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**Manuscript title:** The Couplings of Rock/Carbonate Groundwater/Cement Leachate

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**Abstract**

Hyper-alkaline cement leachates generated from the cement buffer of a nuclear waste disposal site have significant influences on the mineralogy of the host rock, creating a chemically disturbed zone (CDZ). Three major types of cement leachates are formed during the evolution process. Most of the existing scenario modelling research has been focused on the influence of the cement leachate on the host rock. However, the influence of the groundwater in the host rock on the evolution of the CDZ remains unexplored. This paper presents a numerical scenario modelling of the couplings among carbonate groundwater, cement leachates and rock minerals. The results reveal that the high carbonate groundwater significantly affects the precipitation of calcium silicate hydrate (C-S-H) and calcite, and consequently alters the physical and chemical properties of the host rock. This finding provides an essential guide for selection of the location of geological disposal facility (GDF) in terms of the groundwater chemistry.

**Notation**

$A_0$	Initial surface area (m <sup>2</sup> )
$C_i$	Concentration of $i$ th chemical component (mol/L),
$m_{0k}$	Initial moles of solid
$m_k$	Moles of solid at a given time
$n$	2/3, for uniformly dissolving spheres and cubes (normally for experiment)
$\frac{\partial q}{\partial t}$	The change in concentration in the solid phase due to reactions ( $q$ has the same as $C_i$ )
$r_k$	Specific reaction rate (mol/m <sup>2</sup> /s) at 25 °C
$R_k$	Dissolution rate (mol/L/s)
$u_\alpha$	Darcy velocity in $\alpha$ direction (m/s), in which $\alpha=1, 2$ or $3$ , representing space coordinate,
$V$	Solution volume (L)
$\phi$	Porosity

## Introduction

The concept of geological disposal of radioactive waste has been considered in many countries such as Canada, Switzerland, France, and United Kingdom (Nuclear Energy Agency(NEA), 2008, NDA, 2010, Moyce et al., 2014). Cement is normally used as a backfill, surrounding stainless steel canisters containing radioactive waste. In the post-closure stage, the cement may generate hyper-alkaline leachates during the resaturation process, which strongly react with the host rock and groundwater. The transport of these leachates create a chemically disturbed zone (CDZ) with steep biogeochemical gradients, promoting dissolution and precipitation of phases and finally affecting the radionuclides transport (Chen et al., 2015). The long-term assessment and prediction of this reactive transport process is significant for the safety assessment of the nuclear waste disposal, but remains a challenge due to the complexity of coupled multiple chemical reactions and multiple physical processes (Marshall, 2014).

There are three major types of cement leachates during the evolution processes (Moyce et al., 2014): Young Cement Leachate (YCL), Intermediate Cement Leachate (ICL) and Old Cement Leachate (OCL), reflecting the evolution age of the cement materials. The natural analogue of these leachates may be described as ‘Western Springs’, ‘Eastern Springs’ and ‘Daba Region’ in Jordan, respectively (Clark et al., 1994, Alexander et al., 1992, Khoury et al., 1992). ‘Western Springs (YCL)’ is the analogue of early stage post-closure leachate dominated by Sodium Hydroxide (NaOH) and Potassium Hydroxide (KOH) with pH around 13. ‘Eastern Springs (ICL)’ is a middle-stage leachate dominated by Calcium Hydroxide ( $\text{Ca}(\text{OH})_2$ ) with pH around 12 (Wallace et al., 2013). ‘Daba Region (OCL)’ has a pH around 10.5 and it is usually

the late-stage of the post-closure leachate with dominating Calcium-Silicate-Hydrate (C-S-H) phases. These three different leachates (see Table 1 for detailed compositions) are expected to be produced in three different stages in the long-term evolution of a geological disposal facility (GDF) (Chen et al., 2015).

There have been many studies that have evaluated the interactions between the hyper-alkaline leachates and various geological materials. For examples: Adler et al. (1998) investigated the influence on an argillaceous rock; Steefel and Lichtner (1998) simulated the infiltration of hyperalkaline leachates along discrete fractures; Soler (2003) studied the interactions between the leachates and a fractured marl; and Savage et al. (2002) modelled the interactions between bentonite and hyper-alkaline fluids. In addition, Berner (1998) and Neall (1994) presented that changes in porosity were likely to happen in the case of the host matrix variation due to primary phase dissolution and secondary phase precipitation; Bérubé et al. (1990) found that the dolomite in the rock possibly experienced dedolomitisation and caused the significant increase in the amount of carbonate and magnesium.

The relative short timescale of experimental studies presents a limitation for fully understanding the long-term safety issues of nuclear waste disposal. Therefore, long-term scenario modelling study is an effective way to bridge the knowledge gap. Most recently, Moyce et al. (2014) extended the timescale to 15 years for laboratory experiments to study the interactions between the cement leachates and the host rock, which was analysed and interpreted via geochemical modelling later (Chen and Thornton, 2018). Based on the experimental study (Moyce et al., 2014), Chen et al. (2015) developed a long-term (e.g. 5,000

years) scenario modelling to investigate the influence of YCL on the physical porosity and mineral evolution of the host rock. This modelling provided a clear evidence that the porosity would be affected by the long-term multiple chemical reactions within the host rock. However, to focus on the interactions between leachates and the host rock, the study assumed that the background water in the host rock was pure water.

Groundwater chemistry may also significantly affect the CDZ due to the strong couplings between the groundwater, the leachate, and the host rock. For example, Spycher et al. (2003) studied the fluid chemistry and mineral alteration around a potential nuclear waste emplacement tunnel, and they found that after heating and boiling during the first hundred years in a nuclear waste disposal site, the CO<sub>2</sub> discharged from pore water would cause the raising of pH and precipitation of calcite. This CO<sub>2</sub> would dissolve again in the condensation zone, causing the decreasing of pH, redissolving of calcite and increasing of alteration of feldspar to clays. The effect of the groundwater that may infiltrate into an emplacement drift is important in assessing the rate of corrosion of waste container (Spycher et al., 2003). The chemistry of the groundwater may affect the transport of radionuclides from the GDF via the process of speciation, solubility, and sorption etc. There are specific requirements on the geochemical environment (including groundwater chemistry) of host formation in a radioactive waste disposal site. Metz et al. (2003) claimed that “the geochemical environment of such a formation must fulfill the following requirements: high radionuclide retention capacity, high chemical buffering capacity, and favorable composition of formation water with respect to radionuclide solubility”. These requirements aim to ensure the stable storage of radioactive

waste and minimize the transport of radionuclides to the geosphere.

