

Coupled Phenomena in Environmental Geotechnics

Editors: Mario Manassero Andrea Dominijanni Sebastiano Foti Guido Musso



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From theoretical and experimental research to practical applications

Editors

Mario Manassero, Andrea Dominijanni, Sebastiano Foti & Guido Musso

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Preface

Environmental Geotechnics deals with a wide variety of applications, such as the characterization of polluted sites and landfill waste, the design of containment systems for subsoil pollutant control, radioactive waste disposal, geo-energy exploitation and bacteria-driven soil modification, among others. In order to obtain reliable and effective predictions of the actual behavior and performance of these very complex systems, theoretical and experimental research and advanced design procedures need to take into account the coupled hydro-bio-chemo-mechanical phenomena that occur at very different scales. Future progress in the scientific state of the art and substantial advancements in standard practices will therefore be closely related to the development of shared knowledge among different disciplines. The extension and refinement of theoretical modelling and the experimentation capabilities stimulated by geo-environmental applications more in general provide the framework for substantial advancements in the soil and rock mechanics fields.

The International Society for Soil Mechanics and Geotechnical Engineering (ISSMGE) has contributed to these developments through the activities of an ad hoc Committee (TC 215 – Environmental Geotechnics – formerly TC 5). The committee was established under the ISSMGE presidency of Prof. M. Jamiolkowski (1994–1997) and has been very active ever since. Several very lively conferences, symposia and workshops have been organised culminating in the 6th Edition of the International Conference on Environmental Geotechnics (TC 215 – ICEG) which was held in New Delhi, India (2010).

Following this tradition, the international symposium, organised by ISSMGE TC 215 in July 2013 in Torino (Italy) has focused on 'Coupled Phenomena in Environmental Geotechnics – from theoretical and experimental research to practical applications'. The conference has been considered an opportunity to discuss and share knowledge, skills and front-edge research activities in the field. By including contributions not only from the geotechnical community, but also from related and complementary disciplines, the conference has gathered new experimental evidence, contributions to theoretical developments and innovative applications.

The present volume collects the special lectures and the papers that have been presented at the symposium, which cover a wide range of fundamental and applied research on geo-environmental engineering topics. Four sessions of the symposium have dealt with landfills: waste characterization, stability problems, lining and capping systems. Three sessions have been devoted to polluted sites and their interaction with aquifers both in terms of characterization and remediation strategies. The remaining two sessions have focused on the emerging topics of energy issues and bio-chemical processes.

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Special papers Keynote lectures This page intentionally left blank

Recent advances in understanding and improving the performance of lining and capping systems for landfill and mining applications

R. Kerry Rowe

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ABSTRACT: The available evidence suggests that both geosynthetic clay liners (GCLs) and composite liners with a geomembrane (GMB) over a clay liner have performed extremely well at controlling leakage in field applications for a couple of decades. However there have also been some problems reported and recent research has allowed us to have a much better understanding of the key design and construction factors affecting good and poor performance. This paper examines some of these issues including factors affecting GCL performance such as the water retention curve of GCLs, subgrade grain size and initial water content, GCL water content and normal stress on the GCL, the effect of daily thermal cycles on hydration, GCL panel shrinkage, and cation exchange. Factors affecting composite liner performance examined include the potential for desiccation of the clay liner under a sustained thermal gradient, GMB/GCL interface transmissivity, wrinkles in the GMB when the ballast layer is placed over the composite liner, and the potential interaction between wrinkles and GCL panel overlaps. Recent insights regarding leakage through composite liners are discussed. Although a number of potential issues with liner performance are discussed, it is concluded that all can be addressed by appropriate design, material selection, construction, and operations.

1 INTRODUCTION

Liners have been an essential component of modern municipal solid waste (MSW) and hazardous waste landfills for 20–30 years and more recently are becoming an essential component of many mining undertakings where applications include ponds for storage of liquids generated by mining, and liners for tailings dams and heap leach pads. Likewise, covers have been an important part of landfill design for decades. In mining, for many years there has been a recognized need for engineered covers for minimizing impacts due to acid generating waste rock however there is growing need for covers for other mine waste (e.g., arsenic bearing gold mine tailings).

High density polyethylene (HDPE) geomembranes (GMBs) have been used in landfill liners and covers, and for liners in ponds and heap leach pads for mining applications, but there has also been growing use of linear low density polyethylene (LLDPE) GMB liners in heap leach applications. Geosynthetic clay liners (GCLs) and compacted clay liners (CCLs) have been used alone in covers and in some bottom liners, however GCLs used in landfill applications are most commonly used with a GMB to form a composite liner.

Given the long history of the use of liners in landfill applications and the research and monitoring that has been conducted with respect to that application, it is known that well designed and constructed composite bottom liners have performed very well in landfills (Bonaparte et al. 2002; Rowe 2005; Mitchell et al. 2007; Rowe 2012a). However there have also been challenges when the liners have been exposed to conditions not anticipated in the design and where, until very recently, there has been a paucity of research. An example of this is landfills that, due to their operations (e.g., as bioreactors) or the nature of the waste being disposed (e.g., combustion ash, aluminum production wastes etc.), are resulting in temperatures (Table 1) on or near the liner that raise concerns regarding their long-term and, in some cases, even short-term viability (Jafari et al. 2013). High liner temperatures can also be found in mining applications involving, for example, brine ponds and some heap leach pads (Table 1). There is a need for research to examine the effect of these temperatures and the exposure to different chemicals on short- and long-term liner performance.

Liners in landfill and mining covers/caps have exhibited both good and poor performance over the years. If intact, GMBs are excellent barriers to the advective migration of fluids (liquids and gases) but once they have a hole(s) or opening (e.g., due to inferior welding), they can readily transmit relatively large volumes of fluid through the hole(s) and it is for this reason that they are often used in conjunction with a clay liner to form a composite system (e.g., Rowe et al. 2004; Rowe 2005, 2012a).

When used alone, but also in some cases when used as part of a composite liner, GCLs used in covers have had mixed success (sometimes performing very well and sometimes not) in both landfill and mining applications (e.g., Melchior 2002; Adu-Wusu et al. 2002;

Table 1. Temperature on (or near) liners for different environments (after Rowe, R.K. (2012a). "Short and long-term leakage through composite liners", *Canadian Geotechnical Journal*, 49(2): 141–169.)

