    0.044
   FeCl+                      7.853e-007  5.743e-007    -6.105    -6.241   -0.136
   FeSO4                      4.274e-007  4.728e-007    -6.369    -6.325    0.044
   Fe(HS)3-                   1.356e-007  9.920e-008    -6.868    -7.004   -0.136
   FeHCO3+                    1.217e-009  8.897e-010    -8.915    -9.051   -0.136
   FeOH+                      8.034e-010  5.875e-010    -9.095    -9.231   -0.136
   FeCO3                      1.024e-011  1.133e-011   -10.990   -10.946    0.044
   FeHSO4+                    3.754e-012  2.746e-012   -11.425   -11.561   -0.136
   Fe(OH)2                    5.041e-015  5.577e-015   -14.298   -14.254    0.044
   Fe(OH)3-                   3.160e-019  2.311e-019   -18.500   -18.636   -0.136
Fe(3)          2.347e-015
   Fe(OH)2+                   2.123e-015  1.553e-015   -14.673   -14.809   -0.136
   Fe(OH)3                    2.016e-016  2.231e-016   -15.695   -15.652    0.044
   FeOH+2                     1.470e-017  4.204e-018   -16.833   -17.376   -0.544
   FeH2PO4+2                  7.564e-018  2.163e-018   -17.121   -17.665   -0.544
   Fe(OH)4-                   3.102e-019  2.269e-019   -18.508   -18.644   -0.136
   FeHPO4+                    2.079e-019  1.521e-019   -18.682   -18.818   -0.136
   FeCl+2                     1.540e-020  4.404e-021   -19.813   -20.356   -0.544
   FeSO4+                     1.397e-020  1.022e-020   -19.855   -19.991   -0.136
   Fe+3                       9.759e-021  5.839e-022   -20.011   -21.234   -1.223
   FeCl2+                     6.717e-021  4.912e-021   -20.173   -20.309   -0.136
   Fe(SO4)2-                  4.879e-022  3.568e-022   -21.312   -21.448   -0.136
   FeCl3                      1.109e-022  1.227e-022   -21.955   -21.911    0.044
   FeHSO4+2                   8.451e-026  2.417e-026   -25.073   -25.617   -0.544
   Fe2(OH)2+4                 7.108e-032  4.758e-034   -31.148   -33.323   -2.174
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     Fe3(OH)4+5              0.000e+000  0.000e+000   -42.414   -45.812    -3.397
H(0)             7.415e-011
     H2                      3.707e-011  4.101e-011   -10.431   -10.387     0.044
K                1.578e-001
     K+                      1.560e-001  1.019e-001    -0.807    -0.992    -0.185
     KSO4-                   1.562e-003  1.143e-003    -2.806    -2.942    -0.136
     KHPO4-                  2.628e-004  1.922e-004    -3.580    -3.716    -0.136
Mn(2)            3.729e-005
     Mn+2                    2.481e-005  7.095e-006    -4.605    -5.149    -0.544
     MnCl+                   9.870e-006  7.218e-006    -5.006    -5.142    -0.136
     MnSO4                   1.820e-006  2.014e-006    -5.740    -5.696     0.044
     MnCl2                   7.112e-007  7.868e-007    -6.148    -6.104     0.044
     MnCl3-                  7.400e-008  5.412e-008    -7.131    -7.267    -0.136
     MnHCO3+                 4.618e-009  3.377e-009    -8.336    -8.471    -0.136
     MnOH+                   2.781e-010  2.034e-010    -9.556    -9.692    -0.136
     MnCO3                   1.444e-010  1.598e-010    -9.840    -9.796     0.044
     Mn(OH)3-                2.133e-022  1.560e-022   -21.671   -21.807    -0.136
     Mn(NO3)2                0.000e+000  0.000e+000  -164.885  -164.842     0.044
Mn(3)            1.345e-032
     Mn+3                    1.345e-032  8.047e-034   -31.871   -33.094    -1.223
Mn(6)            0.000e+000
     MnO4-2                  0.000e+000  0.000e+000   -84.382   -84.925    -0.544
Mn(7)            0.000e+000
