

Reactive Transport Modelling in Sedimentary Rock: State-of-Science Review

NWMO TR-2007-12

December 2007

K. U. Mayer¹ and K. T. B. MacQuarrie²

¹University of British Columbia, ²University of New Brunswick

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Nuclear Waste Management Organization
22 St. Clair Avenue East, 6th Floor
Toronto, Ontario
M4T 2S3
Canada

Tel: 416-934-9814
Web: www.nwmo.ca

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ABSTRACT

Title: Reactive Transport Modelling in Sedimentary Rock: State-of-Science Review
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Author(s): K. U. Mayer¹ and K. T. B. MacQuarrie²
Company: ¹University of British Columbia, ²University of New Brunswick
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Abstract

To assess the suitability of sedimentary rock units for hosting deep geological repositories (DGR) for used nuclear fuel, it is necessary to investigate the long term geochemical stability of these formations. Multicomponent reactive transport modelling provides a viable method to evaluate conceptual models and to assess parameter sensitivity in the context of rock-water interaction, and can thus support and complement expensive field investigations. In this report, hydrogeological and hydrogeochemical data are reviewed to identify the relevant transport and reaction processes that control groundwater evolution and composition. In addition, previous reactive transport modelling efforts in similar settings are reviewed to assess the current status of reactive transport modelling in sedimentary rock formations. Based on this information, model capabilities and formulation gaps are identified. In addition, recommendations are made on how reactive transport modelling could be used most effectively to evaluate redox stability and salinity evolution in sedimentary rock units in response to periods of glaciation and deglaciation. It is found that reactive transport modelling has not been previously used to assess such a scenario. However, modelling studies of seawater ingress and CO₂ sequestration in sedimentary rocks show promising results and suggest that modelling of the geochemical evolution in a 2D-subsection of a sedimentary basin is a realistic goal. Although there are advanced multicomponent reactive transport models that consider a wide range of the required processes including aqueous speciation, ion exchange, mineral dissolution-precipitation, microbially-mediated redox reactions, density coupling between flow and reactive transport, as well as porosity and permeability changes, none of the currently available codes is capable of capturing all processes of relevance. The MIN3P code belongs to this group of codes and it is recommended that the capabilities of this model be expanded to include a) the Pitzer ion interaction model, b) a modified formulation for microbially-mediated reactions that accounts for inhibition as a function of salinity, c) a formulation for multicomponent and species-dependent diffusion, and d) discretization methods that facilitate the generation of unstructured grids that are better capable of dealing with irregular geometry and outcropping aquifer and aquitard units. Furthermore, it is recommended that the enhanced code be used to investigate a series of conceptual models for sedimentary units; within the context of these models, the effect of parameter uncertainty can be evaluated with respect to recharge penetration depth, redox stability and salinity evolution.

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1. INTRODUCTION

Sedimentary rock units are currently being investigated for their potential to implement the deep geological repository (DGR) concept for used nuclear fuel. For example, the sedimentary rocks of southern Ontario possess many characteristics that are considered favourable for repository siting and long-term waste isolation (Mazurek, 2004), including the potential presence of reducing mineral phases and diffusion-controlled mass transport. Within the time frame of one million years that is deemed necessary to demonstrate repository safety, significant climatic and hydrologic changes may occur as a result of glaciation/deglaciation cycles. Evidence indicates that past glaciations have previously modified groundwater flow systems (e.g. McIntosh and Walter, 2005, 2006), and it is believed that future glacial cycles have the potential to cause recharge of dilute glacial melt water containing relatively high concentrations of dissolved oxygen (Guimerà et al., 1999, Sidborn, 2007), particularly in shallower flow systems within sedimentary basins (McIntosh and Walter, 2005, Person et al., 2007). To demonstrate stability within DGR host rocks, an understanding of far-field geochemical conditions and their evolution over geologic time scales is required.

Reactive transport modelling is one approach that can be employed to assess the geochemical and redox stability within sedimentary rock sequences. For example, reactive transport modelling can clearly and convincingly demonstrate the degree to which dissolved oxygen may be attenuated in the recharge region of a DGR host rock (e.g. Spiessl et al., 2007), how rock-water interaction may cause groundwater salinity to vary along flow paths in aquifers, or how diffusive transport of reactive solutes may evolve in the pore waters of low permeability aquitard units (e.g. Pearson et al., 2002). These types of reactive transport investigations can therefore complement field investigations and assist in supporting the safety case for a DGR. However, before reactive transport modelling can be undertaken, the applicability of models to sedimentary rock systems must be assessed and suitable conceptual models must be developed.

The primary objectives of this report are to provide a review and assessment of the applicability of reactive transport models for simulating long-term geochemical evolution in sedimentary rock basins. The review deals primarily with the issue of past and potential future, glacial melt water ingress into sedimentary rock units that could serve as a host for a DGR. As noted above, reactive transport modelling can also be valuable for interpreting processes that do not directly result from the ingress of glacial waters. To provide a sound basis for evaluating model capabilities and limitations, both groundwater flow and geochemical reaction processes are reviewed. Evidence is presented for past modification of groundwater flow systems during glacial periods, and conceptual models for future flow system modifications and geochemical reactions are proposed.

Previously published studies which have utilized reactive transport modelling to interpret observations or make predictions of geochemical evolution in sedimentary rock sequences are reviewed with the objective of identifying modelling approaches, data requirements, and important feedbacks between reaction and flow processes. These studies therefore assist in determining the capabilities that are required in reactive transport models.

This review for sedimentary rocks is similar in scope to a recent review of reactive transport modelling in fractured crystalline rocks of the Canadian Shield (MacQuarrie and Mayer, 2005). However, unlike the previous review, numerical formulations for reactive

transport models and a comparison of the capabilities of current reactive transport models are not described in detail because these issues have been dealt with previously (e.g. MacQuarrie and Mayer, 2005) and they are independent of the particular rock type. Also, because recent reactive transport simulations in fractured crystalline rocks have been undertaken using the MIN3P code (Mayer et al., 2002, Spiessl et al., 2007), when assessing model requirements, outstanding modelling issues, and making recommendations for future modelling work in sedimentary rocks, we do so by considering both the conceptual models proposed and the current capabilities of the reactive transport code MIN3P.

2. REVIEW OF GEOSCIENTIFIC LITERATURE ON LONG-TERM HYDROGEOLOGICAL AND GEOCHEMICAL EVOLUTION IN SEDIMENTARY FORMATIONS

To provide the necessary background for developing conceptual models for reactive transport in sedimentary rock sequences, this section provides a summary of controlling hydrogeological and geochemical processes that affect groundwater flow and reactive transport on the spatial and time scales of interest.

2.1 HYDROGEOLOGICAL ASPECTS AND FLOW PROCESSES

Currently, the zone of active groundwater circulation in sedimentary basins is limited mostly to glacial drift aquifers and shallow fractured rock (Figure 1, McIntosh and Walter, 2005, Person et al., 2007), in part because the relatively flat landscape in many sedimentary basins does not provide the topographic relief to drive groundwater flow to depths greater than 50-100 m (McIntosh and Walter, 2005). In addition, the salinities of groundwaters at greater depth are characteristic of brines (Wilson and Long, 1993a,b, McIntosh and Walter 2005, 2006) and the resulting density gradient further inhibits groundwater flow into deeper units (Mazurek, 2004).

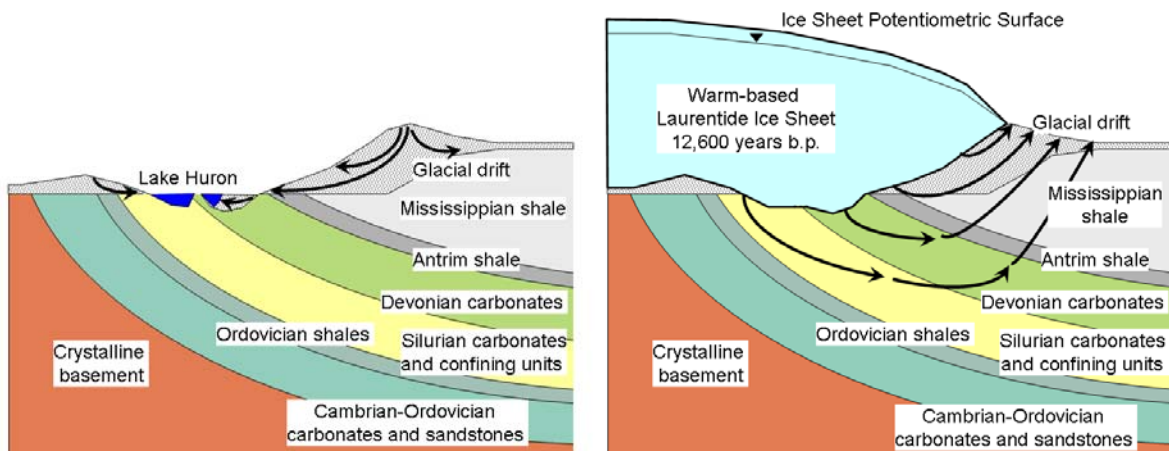


Figure 1: Conceptual model of flow system evolution during glaciation/deglaciation conditions involving a warm-based glacier in the northern section of the Michigan Basin. The left diagram depicts the present day flow system. The ingress of glacial melt water into outcropping aquifer units, displacement of basal brines, and discharge through overlying shale units is displayed on the right for comparison (modified after McIntosh and Walter, 2005).

However, present day conditions are not necessarily reflective of past groundwater flow dynamics. There is evidence that groundwater flow regimes have been reorganized on the basin scale during periods of glaciation and deglaciation. During the Pleistocene, sedimentary basins located in the northern United States and southern Canada, namely the Michigan, Appalachian, Illinois, Forest City, Alberta and Williston basins, were covered periodically by ice sheets of significant thickness (Person et al., 2007). For example, Peltier (2002) conducted a series of simulations using the University of Toronto's Glacial Systems Model that produced ice sheet thicknesses of greater than 2km in southern Ontario, which is underlain by the Michigan and Appalachian basins. In the case of a warm-based ice sheet, hydraulic heads at the ground surface may reach up to 90% of the ice sheet thickness (Person et al., 2003, 2007), as was observed under present day conditions for a basal drainage system of a West Antarctic ice stream (Engelhard and Kamb, 1997). In this case, for an average ice sheet thickness of 1000 m, observed water levels in boreholes that connected to the basal drainage system were typically 100 m below the ice surface. It can be hypothesized that these significant hydraulic heads completely overwhelmed existing land topography and groundwater density stratification (Boulton et al., 1993, Person et al., 2003, 2007). As a result, present-day groundwater divides may not be relevant during periods of glaciation and deglaciation and the flow system may be significantly altered (Figure 1). Conceptual two-dimensional simulations for a sedimentary basin composed of four aquifers separated by aquitards suggest that past recharge rates under warm-based glaciers may have exceeded present-date recharge by a factor of up to 10 (Person et al, 2007).