Environment	Temp. (°C)	Ref. ^a
Normal MSW landfills (limited moisture addition)	30–40	1,2,3,4,5
Wet landfills (e.g. bioreactor landfills) where there is a significant amount of moisture	40–60	5,6,7
Unusual MSW landfills	60-80 ^b	5
	50-60°	5
Ash monofills	46	8
	50–90 ^b	5
	65–70 ^c	5
MSW with aluminum production waste and leachate recirculation	85 ^d	9,10
	>143 ^e	9,10
Nickel heap leach pad	70	11
Ponds for highly saline fluid	70–93	12

^aReference: 1. Brune *et al.* (1991); 2. Rowe (2005); 3. Koerner & Koerner (2006); 4. Needham & Knox (2008); 5. Author's files; 6. Yoshida & Rowe (2003); 7. Koerner et al. (2008); 8. Klein et al. (2001); 9. Calder and Stark (2010); 10. Stark et al. (2012); 11. Abdelaal et al. (2011); 12. Lichtwardt & Comer (1997).

^bNo monitors on liner so liner temperature is unknown, temperature given is in waste about 3 m above liner.

^cLeachate temperature.

^dTemperature in leachate collection pipes.

^eTemperature in waste.

Renken et al. 2005; Meer & Benson 2007; Benson et al. 2010; Scalia & Benson 2011; Hosney & Rowe 2013) begging the question as to what are the factors affecting good versus poor performance?

This paper seeks to examine some recent advances in the understanding of factors affecting the performance of liners in both bottom liner and capping systems for landfill and mining applications and the implications of this new understanding regarding strategies that might be considered for improving liner performance in these applications. Since the theme of this paper is recent advances, emphasis will be placed on research published in the last few years and research about to be published, although other publications will be referenced when required to place the current advances in context. Also, because of space limitations, attention will be focused on advances in understanding related to leakage through GCLs both when used alone and when used in composite liners. The many recent advances with respect to understanding GMB performance, diffusion through liners, and liner stability relevant to the performance of both bottom liners and capping systems are not addressed here.

2 GEOSYNTHETIC CLAY LINERS

GCLs are manufactured and delivered to site on rolls that are laid down with adjacent panels overlapped

to provide a continuous layer of GCL. As manufactured, the most commonly used GCLs comprise a lower "carrier" geotextile, a layer of bentonite, and an upper "cover" geotextile. The GCL is held together by needle-punching the upper cover geotextile fibres through the bentonite and into the carrier geotextile. Many GCLs meet this broad description. For example, one single Canadian manufacturer has over 50 different GCLs that they manufacture fitting this description, with the different products having different characteristics suitable to different design/site conditions. Understanding why GCLs perform remarkably well in many situations and not well in some others requires an understanding of the many factors that can affect the performance of a GCL which include (but are not limited to): (a) the type of bentonite, (b) whether or not there is a polymer in the bentonite, (c) the mass per unit area, M_A , of bentonite, (d) the type and M_A of the geotextiles used, (e) the amount of needle-punching, (f) whether or not the needle-punched fibres are thermally fused to the carrier geotextile, (g) the presence or absence of a geofilm bonded to the GCL, the nature of the geofilm, and how the geofilm is bonded to the carrier geotextile, (h) the characteristics of the GCL panel overlap, (i) whether or not the GCL is part of a composite liner, (j) the presence of wrinkles in the GMB, (k) the initial water content and particle size distribution of the soil above and/or below the GCL, (1) geochemical interactions between the bentonite and the pore water in the soil adjacent to the GCL, (m) possible interaction of the bentonite with the fluid to be retained, (n) the amount of cover soil over the GCL, (o) the level of exposure to thermal cycles, (p) sustained thermal gradients, and (q) the stress on the GCL. The following subsections will explore some aspects of the performance of GCLs and will include consideration of the role of some of the factors noted above. Ongoing research will shed light on other factors not discussed here.

2.1 Water retention curve of GCLs

The performance of a GCL as a barrier to fluids (either liquid or gas) is intimately linked to the uptake of moisture by the bentonite in the GCL and its resulting degree of saturation. It is often implicitly assumed by designers that the GCL will be hydrated when it is needed to act as a fluid barrier. However whether or not this assumption is realized will depend on many factors. One key factor is the water retention curve (WRC) of the GCL itself (e.g., Daniel et al. 1993; Barroso et al. 2006; Southen & Rowe 2007; Acikel et al. 2011; Beddoe et al. 2010, 2011). A GCL's WRC describes the relationship between the water content of the GCL and the suction in the bentonite. The off-the-roll GCL has a very low water content and very high suction. When the GCL is placed on a subgrade with lower suction, the GCL will uptake (suck) water from that soil. This will cause the GCL water content to increase and its suction to decrease. One can expect that the uptake of water would continue until the suction in the GCL had

decreased sufficiently to come into equilibrium with the suction in the soil in direct contact with the GCL (i.e., the adjacent soil). Thus intuitively one may expect that the final equilibrium water content of the GCL will depend on the WRC of the GCL (discussed in this section) and the WRC of the adjacent soil together with the initial water content of this soil which will control it's suction (Section 2.2).

Under isothermal conditions one can expect the GCL to start at a very high suction (corresponding to its off-the-roll water content) and to move up what is called the wetting curve as it takes up moisture until it comes into equilibrium with the adjacent soil. As the GCL takes up moisture, the bentonite swells and is constrained by the needle-punching between the cover and carrier geotextiles and the overburden stress. When the overburden stress is low, most of the resistance is provided by the needle-punched fibres. If the needle punched fibres are not well anchored they can be pulled out of the carrier geotextile and there is a permanent change in the GCL. The extent of this change will depend on how well the fibres are anchored (e.g., thermally fused or not). As the GCL pulls out fibres, the reduction in resistance allows the void ratio of the GCL to increase and hence more water is required to saturate the GCL than if the fibres had not pulled out (or if there were a higher overburden stress).

If a GCL has experienced an increase in water content by moving up the wetting curve and is then heated (as discussed in later sections), the heat can drive the moisture out of the GCL and the suction increases as the water content decreases along what is called the drying curve. In general, the drying curve is different to the wetting curve and the greater the pullout of fibres during wetting the greater one might expect the difference between the wetting and drying curves to be. Thus to fully understand the hydration of a GCL, one needs to know the WRC in wetting. To understand how the GCL will respond to thermal cycles, one also needs to understand the WRC in drying.