To provide more realistic modelling for guidance on nuclear safety assessment, this paper focuses on the analysis of interactions between high carbon groundwater, cement leachates (YCL, ICL and OCL) and host rock minerals, which is a major step forward from previous work (Chen et al., 2015) towards a more realistic scenario modelling for the applications in nuclear waste disposal industry.

### **The high carbon groundwater and the leachates**

In general, there are three major types of groundwater chemistry for a potential selected host rock. They are low carbonate groundwater, high carbonate groundwater, and saline, respectively. Typical compositions of three types of groundwater are listed in Table 2. It shows that saline and low carbonate groundwater tend to be neutral while high carbonate groundwater has a pH of 8.77, which is alkaline. Saline groundwater is a kind of chloride-rich groundwater, which will cause the corrosion of barrier of nuclear waste and endanger the surrounding environment (Molecke, 1983).

Groundwater will react with the surrounding minerals while moving through the ground. Carbonate minerals, such as limestone and dolomitic limestone, are easier to react with groundwater than other kinds of minerals like silicate minerals. This kind of reaction is the main cause of carbonate groundwater. The most typical reaction occurs between calcium carbonate, carbon dioxide, and water, presented as below:



The reaction will lead to an acidic condition in water, which will increase the dissolution

of carbonate mineral and change the porosity in the rock (Cerar and Urbanc, 2013).

The concentration of carbonate in carbonate groundwater is expressed as the concentration of carbon element (C). High carbonate has a higher concentration ( $2.8 \times 10^{-3}$  mol/kg) of C than low carbonate groundwater ( $1.6 \times 10^{-4}$  mol/kg). High concentration of carbonate could have an influence on precipitation of the secondary minerals like C-S-H gel and calcite.

### Mineral kinetic evolution and chemical reactive transport

Kinetics of mineral dissolution and precipitation have strong control on the evolution of the CDZ. Mineral dissolution rate is controlled by pH and temperature and can be described as (Appelo and Postma, 2010)

$$R_k = r_k \frac{A_0}{V} \left( \frac{m_k}{m_{0k}} \right)^n \quad (1)$$

where

$R_k$  = dissolution rate (mol/L/s),

$r_k$  = specific reaction rate (mol/m<sup>2</sup>/s) at 25 °C,

$A_0$  = initial surface area (m<sup>2</sup>),

$V$  = solution volume (L),

$m_k$  = moles of solid at a given time,

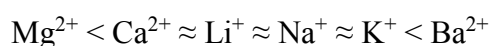
$m_{0k}$  = initial moles of solid,

$n = 2/3$ , for uniformly dissolving spheres and cubes (normally for experiment), and

$\left( \frac{m_k}{m_{0k}} \right)^n$  is to account for changes in  $\frac{A_0}{V}$ .

The surface area  $A_0$  of the mineral is of great importance because it will influence the kinetics of precipitation and dissolution, and it also has an impact on surface reactions, adsorption, and heterogeneous catalysis. The surface area of minerals in sandstone is obtained from literature including experimental studies and published modeling assumptions (Nagy, 1995, Chen et al., 2015).

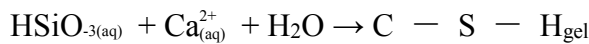
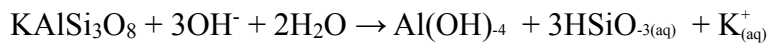
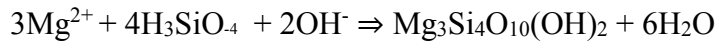
Much research on kinetics of mineral dissolution have been conducted under acidic conditions (pH 1~5) (Anbeek, 1993, Chou et al., 1989, Holdren and Speyer, 1985), which can only be used as references about dissolution kinetics in this study. Dove and Nix in 1997 investigated the influence of alkaline earth cations ( $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Ba^{2+}$ ) on quartz dissolution, which is applied in this study because quartz is one of the major primary minerals, and Mg and Ca are the major elements which will lead to secondary minerals' precipitation. Quartz is the most abundant silicate although it is the least reactive (Dove and Nix, 1997), and the dissolution of quartz in host rock will affect the CDZ (Chen et al., 2015). The influence of alkaline earth cations is compared and the order is (Dove and Nix, 1997):



Previous research has identified that the dissolution rate of quartz is enhanced more by  $Na^+$  and  $K^+$  than by  $Mg^{2+}$  and  $Ca^{2+}$  (House, 1994). Schwartzentruber et al. (Schwartzentruber et al., 1987) studied quartz dissolution rate in alkaline solutions with both short-term and long-term experiments. The short-term experiments were designed for initial dissolution rate determination of quartz in alkaline solutions, while the long-term experiments were designed for determination of quartz reaction rate in equilibrium. The results have shown that the dissolution rate of quartz

increases in NaOH solution which is the main component in YCL. A similar result could also be found in an experiment done by Knauss and Wolery (Knauss and Wolery, 1988). As a typical aluminosilicate, K-feldspar ( $\text{KAlSi}_3\text{O}_8$ ) is a major primary mineral in the host rock that will be considered in this study (see Table 3). A research done by Oelkers et al. (Oelkers et al., 1994) has showed that the concentration of Al and Si in groundwater will influence the dissolution rate of aluminosilicate. High concentration of Al will decrease the dissolution rate while high concentration of Si will increase the dissolution rate.

Evolution of primary and secondary phases presents a key coupling between groundwater and minerals. For example, the chemical reaction links between k-feldspar, dolomite, talc, magnesium hydroxide are listed as follows:



In this study, the chemical transport in host rock can be described as follows (Appelo and Postma, 2010):

$$\frac{\partial(\phi C_i)}{\partial t} = \frac{\partial}{\partial x_a} \left[ \phi D_{\alpha\beta}^i \frac{\partial C_i}{\partial x_\beta} \right] - \frac{\partial(u_\alpha C_i)}{\partial x_a} - \frac{\partial q}{\partial t} \quad (2)$$

where

$C_i$  = concentration of  $i$ th chemical component (mol/L),

$u_\alpha$  = Darcy velocity in  $\alpha$  direction (m/s), in which  $\alpha=1, 2$  or  $3$ , representing space

coordinate,

$\phi$  = porosity, and

$\frac{\partial q}{\partial t}$  = the change in concentration in the solid phase due to reactions ( $q$  has the same unit as  $C_i$ ).