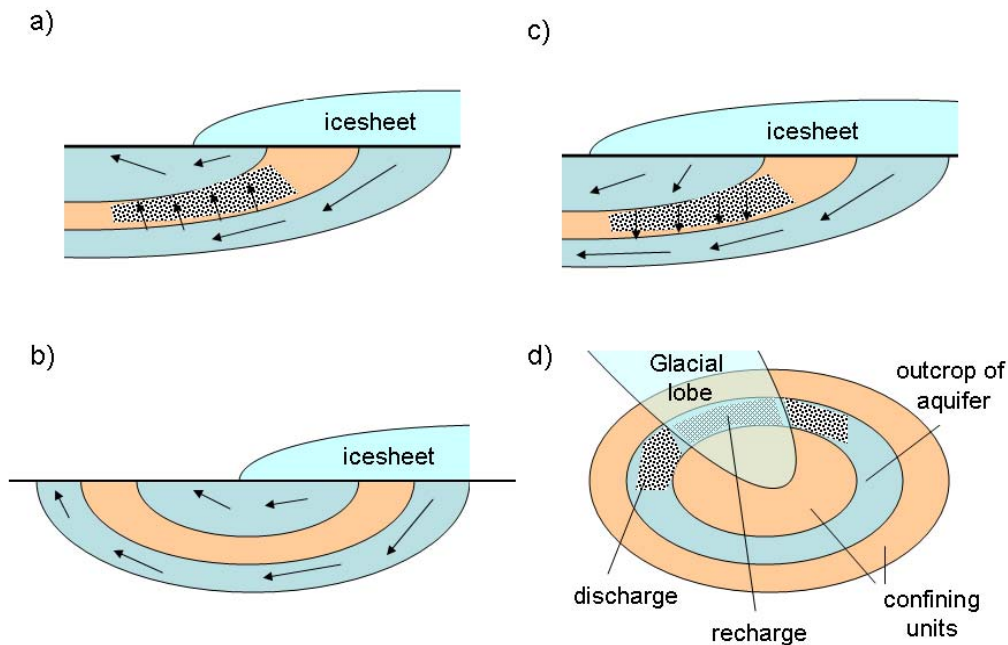


Figure 2: Potential mechanisms of melt water infiltration a) ingress through subcrops or outcrops of aquifers and flow through fractured confining units, b) ingress through subcrops or outcrops of aquifers and displacement of resident groundwaters through aquifers (after Person et al., 2007), c) vertical ingress through confining units (Siegel, 1991), d) hypothetical 3D-effects during advancement of glacial lobe. Sedimentary basins as shown in this figure are typically characterized by a spatial extent ranging from 100 - 500km.

Several conceptual models have been proposed to explain recharge into sedimentary units during glacial periods. For example, McIntosh and Walter (2005, 2006) suggest that the ingress of glacial melt water into Silurian-Devonian carbonate aquifers in the northern Michigan basin took place through subcrops or outcrops at the basin margins. This concept implies that recharge occurs directly into the permeable rock units, but not through the overlying confining beds (Figure 1, Figure 2a).

It is clear that significant recharge can only occur if groundwater that is initially present can be displaced by the recharging water. This implies that groundwater must either migrate deeper into the rock units (Figure 2b), migrate laterally to a discharge point located in the same unit (Figure 2d), or it must discharge to the ground surface after moving through overlying aquitards (Figure 2a). Considering the low hydraulic conductivity of the confining beds in sedimentary basins (mostly composed of shales), the potential for vertical discharge through these units is limited. However, due to high hydraulic heads below ice sheets, significant vertical gradients may develop, which may facilitate vertical discharge. In addition, mechanical loading introduced by the weight of the advancing or retreating glacier may have caused fracturing of the confining units thereby increasing their effective hydraulic conductivity and providing a pathway for egress of groundwater (Person et al., 2007, Figure 2a).

For example, in the northern Michigan basin, there is evidence that meteoric water has migrated into the Silurian and Devonian aquifers and subsequently into the overlying fractured organic rich Devonian shale units (McIntosh and Walter, 2005, 2006). Glacial melt water is estimated to comprise up to 50% of the shale formation water with an increasing contribution towards the shale outcrop (Figure 1). Recharge into outcropping Silurian/Devonian aquifers is also believed to have provided a pathway for ingress of melt water into the Illinois basin (McIntosh and Walter, 2005) and the Williston basin (Grasby and Betcher, 2002). Ingress of glacial melt water may also have affected deeper units (i.e. Cambrian/Ordovician rock units), as evidenced by anomalous fluid pressures (McIntosh and Walter, 2005, 2006 and references therein).

Person et al. (2003) used this concept to explain the relatively dilute water composition in sedimentary units in the Atlantic continental shelf. In a modelling study, dilute water compositions present today in the shelf deposits could only be reproduced by assuming enhanced recharge during periods of glacial melt water production. McIntosh et al. (2005) conducted density-dependent flow and transport simulations for the northern Michigan Basin under glacial boundary conditions. Their results show that high hydraulic heads during basal melting could result in penetration to depths of ~ 300 m in rocks at the basin margin, consistent with field observations.

In a more recent modelling study, Person et al. (2007) suggested an alternative conceptual model, which assumed basin wide flow and displacement of the groundwater towards the opposite end of the basin margin (Figure 2b). This conceptual model was discussed for the Williston basin and a sensitivity analysis was conducted that assumed that hydraulic conductivity declined with depth; however, the decrease was limited to one order of magnitude and porosity was assumed to be constant with depth (Person et al., 2007).

Siegel et al (1991) suggested yet another concept and proposed that recharge into the Cambrian-Ordovician aquifer of Iowa (Illinois and Forest City basins) occurred vertically downward through hundreds of metres of confining beds under the Des Moines glacial lobe. This scenario was deemed more likely than infiltration through aquifer outcrops at distant locations in southern Minnesota. Vertical recharge was assumed to occur predominately

through vertical sets of fractures (Figure 2c) and numerical modelling based on reasonable aquitard parameters (bulk hydraulic conductivity: $K = 10^{-11} \text{ ms}^{-1}$, $\phi = 0.001$) suggests that this hypothesis is plausible. Simulations conducted by Boulton et al. (1994) for a two-dimensional cross-section of a major aquifer system in the Netherlands also indicated that vertical ingress through thick aquitards (300-1000m) is possible under a warm-based ice sheet. The simulated recharge quantity was significant, considering that subglacial catchments for groundwater flow extended from the ice divide to the glacier margin (on the order of 1000 km). The simulations showed high horizontal gradients during glacial melt water production (one to two orders of magnitude larger than under present day conditions), large vertical gradients in some regions, and ingress of melt water to depths of approximately 1,500 m. However, it must be noted that these simulations assumed a specified flux in a region of basal melting that extended over 100's of km and were based on a hydraulic conductivity for the main aquitard unit of approximately $5 \times 10^{-7} \text{ ms}^{-1}$, which is orders of magnitude higher than typical values for clay and shale aquitards ($1 \times 10^{-11} \text{ ms}^{-1}$, Mazurek, 2004).

One mechanism for glacial melt water recharge and discharge which, to the best of our knowledge, has not been discussed to date is the introduction of melt water caused by 3-D effects during the presence of a glacial lobe over a sedimentary basin (Figure 2d). While high hydraulic heads may exist underneath the ice sheet, hydraulic heads adjacent to the glacial lobe are limited by ground surface elevation or the water level of surface water bodies. Recharge may therefore occur into a permeable sedimentary unit and may be driven out laterally into zones of lower hydraulic head within the same unit. Unlike the scenarios shown in Figures 2a and 2b, this case does not require flow through low permeability confining units. In addition, kilometre-deep displacement of formation waters (as shown in Figure 2b), which is questionable due to depth-dependent decreases in formation permeability, fluid density contrasts between fresh recharge water and resident brines, and the lack of an exfiltration zone, is not required if lateral discharge can occur.

Following complete retreat of continental ice sheets, it can be envisioned that the flow regime in the aquifer units continues to evolve. Zones of overpressurization or displaced water of high salinity may provide the driving force for upward movement of groundwater. Evidence for this type of groundwater regime is provided by the presence of saline springs along basin margins (Grasby and Betcher, 2002 as referenced by McIntosh and Walter, 2005, Ferguson et al., 2007). Person et al. (2007) also report reflux of cold climate recharge for the Williston basin; however, the chemical composition of the discharging water has been altered to a brine due to rock-water interactions. In addition, upward migration may also be driven by gas production at depth, which may increase hydraulic head in the region of gas generation and may induce basin-scale groundwater flow towards the basin margins (Mazurek, 2004).

2.2 ISOTOPIC EVIDENCE FOR PAST GLACIAL MELTWATER RECHARGE

Evidence for past glacial melt water recharge, as discussed above, is provided by anomalous $\delta^{18}\text{O}$ and δD signatures of groundwater in comparison to precipitation formed under current climate conditions. Groundwater to depths of up to 300 metres in Silurian-Devonian aquifers and shales along the northern margin of the Michigan Basin have $\delta^{18}\text{O}$ of -15 to -10‰ and δD values of -100 to -75 ‰ (McIntosh and Walter, 2005, 2006), indicating Pleistocene recharge into these regions. Siegel et al. (1991) also provided evidence for Pleistocene recharge into the Cambrian-Ordovician aquifer of Iowa. Most recently, Person et al. (2007) conducted a review

that compiled isotopic data from various sedimentary basins and suggested that recharge of Pleistocene waters is a common feature at the margins of sedimentary basins.

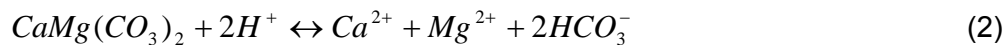
On the other hand, data presented by Dollar et al. (1991) for southwestern Ontario supports recent (< 10,000 years) ingress of freshwater only into Devonian units (to a depth of < 100 m). Unlike the situation in the northern part of the Michigan basin (McIntosh and Walter, 2005, 2006), available oxygen isotopic data suggests that deeper units (Silurian, Ordovician and Cambrian) have not been affected by recharge of meteoric water. These units show a signature of very long residence times and in situ-rock-water interaction (Mazurek, 2004).

In summary, although ingress of meteoric water seems to be common, isotopic data suggests maximum ingress depths of approximately 300 m.

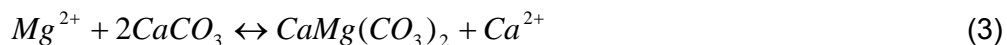
2.3 GEOCHEMICAL ASPECTS AND CONTROLLING REACTIONS

The initially low salinity of recharging freshwater may be significantly increased due to rock-water interaction (e.g. Wilson and Long, 1993a, McIntosh and Walter, 2005), a process which may completely overwhelm the freshwater signature. The presence of high salinity groundwater at depth therefore does not provide conclusive evidence for the absence of glacial melt water recharge. This argument is supported by previous studies, which suggest that rock-water interaction has played a dominant role in determining the composition of deep basal brines. Evaporation alone was found to be insufficient for explaining observed water compositions in many cases (e.g. Wilson and Long, 1993a,b, McIntosh and Walter, 2006). The main geochemical processes affecting major ion composition could include carbonate mineral dissolution, dolomitization (Wilson and Long, 1993a,b, McIntosh and Walter, 2006), dedolomitization (McIntosh and Walter, 2006), halite dissolution (Wilson and Long, 1993a,b), anhydrite dissolution (McIntosh and Walter, 2006), ion exchange of Na with Ca (Wilson and Long, 1993a, McIntosh and Walter, 2006), and to a lesser degree dissolution-precipitation of Al-silicate phases (Wilson and Long, 1993a, McIntosh and Walter, 2006).