     MnO4-                   0.000e+000  0.000e+000   -96.609   -96.745    -0.136
N(-3)            1.094e-002
     NH4+                    1.072e-002  7.839e-003    -1.970    -2.106    -0.136
     NH4SO4-                 2.204e-004  1.612e-004    -3.657    -3.793    -0.136
     NH3                     4.571e-006  5.057e-006    -5.340    -5.296     0.044
N(0)             6.174e-002
     N2                      3.087e-002  3.415e-002    -1.510    -1.467     0.044
N(3)             0.000e+000
     NO2-                    0.000e+000  0.000e+000   -58.671   -58.807    -0.136
N(5)             0.000e+000
     NO3-                    0.000e+000  0.000e+000   -80.010   -80.146    -0.136
     Mn(NO3)2                0.000e+000  0.000e+000  -164.885  -164.842     0.044
Na               2.615e-001
     Na+                     2.590e-001  1.844e-001    -0.587    -0.734    -0.148
     NaSO4-                  2.017e-003  1.475e-003    -2.695    -2.831    -0.136
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    NaHPO4-               4.757e-004  3.479e-004   -3.323    -3.459    -0.136
    NaHCO3               5.005e-007  5.537e-007   -6.301    -6.257     0.044
    NaCO3-               1.331e-009  9.734e-010   -8.876    -9.012    -0.136
Ni           1.131e-006
    Ni+2                 7.676e-007  2.196e-007   -6.115    -6.658    -0.544
    NiCl+                1.883e-007  1.377e-007   -6.725    -6.861    -0.136
    NiCl2                1.129e-007  1.249e-007   -6.947    -6.904     0.044
    NiSO4                6.176e-008  6.833e-008   -7.209    -7.165     0.044
    NiCO3                4.171e-010  4.614e-010   -9.380    -9.336     0.044
    NiHCO3+              2.213e-010  1.618e-010   -9.655    -9.791    -0.136
    NiOH+                4.622e-011  3.380e-011  -10.335   -10.471    -0.136
    Ni(SO4)2-2           2.048e-011  5.857e-012  -10.689   -11.232    -0.544
    Ni(OH)2              2.468e-014  2.731e-014  -13.608   -13.564     0.044
    Ni(CO3)2-2           7.948e-016  2.273e-016  -15.100   -15.643    -0.544
    Ni(OH)3-             4.164e-019  3.045e-019  -18.380   -18.516    -0.136
O(0)         0.000e+000
    O2                   0.000e+000  0.000e+000  -71.663   -71.619     0.044
P            2.315e-002
    H2PO4-               1.882e-002  1.377e-002   -1.725    -1.861    -0.136
    HPO4-2               3.382e-003  9.675e-004   -2.471    -3.014    -0.544
    NaHPO4-              4.757e-004  3.479e-004   -3.323    -3.459    -0.136
    KHPO4-               2.628e-004  1.922e-004   -3.580    -3.716    -0.136
    CaH2PO4+             9.232e-005  6.752e-005   -4.035    -4.171    -0.136
    CaHPO4               9.192e-005  1.017e-004   -4.037    -3.993     0.044
    FeH2PO4+             1.572e-005  1.149e-005   -4.804    -4.940    -0.136
    FeHPO4               5.800e-006  6.417e-006   -5.237    -5.193     0.044
    CaPO4-               3.724e-007  2.724e-007   -6.429    -6.565    -0.136
    PO4-3                8.252e-009  4.938e-010   -8.083    -9.306    -1.223
    FeH2PO4+2            7.564e-018  2.163e-018  -17.121   -17.665    -0.544
    FeHPO4+              2.079e-019  1.521e-019  -18.682   -18.818    -0.136
S(-2)        7.752e-004
    H2S                  5.932e-004  6.563e-004   -3.227    -3.183     0.044
    HS-                  1.162e-004  8.497e-005   -3.935    -4.071    -0.136
    Zn(HS)2              1.152e-005  1.274e-005   -4.939    -4.895     0.044
    Fe(HS)2              9.690e-006  1.072e-005   -5.014    -4.970     0.044