Despite its importance to the uptake of moisture, the WRC of GCLs has received very little study. probably because of the inherent difficulty of experimentally obtaining the WRC of the bentonite when encased in geotextiles and the wide range of suctions that need to be investigated (Beddoe et al. 2010). Beddoe et al. (2011) obtained the wetting and drying WRCs of four GCL products under 2 kPa normal stress. They showed that this wetting curve varied quite substantially depending on the characteristic of the GCL as manufactured. At a given suction, the gravimetric water content was lowest for a GCL (denoted as GCL2) which was thermally treated to fuse the needle-punched fibres to the scrim reinforced nonwoven (i.e., a combination of a woven and nonwoven) carrier geotextile. This GCL reached a higher degree of saturation at a given moisture content than the other GCLs tested. The wetting curves for GCL1 (which was thermally treated to fuse the needle-punched fibres to the woven carrier geotextile) and GCL4 (with a simple needle-punched nonwoven carrier and only

Table 2. GCL Gravimetric water content of four different GCL products at saturation at 2 kPa (adapted from Beddoe et al. 2011).

	Water content at saturation			
Product	Mean (%)	Std. deviation (%)		
GCL1	166	10		
GCL2	130	5		
GCL3	205	16		
GCL4	194	8		

mechanical bonding) crossed at a suction of 10 kPa. GCL3 (with a woven carrier and only mechanical bonding) had the highest water content at any given suction.

There is always variability in manufactured products like GMBs, GCLs, and geotextiles. Recognizing this, GCLs are produced to meet minimum average roll values (MARV). The effect of the GCL characteristics, as manufactured, and the related variability is most evident for a GCL that is fully hydrated at low stress (e.g., below a GMB with little or no cover over the GMB). When saturated, there was a significant difference in the average water content and variation in saturated water content for the four most commonly used GCLs in North America (Table 2). At saturation, GCL2 had by far the lowest water content and the lowest variability (standard deviation) because the needle-punched fibres were most effectively and consistently bonded to the carrier geotextile thereby minimising fibre pullout as the bentonite hydrates and providing the best confinement of the bentonite. For GCL1, the thermal treatment resulted in the next lowest saturated water content but the bonding to the woven carrier was not as consistent as that to the scrim-reinforced nonwoven carrier of GCL2. GCL4 had a substantially higher saturated water content than GCL1 or GCL2. GCL3 had the highest mean water content and by far the highest variability indicating that the mechanical bonding of the needle-punched fibres to a woven GCL was least effective and most inconsistent in terms of constraining the bentonite as it tried to swell at low stress. Since it is the degree of saturation, rather than the actual water content, that most affects GCL performance and since both the hydraulic conductivity and diffusion coefficient are lower with a lower bulk void ratio (Petrov & Rowe 1997; Lake & Rowe 2000a,b), it follows that the lower the saturated water content the better the performance as a hydraulic and diffusive barrier (other things being equal).

Swelling of the GCL at low stress results in some pull-out of fibres that are not well anchored. This is manifested as a difference in the drying and wetting WRCs and the degree of hysteresis if the GCL is subjected to drying after hydration. The hysteresis was by far the least for GCL2 for which there was very little difference between the wetting and drying curves. Thus in field applications where the GCL may be exposed to wetting and drying cycles, such as when a GCL is below a GMB that is left exposed, one might infer that GCL2 will be less susceptible to the moisture changes that result in shrinkage of the GCL and hence predict less shrinkage for GCL2 than the other three GCLs in a real field situation.

Southen & Rowe (2007) demonstrated that the WRC for a GCL was dependent on the applied stress based on tests at 0.5 kPa and 100 kPa. This is important in modelling moisture loss and possible desiccation of GCLs when subject to a sustained thermal gradient discussed later. At present there is very limited data on GCL WRCs at stresses greater than 2 kPa. Thus, more research is required to obtain WRCs for different GCLs at different stress levels.

2.2 Isothermal moisture uptake by a GCL

When a GCL is placed on soil containing water, the suctions in the bentonite will induce moisture migration from the soil to the GCL until the suction in the GCL is in equilibrium with the suction in the adjacent soil. The rate at which this process takes place and the time to equilibrium will be dependent on the hydraulic conductivity of the soil adjacent to the GCL. This hydraulic conductivity will depend on the water content of the soil and can be expected to reduce as water is transferred from the soil to the GCL. The suction at which equilibrium is reached will depend on the WRCs of both the GCL and soil from which it is hydrating. Despite its importance, this has received remarkably little attention. Daniel et al. (1993) reported that an initially air dry GCL reached water content, w, of 88% after 40-45 days resting on sand at 3% gravimetric water content. Eberle & von Maubeuge (1998) showed that an initially air dry GCL resting on a sand with a water content, w_{fdn} , of 8–10%, reached w = 100%in less than 24 hours and w = 140% after 60 days. However, the effect of GCL type, subsoil grain-size distribution and water content has only recently been published (Rayhani et al. 2011; Anderson et al. 2012; Chevrier et al. 2012).

Rayhani et al. (2011) examined the moisture uptake of three GCLs (those denoted as GCL1, GCL2 and GCL4 in the Beddoe et al. 2011 study and described above) in a composite liner under isothermal conditions at 22°C. Tests were conducted for the GCLs resting on a silty sand subgrade (SM: 35% non-plastic fines and standard Proctor optimum water content, w_{opt} , of 11.4%; Table 3) and a poorly graded sand subgrade (SP: 5% non-plastic fines, $w_{opt} = 10.3\%$; Table 4). Because of the presence of an overlying GMB, all water up-take was from the subgrade below.

When the GCLs were placed on the silty sand subgrade at a water content corresponding to field capacity ($w_{fdn} = 21\%$), GCL2 was essentially hydrated in 5 weeks ($S_r = 97\%$, Table 3) and GCL1 and GCL4 had S_r of about 90%. All GCLs had fully hydrated after 30 weeks, however there was a significant difference in the final water content, w_f , between GCL2 ($w_f = 116\%$) and GCL1 ($w_f = 141\%$) and GCL4

Table 3. Hydration of GCLs with time resting on silty sand at different initial water contents, w_{fdn} (adapted from Rayhani et al. 2011).

GCL	Week	5	10	20	30	30	
	SubgradeDegree of saturation, S_r w_{jchn} (%)(%)						
GCL1	5	25	25	24	24	34	
GCL1	10	52	57	62	62	86	
GCL1	16	60	68	72	73	102	
GCL1	21	91	100	100	100	141	
GCL2	5	32	33	34	34	40	
GCL2	10	63	69	74	74	85	
GCL2	16	66	70	75	77	88	
GCL2	21	97	100	100	100	116	
GCL4	5	32	41	50	55	83	
GCL4	10	50	61	66	68	102	
GCL4	16	57	68	73	76	114	
GCL4	21	89	94	99	99	149	

Table 4. Hydration of GCLs with time resting on poorly graded sand at different initial water contents (adapted from Rayhani et al. 2011).