Dissolution and precipitation reactions for the carbonate minerals calcite and dolomite are given by the following:

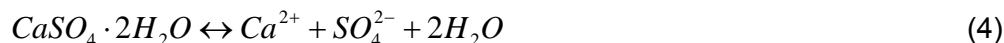


In groundwaters that are relatively depleted in Ca, but enriched in Mg, it is possible that calcite dissolves and dolomite precipitates, leading to the process of dolomitization (Wilson and Long, 1993a,b, Mazurek, 2004, McIntosh and Walter, 2006):



This reaction is important because it can enhance porosity and hydraulic conductivity of the sediments (Weaver et al., 1995) and can provide a feedback on flow and transport processes.

The salinity of the groundwater is mainly controlled by the dissolution of evaporite minerals including gypsum:



anhydrite (McIntosh and Walter, 2006):



and halite (e.g.: Wilson and Long, 1993a,b):



Ion exchange reactions with clays may have an additional effect on groundwater composition (McIntosh and Walter, 2006), although this class of reactions does not significantly affect salinity:

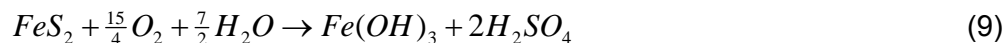


It can be expected that the reactions described by equations 1-7 will also take place in response to the infiltration of glacial melt water. These reactions will significantly increase the salinity of the groundwater and its density, while maintaining a circum-neutral pH value. As previously mentioned, some groundwaters that have been identified as Pleistocene recharge, based on their isotopic signature, have attained the geochemical composition of a brine (e.g. McIntosh and Walter, 2005, 2006). Considering that changes in salinity are also associated with changes in fluid density, a direct feedback between geochemical reactions and flow and transport processes can be expected.

In terms of redox state, the significant organic carbon content typically present in sedimentary formations, the abundance of hydrocarbon deposits, and the occurrence of methanogenic conditions, suggest the development of highly reducing conditions at shallow depths (McIntosh and Walter, 2005, 2006). In this type of environment, oxygen in recharge water is rapidly consumed by reaction with organic carbon contained in the sediments:



Depending on the depositional history, it can also be expected that pyrite, other sulfide minerals, and Fe(II)-containing mineral phases supply further redox reduction capacity (Dollar et al., 1991, McIntosh and Walter, 2005). For example, the oxidation of pyrite also consumes oxygen:



For the Michigan basin, McIntosh and Walter (2006) showed that pyrite oxidation is occurring in the shallowest portion of the aquifers.

At greater depth, sulfate reduction and methanogenesis are the dominant redox processes in sedimentary basins (Wilson and Long, 1993, Martini et al., 1998, McIntosh et al.,

2002, 2004, McIntosh and Walter, 2005, 2006). Sulfate reduction may occur if sulfate rich groundwater is displaced into regions with high labile organic carbon content:



Sulfate may also originate from the oxidation of pyrite by oxygen (equation 9). If sulfate becomes depleted, and organic carbon is still present, it is likely that further organic matter degradation by fermenters and methanogenic bacteria takes place:



However, microbially mediated reactions are inhibited under highly saline conditions, which may explain the persistence of sulfate over long periods of time despite the presence of organic matter. Recent work by Martini et al. (1998) and McIntosh and Walter (2005, 2006) provide evidence that the ingress of glacial melt water into Silurian/Devonian aquifers of the northern Michigan basin and its subsequent ingress into the overlying Antrim shale has enhanced microbial activity and has caused significant microbially-mediated gas production (predominantly methane). In this case, the groundwater signature remained relatively fresh due to the lack of soluble mineral phases such as halite, which facilitated the enhancement of microbial activity and led to the generation of economically viable gas deposits in the Michigan basin (McIntosh and Walter, 2006).

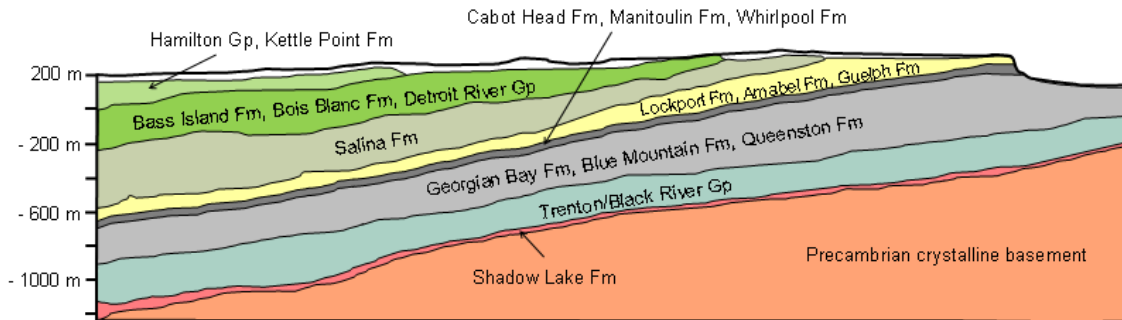
In summary, the literature suggests that rock-water interaction will increase the salinity of ingressing glacial melt water. The degree of salinity gain is controlled by sediment composition and the availability of soluble minerals such as halite and other evaporate mineral phases. The literature also suggests a strong redox buffer capacity likely capable of buffering glacial melt water that may contain a significant degree of excess air with dissolved O_2 concentrations elevated by a factor of up to five (MacQuarrie and Mayer, 2005).

3. APPLICATION OF FLOW AND REACTION CONCEPTS TO SEDIMENTARY ROCK SEQUENCES IN SOUTHWESTERN ONTARIO

The general hydrogeological and geochemical concepts discussed above are now put into the context of the Canadian portion of the Michigan Basin. This is done to provide a more definitive example of how groundwater flow and geochemical reactions may be invoked to constrain the hydrogeological and geochemical evolution at a specific site. This sedimentary basin has been selected for discussion because of the relative abundance of data that has been assembled by others for the region underlying southwestern Ontario (e.g. Mazurek, 2004) and for the northern part of the Michigan basin (McIntosh and Walter, 2005, 2006). However, with sufficient data similar site-specific conceptualizations could be developed for other sedimentary basins.

As pointed out by Dollar et al. (1991), the Michigan basin is a remarkably circular feature consisting of symmetrical bands of outcropping aquifer and aquitard units, which supports the translation of flow and reactive transport concepts from the region of the basin investigated by McIntosh and Walter (2005, 2006) to southwestern Ontario. However, differences may exist in aquifer hydraulic conductivity and fracturing of the aquitards in these two regions of the basin, which may affect system evolution in the two regions in different ways. In addition, it is also important to evaluate if the nature of glaciation has been similar in both regions, considering that recharge will be very different under warm-based and polar-based glaciers (Person et al.,

2007). Recently, a comprehensive geosynthesis of the existing geoscientific literature for Southern Ontario has been conducted (Mazurek, 2004). The hydrogeological and hydrogeochemical information for southwestern Ontario and its interpretation with respect to Quaternary glaciations (Mazurek, 2004) provides the framework for discussing the applicability of the concepts put forward by McIntosh and Walter (2005, 2006) for the northern Michigan basin.



after Mazurek, 2004



Figure 3: Cross-sectional view of region under consideration. Ordovician units include sandstones and dolostones (Shadow Lake Fm), limestones (Trenton- Black River Gp (cf. Simcoe Gp)), and shales (Blue Mountain Fm, Georgian Bay Fm, and Queenston Fm). Silurian units include the Cabot Head Fm (shale), Manitoulin Fm (dolomite), Whirlpool Fm (sandstone), a group of dolomites (Lockport Fm, Amabel Fm, Guelph, Fm), the Salina Fm (evaporates with limestones), and Bass Island Fm (dolomite). The Bois Blanc Fm (dolomite), Detroit River Gp (dolomite and limestones), Hamilton Gp (shales and limestones) and Kettle Point Fm (shale) are Devonian in age.

A cross-section of the sedimentary units of southwestern Ontario (Figure 3; after Mazurek, 2004) shows that several major formations overlie the Precambrian crystalline basement, and that these gradually dip to the southwest towards the center of the Michigan basin. The stratigraphic sequence includes Middle and Upper Ordovician units (limestones and shales), as well as Silurian and Devonian units. In the region of the Algonquin Arch, which underlies southwestern Ontario, pre-existing Cambrian and Lower Ordovician rocks have been eroded prior to deposition of the younger rock formations (Ziegler and Longstaffe, 2000). Middle and Upper Ordovician rocks include the units that have recently been identified as most suitable for the purpose of long-term radioactive waste management (Mazurek, 2004). Ordovician limestones constitute most of the Trenton and Black River Groups (cf. Simcoe Gp.), while Ordovician shale units include the Blue Mountain Formation, Georgian Bay Formation and Queenston Formation (Mazurek, 2004).

3.1 HYDRAULIC CONDUCTIVITIES FOR SEDIMENTARY ROCK UNITS

To apply the concepts introduced in section 2 in a site specific context, it is useful to compare the hydraulic conductivities of the sedimentary rock units in southwestern Ontario to the values reported for other sedimentary basins, and most importantly for the northern Michigan basin (McIntosh and Walter, 2005, 2006). Such an assessment will help to develop a framework for evaluation of the ingress mechanisms depicted in Figure 2. For rock units that can potentially act as aquifers (sandstones and carbonates), a comparison of horizontal hydraulic conductivities is informative, while vertical hydraulic conductivities and, in particular, evidence for the presence of vertical fractures are most relevant for the confining units (typically shales).

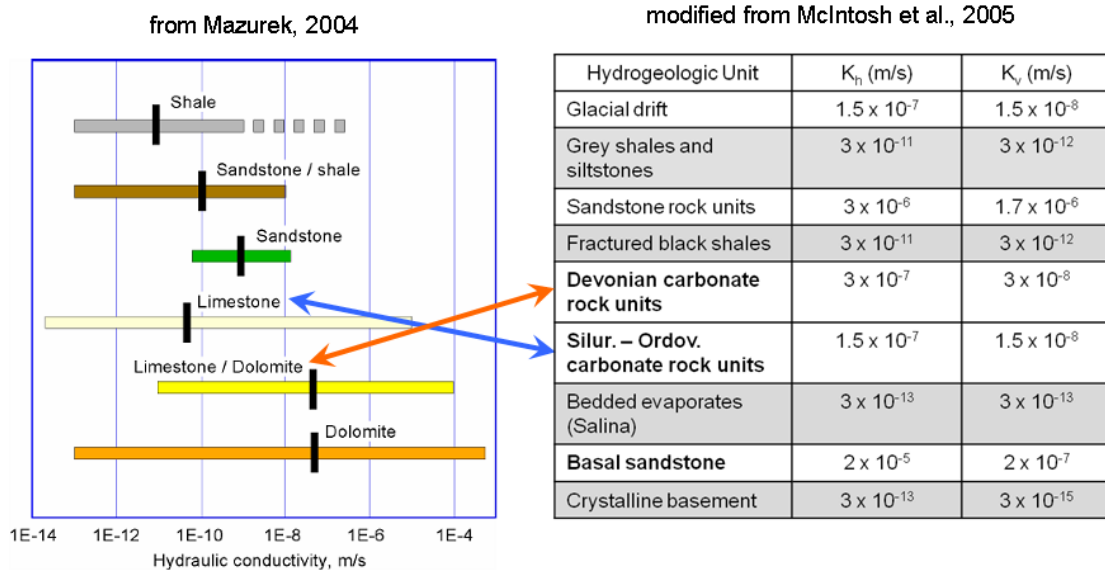


Figure 4: Comparison of hydraulic conductivity values for region of interest from a) Mazurek (2004) and b) McIntosh et al., 2005. Hydraulic conductivities for the Devonian carbonate rock units selected by McIntosh et al. (2005) compare well with the average values by Mazurek (2004). Hydraulic conductivities for the Silurian-Ordovician carbonate rock units used by McIntosh et al. (2005) are more than 3 orders of magnitude higher than average values reported by Mazurek (2004). Hydraulic conductivities reported by McIntosh et al. (2005) originate from a conference poster and cannot be traced back to original references.