    Cu(HS)3-             7.423e-006  5.428e-006   -5.129    -5.265    -0.136
    Fe(HS)3-             1.356e-007  9.920e-008   -6.868    -7.004    -0.136
    S5-2                 5.781e-008  2.444e-008   -7.238    -7.612    -0.374
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    S4-2                 3.795e-008  1.426e-008    -7.421    -7.846    -0.425
    S6-2                 2.728e-008  1.265e-008    -7.564    -7.898    -0.334
    Zn(HS)3-             2.140e-008  1.565e-008    -7.670    -7.806    -0.136
    S-2                  4.062e-011  1.162e-011   -10.391   -10.935    -0.544
    S3-2                 1.562e-011  5.025e-012   -10.806   -11.299    -0.493
    S2-2                 1.033e-012  2.852e-013   -11.986   -12.545    -0.559
S(6)           1.122e-002
    SO4-2                7.364e-003  1.596e-003    -2.133    -2.797    -0.664
    NaSO4-               2.017e-003  1.475e-003    -2.695    -2.831    -0.136
    KSO4-                1.562e-003  1.143e-003    -2.806    -2.942    -0.136
    NH4SO4-              2.204e-004  1.612e-004    -3.657    -3.793    -0.136
    CaSO4                5.518e-005  6.105e-005    -4.258    -4.214     0.044
    MnSO4                1.820e-006  2.014e-006    -5.740    -5.696     0.044
    FeSO4                4.274e-007  4.728e-007    -6.369    -6.325     0.044
    HSO4-                1.874e-007  1.371e-007    -6.727    -6.863    -0.136
    NiSO4                6.176e-008  6.833e-008    -7.209    -7.165     0.044
    CaHSO4+              4.320e-010  3.159e-010    -9.365    -9.500    -0.136
    Ni(SO4)2-2           2.048e-011  5.857e-012   -10.689   -11.232    -0.544
    FeHSO4+              3.754e-012  2.746e-012   -11.425   -11.561    -0.136
    ZnSO4                6.852e-013  7.580e-013   -12.164   -12.120     0.044
    Zn(SO4)2-2           3.438e-014  9.834e-015   -13.464   -14.007    -0.544
    CuSO4                3.281e-020  3.630e-020   -19.484   -19.440     0.044
    FeSO4+               1.397e-020  1.022e-020   -19.855   -19.991    -0.136
    Fe(SO4)2-            4.879e-022  3.568e-022   -21.312   -21.448    -0.136
    FeHSO4+2             8.451e-026  2.417e-026   -25.073   -25.617    -0.544
Zn             1.154e-005
    Zn(HS)2              1.152e-005  1.274e-005    -4.939    -4.895     0.044
    Zn(HS)3-             2.140e-008  1.565e-008    -7.670    -7.806    -0.136
    Zn+2                 7.083e-012  2.026e-012   -11.150   -11.693    -0.544
    ZnCl+                1.862e-012  1.362e-012   -11.730   -11.866    -0.136
    ZnSO4                6.852e-013  7.580e-013   -12.164   -12.120     0.044
    ZnCl2                3.218e-013  3.561e-013   -12.492   -12.448     0.044
    ZnCl3-               1.364e-013  9.976e-014   -12.865   -13.001    -0.136
    ZnCl4-2              4.365e-014  1.249e-014   -13.360   -13.904    -0.544
    Zn(SO4)2-2           3.438e-014  9.834e-015   -13.464   -14.007    -0.544
    ZnOHCl               1.689e-014  1.868e-014   -13.772   -13.729     0.044
    ZnOH+                3.387e-015  2.477e-015   -14.470   -14.606    -0.136
    ZnHCO3+              1.862e-015  1.362e-015   -14.730   -14.866    -0.136
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ZnCO3                       1.036e-016  1.146e-016  -15.985  -15.941    0.044
Zn(OH)2                     2.867e-017  3.172e-017  -16.543  -16.499    0.044
Zn(CO3)2-2                  2.428e-021  6.946e-022  -20.615  -21.158   -0.544
Zn(OH)3-                    1.530e-022  1.119e-022  -21.815  -21.951   -0.136
Zn(OH)4-2                   6.912e-029  1.977e-029  -28.160  -28.704   -0.544