	Week	5	10	20	30	30
GCL	Subgrade w _{fdn} (%)	Degr (%)	ee of sa	turation	l	^w f (%)
GCL2 GCL2	2 10	26 68	27 75	27 76	27 78	31 90

($w_f = 149\%$). When the GCLs were placed on silty sand at $w_{fdn} = 10\%$ (i.e., just below w_{opt}), GCL2 hydrated to $S_r = 74\%$ ($w_f = 85\%$) in 20 weeks, GCL1 took 30 weeks to reach $S_r = 62\%$ ($w_f = 86\%$), and GCL4 took 30 weeks to reach $S_r = 68\%$ ($w_f = 102\%$). Thus when placed on silty sand at w_{fdn} just below w_{opt} , the GCLs would only be partially hydrated from the subgrade at low stress. If the stress on the GCL increased (e.g., due to placing sufficient cover soil or material to be contained by the liner), one would expect an increase in S_r (Siemens et al. 2012).

For the same soil initial water content $w_{fdn} = 10\%$, the GCL placed on the sand (SP; Table 4) hydrated faster and to a slightly higher final water content than when on the silty sand (SM; Table 3). When GCL2 was placed on soil close to its residual water content (5% for the silty sand and 2% for the sand) it only hydrated to $S_r = 34\%$ ($w_f = 40\%$) and $S_r = 27\%$ ($w_f = 31\%$) respectively, highlighting the need for the GCL to be placed on soil with sufficient moisture to allow reasonable hydration of the GCL.

Rayhani et al. (2011) reported that the hydration was not significantly affected by whether the cover or carrier GCL rested on the subgrade, and inferred that the WRC of the GCLs were not affected by whether the carrier geotextile was placed up or down.

Table 5. Hydration of GCLs with time resting on clayey sand at different initial water contents (adapted from Anderson et al. 2012).

	Week	1	22	22
GCL	Subgrade w _{fdn} (%)	S _r (%)		w (%)
GCL1	5	17	16	24
GCL1	10	26	59	85
GCL1	15	28	67	98
GCL1	20	29	90	130
GCL2	5	18	18	22
GCL2	10	26	67	79
GCL2	15	27	75	88
GCL2	20	29	90	106
GCL3	5	13	12	23
GCL3	10	21	48	90
GCL3	15	22	52	99
GCL3	20	24	92	174

Anderson et al. (2012) examined the hydration of GCL1, GCL2 and GCL3 resting on a clayey sand (Table 5). The clayey sand had 21% fines (12% clay size) and $w_{opt} = 11.3\%$. When the subsoil had a water content of 20%, all GCLs hydrated to a S_r of about 90%. When the subsoil water content was at a little below optimum ($w_{fdn} = 10\%$), GCL2 hydrated to a $S_r = 67\%$ (w = 79%) compared to $S_r = 59\%$ ($w_f = 85\%$) for GCL1 and $S_r = 48\%$ ($w_f = 90\%$) for GCL3. At a subsoil water content of 5% there was very little hydration and after 22 weeks S_r was only 18, 16 and 12% for GCL2, GCL1, and GCL3 respectively.

Anderson et al. (2012) compared their results with those obtained by Rayhani et al. (2011) under otherwise similar conditions and concluded that the subsoil affected both the rate and degree of hydration. For example, the time it took to reach a value of $S_r = 60\%$ ranged from 2 weeks over the sand (SP), to 5 weeks over the silty sand (SM), to 8 weeks over the clayey sand (SC).

Also for otherwise comparable conditions, the final equilibrium value of S_r was (slightly) higher for the GCL over the sand (SP) than over the silty sand (SM) which was higher than for the GCL over the clayey sand (SC). These differences are due to the different WRCs of the three subgrades.

Chevrier et al. (2012) obtained similar findings with respect to the effect of subgrade grain size and initial water content but at a stress of 4 kPa which was slightly greater than the 2 kPa used in the Rayhani et al. (2011) and Anderson et al. (2012) studies. Chevrier et al. (2012) also demonstrated that the rate of hydration was temperature dependent, with faster hydration at 45°C than at 20°C than at 5°C.

The French Committee for Geosynthetics (Fascicule, 1998) requires that the water content of the bentonite in GCLs used in liners should be at least 100%, presumably with the objective of ensuring that

the GCL has a high degree of saturation prior to contact with leachate. The work described above has indicated that whether or not this will happen is highly dependent on the initial moisture content and grain size characteristics of the subgrade below the GCL. The work cited above also shows that the degree of saturation when this criterion is met can be highly dependent on the type of GCL. For example at w = 98-102%, GCL1, GCL3 and GCL4 had S_r of 67–73%, 52%, and 68% respectively (see Tables 3 and 5). When GCL2 was at w = 116% it had $S_r = 100\%$ but at a similar w = 114%GCL 4 only had $S_r = 76\%$ (see Table 3). Thus, while w = 100% would appear to be a reasonable requirement for the scrim-reinforced and thermally treated GCL2 it appears quite inadequate for the other GCLs (especially GCL3).

2.3 Modelling isothermal moisture uptake

Siemens et al. (2012) used the WRCs from Beddoe et al. (2011) together with the isothermal hydration data from Rayhani et al. (2011) to calibrate a numerical model for GCL hydration. They then performed sensitivity analyses to examine the effect of different subgrades (with different WRC and w_{fdn}). These results showed that for a given GCL WRC, the final equilibrium water content, and hence S_r , was governed by the initial suction in the subgrade (which depended on the subgrade WRC and w_{fdn}). Based on this observation, they proposed a method for assessing the likely equilibrium water content of the GCL (and hence S_r). In essence, knowing the WRC of the subgrade (which can be inferred from its grain size distribution) and w_{fdn} , one can infer the suction in the subgrade and then, using the wetting WRC of the GCL (e.g., from Beddoe et al. 2011), one can deduce the value of w_f for that suction and hence calculate the likely value of S_r (knowing the likely saturated water content for that GCL). Conversely, knowing the desired value of S_r , one can calculate the required equilibrium value of w_f for the GCL and hence, from the WRC, the corresponding suction. Using this suction and the WRC for the subgrade one can then deduce the value of w_{fdn} required to achieve the desired hydration of the GCL.