## Methodology

Laboratory experiments are often limited to short timescales, whereas the reaction between rock and groundwater could last more than hundreds of years. To understand the long-term reaction and influence, theoretical analysis and numerical modelling are applied in this study. Such model has also been validated through comparison with a 15 years experiment (Chen and Thornton, 2018).

### *Software employed*

In this study, geochemical code PHREEQC (Parkhurst and Appelo, 1999) is used to perform the numerical simulations and analyses. PHREEQC is a computer program designed for a wide range of aqueous geochemical calculations, and it can use several types of aqueous models such as two ion-association aqueous models to achieve index calculation, transport calculation and inverse modeling. The advection-reaction-dispersion equation (equation 2) is “solved with an explicit finite difference scheme that is forward in time, central in space for dispersion, and upwind for advective transport” (Parkhurst, 1995). The initial conditions of rock and groundwater including pH, the concentration of composition, temperature, and density will be

input to PHREEQC, and the kinetics part is also necessary to shape the graphs which would come out after running the program (Parkhurst and Appelo, 1999).

#### *The mesh of the model*

The conceptual model is shown in Figure 1, which represents 100-meters length in the host rock around the nuclear waste container. There are 20 cells and the length of each cell is five meters (Chen et al. 2015).

#### *Time scales/steps input for the modelling*

In this study, the influence of YCL, ICL, and OCL are considered over timescales around 0~25,000, 25,000~50,000, and 50,000~100,000 years, respectively (Figure 1). When YCL breaks through the host rock after 25000 years, it will be followed by the YCL for the next 25000 years. Finally, OCL will follow closely behind ICL to permeate through the rock in the last 50000 years. The time step  $1.0 \times 10^8$  s is selected based on the numerical stability and efficiency.

#### *Primary minerals input for the modelling*

The selected host rock for this study is Bromsgrove Sandstone Formation which is from central England. This sandstone represents a generic rock formation, and its basic composition is mineralogically and geochemically similar to low-permeability geological materials which are expected to be a host rock for a GDF. This Permo-Triassic sandstone is mainly composed of quartz (75.5%) and K-feldspar (16%). The detailed composition of Bromsgrove Sandstone is shown in Table 3. Quartz and K-feldspar are mainly discussed because of their high percentage

in sandstone and the influence of mineralogy in water-rock interaction. According to the relevant research results from the laboratory, phlogopite, apatite, and TiO<sub>2</sub> are omitted from the simulations, since they account for very low percentages (0.2%~0.3%) in sandstone and they also have little influence on the geochemical process. The rate constants of these primary minerals provided by PHREEQC are used for this research (Chen et al., 2015).

#### *Leachate and groundwater chemistry input for the modelling*

The flow rate of the leachate is assumed to be  $1 \times 10^{-3}$  m/year based on Bromsgrove Sandstone permeability over time scales around 100,000 years, and the dispersivity is assumed to be 0.0105 m/s (Chen et al. 2015). The compositions of leachates and groundwater are listed in Table 1 and Table 2, respectively. High carbonate groundwater is selected for this study.

#### *Secondary minerals input for the modelling*

The choice of secondary minerals is based on the experiments with calcite, talc, and C-S-H gel (Moyce et al., 2014). Figure 2 shows the conceptual model of mineral dissolution and precipitation. Only four kinds of primary minerals and three kinds of secondary minerals are included in this model because they are the most important. Further attention will be focused on calcite and C-S-H gel.

#### *Key functions included in the model*

The modelling covers the following aspects:

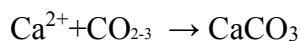
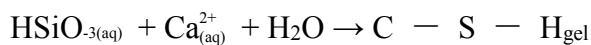
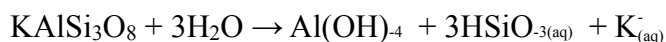
1. The chemical property of the fluid and multiple mineral alterations affected by the cement leachates,

2. The mixing process of high pH plume with the background groundwater,
3. The multiple chemical reactions during the high alkaline plume transport,
4. The kinetics (including dissolution and precipitation) of primary minerals, and
5. The evolution of the secondary minerals.

## Results and discussions

### $Ca^{2+}$ (Figure 3)

Figures 3(a), 3(b), and 3(c) illustrate the distribution of  $Ca^{2+}$  in the host rock at different evolution time for YCL (from 0 to 25000 years), ICL (from 25000 to 50000 years), and OCL (from 50000 to 100000 years), respectively. The affected zone by YCL expands to around 32.5 meters after 25000 years. In the area around the inlet point, the  $Ca^{2+}$  concentration decreases to a minimum due to the precipitation of secondary phase minerals (e.g. C-S-H gel and calcite). The mineral transformation from calcite to C-S-H gel due to high pH in the YCL may be described as follows (Moyce et al., 2014) :

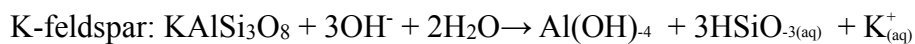
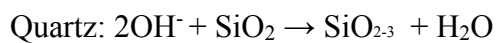


When the YCL moves forward to the near field, the  $Ca^{2+}$  concentration rises up significantly due to the precipitation process slowing down and the introduction of  $Ca^{2+}$  concentration in the YCL, which is  $1.35 \times 10^{-4}$  mol/L. In the far field, the  $Ca^{2+}$  concentration is unaffected, which remains closely at the level in groundwater ( $8.8 \times 10^{-5}$  mol/L).

After 25000 years, the concentration of  $\text{Ca}^{2+}$  in the host rock (Figure 3(b)) keeps close to  $1.62 \times 10^{-2}$  mol/L in the near field due to much higher initial  $\text{Ca}^{2+}$  concentration in the ICL than YCL, and then in the far field the  $\text{Ca}^{2+}$  concentration decreases to the level in groundwater ( $8.8 \times 10^{-5}$  mol/L). When the OCL enters into the host rock (Figure 3(c)), the  $\text{Ca}^{2+}$  is diluted in the area close to GDF by much lower initial  $\text{Ca}^{2+}$  concentration ( $2.01 \times 10^{-4}$  mol/L) in OCL, while in the intermediate field the  $\text{Ca}^{2+}$  concentration still keeps as high as about  $1.6 \times 10^{-2}$  mol/L, which is mainly caused by the high  $\text{Ca}^{2+}$  concentration in the ICL. The shapes of  $\text{Ca}^{2+}$  concentration curves at different evolution time are quite similar.