3.1.1 Horizontal Hydraulic Conductivities of Sandstone and Carbonate Rock Units

McIntosh et al. (2005) employed a density dependent flow and transport model to simulate ingress of glacial melt water into the sedimentary units of the northern Michigan basin under glacial loading. These simulations predicted fairly deep ingress of melt water (~ 300 m) into Devonian, Silurian, Ordovician and Cambrian rock units. Figure 4 presents the hydraulic conductivity values that were used by McIntosh et al. (2005) for the respective units. These values can be compared to a compilation of hydraulic conductivity data for sedimentary rocks underlying southwestern Ontario (Mazurek, 2004). The data presented by Mazurek (2004)

stems from in-situ packer tests in boreholes and are generally considered conservative estimates of hydraulic conductivity (i.e. actual hydraulic conductivities may be lower).

While geometric means (shown as black bars in chart by Mazurek (2004), Figure 4) for all shale formations and Devonian carbonate rock units are in good agreement, McIntosh et al. (2005) have assigned significantly larger hydraulic conductivity values for the Silurian and Ordovician rock formations (up to 3 orders of magnitude higher, these values originate from a conference poster and cannot be traced back to original references). These are the units which were simulated to have some of the deepest ingress of glacial melt water (McIntosh et al., 2005). It must be noted that hydraulic conductivity values for limestones compiled by Mazurek (2004) also encompass more shallow units, and the maximum values for Silurian-Ordovician carbonate rock units were $< 10^{-8} \text{ ms}^{-1}$ with a geometric mean on the order of 10^{-11} ms^{-1} (see Figure 6-9 in Mazurek, 2004). This provides further support that the high hydraulic conductivity values used by McIntosh may not be applicable for the Ordovician and Silurian rocks of southwestern Ontario. However, the review by Mazurek (2004) also provides evidence that Ordovician limestones may locally be more permeable. The enhanced hydraulic conductivity is believed to be caused by local dolomitization along faults (Mazurek, 2004). Such a local hydraulic conductivity enhancement is supported by isotopic data, which suggests mixing of waters between sandstone units and Ordovician limestones (see section 3.2, Dollar et al., 1991)

McIntosh et al. (2005) also used a relatively high hydraulic conductivity of $2.0 \times 10^{-5} \text{ m s}^{-1}$ for the basal sandstone unit (3 orders of magnitude larger than the highest measured sandstone value in southwestern Ontario). The basal sandstone units in southwestern Ontario are thin and restricted to the Shadow Lake formation. In addition, there are facies changes in the Shadow Lake formation across southern Ontario with gradation to a dolostone towards the region where this unit outcrops. Although Cambrian sandstones are present in the northern part of the Michigan basin, these were eroded in the region of the Algonquin Arch prior to deposition of the overlying units (Ziegler and Longstaffe, 2000). As a result, Cambrian units do not outcrop at the basin margin in the region north of Toronto. The hydraulic conductivity reported in the compilation by Mazurek (2004) for sandstones is based on a single unit located in Silurian rocks (Whirlpool formation), and may not be representative for sandstones contained in the Shadow Lake Fm. In regions where the Cambrian sandstones were not eroded, large flows obtained from wells support relatively high permeabilities in these rocks (Dollar et al., 1991).

3.1.2 Vertical Hydraulic Conductivities in Confining Units (Shales) and Evidence for Fracturing

Considering the low hydraulic conductivity of the confining beds, the presence of fractures and fault zones is a key factor for vertical migration through aquitards. The presence of fractures could provide a major control for the overall evolution of the flow field during glacial melt water ingress (Figures 2a and 2c). As summarized by Mazurek (2004), Sanford et al. (1985) developed a conceptual fracture network model for southwestern Ontario. The presence of three fracture systems was hypothesized; however, only a small density of faults was predicted for the Bruce Megablock when compared to the Niagara Megablock. In addition only one of the three fracture systems is thought to be prevalent in the Bruce Megablock (Sanford et al., 1985). Reactivation of the fracture zones is believed to be restricted to orogenic events, the most recent of which occurred approximately 250 million years ago during the late Paleozoic-early Mesozoic (Sanford et al., 1985). Although some evidence exists for the presence of neotectonic fractures in the Lockport Formation of southwestern Ontario, these features are associated with the retreat of the Niagara escarpment (Gross and Engelder, 1991). Fluid overpressures have

been identified in Silurian and Devonian formations in southern Ontario (Raven et al., 1992, Novakowski and Lapcevic, 1988). The fact that supernormal pressures exist suggest that fracturing is limited at present time and that the bulk hydraulic conductivity is very low (Raven et al., 1992). Overall, except for one local example in the Devonian units overlying the Salina formations (Weaver et al., 1995), there is very little evidence for vertical fracturing of the confining units and the hydraulic conductivity both in vertical and horizontal directions is likely low. This suggests that the potential for vertical flow through aquitards, as has been depicted in Figure 2a and c, is low.

3.2 ISOTOPIC EVIDENCE FOR PAST GLACIAL MELT WATER RECHARGE

Information on the isotopic composition of groundwater is also useful to determine if infiltration of glacial melt water has occurred in southwestern Ontario. In this context, it must be acknowledged that extensive data sets, such as those for the northern Michigan basin, do not currently exist for the Ontario portion of the basin margin. In southwestern Ontario, groundwater with a Pleistocene isotopic recharge signature is most abundant in very shallow Quaternary aquifers (maximum depth of 50 m) that overlie the older sedimentary rocks (Desaulniers et al., 1981, 1986, Husain et al., 2004). As noted in section 2.2., Dollar et al. (1991) suggest that Pleistocene recharge may also have occurred into the Dundee Formation (Middle Devonian, Figure 3). It is worthwhile noting that all groundwater with cold water isotopic signatures from Devonian formations were sampled at depths of less than 100 m, in regions where these formations subcrop. The ingress mechanism is not discussed; however, it is suggested that the dissolution of evaporite deposits in the underlying Salina Formation may have caused the formation of collapse breccias within the Devonian units. The presence of these collapse structures may have made the Dundee Formation more accessible to ingress of glacial melt water (Dollar et al., 1991, Mazurek, 2004).

For the remaining units (Silurian, Ordovician and Cambrian), the isotopic signature and chemical composition of groundwater sampled from oil and/or gas producing reservoirs does not provide evidence for past ingress of glacial melt water (Dollar et al., 1991). In addition, most units show characteristic chemical and isotopic composition indicating very limited flow across unit boundaries. An exception is a limited number of brine samples from hydrocarbon-producing wells within the Cambrian and lower Ordovician rock formations (Dollar et al., 1991, Mazurek, 2004) which show overlap in their stable water isotopic signatures. This suggests local exchange occurred between the units through a possible hydraulic or diffusive connection.

3.3 GEOCHEMICAL ASPECTS AND CONTROLLING REACTIONS

The long term geochemical evolution of groundwater is largely controlled by the composition of the sedimentary rock sequences hosting the groundwaters (McIntosh and Walter, 2006). As a result, groundwater in southwestern Ontario has been affected by processes similar to those identified in other sedimentary basins including the northern region of the Michigan basin. In the case of future melt water ingress, the salinity of recharge waters is expected to be controlled by the presence of halite and other highly soluble mineral phases. In southwestern Ontario, these mineral phases are only abundant in the Silurian Salina Formation (Dollar et al., 1991). On the other hand, carbonate minerals are ubiquitous, and even the shale units contain a significant carbonate mineral fraction (Mazurek, 2004). It can be expected that equilibration of groundwater with these phases will maintain pH values at circum-neutral levels. Organic carbon and reducing

mineral phases including pyrite and Fe(II) bearing chlorite are abundant in the Ordovician formations (Mazurek, 2004), suggesting that redox processes are similar to those in the northern Michigan basin. Both sulfate reduction and methanogenesis cause the production of fairly insoluble gases. For example, dissolved hydrogen sulfide has been identified in the Queenston Formation (Mazurek, 2004).

4. PREVIOUS INVESTIGATIONS OF REACTIVE TRANSPORT IN SIMILAR SETTINGS

As demonstrated by the review of recent literature presented in Appendix A, multicomponent reactive transport modelling in sedimentary basins has been rather limited, and relatively few studies have dealt with the long-term evolution of geochemical conditions in sedimentary rock environments. One notable exception is the study by Pearson et al. (2002), who applied one-dimensional reactive transport modelling to the Opalinus Clay formation in a specific attempt to better interpret the dilution of sea water in the formation by fresh water present in the bounding aquifers.

A number of studies have used reactive transport simulations to investigate CO₂ sequestration in geological settings that share some similarities with the sedimentary rock sequences being considered for waste repositories. These modelling investigations are typically localized to either consider processes in the shale cap rocks, or the immediate vicinity of the sandstone-shale interface (e.g. Gaus et al., 2005, Xu et al., 2005, Figure 5). These studies have, however, highlighted the importance of having detailed initial mineralogical characterization in aquitard formations (see Appendix A for details).

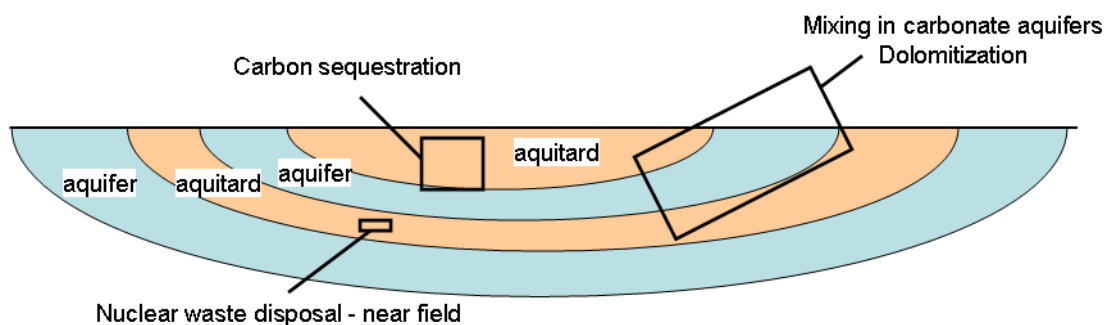


Figure 5: Schematic representation of modelling domains, shown in relation to a sedimentary basin cross section, used in previous reactive transport studies. These studies include the characterization of diffusive transport in rock formations considered for deep geologic repositories, natural analogue studies for uranium migration and attenuation, several modelling studies on geologic carbon sequestration, and the simulation of the interactions between saline and fresh waters in coastal aquifer systems (see Appendix A).