To apply the approach above, one needs the wetting WRC of the GCL. This has only been developed for a limited number of GCLs and mostly at low stress (<2 kPa); there is a need for wetting WRC for a range of hydrating stresses. This information void leaves open the question as to what effect does the stress on the GCL at the time of hydration have on the WRC and hence the value of S_r that can be achieved for a given subgrade? To provide some insight, Siemens et al. (2013) used the WRC data from Beddoe et al. (2011) and that at 0.5 kPa and 100 kPa from Southen & Rowe (2007), the consolidation characteristics of GCLs from Lake & Rowe (2000a), and the GCL hydraulic conductivity data at various confining stresses from Rowe & Hosney (2013) in conjunction with the numerical procedure developed by Siemens et al. (2012) to provide the basis for a numerical investigation of the possible

effects of higher confining stress on the hydration behaviour of GCLs. Their results indicated that hydration of a GCL at a higher confining stress would result in a higher S_r (other things being equal), with the magnitude of this difference being dependent on w_{fdn} . These findings provide encouragement for laboratory studies of the effect of stress on the WRC of GCLs.

Since adequate hydration of a GCL is key to good performance as a barrier, their performance in covers and liners can be improved by paying attention to the water content of the subsoil upon which they are placed and the selection of an appropriate GCL, especially under more challenging conditions.

2.4 Effect of moisture uptake and stress on gas permeability

An example of the linkage between the GCL WRC and moisture uptake and the potential engineering performance of GCLs as a gas barrier has been recently reported by Rouf et al. (2013). They examined the gas permeability of a GCL somewhat similar to GCL2 discussed earlier (the main difference being the use of powdered Trugel bentonite in this case and granular Wyoming bentonite in GCL2). Experiments were performed for a range of water contents and suctions for stresses of 2 kPa and 20 kPa.

At low water content (w < 50% and suctions > 1.6 MPa) the gas permeability was very high and not much affected by stress. However as the water content increased, there was not only a substantial (orders of magnitude) decrease in gas permeability but also a significant effect of the difference in stress between 2 kPa and 20 kPa. This was likely due to the change in the WRC with applied stress which resulted in a higher degree of saturation and lower void ratio at a given water content at 20 kPa than at 2 kPa.

2.5 GCL moisture uptake with daily thermal cycles

Isothermal conditions, as examined above, represent ideal conditions for hydration. If a GCL is used as part of a composite liner that is left exposed to the sun, the GCL will be subject to thermal cycles. Rowe et al. (2011b) examined the same GCLs and silty sand subsoil as Rayhani et al. (2011) (discussed in a previous section) but subjected the GCL to daily thermal cycles. Based on observations at the Queen's University environmental liner test site (QUELTS) located north of Kingston, Ontario, Canada, in the summer the GMB can heat to up to 60°C on a sunny day and cool to 20°C in the evening. For the laboratory study this was idealized as a daily cycle where a GMB above the GCL resting on the silty sand was heated to 60°C for 12 hours and then allowed to cool to 20°C over the next 12 hours.

For GCLs over silty sand with w_{fdn} of 5%, 10% and 16%, after 7 weeks of daily thermal cycles the GCLs at the end of the heating cycle had S_r of only 9–24% (Table 6). These values are very low compared to

Table 6. Hydration of GCLs resting on silty sand when subjected to daily thermal cycles of $20-60^{\circ}$ C; values given are immediately following the heating period (adapted from Rowe et al. 2011b).

GCL	Week Subgrade w _{fdn} (%)	1	7	7 w (%)
		S _r (%)		
GCL1	5	15	16	23
GCL1	10	23	25	35
GCL1	16	24	22	30
GCL1	21	52	81	113
GCL2	5	16	14	16
GCL2	10	15	14	16
GCL2	16	20	24	27
GCL2	21	66	100	117
GCL4	5	13	9	14
GCL4	16	10	11	17
GCL4	21	45	85	127

the values obtained under isothermal conditions, especially for subsoil with w_{fdn} of 10% and 16% (Table 3). However for $w_{fdn} = 21\%$ (just below field capacity), even with daily thermal cycles S_r was 100% for GCL2, 81% for GCL1, and 85% for GCL4 (Table 6). Thus the effect of the daily cycles was very sensitive to w_{fdn} .

A key consideration with respect to possible shrinkage of the GCLs is the change in water content during a daily cycle (i.e., between the end of the cool period and the end of the hot period). After a few weeks of daily cycles, for $w_{fdn} = 16\%$ GCL1 experienced a ~13% change in water content during a cycle compared to ~10% for GCL4 and ~2% for GCL2. These differences are related to the difference in the WRC discussed earlier. Thus, Rowe et al. (2011b) predicted that, for the conditions examined and to the extent that shrinkage is dependent on a change in moisture over a daily cycle, the susceptibility to shrinkage would be GCL1 \geq GCL4 > GCL2.

Anderson et al. (2012) examined the performance of GCL2 and GCL3 over the same clayey sand subgrade as examined for isothermal conditions and discussed in the previous section (Table 5). For w_{fdn} of 5%, 10% and 15%, after 6 weeks of daily thermal cycles the GCLs at the end of the heating cycle had S_r of only 9–14% (Table 7). Comparing results for GCL2 in Tables 6 and 7, it appears that the clayey sand suppressed the hydration of the GCLs even more than the silty sand at the end of the heating cycle. This effect is even more evident comparing results for subsoil with w_{fdn} of 20–21% where, for the silty sand, GCL2 was fully hydrated ($S_r = 100\%$) but for the clayey sand it only reached $S_r = 56\%$.

For a GCL in an exposed composite liner, the cases of isothermal hydration at 20°C and daily thermal cycles from 20 to 60°C represent two extremes in one sense but neither represents a worst case for GCL shrinkage and neither is likely to be realised given that

Table 7. Hydration of GCLs resting on clayey sand when subjected to daily thermal cycles of 22–56°C; values given are immediately following the heating period (adapted from Anderson et al. 2012).

GCL	Week Subgrade w _{fdn} (%)	1	6	6 w (%)
		S _r (%)		
GCL2	5	11	11	13
GCL2	10	11	13	16
GCL2	15	12	14	16
GCL2	20	21	56	66
GCL3	5	9	9	16
GCL3	10	9	10	20
GCL3	15	9	10	18
GCL3	20	25	48	92

(gap + original design overlap of 150 mm). Data from Koerner & Koerner (2005) and Thiel et al. (2006). GCL¹ Slope (mm) (months)

Table 8. Summary of observed GCL panel separation

	220	450	60
N/W	18°	350	15
N/W	4°	450	2
N/N	34°	1350	36
N/N	18°	450	5
N/N	4°	600	2
N/N	2–4°	300	2

¹Cover geotextile/carrier geotextile; W = woven geotextile; N = nonwoven geotextile.

the weather and cloud cover are likely to change from day to day. A worse case, for example, is if there is a period of cloudy weather where the GCL can hydrate almost isothermally followed by a hot sunny day when the moisture can evaporate or be driven back into the soil, followed by another period of cooler/cloudier weather; thereby allowing larger changes in the water content of the GCL when heated.