#### *SiO<sub>2</sub>(aq) or Silicon (Figure 4)*

Figures 4(a), 4(b), and 4(c) show the distribution of the silicon concentration in the host rock at different evolution for YCL (from 0 to 25000 years), ICL (from 25000 to 50000 years), and OCL (from 50000 to 100000 years), respectively. As shown in Figure 4(a), the concentration of silicon increases steadily with distance in the area close to GDF. Silicon is generated from the kinetic dissolution of quartz, K-feldspar, illite, kaolinite and muscovite as follows:



The silicon concentration peaks around  $3.02 \times 10^{-3}$  mol/L at the point of 22.5 meters (25,000 years), when the leachate source changes from YCL to ICL. It continuously goes up

with evolution time and the peaks move towards the far field of the host rock, due to more mineral dissolution. In the near field, the silicon concentration drops to 0 due to the precipitation of C-S-H phases (Figure 4(b), and Figure 5 for C-S-H phases). During the process of OCL injection (Figure 4(c)), the pH is much lower, causing the redissolution of C-S-H gel and release of silicon minerals in the near field of the inlet, which slightly increases the silicon concentration in the near field (e.g. 0-20 meters).

*Calcium silicate hydrate gel or C-S-H gel (Figures 5 and 6)*

Figures 5 and 6 display the distributions of the concentration and saturation index of C-S-H gel in the host rock at different evolution time. Here, saturation index (SI) is an index showing whether a water will tend to dissolve or precipitate a particular mineral. Its value is negative when the mineral may be dissolved, positive when it may be precipitated, and zero when the water and mineral are at chemical equilibrium. During the process of YCL injection (Figure 5(a)), at each evolution time, the concentration of C-S-H gel rises with the distance in the area close to GDF as the precipitation of C-S-H gel occurs, and peaks at the distance of around 7.5 meters, then decreases to the level of unaffected zone. Both the peak concentration and the influence distance increases with the evolution time, and the maximum peak reaches to  $6.14 \times 10^{-6}$  mol/L' at evolution time of 25000 years.

As shown in Figure 6(a), the dissolution of C-S-H gel doesn't happen in the area close to GDF since the saturation index is close to zero. As shown in Figure 5(b), the injection of ICL further increases the precipitation peak to  $8.88 \times 10^{-5}$  mol/L due to additional calcium supply

from ICL, This can be also explained by Figure 6(b), where the saturation index in longer distance is close to zero (i.e., no dissolution).

The C-S-H gel evolutions during the process of OCL injection (Figures 5(c) & 6(c)) are different from those for YCL and ICL. The peak of precipitation of C-S-H gel is decreased with evolution time because both the pH value and calcium concentration in OCL are lower than those in YCL and ICL, resulting in C-S-H gel re-dissolving, which is also confirmed by Figure 6(c) as the saturation index is below zero in the area close to GDF.

#### *Calcite (Figures 7 and 8)*

Figures 7 and 8 demonstrate the distributions of the concentration and saturation index of calcite in the host rock at different evolution time. Calcite is initially at equilibrium condition before the injection, and starts to precipitate during the process of YCL injection (0-25,000) as YCL contains  $1.35 \times 10^{-4}$  mol/L  $\text{Ca}(\text{OH})_2$  which can contribute to forming calcite in the early time (Figure 7(a)). For example, the peak of precipitated calcite concentration in 5,000 years reaches to  $6.03 \times 10^{-5}$  mol/L. However, calcite will redissolve rapidly and the calcite will be transformed to C-S-H gel during the injection of YCL (Figures 7(a) & 5(a)), which is also confirmed by Figure 8(a) as the saturation index is below zero in the area close to GDF.

ICL has higher calcium concentration ( $1.62 \times 10^{-2}$  mol/L  $\text{Ca}(\text{OH})_2$ ) than YCL, and the pH in ICL is lower than YCL, so it may generate more calcite. However, during the period from 25,000 to 40,000 years, the peak of calcite concentration is still decreased from  $1.11 \times 10^{-6}$  mol/L to  $3.67 \times 10^{-7}$  mol/L. This peak is beginning to reverse from 40000 to 50000 years as C-S-H gel starts to dissolve back to calcium and contributes to increasing calcite concentration

(Figures 7(b) & 8(b)). Therefore, the precipitation of calcite is contributed not only by the calcium concentration from ICL but also by the C-S-H dissolution.

During the process of OCL permeation (Figures 7(c) & 8(c)), calcite concentration rises steadily over the last fifty thousand years. The  $\text{Ca}^{2+}$  concentration in OCL is low, but the overall  $\text{Ca}^{2+}$  concentration is increased by the permeation of ICL and the C-S-H dissolution caused by lower pH, which is the main reason for the increase of calcite.

## Conclusions

In this study, PHREEQC software is used to analyze the influence of high carbonate groundwater on the process of three different cement leachates (i.e. YCL (0~25000years), ICL (25000~50000years) and OCL (50000~100000 years)) breaking through Bromsgrove Sandstone, resulting in a series of complex geochemical reactions and physical processes. This is significant to understand the long-term performance of nuclear waste disposal facilities, and provides an essential guide for selection of the location of geologic disposal facility (GDF) in terms of the groundwater chemistry as C-S-H gel evolution presents an important uncertainty for the safety of nuclear waste disposal.

This research discusses the evolution of element concentration, pH variation and secondary phase minerals. Through the analyses of the simulation data, the following conclusions can be drawn: (1) Three different high alkaline leachates represent three distinct periods, so the effects on the host rock are different at these three periods over 100000 years. Furthermore, the same leachate exerts different effects at different distances in the same period. (2) During YCL, ICL, and OCL phases, the chemical property of the host rock and the fluid

will experience significant alteration which includes the increase or decrease in the concentration of elements, dissolution and precipitation of multiple minerals as well as the formation and re-dissolution of secondary minerals (e.g. C-S-H gel). (3) The primary minerals may promote the generation of the secondary minerals. For example, the dissolution of quartz and K-feldspar can provide silicon for the precipitation of C-S-H gel. (4) The secondary minerals studied in this study are most likely to be created in the near field of a nuclear waste container. In contrast, the generation of calcite will move forward to the far field with time.