Although no previous studies have directly considered the ingress of dilute glacial melt waters into sedimentary basins, several large scale simulation studies (Figure 5) have focused on the mixing of different water types in carbonate aquifers with spatial and time scales (e.g. 10,000 to 1 million years) that are relevant to nuclear waste isolation. In addition, the influence

of variable fluid densities (Rezaei et al., 2005), heat transport, and high ionic strength on aqueous geochemistry have been considered in some studies (Jones and Xiao, 2005). As noted by the review in Appendix A, one relatively common focus of previous studies has been the simulation of porosity evolution in aquifers and aquitards, and in some cases the feedback between porosity and permeability (Jones and Xiao, 2005).

5. A REACTIVE TRANSPORT MODELLING FRAMEWORK FOR SEDIMENTARY ROCK SEQUENCES

In this section a general framework is developed that describes the interactions between fluid flow and the geochemical evolution of groundwater in sedimentary basins subjected to glacial cycles. This model integrates information for sedimentary basins and also includes information from previous reactive transport modelling studies in sedimentary rocks (Appendix A). The key governing equations that are required to simulate such a system are also summarized.

5.1 GENERAL CONCEPTUAL MODEL

Based on the review conducted in section 2, it appears possible that glacial melt water with a fresh water signature, and elevated O₂ concentration, may recharge into outcropping carbonate and/or sandstone formations at the margins of sedimentary basins (Figure 6). To what depth this recharge migrates is dependent on the driving force (i.e. hydraulic gradients) imposed by the water table in an overlying warm-based ice sheet during periods of glaciation, and the permeabilities of the various rock formations. If the driving force and hydraulic conductivities are sufficiently high, dense brines which are present at depth and are stagnant under present day conditions may be mobilized and displaced. Theoretically, displacement within the aquifer may result in groundwater flow to greater depth or in lateral directions. Alternatively, displacement may occur upwards through overlying confining units. It must be clarified that little evidence exists for upward migration of brines in the geologic past.

To what degree geochemical reactions modify water quality during the recharge process will depend on the composition of the rock units. Generally, the dissolution of carbonate minerals is expected to keep the pH in a circum-neutral range. Overall, mineral dissolution, including the dissolution of soluble phases, such as anhydrite, gypsum and halite will increase the ionic strength of the solution, and as a result also the solution density. If solution density is affected significantly, the fluid flow may be impacted leading to a direct coupling between reaction processes, transport and flow. Groundwater composition may be further affected by ion exchange reactions. An additional feedback mechanism between reactions, flow and transport may be caused by porosity and permeability enhancement or reduction due to mineral dissolution-precipitation reactions.

Furthermore, it is likely that organic matter and reduced mineral phases such as pyrite, chlorite and other Fe(II)- and sulfide-bearing phases lead to the consumption of oxygen that is dissolved in the recharge water (Figure 6). Other redox reactions such as sulfate reduction or methane generation may also play a role. A feedback may exist between fluid density and the rate of these reactions, considering that highly saline conditions tend to strongly inhibit microbial activity (McIntosh and Walter, 2005).

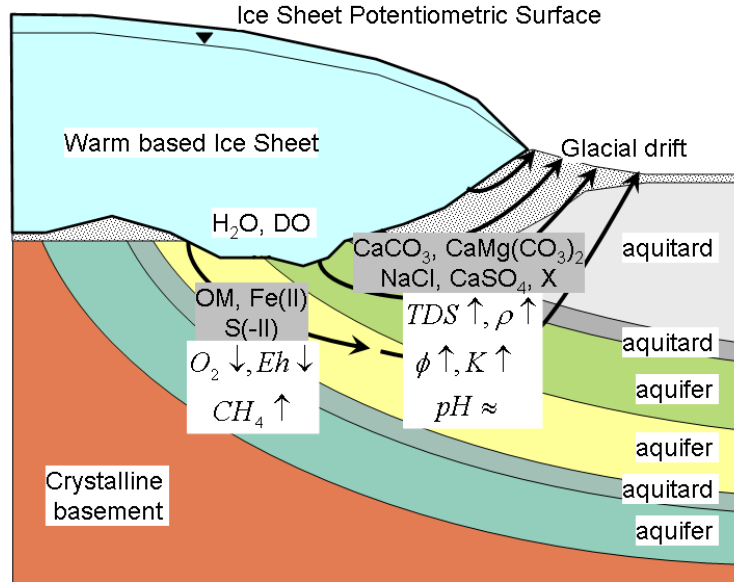


Figure 6: Conceptual model for groundwater evolution in response to melt water ingress. High hydraulic gradients cause enhanced recharge of melt water containing high dissolved oxygen (DO). Carbonate and evaporite mineral dissolution causes an increase in TDS and fluid density, possibly associated with porosity and permeability increase. The presence of reduced mineral phases and organic matter (OM) causes oxygen consumption, possibly sulfate reduction and methanogenesis. Solid phase constituents are shown in grey boxes (modified after McIntosh and Walter, 2005).

5.2 GOVERNING EQUATIONS

To describe reactive transport in sedimentary basins, it is necessary to consider the coupling between density-dependent flow and transport and geochemical reactions (e.g. Rezaei et al., 2005, Jones and Xiao, 2005). The governing equation for density-dependent fluid flow in saturated porous media can be written as (Bear, 1979):

$$\frac{\partial}{\partial t}(\phi\rho) + \nabla \cdot (\rho q_a) = \rho Q_a \quad (12)$$

where ϕ is the porosity [L^3 void L^{-3} porous medium], ρ is the fluid density [ML^{-3}], q_a is the specific discharge vector [LT^{-1}], and Q_a represents fluid sources/sinks [T^{-1}]. The corresponding reactive transport equations for N_c aqueous components can be written in terms of the total component concentration T_j^a :

$$\frac{\partial}{\partial t}(\phi T_j^a) + \nabla \cdot (q_a T_j^a) - \nabla \cdot (\phi D_a \nabla T_j^a) = Q_j^{a,a} + Q_j^{a,s} + Q_j^{a,ext} \quad j = 1, N_c \quad (13)$$

where D_a is the dispersion tensor, $Q_j^{a,a}$ [$mol\ dm^{-3}$ porous medium] and $Q_j^{a,s}$ [$mol\ dm^{-3}$ porous medium] are internal source and sink terms from kinetic intra-aqueous and heterogeneous reactions, and $Q_j^{a,ext}$ [$mol\ dm^{-3}$ porous medium] is an external source and sink term (Mayer et

al., 2002). This equation also implicitly considers equilibrium reactions through the total concentration terms T_j^a (Mayer et al., 2002, MacQuarrie and Mayer, 2005).

The fact that fluid density is directly related to solution chemistry can be expressed as a linear function of total dissolved solute concentrations c_t (Voss and Souza, 1987, Kharaka et al., 1988, Guo and Langevin, 2002):

$$\rho = \rho_0 + \frac{\partial \rho}{\partial c_t} c_t \quad (14)$$

where ρ_0 is the freshwater density and $\partial \rho / \partial c_t$ is a unitless constant, approximately 0.688 (Kharaka et al., 1988). The total solute concentration c_t is calculated based on the sum of the total concentrations T_j^a . Alternatively, more sophisticated relationships can be used which are based on the Pitzer ion interaction model (Monnin, 1989). In any case, this relationship directly accounts for the coupling between fluid flow and reactive solute transport.

The reduction in aquifer hydraulic conductivity due to the dissolution and precipitation of minerals can be described by a number of different permeability-porosity relationships (MacQuarrie and Mayer, 2005). A model commonly used is provided by the Carman-Kozeny relationship (e.g.: Le Gallo et al. 1998):

$$k^t = \left[\frac{\phi^3}{(1-\phi)^2} \right]^t \left[\frac{(1-\phi)^2}{\phi^3} \right]^{initial} k^{initial} \quad (15)$$

where k^t and $k^{initial}$ represent the current and initial media permeabilities. Additional functional relationships can be included, for example to describe reaction rates as a function of salinity.

6. OUTSTANDING ISSUES FOR REACTIVE TRANSPORT MODELLING

This section assesses the general applicability and limitations of reactive transport codes for modelling rock-water interactions, including the attenuation of oxygen and mineral precipitation-dissolution reactions and related porosity changes for the more dilute, shallow groundwater in sedimentary formations and for the highly saline groundwater found at depth.

Numerous models exist that are capable of simulating the transport processes and biogeochemical reactions (dissolution-precipitation, ion exchange, and microbially mediated oxidation reduction reactions) relevant in sedimentary basins (e.g.: review by MacQuarrie and Mayer, 2005). However, considering the significant salinity gradients that may be present, a coupled treatment of geochemical reactions and density dependent flow and transport is needed and fewer codes meet these requirements (Freedman and Ibaraki, 2002, Lichtner et al., 2004, Kim et al., 2004, Mao et al., 2006, Henderson and Mayer, 2007). Although these codes are theoretically suitable, they have not been used to date to evaluate the long-term geochemical evolution in sedimentary basins. The effect of dissolution-precipitation reactions on porosity and permeability has also been implemented in reactive transport codes (e.g., Steefel and Lasaga, 1994, Bethke, 2002, Lichtner et al. 2004, Henderson and Mayer, 2007). In addition, the capability of these models to deal with strong salinity contrasts, locally diffusion-controlled transport, microbially mediated gas production, and relatively complex geometries needs to be evaluated.

6.1 REACTIVE TRANSPORT MODELLING IN HIGHLY SALINE SOLUTION

An important aspect of reactive transport modelling is the appropriate evaluation of activity coefficients both under dilute and highly saline conditions. Most reactive transport codes rely on the Davis equation or some form of the extended Debye-Huckel equation to determine the activity of dissolved ions as a function of ionic strength. However, these activity relationships are only applicable in relatively dilute solutions up to an ionic strength similar to that of sea water. Highly saline solutions and brines found in sedimentary basins require an alternative approach for calculating the activities of dissolved ions. One of the most common approaches is the Pitzer ion interaction model (Pitzer, 1973, Pitzer, 1991). The Pitzer ion interaction model is based on a virial expansion, which reduces to a modified Debye-Huckel formulation at low concentrations (Lichtner and Felmy, 2003). In addition to the effects of the formation of complexes and ion pairing, activity coefficients calculated using the Pitzer formalism account for electrostatic interactions and ion hydration effects (Lichtner and Felmy, 2003).

The Pitzer equations have been implemented in geochemical equilibrium models to extend their applicability to high ionic strength solutions. For example, the Pitzer formalisms were introduced into the PHREEQE code, resulting in PHRQPITZ (e.g. Plummer et al., 1988, Plummer and Parkhurst, 1990). More recently, the Pitzer equations were also successfully implemented in a number of reactive transport codes (Bethke, 2002, Lichtner and Felmy, 2003, Bachler and Kohl, 2005, Zhang et al., 2005) and in version 2.12 of PHREEQC (Parkhurst and Appelo, 1999), which is also available in PHAST (Parkhurst et al., 2004). Although the Pitzer ion-interaction model is complex in nature, implementing the equations in reactive transport models does not pose a major difficulty. The activity coefficients are calculated on a nodal basis and can be lagged a time step behind the reactive transport calculations (Lichtner and Felmy, 2003), which simplifies the solution algorithm while not significantly affecting the accuracy of the results. In addition, a numerical implementation of the Pitzer equations is available as public domain software through the USGS (PHRQPITZ, e.g. Plummer et al., 1988, Plummer and Parkhurst, 1990). This computer code and the associated database can be modified and implemented in other reactive transport models. Applications of reactive transport models that include activity corrections based on the Pitzer equations include the assessment of contaminant transport at the Hanford tank farm (Lichtner et al., 2004, Zhang et al., 2005), dolomitization in a regional carbonate aquifer (Jones and Xiao, 2005), and the simulation of a geothermal energy system (Bachler and Kohl, 2005).