2.6 GCL shrinkage

GCL manufacturers recommend that the GCL be placed under dry weather conditions and be covered with a ballast layer (typically 0.3 m or more of cover soil) shortly after placement. When covered by a GMB to form a composite liner this recommendation is often more honoured in the breach that the observance. There can be a variety of reasons for this but a common one is that the cover soil on the side slopes cannot be adequately placed quickly for the length of slope that has been installed and so the liner system is left exposed for months and sometimes many years. Covering the composite liner in a timely manner avoids a number of potential problems not the least of which is the potential for shrinkage of the GCL below the exposed GMB.

The potential for shrinkage was reported by Thiel & Richardson (2005) for cases where a GMB was opened to discover that the GCL had shrunk to the point that the GCL panels that had originally been overlapped by 150 mm had shrunk sufficiently to leave a significant gap between the panels. Koerner & Koerner (2005) and Thiel et al. (2006) reported other cases (Table 8) which corresponded to shrinkage of the overlap by 300–1350 mm and shrinkage strains ranging from 7% to 31%. These cases demonstrated that there could be significant shrinkage in periods of as little as two months on both relatively flat (2–4°) slopes as well as side slopes of 18° to 34°. However there are also cases where GCLs have been installed and no significant shrinkage was observed. Thiel and Rowe

(2010) discussed a number of such cases as briefly summarized below.

GCLs (similar to GCL3 and GCL4) that had experienced significant shrinkage in several cases reported in Table 8 were installed on a 3H:1V (18°) slope with a silty clay subgrade having $w_{fdn} = 5\%$ (CETCO 2006). Water was sprayed on the GCL after placement to raise the GCL water content to 40-45% and it was then covered with a GMB. Over a 10 month period, during which GMB temperatures were reported to reach over 60°C, the GCL water content was reported to have gone from an initial high of about 45% to a low of 11%. The GCL panels only experienced shrinkage strains of 0.6%-0.9% and overlap movements of only 25 mm to 37 mm. In this case the low shrinkage was probably due to a number of factors including the low initial water content of the subsoil (which limited the rate and amount of hydration in cool periods) and the fact that the GMB did not appear to have been welded so there was potential for moisture loss at the GMB panel edges to the atmosphere that could be expected to have reduced the moisture cycles.

Gassner (2009) installed a GCL very similar to GCL1 on a 55 m long 3H:1V slope and covered it with a GMB and white geotextile. After 18 months of exposure in Melbourne, Australia, the inspection of 1 m of the overlap one-third of the way down the slope indicated shrinkage of only 50 mm to 80 mm and the 300 mm overlap used in this case appeared adequate.

Thiel & Rowe (2010) reported that four different GCL test plots were constructed on a 40 m long 3H:1V slope at one of the sites where there had been significant panel separation on relatively flat areas (Table 8). After it was covered with a GMB, the overlaps below the GMB were periodically inspected. Over a period of 7 months there was reported to be no notable panel shrinkage, but a high value of S_r , "flowing" water, and internal bentonite erosion resulting from the flowing water were reported.

It is apparent that the shrinkage is a result of wet-dry cycling. However the fact that in some case there was shrinkage that caused a large gap between the GCL panels and in other cases there was no significant shrinkage indicates that this is a complex issue. The potential for GCL shrinkage has been the subject of a number of laboratory studies (Thiel *et al.* 2006; Bostwick *et al.* 2010; Rowe *et al.* 2010a, 2011a; Brachman *et al.* 2010; Joshi *et al.* 2011) as briefly summarized below.

Experiments have been conducted on GCLs placed in a pan and subjected to artificial wet-dry cycling by adding a prescribed amount of water and then drying the GCL in an oven at 60°C (Thiel et al. 2006; Bostwick et al. 2010; Rowe et al. 2011a). These experiments showed that all eight GCLs tested have the potential to shrink significantly, although the method of manufacture did have an effect with some types of GCL shrinking more than others. However when the GCL is used as part of an exposed composite liner in the field, the moisture cycles experienced by the GCL will depend on the WRCs of the GCL and the subgrade (which will depend on the type of GCL and grain size distribution of the subgrade), the initial water content of the subgrade, and the length and nature of the thermal cycles as discussed above.

Bostwick et al. (2010) reported that the dry mass per unit area of a GCL did not significantly affect shrinkage provided that the bentonite was evenly distributed. However, much higher shrinkage was reported for GCLs with an uneven distribution of bentonite (generally samples with a low average mass per unit area). GCLs with a lower mass per unit area appear to have an increased probability of variability in the distribution of bentonite and, GCLs with little to no bentonite in some areas experience higher shrinkage under otherwise similar test conditions. Thus the level of quality control needed to ensure sufficient bentonite at every location on a GCL roll appears to increase as the average mass of bentonite per unit area is decreased. Bostwick et al. (2010) also noted that the maximum shrinkage of 14.4% observed for GCL4 in their study was well below the maximum of 23% observed by Thiel et al. (2006) for nominally the same product using the same test method, suggesting that there can be a difference in shrinkage of different rolls of nominally the same product under otherwise similar conditions which, presumably, is related to difference in the variability of the product being produced at different times but having the same designation. Bostwick et al. (2010) and Rowe et al. (2011a) found that some products exhibited considerable variability while other products had quite small variability.

Rowe et al. (2011a) examined eight different GCLs subjected to laboratory wetting and drying cycles. They reported that the off-the-roll water content could affect the initial shrinkage but did not significantly change the final shrinkage (i.e., after many cycles). They also reported that when GCLs with granular bentonite were wetted to a water content $\geq 60\%$ in each cycle, the actual water content did not have much effect on the final equilibrium shrinkage but it did change the rate of shrinkage. A higher water content in the hydration cycle resulted in the maximum shrinkage being reached in fewer cycles.

shrinkage of a needle-punched GCL with a thermally treated scrim-reinforced nonwoven carrier geotextile and granular bentonite (GCL2) was less than that for a needle-punched GCL with a simple nonwoven carrier and granular bentonite (GCL4). It is significant that, in their experiments, the shrinkage strain required to cause the loss of a 150–300 mm panel overlap could be developed in as little as about five wet-dry cycles and this helps explain why panel overlap has been lost in as little as two months in some field situations (Table 8). Thus the conditions that would allow this number of significant hydration cycles become important.