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**Table 1.** Compositions of cement leachates

Type of cement leachates	Young Cement Leachate (YCL)	Intermediate Cement Leachate (ICL)	Old Cement Leachate (OCL)
KOH	5.2 g L <sup>-1</sup>		
NaOH	3.8 g L <sup>-1</sup>		
Ca(OH) <sub>2</sub>	0.01 g L <sup>-1</sup>	1.2 g L <sup>-1</sup>	15 mg L <sup>-1</sup>
KCl		0.296 g L <sup>-1</sup>	
NaCl		0.01 g L <sup>-1</sup>	
pH	~ 13.1	~ 12.3 - 12.4	10.4-10.5

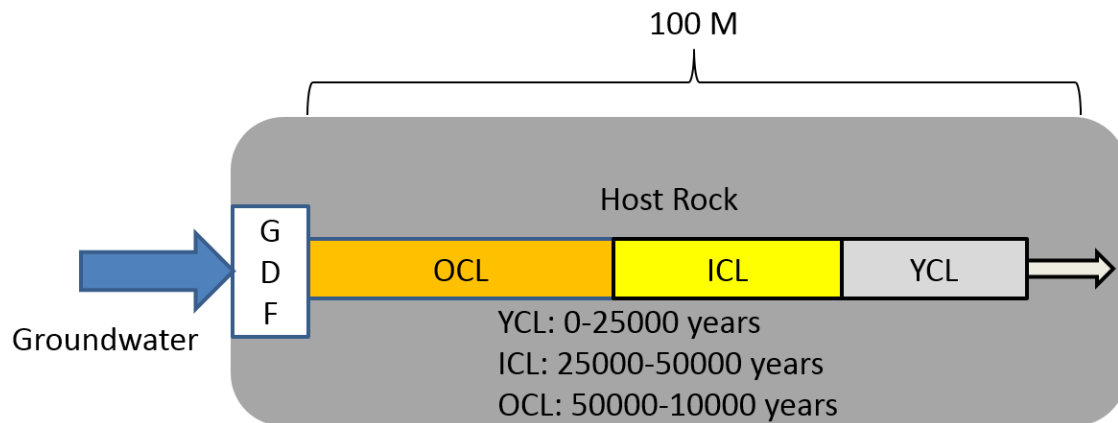
**Table 2.** Typical compositions of groundwater at 25°C

	<b>Saline (mol kg<sup>-1</sup>) (Bond and Tweed, 1995)</b>	<b>High carbonate (mol kg<sup>-1</sup>) (Nirex, 1994)</b>	<b>Low carbonate (mol kg<sup>-1</sup>) (Nirex, 1994)</b>
<b>Na</b>	3.7e-1	8.4e-3	8.2e-2
<b>K</b>	4.4e-3	3.8e-5	2.5e-4
<b>Mg</b>	5.7e-3	3.3e-5	6.8e-4
<b>Ca</b>	2.9e-2	8.8e-5	4.8e-2
<b>Sr</b>	2.0e-3	2.0e-5	9.9e-4
<b>Al</b>	1.7e-6	4.6e-7	5.4e-8
<b>C</b>	1.0e-3	2.8e-3	1.6e-4
<b>Si</b>	2.5e-4	1.1e-4	7.6e-5
<b>Cl</b>	4.2e-1	5.3e-3	1.7e-1
<b>SO<sub>4</sub><sup>2-</sup></b>	1.2e-2	2.8e-4	6.4e-3
<b>pH</b>	7.22	8.75	7.73

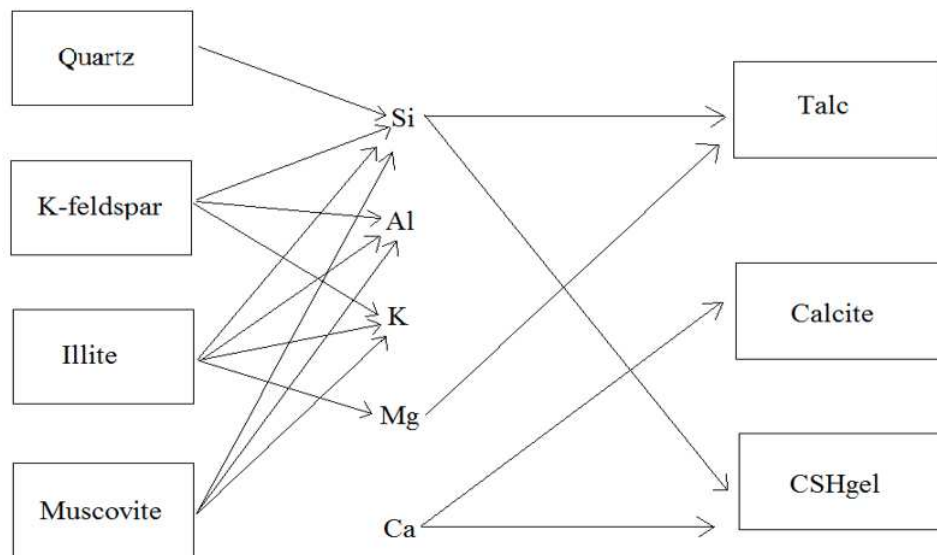
**Table 1.** Composition of Bromsgrove Sandstone and its conceptualization within modelling

Mineralogy	Modal composition (%)	Modelling approach (Toughreact, Petrasim, and Phreeqc)
Quartz	75.5	Modeled (Kinetics)
K feldspar ( $\text{KAlSi}_3\text{O}_8$ )	16	Modeled (Kinetics)
Albite ( $\text{NaAlSi}_3\text{O}_8$ )	0	0
Illite/Chlorite/Smectite	3.7	Modeled (Illite only, Kinetics)
Kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ )	3.5	Modeled (Kinetics)
Dolomite	0	0
Calcite	0	0
Muscovite	0.7	Modeled (Kinetics)
Biotite	0	0
Phlogopite	0.2	Not modeled
Zircon	0	0
Apatite	0.2	Not modeled
$\text{TiO}_2$	0.3	Not modeled
Ilmenite	0	0
Magnetite	0	0
Fe Oxide or Oxyhydroxide	0	0
Porosity	18.4	18.4(Modeled)