One of the main limitations of the Pitzer approach is that a large number of ion interaction parameters are required. These parameters can only be obtained through extensive laboratory experimentation over a range of pressures and temperatures (Lichtner and Felmy, 2003). As a result, parameters are only available for a select group of ions. However, progress has been made during recent years and in addition to the available ion interaction parameters for major ions, Pitzer coefficients have been obtained for select Si and Al species (Park and Englezos, 1999, Felmy et al., 2001). Moller et al. (2007) report further progress with respect to the inclusion of Al and Si species into the Pitzer equations, and data for select trace elements are also becoming available (Lichtner and Felmy, 2003).

For the reactions that control salinity in sedimentary basins (equations 1-6), the present set of Pitzer parameters already provides a suitable foundation for reactive transport calculations. Combined with the fact that source code is available, there appear to be no major obstacles for implementing the Pitzer ion interaction equations into reactive transport models.

For the investigation of the long-term evolution of groundwater geochemistry in sedimentary basins, it is also not anticipated that the computational burden associated with using the Pitzer activity correction will be limiting.

6.2 SPECIES DEPENDENT MULTICOMPONENT DIFFUSION

Due to the low permeability of aquitard units, mass transport in these rocks is often diffusion-controlled (Mazurek, 2004). Although diffusive transport is commonly described by Fick's law, it is well known that its applicability is limited, in particular in electrolyte solutions and in fine grained porous media rich in clay minerals (Oelkers, 1996, Appelo and Wersin, 2007).

Fick's law assumes that diffusion is solely a function of a concentration gradient, and that interactions between different solutes do not take place. This is not strictly true because many ions present in solution carry a charge. As a result, the migration of ions by diffusion causes a charge imbalance, resulting in an electrical field that drives electrochemical migration to counteract the charge imbalance (Lichtner, 1996). The generation of a charge imbalance due to diffusive migration is aggravated because each ion has a unique diffusion coefficient (Lichtner, 1996), leading to different rates of migration. Failure to account for the effect of electrical potential and interactions between the ions can lead to large errors in mass balance calculations (Oelkers, 1996, Li et al., 2007). In extreme cases, "diffusion" of a charged ion can occur in the direction against its concentration gradient. This is of particular importance in regions of steep concentration gradients, such as boundaries between aquifer and aquitard units and in solutions with high ionic strength. As a result, to adequately describe multicomponent transport in diffusion-dominated systems, a formulation is required that includes species-dependent diffusion coefficients and an electrochemical migration term (Lichtner, 1996, Oelkers, 1996, Giambalvo et al., 2002).

Additional complications are introduced if diffusion occurs in fine grained deposits containing reactive mineral surfaces with high surface areas. In these materials, charged ions participate in surface complexation reactions. Most mineral surfaces are negatively charged, which favors surface complexation of cations. Some cations do not form inner-sphere surface complexes at the mineral surface, but remain predominantly in the diffusive double layer (DDL), a layer of stagnant water surrounding the minerals. The ions remain mobile in this region and are still able to diffuse along a concentration gradient. These processes enhance cation migration, but limit the migration of negatively charged species by anion exclusion (Appelo and Wersin, 2007). The thickness of the diffusive double layer is a function of salinity and decreases with increasing ionic strength (Stumm and Morgan, 1996, Boudreau et al., 2004). However, according to Appelo and Wersin (2007), even for solutions with an ionic strength similar to seawater, a significant fraction of cation migration may occur in the DDL.

Despite the shortcomings of Fick's law, multicomponent diffusion formulations have not been used commonly in reactive transport modelling studies. For example, Pearson et al. (2002) conducted a reactive transport study for the Opalinus Clay under diffusion-controlled conditions based on Fick's law. The authors of this work acknowledge that the mismatch of observed and simulated data and uncertainties of the model predictions may be partially attributable to the use of a single diffusion coefficient for all species. More recently, Appelo and Wersin (2007) used a modified version of PHREEQC to simulate multicomponent diffusive transport of tritium, iodide, and sodium in Opalinus clay and accounted for surface complexation reactions. Laboratory data and simulations demonstrated that tortuosity was increased for iodide (a negatively charged ion) due to anion exclusion, while it was lowered for sodium

(positively charged) due to enhanced migration in the diffusive double layer. Other applications of multicomponent diffusion models have focused on migration of Cl^- , Na^+ , K^+ and OH^- in concrete (Truc, 2000, Lorente et al, 2003).

Mathematical formulations for multicomponent diffusion controlled by electrochemical gradients, including species-dependent diffusion coefficients, and considering surface complexation are available (Oelkers, 1996, Truc et al., 2000, Appelo and Wersin, 2007). The development effort associated with the implementation of multicomponent diffusion into reactive transport models is considered moderate.

6.3 OTHER PROCESSES AND DISCRETIZATION ISSUES

The occurrence of glaciation and deglaciation events contributes additional complexity to the system under consideration. The advance of an ice sheet over sedimentary rocks affects the stress regime in the subsurface, which may in turn affect porosity and hydraulic conductivity of both aquifer and aquitard units. The weight of the ice sheet may also result in a change in land surface elevation due to compression of the lithosphere with subsequent rebound following deglaciation. Together, these processes cause transient changes in boundary conditions and system properties which may affect the flow regime and reactive transport. However, to date there have been no attempts to implement or couple these processes within a reactive transport modelling context. Considering the significant complexity associated with simulating glacial compression and rebound, as well as multicomponent reactive transport, it does not appear to be warranted to develop a combined model at this stage. The development effort is expected to be significant, and computational requirements would likely be prohibitive and not allow beneficial use of such a model.

As pointed out by Martini et al. (1998) and McIntosh et al. (2002, 2004), the generation of biogenic gas (predominantly methane) may occur in sedimentary rock systems, in particular if fresh water ingress occurs into units with abundant organic matter. Although gas solubility increases with depth, exsolution may occur if gas generation is significant. Under these conditions, it may be possible that resident groundwater is displaced, that gas is transported towards the ground surface along bedding planes or fracture systems, and that the relative permeability for water flow is reduced. An adequate description of these processes would require a multi-phase flow approach coupled with a reactive transport model. Modelling techniques and formulations for implementing multi-phase flow are available; however, the effort of implementation into a reactive transport model is significant because gas migration and generation need to be coupled directly. The TOUGH-REACT code (Xu and Pruess, 2001), which has been applied at the Yucca Mountain site (Spycher et al., 2003), is probably the most advanced reactive transport code that contains multi-phase capabilities. However, simulations that couple multi-phase flow and reactive transport on the time and spatial scales of interest in the current context are beyond today's computing capabilities. To adequately describe gas generation, it will also be necessary to account for the fact that microbially mediated reactions are inhibited in the presence of highly saline solutions or brines. Including inhibition as a function of salinity is not a common feature in reactive transport codes; however, provided that a functional relationship is available that adequately describes this dependence, its numerical implementation is expected to be straightforward.

Flow, transport and reaction processes can also be affected by heat flow, which is not often included in reactive transport models. Temperature is directly coupled to fluid density; however, for the strong salinity gradients observed in sedimentary basins, it can be expected

that salinity-induced density gradients will overwhelm temperature-induced density changes. The effect of temperature on mineral solubilities and biogeochemical reaction rates may be more significant. Although the simulation of heat flow may be required for the investigation of reactive transport in the near field of a nuclear waste repository (Spycher et al., 2003), it may be sufficient to base simulations on a depth-dependent temperature profile (e.g. Mayer et al., 2006) if the temperature field is a function of depth, for example determined by a geothermal gradient. Formulations for heat flow and conduction in the subsurface area available and the implementation effort is considered moderate.

Lastly, most reactive transport models developed to date rely on an orthogonal grid structure, which is typically chosen to facilitate local mass conservation – a requirement for reactive transport codes. However, such a discretization scheme makes it awkward, although not impossible, to discretize sedimentary basins including multiple aquitard and aquifer formations. This is particularly true near basin margins, where these units outcrop. A more suitable formulation would be provided by a control volume finite element discretization (e.g. Durlofsky, 1994), which to the best of our knowledge has not been incorporated to date in multicomponent reactive transport models. The effort for implementing an unstructured grid is considered moderate to significant.

7. RECOMMENDATIONS AND FUTURE WORK

Although modelling studies have been conducted to evaluate the influence of glacial recharge into sedimentary basins (Boulton et al., 1994, Person et al., 2003, McIntosh et al., 2005, Person et al., 2007), none of these studies have considered the effect of geochemical reactions on groundwater salinity, pH or redox conditions. The major recommendation of this review is that work needs to be initiated in this area to, as mentioned in Section 1, provide a means to demonstrate how groundwater composition could evolve in relation to hydrological perturbations that may result from glaciation of sedimentary rock sequences.

Three major categories of recommendations are made which relate to a) model developments and improvements, b) model applications to evaluate the conceptual models discussed in this report, and c) model parameters and boundary conditions that are required to constrain the simulations.

7.1 MODEL DEVELOPMENT AND IMPROVEMENTS

None of the computer codes currently available is capable of simulating reactive transport in sedimentary basins over time scales of > 10,000 years, while including all processes introduced above. The review conducted by MacQuarrie and Mayer (2005) compared different reactive transport modelling techniques and model implementations and demonstrated that the MIN3P code (Mayer et al., 2002) has comparable capabilities to other state-of-the-science reactive transport models. The MIN3P code has previously been used to assess redox stability in crystalline rock of the Canadian Shield (Spiessl et al., 2007), and we recommend to further improve this model to meet the needs for simulations in sedimentary systems. Specifically within the context of the MIN3P code, there is a need to address several of the outstanding issues discussed in Section 6. Namely, we are recommending that the code be improved to handle the following situations:

- High ionic strength solutions – as identified throughout this report, the presence of brines in sedimentary formations, or the evolution of fresh water towards a brine, means that there is a need to have specific formulations for activity coefficients and ionic strength effects. Implementation of the Pitzer formulations currently appears to be the most appropriate way to deal with this need.
- Species dependent diffusion – the inclusion of species dependent diffusion has been identified as important to adequately describe diffusion dominated transport, particularly when dealing with low hydraulic conductivity units. Diffusion coefficients among species vary by a factor of up to 10 (Lichtner, 1996), diffusive transport may be significantly affected by electrochemical forces, under extreme conditions causing diffusion against the concentration gradient (Oelkers, 1996), and interactions with charged mineral surfaces in fine grained deposits causes significant differences in migration characteristics between anions and cations (Appelo and Wersin, 2007). These considerations suggest that using a single diffusion coefficient for all species, and ignoring electrochemical migration and the effect of surface charge can lead to an erroneous assessment of transport behaviour under diffusion controlled conditions. It is recommended that species dependent diffusion be implemented in MIN3P because this will allow the code to more comprehensively deal with diffusion-controlled reactive transport.
- Inhibition of microbial activity as a function of salinity – an interesting and potentially important finding of the review is that high salinity solutions may act to retard microbial activity. Such an effect may have significant implications for simulating reactive transport in sedimentary rock sequences and it is recommended that formulations which simulate this effect should be developed and implemented in MIN3P. In this context, it can also be evaluated to what degree rates of kinetically controlled inorganic reactions are affected by changes in fluid density.