---------------------------Saturation indices-----------------------------


     Phase            SI log IAP  log KT


     Anhydrite       -2.15   -6.51   -4.36   CaSO4
     Anilite          8.43  -23.45  -31.88   Cu0.25Cu1.5S
     Antlerite      -43.76  -35.47    8.29   Cu3(OH)4SO4
     Aragonite       -4.93  -13.26   -8.34   CaCO3
     Atacamite      -27.71  -20.37    7.34   Cu2(OH)3Cl
     Azurite        -46.95  -43.20    3.75   Cu3(OH)2(CO3)2
     Bianchite      -12.76  -14.53   -1.76   ZnSO4:6H2O
     Birnessite     -29.42   14.18   43.60   MnO2
     Bixbyite       -29.27  -29.89   -0.61   Mn2O3
     BlaubleiI        6.33  -17.83  -24.16   Cu0.9Cu0.2S
     BlaubleiII       6.85  -20.43  -27.28   Cu0.6Cu0.8S
     Brochantite    -57.67  -42.33   15.34   Cu4(OH)6SO4
     Bunsenite       -7.01    5.44   12.45   NiO
     Calcite         -4.78  -13.26   -8.48   CaCO3
     CH4(g)          -6.65   -9.51   -2.86   CH4
     Chalcanthite   -19.14  -21.78   -2.64   CuSO4:5H2O
     Chalcocite       9.01  -25.61  -34.62   Cu2S
     Chalcopyrite    14.50  -20.77  -35.27   CuFeS2
     CO2(g)          -3.50   -4.97   -1.47   CO2
     Covellite        5.30  -16.97  -22.27   CuS
     Cu(OH)2        -15.50   -6.86    8.64   Cu(OH)2
     Cu2(OH)3NO3   -109.15  -99.91    9.24   Cu2(OH)3NO3
     Cu2SO4         -28.44  -30.39   -1.95   Cu2SO4
     Cu3(PO4)2      -38.62  -75.47  -36.85   Cu3(PO4)2
     Cu3(PO4)2:3H2O -40.37  -75.49  -35.12   Cu3(PO4)2:3H2O
     CuCO3          -18.87  -28.50   -9.63   CuCO3
     CuMetal         -2.60  -11.36   -8.76   Cu
     CuOCuSO4       -40.13  -28.60   11.53   CuO:CuSO4
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CupricFerrite    -18.90   -13.02     5.88   CuFe2O4
Cuprite          -13.94   -15.49    -1.55   Cu2O
CuprousFerrite    -1.91   -10.83    -8.92   CuFeO2
CuSO4            -24.76   -21.75     3.01   CuSO4
Djurleite          8.88   -25.04   -33.92   Cu0.066Cu1.868S
Fe(OH)2.7Cl.3     -2.05    -5.09    -3.04   Fe(OH)2.7Cl0.3
Fe(OH)3(a)        -7.98    -3.09     4.89   Fe(OH)3
Fe3(OH)8         -20.09     0.13    20.22   Fe3(OH)8
FeS(ppt)           0.12    -3.80    -3.92   FeS
Fix_H+            -6.05    -6.05     0.00   H+
Goethite          -2.09    -3.09    -1.00   FeOOH
Goslarite        -12.58   -14.54    -1.96   ZnSO4:7H2O
Greigite           4.72   -40.31   -45.03   Fe3S4
Gypsum            -1.95    -6.53    -4.58   CaSO4:2H2O
H2(g)             -7.24   -10.39    -3.15   H2
H2O(g)            -1.52    -0.01     1.51   H2O
H2S(g)            -2.19    -3.18    -1.00   H2S
Halite            -2.92    -1.34     1.58   NaCl
Hausmannite      -32.94    28.09    61.03   Mn3O4
Hematite          -2.16    -6.16    -4.01   Fe2O3
Hydroxyapatite    -0.00    -3.42    -3.42   Ca5(PO4)3OH
Jarosite(ss)     -25.18   -35.01    -9.83   (K0.77Na0.03H0.2)Fe3(SO4)2(OH)6
Jarosite-K       -24.79   -34.00    -9.21   KFe3(SO4)2(OH)6
Jarosite-Na      -28.47   -33.75    -5.28   NaFe3(SO4)2(OH)6
JarositeH        -33.68   -39.07    -5.39   (H3O)Fe3(SO4)2(OH)6
Langite          -59.12   -42.33    16.79   Cu4(OH)6SO4:H2O
Mackinawite        0.85    -3.80    -4.65   FeS
Maghemite        -12.55    -6.16     6.39   Fe2O3
Magnetite         -3.58     0.16     3.74   Fe3O4
Malachite        -30.18   -25.03     5.15   Cu2(OH)2CO3
Manganite        -14.78    10.56    25.34   MnOOH
Melanothallite   -23.89   -20.16     3.73   CuCl2
Melanterite       -6.41    -8.62    -2.21   FeSO4:7H2O
Millerite          3.37    -4.68    -8.04   NiS