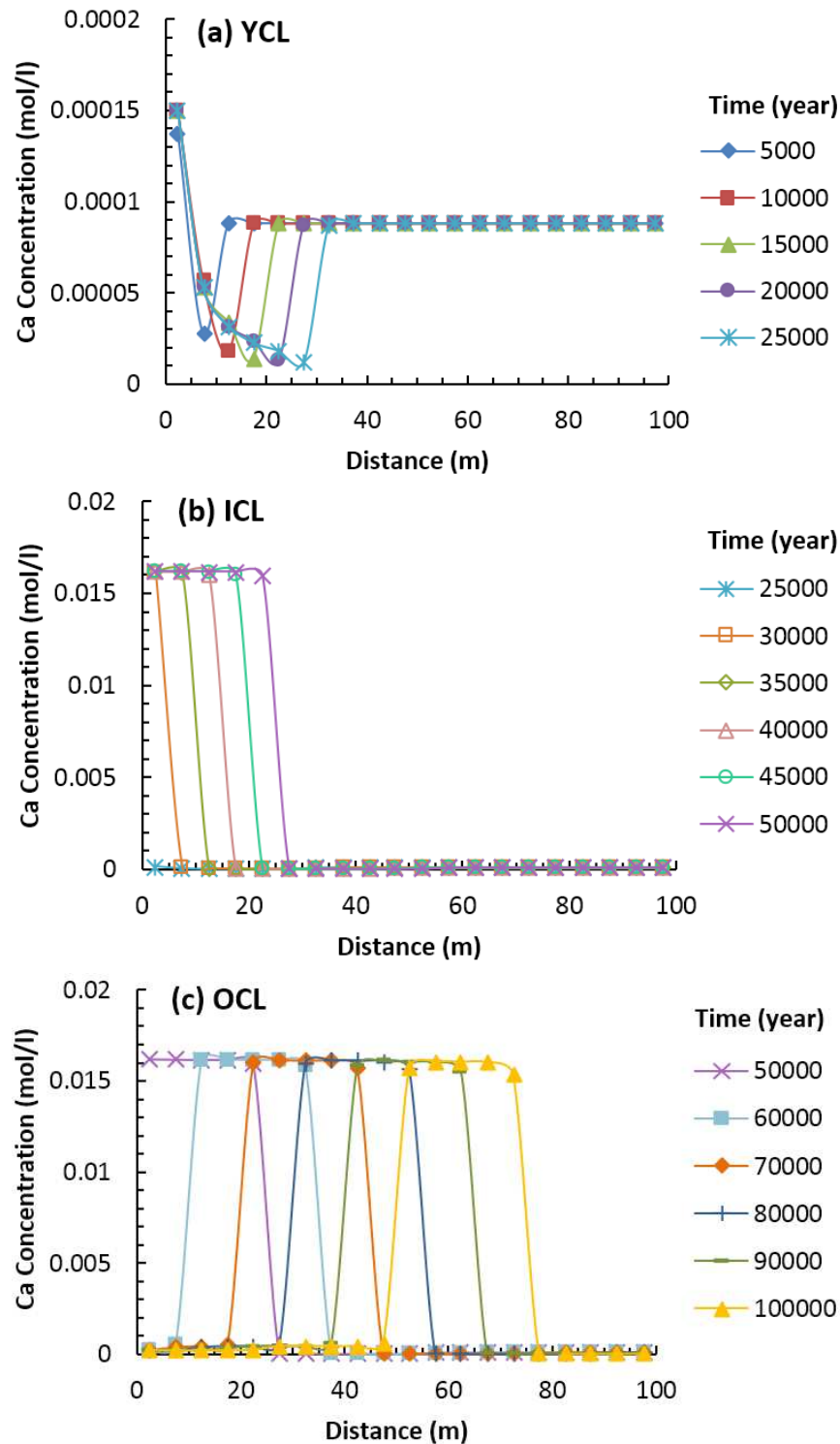
**Figure 1.** Conceptual model



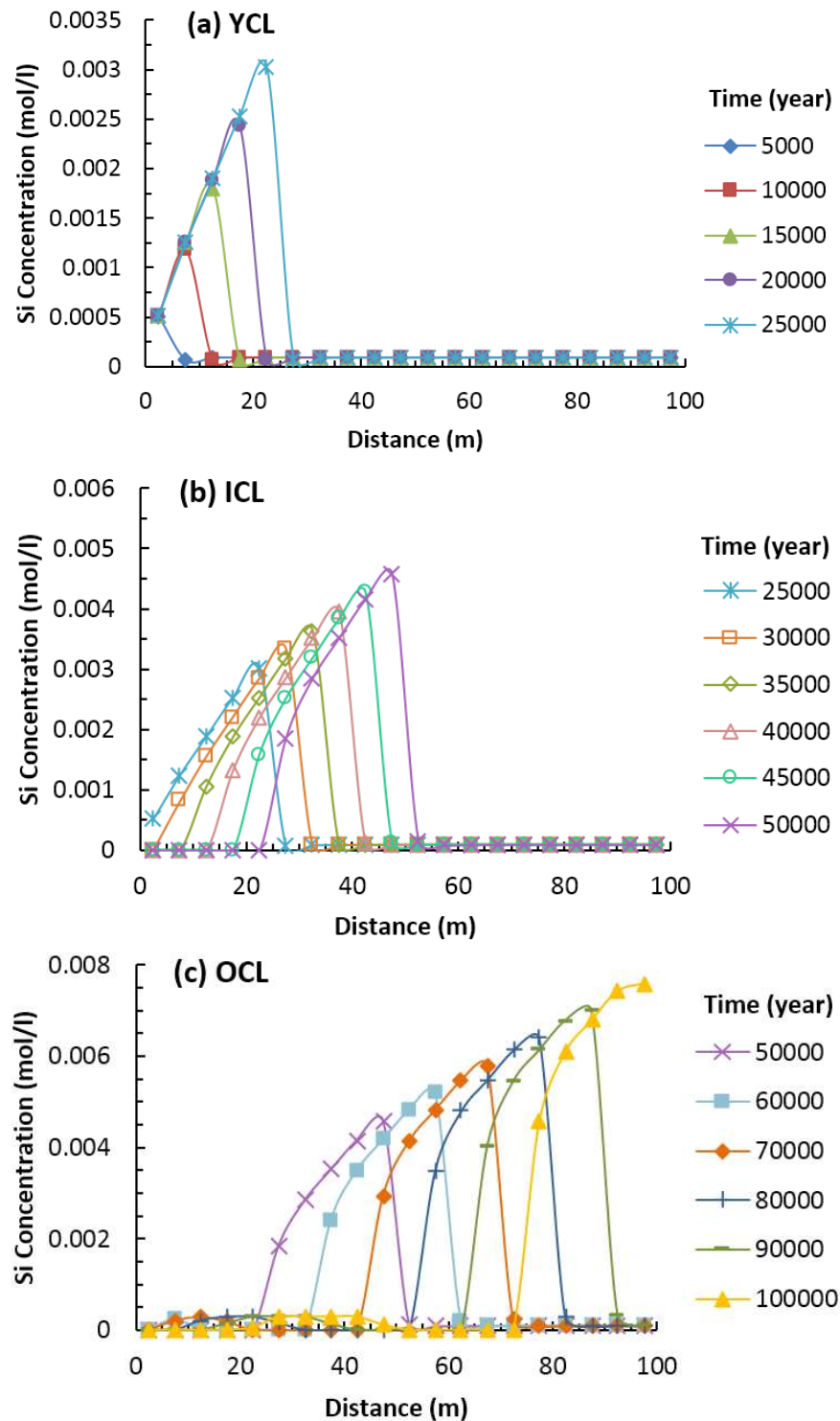
**Figure 2.** Conceptual model of mineral dissolution and precipitation