Other outstanding issues which have been identified in Section 6 will also require future model developments and improvements. Perhaps most importantly is the issue of discretization of domains to adequately deal with sedimentary rock sequences. While the current orthogonal discretization capabilities of MIN3P would allow for simulation of local scale problems (e.g. diffusive-reactive transport within a single horizontal aquitard unit), the simulation of larger scale aquifer-aquitard systems, which dip inward from the basin margin, will benefit from an improved discretization method. It is therefore recommended that work be initiated to implement a method of discretization that will allow for simulation of gently-dipping sedimentary units.

7.2 MODEL APPLICATIONS

Application of reactive transport models to evaluate the potential conceptual models presented in this report is recommended; however, it must be acknowledged this cannot be done in isolation from other studies that are currently aimed at understanding ice sheet dynamics and large-scale regional groundwater flow in sedimentary basins. For example, to conduct reactive transport modelling studies with boundary conditions that adequately reflect the current understanding of future permafrost conditions and glaciation/deglaciation cycles in southern Ontario, it will be necessary to investigate more thoroughly the findings that have been obtained using the University of Toronto's Glacial Systems Model. To evaluate potential 3D effects created by ice sheet lobes that could develop over a portion of the sedimentary basin (e.g. Figure 2d), it may be necessary to conduct more detailed coupled ice sheet-regional groundwater flow modelling in addition to reactive transport modelling. However, the simulation of reactive transport in 3D, on a basin-wide scale, is currently not recommended due to the

significant computational demands of such a model. Reactive transport modelling should focus on assessing geochemical evolution and potential feedbacks between flow, transport and reaction processes in 1D and 2D scenarios. Information gained from these simulations will be useful to assess overall system evolution on a basin-wide scale.

Reactive transport modelling studies in 1D (e.g. for simulating solute profiles in single aquitards) or 2D (as depicted in Section 5) are considered both computationally feasible and informative from the point of view of supporting DGR stability. It is therefore recommended that reactive transport modelling initially be applied to 2D cross sections that focus on the units of interest at the basin margin (as shown in Figures 2a and c), similar to the approaches taken by Person et al. (2003) and McIntosh et al. (2005).

7.3 REQUIRED MODEL PARAMETERS AND PARAMETER UNCERTAINTY

Due to the large number of processes involved, reactive transport simulations require a significant number of input parameters. It is necessary to define the geometry, material parameters, and initial conditions in each of the sedimentary units. In addition, it is required to define boundary conditions for flow and transport and the parameters that control the progress of biogeochemical reactions. The following provides a more detailed summary of the required input parameters:

- Geometry and thicknesses of various sedimentary formations.
- Time frame of simulation.
- Hydraulic conductivities and porosities of various sedimentary units, possibly including spatial or depth-dependent variation within these units.
- Boundary conditions for flow (hydraulic heads or recharge fluxes) and transport (recharge water composition) for present day and future conditions. The boundary conditions must account for the effect of ice sheet advance and retreat including the potential development of permafrost conditions.
- Initial conditions including groundwater composition and sediment composition (mineralogy, organic carbon content, and cation exchange capacity) parameters need to be specified for the various sedimentary units.
- Equilibrium constants and rates of biogeochemical reactions.

The various uncertainties that have been raised with respect to the potential conceptual models, for example the vertical hydraulic conductivities of shale units and local permeability enhancements in limestone units, could then be investigated in a quantitative manner. Likewise, issues related to density distribution and fluid composition, sediment composition (e.g. mineralogy and TOC - information which is currently sparse), and porosity and permeability distributions could be feasibly explored in 2D reactive transport simulations.

8. SUMMARY AND CONCLUSIONS

This review was conducted to determine if multicomponent reactive transport modelling can contribute to the assessment of the long-term geochemical evolution and stability in sedimentary rock systems. A scenario of specific interest is the infiltration of glacial melt water into rock units of sedimentary basins during glaciation and deglaciation cycles. A literature review has shown that there is evidence for the past occurrence of melt water infiltration to

several 100's m depth in a number of sedimentary basins. However, the lack of evidence for deep melt water ingress in southwestern Ontario suggests that processes controlling melt water recharge in that region may differ from other parts of the Michigan basin. The literature shows that geochemical reactions are indeed of importance and control the compositional evolution of the infiltrating melt water, both in terms of salinity and redox state. In addition, diffusion-controlled transport in low permeability units may also be affected by rock-water interaction due to anion exclusion and preferential migration of cations in the diffusive double layer. In both cases, multicomponent reactive transport modelling is required to explain changes in groundwater composition on a mechanistic level and to adequately describe solute transport.

The suitability of existing model formulations for assessing the systems of interest was also evaluated. In terms of geochemical reactions that are of key relevance in sedimentary basins, adequate model formulations are currently available. The most important reactions include aqueous complexation, ion exchange, mineral dissolution-precipitation and microbially mediated oxidation-reduction reactions. Due to the strong salinity contrasts, it is deemed necessary to employ a model that considers the coupling between geochemical reactions and density-dependent flow and transport. To adequately describe diffusive transport in low permeability units, it appears that a formulation that is based on a single average diffusion coefficient for all species is insufficient. Diffusion coefficients among species vary by an order of magnitude, diffusive transport may be affected by electrochemical gradients, and interactions with the diffusive double layer in fine grained deposits cause differences in migration characteristics between cations, anions, and uncharged species. To rigorously describe diffusion dominated transport a multicomponent description with species-dependent diffusion coefficients, electrochemical migration, and surface complexation is required.

To our knowledge, multicomponent reactive transport modelling has not yet been used to investigate the evolution of sedimentary rock sequences in response to glaciation events. However, simulations of CO₂-sequestration and CO₂-escape from aquifers used for sequestration, as well as seawater infiltration into freshwater aquifers show similar characteristics in terms of geochemical complexity, although these studies have been conducted on a smaller scale. The success of these simulations nevertheless suggests that it is feasible to also conduct reactive transport modelling for the scenario of glacial melt water infiltration. For example, reactive transport modelling can be used to clearly and convincingly demonstrate the degree to which dissolved oxygen may be attenuated in the recharge region of a DGR host rock and how rock-water interaction transforms freshwater recharge into groundwater with characteristics of a brine. In terms of diffusion modelling in low permeability media, multicomponent and species-dependent formulations have recently been applied with significant differences in diffusion rates as a function of solution composition and the role of surface complexation reactions (Appelo and Wersin, 2007).

Although multiple reactive transport codes with advanced capabilities exist, none of the currently available models meets all requirements for simulating the geochemical evolution of sedimentary basins in response over time periods of > 10,000 years. The MIN3P code (Mayer et al., 2002) belongs to a select group of state-of-the science reactive transport codes (MacQuarrie and Mayer, 2005) that meet many of the requirements and already contains a geochemistry-density coupling and a relationship to account for permeability and porosity changes. In addition, this code has previously been used to study redox stability in crystalline rocks of the Canadian Shield (Spiessl et al., 2007). To ensure continuity and to improve the capabilities of the MIN3P code for sedimentary rock systems, it is recommended to implement a) the Pitzer ion interaction model, b) a modified formulation for microbially mediated reactions that accounts for inhibition as a function of salinity, c) a formulation for multicomponent and

species-dependent diffusion, and d) discretization methods that facilitate the generation of unstructured grids that are better capable of dealing with irregular geometry and outcropping aquifer and aquitard units.

Multicomponent reactive transport modelling provides an approach to investigate a series of possible conceptual models and assess parameter sensitivity for groundwater evolution in sedimentary rocks. Similar modelling studies would also be useful for reconstructing past melt water infiltration events, and visualizing how groundwater salinity and redox state may have evolved. These studies could be supported by available paleohydrogeologic data.

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**APPENDIX A: A REVIEW OF RECENT STUDIES DEALING WITH REACTIVE TRANSPORT
MODELLING IN SEDIMENTARY ROCK SEQUENCES**

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A.1 REVIEW OF REACTIVE TRANSPORT MODELLING STUDIES

Several recent studies are reviewed here to provide examples of how reactive transport models have been applied in sedimentary rock systems, and to gain an appreciation of the model capabilities that may be required. Because there are few examples that deal directly with issues related to deep geological repositories (DGR), studies from other fields such as CO₂ sequestration have also been considered.

One of the few studies that have directly employed reactive transport modelling for interpreting geochemical data from a potential DGR host rock is that of Pearson et al. (2002). They applied the PHREEQC code to simulate 12 to 15 million years of 1D diffusive transport coupled with geochemical reactions in the Opalinus Clay formation at the Mont Terri Rock Laboratory in northern Switzerland. The objective of the modelling was to better understand the transport and reaction processes that were responsible for dilution of sea water, which was assumed to be initially present in the claystone pores, by fresh groundwaters that has subsequently invaded adjacent formations. The reactions that were considered included (Pearson et al., 2002): dissolution-precipitation of quartz, calcite, dolomite, pyrite and celestite, plus ion exchange of Na⁺, K⁺, Ca²⁺, Mg²⁺ and Sr²⁺. The measured data and modelling results were in reasonable agreement for the major cations, with the exception of Mg²⁺, while there was a systematic disagreement between the simulated results and measurements for carbonate and pH. Although the reasons for these disagreements were not fully resolved, Pearson et al. (2002) have noted that the model should be considered preliminary because of over-simplified assumptions including invariant boundary conditions, no flow or solute transport through the bottom of the sequence, and the use of a single value of diffusion coefficient for all species.

Gurban et al. (2003) have applied two different modelling approaches, hydrochemical mixing and mass balance (M3 code) and reactive transport (HYTEC code), to two natural analogue reactor zones, Bangombé and OK84 at Okélobondo. Although the two sites differ with respect to the depth of the uranium reaction zone, the geological materials at both consist of sandstones and pelites, which in some locations are rich in manganese. Both sites have waters of relatively low ionic strength and issues related to activity corrections were not discussed. The results of the modelling generally agree with the limited field data, in that uranium is initially oxidized at Okélobondo, but then quickly attenuated down gradient by inorganic reactions, while at Bangombé a redox buffer zone that is rich in organic matter consumes dissolved oxygen and protects uraninite from dissolution. The authors conclude that the two modelling approaches considered are complementary. The mixing and mass balance model can be useful for an initial assessment of the field data and for determining the likely biogeochemical reactions causing deviations from ideal mixing of end members, while the reactive transport model gives a spatial and temporal description of the reactions and can be used to test several hypotheses regarding uranium transport.