The uptake of moisture and the potential of a change in water content are highly dependent on the initial water content and the WRC of the soil below the GCL, and the WRC of the GCL. The thermal cycles experienced by the GCL also will depend on weather conditions as discussed earlier.

Shrinkage may be suppressed by bonding between GCL panels. This could occur due to "gluing" of panels together when supplemental bentonite between GCL panels gets wet and then dries (Brachman et al. 2010), although this is not a reliable method of suppressing shrinkage (e.g., it will be lost when the supplemental bentonite at a location is re-hydrated). A potentially more reliable means of suppressing shrinkage is to heat tack the overlaps. Limited evidence suggests that, when well heat tacked, there is sufficient bond to resist at least some wet-dry cycles (Thiel and Thiel 2009; Rowe et al. 2010a; Joshi et al. 2011), although it is not yet clear to what extent the bond would be sufficient to resist overlap movement under the conditions that resulted in the loss of panel shrinkage reported in Table 8.

The laboratory studies reported above have provided insight regarding the relative performance of different GCLs for idealized conditions; however, to date, there has been no published study examining the field performance of different GCLs side by side under similar field conditions. Brachman et al. (2007) described the construction of the Queen's University environmental liner test site (QUELTS) north of Kingston, Ontario in 2006 to examine the relative performance of four commonly used North American GCLs (GCLs 1-4 discussed earlier) in six different exposed composite liner configurations (some smooth, some textured GMBs) under as identical conditions as possible (Figure 1). This experiment was terminated in 2011 after approximately 5 years. The GMBs and GCLs placed in 2006 were removed in May 2012 and seven new test sections were constructed and have been monitored since that time (Figure 2). Papers describing the findings from QUELTS are in preparation; suffice it to say that some GCLs experienced significant shrinkage while one experienced very little shrinkage in almost 5 years of exposure.

Based on the available evidence to date, it is expected that GCL shrinkage is not a concern if the GCL is placed in accordance with good construction practice and the composite liner is quickly covered with a ballast layer (e.g., cover soil or leachate



Figure 1. Queen's University environmental liner test site (QUELTS) north of Kingston Ontario, Canada during construction in 2006.



Figure 2. QUELTS II following re-construction in 2012.

collection system). If the GCL must be left exposed, its performance in covers and liners can be improved by (a) placing panels with 300 mm of overlap, (b) heat tacking the overlaps, and (c) using a GCL that has shown low shrinkage in the field. These three strategies (especially if used together) will minimize the risk of panel separation. However, at this time, there is no assurance that they will prevent panel separation under worst case conditions; the composite liner should still be covered as quickly as possible.

2.7 Cation exchange

Cation exchange is a well-recognised mechanism whereby the sodium ions in the smectite, which is the component of sodium bentonite responsible for its low hydraulic conductivity, are exchanged with other cations in the permeating fluid, the pore water of the soil adjacent to the GCL or, especially for activated sodium bentonite, in calcium bearing minerals in the bentonite itself. There have been instances where cation exchange (probably coupled with wetdry cycles) has resulted in substantial increases in hydraulic conductivity, k, from the low (typically $k \le 5 \times 10^{-11}$ m/s) values for GCLs as they come off the roll. For example, Benson et al. (2007) reported that after 15 months in a landfill final cover, a GCL similar to GCL4 discussed above and with 760 mm of soil above the GCL experienced an increase in k to between 1.8×10^{-7} m/s and 6.9×10^{-7} m/s and a decrease in swell index (SI) from $\geq 24 \text{ mL/2g}$ to 7-15 mL/2g. These changes were attributed to the exchange of Ca²⁺ and Mg²⁺ in the adjacent soils for Na⁺ in the bentonite together with dehydration.

Meer & Benson (2007) reported findings for GCLs exhumed from four different landfill covers, with 0.75-1 m of soil above the GCL. High $k (10^{-8}-10^{-6} \text{ m/s})$ was reported for samples with water content less than 85%, while the k ranged between $10^{-10}-10^{-9} \text{ m/s}$ for samples with a water content greater than 100% (with the lowest values being obtained from well hydrated samples exhumed after 11 years). Thus the water content of the sample appears to be an important factor.

Scalia & Benson (2011) exhumed GCLs from six composite liners with 0.3–1.1 m of cover soil (thickness depended on site) in landfill final covers after 4.7 to 6.7 years. The *SI* dropped to 7–11 mL/2g (i.e., typical of calcium bentonite) at four sites whereas it was 12-22 mL/2 g at the two other sites. There was an almost 5 order of magnitude variation in *k* over the six sites ($9.3 \times 10^{-12} \le k \le 2.1 \times 10^{-7} \text{ m/s}$).

Rowe & Abdelatty (2012a) examined cation exchange, and its effect on k, for a GCL resting (a) directly on Ca-rich soil (pore water: 1700–1800 mg/L Ca^{2+}) (b) on a 0.3 m foundation layer (pore water: ~200–300 mg/L Ca^{2+}) over the Ca-rich soil, and (c) on the foundation layer alone. All soils were silty sand at an initial water content of 13.9%.

For the GCL on the foundation layer alone, the GCL w increased to a final equilibrium value of 113% after 500 days. There was no change in the k of the GCL. For the GCL directly on the Ca-rich soil, w increased to a maximum of 86% and then decreased to 67% due to cation exchange under isothermal conditions, showing that simple chemical interaction with the subgrade can result in a decrease in GCL water content (other things being equal). A similar trend was observed for the case where the GCL was on the foundation layer over the Ca-rich soil but the maximum w was 96% and it reduced to 80% at equilibrium. There was no desiccation cracking of the GCLs. The value of k (at 15 kPa) increased from the initial value of 3×10^{-11} m/s to 2×10^{-10} m/s when resting directly on the Ca-rich soil and 7×10^{-11} m/s (after 3 years) when on the foundation layer over the Ca-rich soil.

Hosney & Rowe (2013) examined the field performance of three needle-punched GCL products covered with up to 1 m of cover soil (gravelly sand) as part of a cover over an abandoned gold mine in Nova Scotia, Canada. One GCL (GCL1 discussed earlier) had sodium bentonite sandwiched between a woven and a nonwoven geotextile. The other two GCLs had polymer enhanced sodium bentonite and a nonwoven cover geotextile but different carriers: one a scrim reinforced nonwoven geotextile, the other a woven geotextile laminated with a polypropylene film. GCL samples were exhumed after 1 and 2 years. Almost all the moisture uptake occurred in the first year and there was very little change at year 2. All exhumed GCLs had w > 80%.