Mirabilite        -3.22    -4.33    -1.11   Na2SO4:10H2O
Mn2(SO4)3        -68.87   -74.58    -5.71   Mn2(SO4)3
Mn3(PO4)2        -10.23   -34.06   -23.83   Mn3(PO4)2
MnCl2:4H2O        -9.09    -6.38     2.71   MnCl2:4H2O
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MnHPO4             4.78    -8.16   -12.95   MnHPO4
MnS(Green)        -6.97    -3.17    3.80    MnS
MnSO4            -10.61    -7.95    2.67    MnSO4
Morenosite        -7.14    -9.50   -2.36    NiSO4:7H2O
N2(g)              1.79    -1.47   -3.26    N2
Nahcolite         -5.46    -6.01   -0.55    NaHCO3
Nantokite         -7.64   -14.40   -6.76    CuCl
Natron            -9.77   -11.08   -1.31    Na2CO3:10H2O
NH3(g)            -7.07    -5.30    1.77    NH3
Ni(OH)2           -5.36     5.44   10.80    Ni(OH)2
Ni3(PO4)2         -7.29   -38.59  -31.30    Ni3(PO4)2
Ni4(OH)6SO4      -25.15     6.85   32.00    Ni4(OH)6SO4
NiCO3             -9.37   -16.21   -6.84    NiCO3
Nsutite          -28.38    14.18   42.56    MnO2
O2(g)            -68.73   -71.62   -2.89    O2
Portlandite      -14.42     8.38   22.80    Ca(OH)2
Pyrite            11.80    -6.68  -18.48    FeS2
Pyrochroite       -8.25     6.95   15.20    Mn(OH)2
Pyrolusite       -27.20    14.18   41.38    MnO2
Retgersite        -7.45    -9.49   -2.04    NiSO4:6H2O
Rhodochrosite     -3.57   -14.70  -11.13    MnCO3
Rhodochrosite(d)  -4.31   -14.70  -10.39    MnCO3
Siderite          -4.44   -15.33  -10.89    FeCO3
Siderite(d)(3)    -4.88   -15.33  -10.45    FeCO3
Smithsonite      -11.24   -21.24  -10.00    ZnCO3
Sphalerite         1.91    -9.71  -11.62    ZnS
Strengite         -4.15   -30.55  -26.40    FePO4:2H2O
Sulfur            -0.78   -15.81  -15.03    S
Tenorite         -14.47    -6.85    7.62    CuO
Thenardite        -4.09    -4.27   -0.18    Na2SO4
Thermonatrite    -11.15   -11.02    0.13    Na2CO3:H2O
Trona            -16.24   -17.04   -0.80    NaHCO3:Na2CO3:2H2O
Vivianite          0.00   -36.00  -36.00    Fe3(PO4)2:8H2O
Wurtzite          -0.03    -9.71   -9.68    ZnS
Zincite(c)       -10.73     0.41   11.14    ZnO
Zincosite        -17.50   -14.49    3.01    ZnSO4
Zn(NO3)2:6H2O   -175.46  -172.02    3.44    Zn(NO3)2:6H2O
Zn(OH)2-a        -12.05     0.40   12.45    Zn(OH)2
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```
       Zn(OH)2-b          -11.35     0.40    11.75   Zn(OH)2
       Zn(OH)2-c          -11.80     0.40    12.20   Zn(OH)2
       Zn(OH)2-e          -11.10     0.40    11.50   Zn(OH)2
       Zn(OH)2-g          -11.31     0.40    11.71   Zn(OH)2
       Zn2(OH)2SO4        -21.59   -14.09     7.50   Zn2(OH)2SO4
       Zn2(OH)3Cl         -21.05    -5.85    15.20   Zn2(OH)3Cl
       Zn3(PO4)2:4w       -21.68   -53.72   -32.04   Zn3(PO4)2:4H2O
       Zn3O(SO4)2         -47.59   -28.57    19.02   ZnO:2ZnSO4
       Zn4(OH)6SO4        -41.69   -13.29    28.40   Zn4(OH)6SO4
       Zn5(OH)8Cl2        -49.79   -11.29    38.50   Zn5(OH)8Cl2
       ZnCl2              -19.93   -12.90     7.03   ZnCl2
       ZnCO3:H2O          -10.99   -21.25   -10.26   ZnCO3:H2O
       ZnMetal            -32.58    -6.82    25.76   Zn
       ZnO(a)             -10.90     0.41    11.31   ZnO
       ZnS(a)              -0.66    -9.71    -9.05   ZnS
       ZnSO4:H2O          -13.93   -14.50    -0.57   ZnSO4:H2O

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End of simulation.
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Reading input data for simulation 3.
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End of run.
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