Reactive transport modelling has recently been employed in several studies related to the injection (sequestration) of CO₂ into sedimentary rock sequences. Gaus et al. (2005) investigated the major reactions occurring when CO₂ is injected into a saline aquifer which is overlain by up to 250 m of shale cap rock. The reactive transport domain was limited to the shale cap rock, and it was assumed that dissolved CO₂ would migrate vertically upward by diffusion from a supercritical CO₂ gas bubble trapped at the sandstone-shale interface. Gaus et al. (2005) assumed that the cap rock mineralogy was homogeneous, consisting primarily of quartz (21.5% by mass), mica/illite (24.7% by mass), and kaolinite (18%), with an assumed initial porosity of 5%. The modelling investigation was performed in stages, starting with batch modelling (assuming equilibrium or kinetic reactions) and advancing to 1D reactive transport

modelling. Rate constants were selected from the literature, while reactive mineral surface areas were estimated from geometric equations for spheres and a “scaling factor” of 0.001 (ratio of reactive surface area to geometric surface area). Gaus et al. (2005) used the same diffusion coefficient for all species (based on the value for CO₂) and argue that this approach does not affect the accuracy of the results because the variation in diffusion coefficients among various aqueous species is an order of magnitude smaller than the range they computed for the effective diffusion coefficient of CO₂. In addition, although Gaus et al. (2005) note that the Pitzer approach for activity coefficients would be the optimal choice for this problem, this approach was not applied because aluminum speciation was considered crucial and aluminum speciation with the Pitzer approach was not currently possible. Development of aluminum speciation within the context of the Pitzer interaction equations appears to be ongoing (e.g. Moller et al., 2007).

For the equilibrium batch modelling of CO₂ injection, the results suggest large changes in the clay mineral volumes (and porosity), with the dissolution of smectites and illite and precipitation of chalcedony, kaolinite, K-feldspar and large amounts of calcite. When compared to the results of the kinetic batch model at a time of 15,000 years, the equilibrium batch model results are questionable, and the authors caution that the results of equilibrium batch models may be erroneous for assessing the progress of reactions in the shale cap rock.

The PHREEQC code was employed by Gaus et al. (2005) to conduct 1D diffusion-reaction simulations. The results show that if plagioclase is assumed to be present only as albite, then CO₂ migrates at a rate that is comparable to non-reactive diffusion; however, if plagioclase is assumed to be present as a 50:50 albite:anorthite, then CO₂ migration into the cap rock is significantly retarded by reaction with anorthite. Reaction with anorthite limits the migration of elevated CO₂ concentrations to within the lower metre of the cap rock after 3000 years, and the maximum porosity decrease is less than 3%. Not surprisingly, Gaus et al. (2005) conclude that having access to detailed mineralogical data when assessing the impact of geochemical reactions on the safety of CO₂ sequestration remains crucial. Although the feedback of porosity changes on effective diffusion coefficients was not considered in the study, the computed decrease in shale porosity can be expected to cause a reduction in effective diffusion coefficients, which would serve to further limit CO₂ migration into the shale unit.

Xu et al. (2005) have applied the reactive fluid flow and geochemical transport code TOUGHREACT to analyze mass transfer between sandstone and shale layers and CO₂ immobilization through carbonate precipitation. They considered a simplified horizontally bedded sandstone-shale system over a time period of 100,000 years, with the sandstone represented by one model grid block (i.e. perfect mixing) and 1D diffusion being the main transport process in the shale bed. Specific attention was paid to critically evaluating and updating the thermodynamic data for carbonates, chlorite, and kerogen. Even though the salinity of the formation water they were simulating was about 1 mol NaCl/L (i.e. I ~ 1), Xu et al. (2005) used the extended Debye–Hückel equation to compute activity coefficients (with the exception of CO₂(aq)).

Simulation results indicate that most CO₂ sequestration occurs in the sandstone, with the major CO₂ trapping minerals being dawsonite and ankerite. Interesting reversals in transport occur for certain species; for example, Fe²⁺ and Ca²⁺ initially diffuse from the shale into the sandstone to supply reactants for precipitation of siderite and ankerite, but later (~ 100,000 years) the diffusion of these species reverses direction. Xu et al. (2005) conclude that the sequestration time depends on the rates of mineral dissolution and precipitation, which are

products of the kinetic rate constant and reactive surface area. Scaling kinetic rates for all minerals by the same factor is equivalent to scaling the time coordinate.

Although the CO₂ sequestration simulations have been conducted in geological settings that share some similarities with the sedimentary rock sequences being considered for waste repositories, the modelling investigations are typically localized to either consider processes in the shale cap rocks, or the immediate vicinity of the sandstone-shale interface. This is appropriate considering the localized nature of CO₂ injection at significant depths. It does not appear that any long-term changes in surface boundary conditions have been considered in CO₂ sequestration modelling investigations; however, Xu et al. (2005) suggest that regional groundwater flow may be sufficiently slow so as to maintain chemical gradients within the sandstone aquifers.

Reactive transport modelling at larger scales, and considering additional factors such as density-dependent flow, has been conducted to investigate the mixing of saline and fresh water in coastal carbonate aquifers or deep hydrothermal systems. Based on the findings from a 1D reactive transport investigation, which showed that saturation indices cannot be used to predict the extent of calcite dissolution when mixing controls the overall rate of dissolution, Rezaei et al. (2005) simulate seawater-freshwater mixing in a 2D coastal carbonate (i.e. calcite) aquifer. Their study closely parallels earlier work by Sanford and Konikow (1989) and considered fluid density variability, reactive transport, and porosity enhancement by calcite dissolution. Results from the RETRASO model indicate that the maximum dissolution of calcite occurs near the saline side of the groundwater discharge zone because of a very active convection cell that develops there, which enhances mixing and thus reaction rates (Figure A.1). A maximum porosity increase rate of 24% every 10,000 years occurs in this area of the domain; however, over the majority of the mixing zone the rate of porosity increase is between 1 and 5% per 10,000 years. The feedback between porosity and hydraulic conductivity, which was not considered in the modelling, may tend to further focus the zone(s) of dissolution. In this advection-dominated flow system the overall amount of calcite dissolution tends to increase with larger values of dispersivity because larger values will enhance the mixing rate; however, the changes in porosity enhancement as a result of variations in dispersivity were relatively minor (Rezaei et al., 2005).

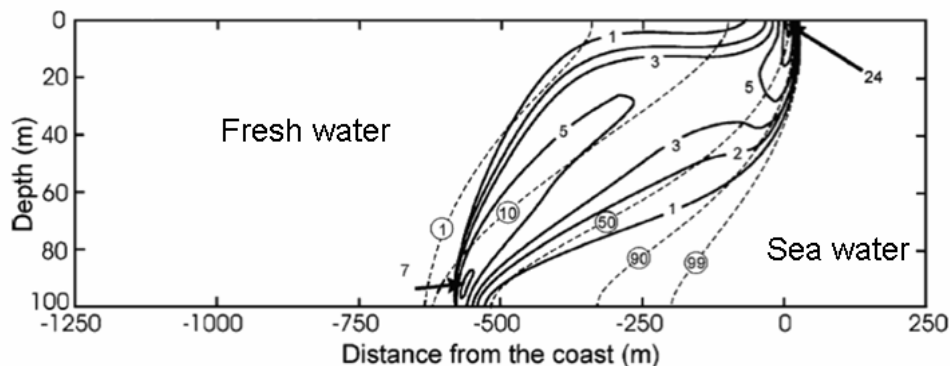


Figure A.1: Example of porosity evolution due to mixing of fresh water and sea water in a coastal aquifer system (Rezaei et al., 2005). The solid contours indicate the porosity increase in % during a simulation period of 10,000 years, while the dashed lines are contours of % sea water.

Corbella et al. (2003) also used the RETRASO model to simulate a relatively high temperature system (150°C) in which a dilute fluid and a brine were mixed. The main conclusion of this work was that the mixing of hydrothermal solutions of different chemistry, and saturated with respect to calcite, causes both precipitation and dissolution of this mineral in separate zones of the domain.

Jones and Xiao (2005) have investigated dolomitization, anhydrite precipitation, and porosity evolution in regional carbonate aquifers. They applied the isothermal Xt2 code (Bethke, 2002) which solves the coupled governing equations of transport (fluid mass and solute mass) and the geochemical system (mass balance, equilibrium reactions, and kinetic reactions) in two dimensions. The modelling scenario considered a hypothetical two-dimensional (500 m deep by 10 km wide) carbonate aquifer, initially containing sea water which is displaced by brines of differing chemistry. The geochemical model included three solid species (calcite, dolomite, and anhydrite) and 32 aqueous species. The Pitzer equations were employed for calculating mineral equilibria in solutions more concentrated than sea water. Because they noted a relatively rapid change in porosity, Jones and Xiao (2005) included a feedback with the aquifer permeability.

Starting with a base case scenario, Jones and Xiao (2005) varied parameters individually to investigate the sensitivity of the dolomite (precipitated), anhydrite (generally precipitated), and porosity distributions for simulation times up to approximately 1 million years. For the range of parameters investigated, they found that dolomitization was critically-dependent on the reflux (i.e. intruding brine groundwater) velocity and the reactive surface area. Temperature was also important because of its effect on the reaction rates. Dolomitization resulted in a porosity increase of 8% (with an initial porosity of 35%) that is consistent with the mole-for-mole replacement theory favored by Weyl (1960). The increase in porosity by dolomitization was offset by the precipitation of anhydrite, which occluded porosity by 0–22% ahead of the dolomitization reaction front (Jones and Xiao, 2005). The feedback relationship between porosity and permeability was a relatively moderate control on the evolution of dolomitization; however, it was noted that predicting crystal size from mineral reactions is beyond the capabilities of current reactive transport models, which thus limits the ability to predict permeability from porosity (Jones and Xiao, 2005).

In studies that have focused on porosity enhancement in carbonate aquifers, it appears that it has not been common to consider interactions with adjacent aquitard units. Again, because these units would be expected to have little influence on the processes occurring in the more permeable carbonate aquifers, this may be a reasonable simplification. Such a conceptual model may be applicable to the investigation of long-term changes in boundary conditions in sedimentary sequences, and could constitute a first-order modelling approach if aquitard units can be assumed to isolate individual aquifers. However, the interaction of aquifers and aquitards will increase in importance if shale units have increased permeabilities caused, for example, by fracturing.

This review of recent literature indicates that several studies have considered various aspects of reactive transport modelling that are relevant to investigation of waste disposal in sedimentary rock sequences of southern Ontario. The study of Pearson et al. (2002) has considered the effects of diffusive transport and reactions driven by fresh water ingress into aquifers bounding a potential host rock (Opalinus Clay), while modelling conducted within the context of CO₂ sequestration has considered in detail the reactive transport processes occurring in shale aquitard units and highlighted the importance of having detailed initial mineralogical characterization. Several studies have also focused on the mixing of different water types in carbonate aquifers with spatial and time scales that are of relevance to nuclear waste isolation

(e.g. 10,000 to 1 million years). In addition, the influence of variable fluid densities, heat transport, and high ionic strength on aqueous geochemistry have been considered in some studies. One common theme of previous studies is that of simulating porosity evolution in aquifers and aquitards, and in some cases the feedback between porosity and permeability. Species-dependent diffusion coefficients have not been commonly applied in reactive transport modelling in sedimentary rock sequences; however, Li et al. (2007) note that large errors can be introduced in saline solutions by using a fixed diffusion coefficient, although the effect of ignoring electrochemical migration appears to be minor.

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