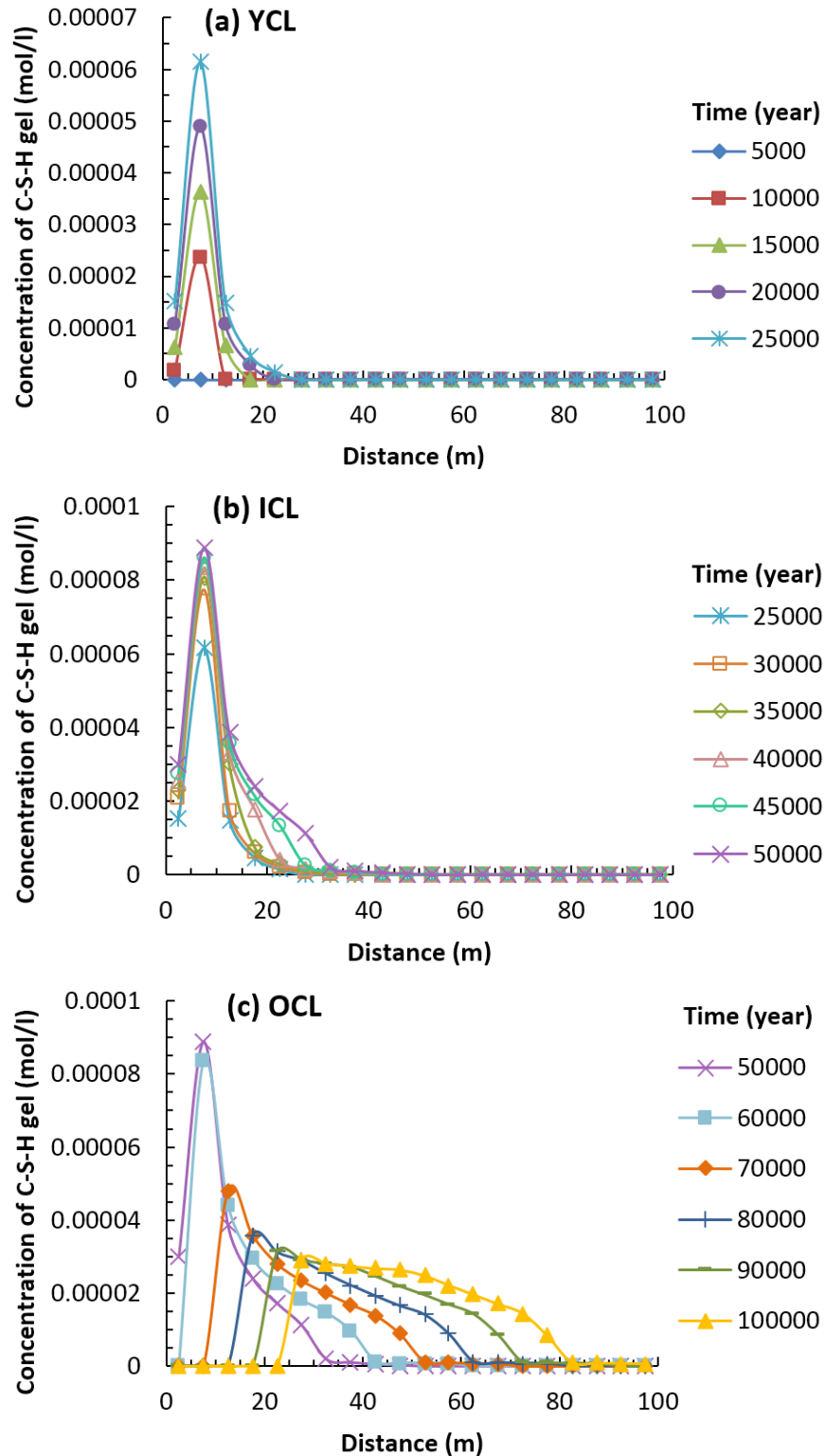
**Figure 3.** Predicted temporal variation in calcium concentration with distance during the migration of the cement leachates through the host rock: (a) YCL, (b) ICL, and (c) OCL



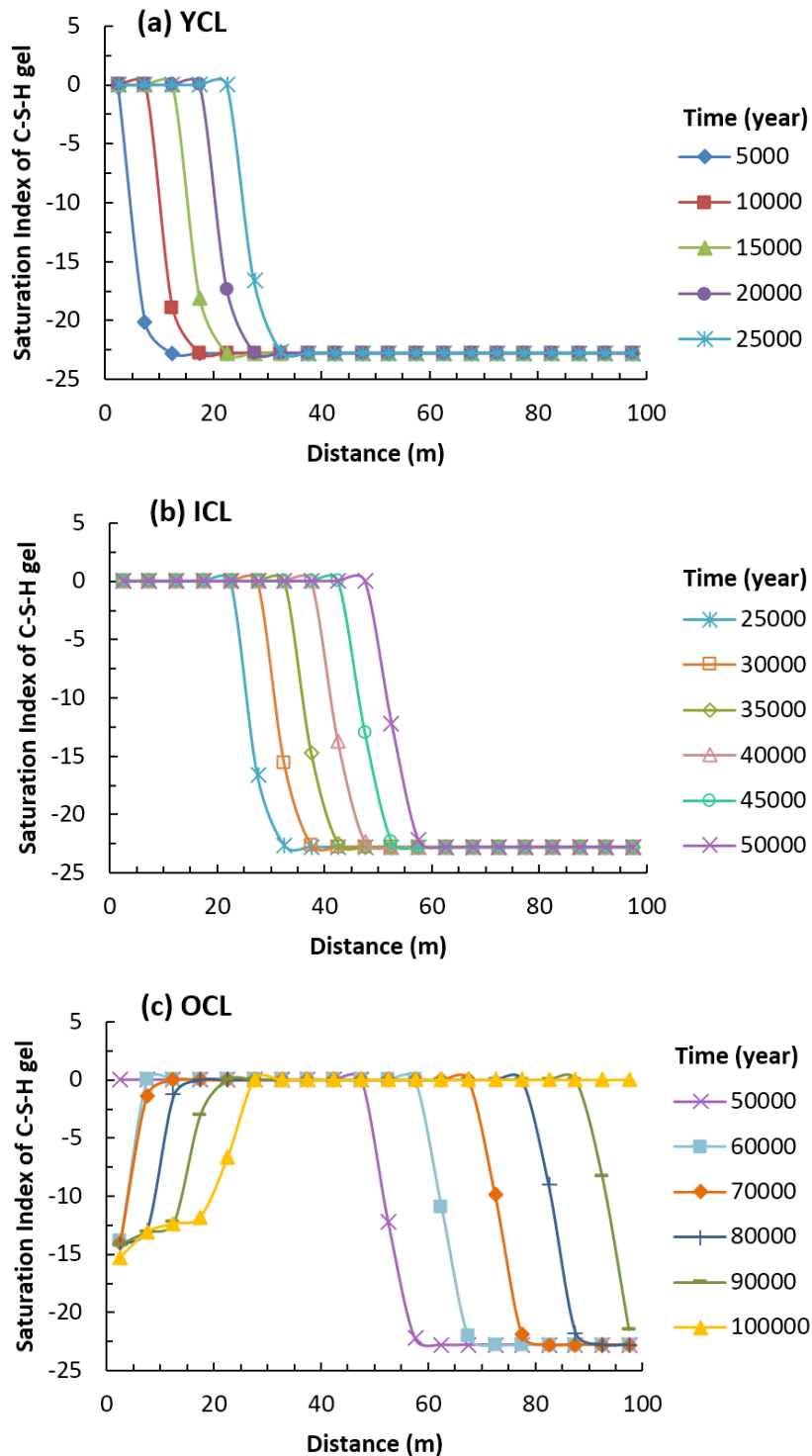
**Figure 4.** Predicted temporal variation in Si concentration with distance during the migration of the cement leachates through the host rock: (a) YCL, (b) ICL, and (c) OCL



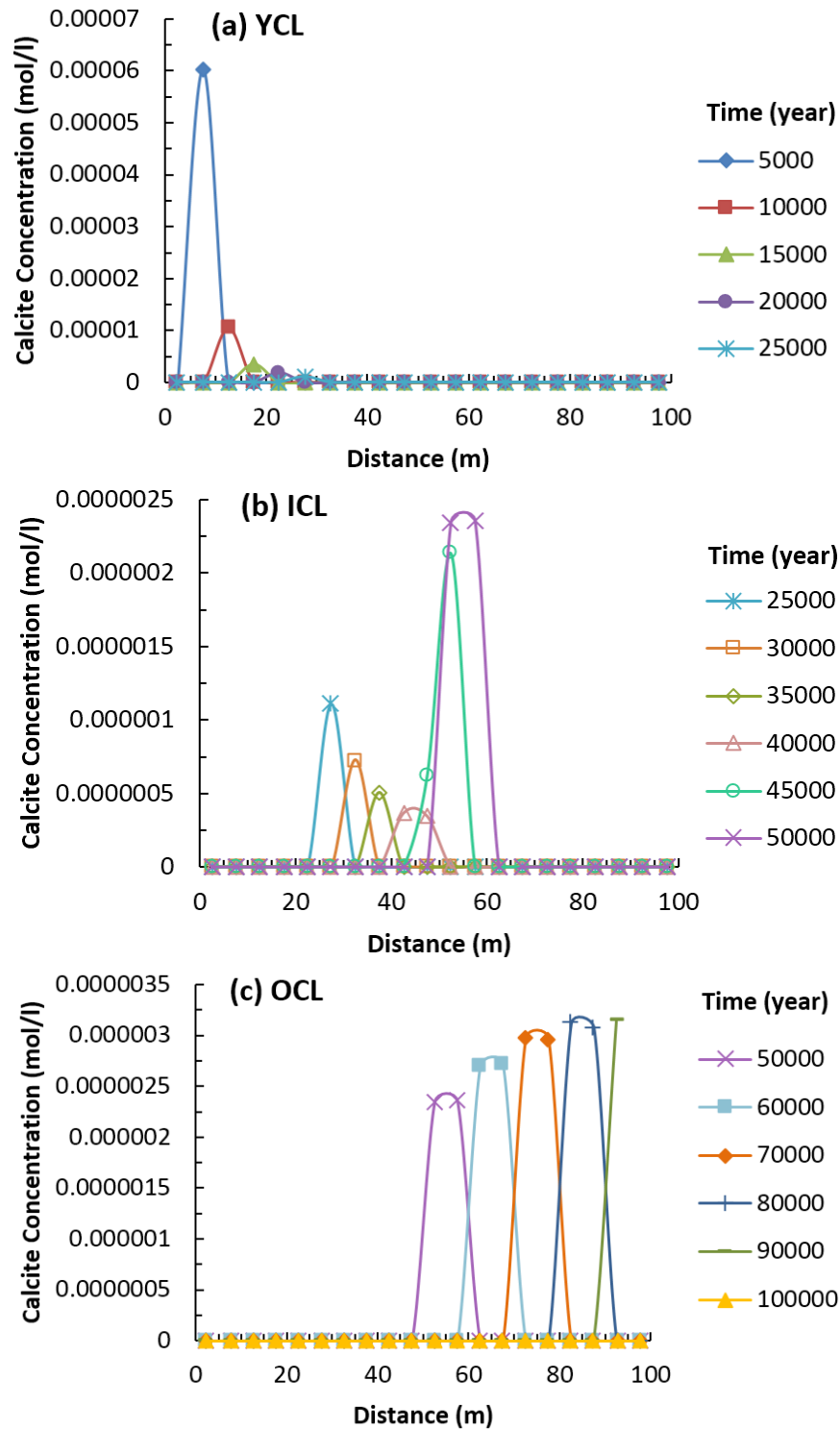
**Figure 5.** Predicted temporal variation in the concentration of C-S-H gel with distance during the migration of the cement leachates through the host rock: (a) YCL, (b) ICL, and (c) OCL



**Figure 6.** Predicted temporal variation in the saturation index of C-S-H gel with distance during the migration of the cement leachates through the host rock: (a) YCL, (b) ICL, and (c) OCL



**Figure 7.** Predicted temporal variation in calcite concentration with distance during the migration of the cement leachates through the host rock: (a) YCL, (b) ICL, and (c) OCL



**Figure 8.** Predicted temporal variation in the saturation index of calcite with distance during the migration of the cement leachates through the host rock: (a) YCL, (b) ICL, and (c) OCL