After 2 years, GCL1 with untreated sodium bentonite experienced almost complete cation exchange (*SI* dropped from 26 to 8–10 mL/2g) but still maintained $k \le 5 \times 10^{-11}$ m/s at locations where there was ≥ 0.7 m of cover soil above the GCL. The *SI* of GCL with polymer enhanced bentonite decreased from 24 to 14 mL/2g and $k \le 3 \times 10^{-11} \text{ m/s}$ when there was $\ge 0.7 \text{ m}$ of cover soil above the GCL. The *SI* of the GCL with polymer enhanced bentonite and a carrier geotextile coated with a geofilm decreased from 25 to 13-15 mL/2g but because the *k* is controlled by the thin geofilm, the *k* value did not change and remained around $5 \times 10^{-12} \text{ m/s}$ (virgin *k* value). After two years of exposure to the natural climatic cycles in this humid climate, all GCLs were performing adequately despite cation exchange when the cover soil $\ge 0.7 \text{ m}$. When the cover above the GCL was reduced to 0.5 m, GCL1 experienced a similar change in *SI* but *k* increased to $1 \times 10^{-10} \text{ m/s}$.

The work described above highlights the complex interaction between variables such as the availability of exchangeable cations (especially Ca^{2+} and Mg^{2+}), w_{fdn} of the subgrade, w of the exhumed GCL, the amount of cover soil above the GCL, and the type of GCL, on the k of GCLs used in covers. While there are certainly cases where there has been a very substantial increase in k of the GCL in covers, there are also cases where it has performed very well, suggesting that performance is related to both local conditions (soil and climate) coupled with the details of the design (including the type of GCL used).

In addition to ensuring the subgrade below the GCL has adequate moisture to allow reasonable hydration of the GCL, as discussed earlier, the performance of GCLs in low stress applications (especially those where they could be subjected to wet-dry cycling) can be improved by (a) ensuring there is sufficient cover soil above the GCL (the amount needed will depend on local conditions/climate), and (b) selecting the appropriate GCL for the application.

3 GCL DESICCATION IN COMPOSITE LINERS

A GCL may desiccate as a result of one or more wetdry cycle. This may occur because the GCL is in an exposed composite liner (i.e., the mechanisms giving rise to shrinkage discussed earlier), the GCL is in a cover liner without adequate cover soil to protect it from significant wet-dry cycles due to climatic cycles, or because it is in a composite bottom liner that initially hydrates (as discussed in Sections 2.2–2.5) and is then dried by the thermal gradient generated by hot waste (e.g., municipal solid waste where there is leachate recirculation or disposal of combustion ash). When it desiccates, the GCL k value will be high but, provided that there is not too much cation exchange, it can quickly reduce again to low values (Southen & Rowe 2005) because of the ability of the sodium bentonite to swell and self-heal on re-wetting (i.e., when it comes into contact with the fluid that is to be contained). However as indicated by some of the cases cited in the previous section, when desiccation is combined with cation exchange the self-healing capacity is reduced or lost, with the magnitude of the effect depending on (a) the amount of cation exchange, (b) the extent of the cracking and the size of the desiccation cracks, and (c) the stress on the GCL (higher stress increases the ability of the GCL to self-heal; other things being equal). The ability to rehydrate to a low k may also be reduced by the chemical composition of the permeant (Petrov & Rowe 1997) even if there was little initial cation exchange.

The size of the desiccation cracks can be expected to affect how well it can self-heal. The larger the cracks the more difficult it will be for the bentonite to selfheal, especially after some cation exchange and at low stress. It is well recognised that desiccation of a GCL is caused by wetting followed by drying; however it is not well recognised that the size of the desiccation cracks is a function of a number of factors. For example, Take et al. (2012a) showed that the size of cracks developed in a GCL's bentonite core depended on both the type of GCL and the rate of drying. They examined the desiccation of GCL2 and GCL4 under isothermal drying at 20°C and 60°C. As discussed earlier, GCL2 had more effective anchorage of its needle-punched fibres than GCL4 (due to the combination of needle-punching to the scrim reinforced carrier geotextile and the thermal bonding of the fibres in GCL2). As a result, GCL2 had much thinner cracks when desiccated than GCL4 (which relied on mechanical anchorage to a nonwoven carrier geotextile for fibre anchorage). Also, for GCL4, the rate of drying was important to crack size, with slow drying giving significantly larger cracks than rapid oven drying at 60°C. The effect of drying rate was much less for GCL2.

A laboratory study of the potential for desiccation of a GCL in a composite liner due to sustained thermal gradient was reported by Southen & Rowe (2004, 2005). This work was extended to consider double composite liners by Azad et al. (2011). These studies showed experimentally that, under some circumstances, desiccation would occur whereas in others there was no desiccation. Factors affecting whether or not there was desiccation included the: (a) initial subsoil water content (higher w_{fdn} decreased the potential for desiccation); (b) type of GCL; (c) bentonite M_A (higher M_A appeared to reduce potential desiccation); (d) carrier geotextile thickness (higher M_A appeared to reduce potential desiccation); (e) temperature gradient (lower gradient decreased the potential for desiccation).

The numerical model DESICCATE (Zhou & Rowe 2003) has been successfully used to model the experimental data discussed above (Southen & Rowe 2011; Azad et al. 2012) and used to examine the effects of factors such as liner temperature, overburden stress, subsoil initial water content, grain size of the subgrade, and depth to the water table (Hoor & Rowe 2013).

Based on the studies to date, and more research is required, it appears that the potential for desiccation can be reduced, and hence the performance of liner systems improved, by ensuring an adequate water content of subsoil and by one or more of the following: (a) limiting the temperature gradient (e.g., by avoiding leachate recirculation or disposing of waste such as combustion ash that would increase liner temperatures – Hoor & Rowe 2013), or (b) removing heat (Rowe et al. 2010b), or (c) providing insulation (Hoor & Rowe 2012).

4 COMPOSITE LINERS OVER A DRAINAGE LAYER

GCLs may be used as part of a primary composite liner in a double liner system. When a GCL is to be placed over a relatively uniform gravel or geonet/ geocomposite drainage layer (e.g., a leak detection layer), there are two issues that need careful consideration in design. First, there is the issue of hydration. Consideration should be given to how the GCL will hydrate when placed on a material that typically has very low water content as placed. For example, if the GCL is hydrated from the leachate it may increase the hydraulic conductivity of the GCL (Petrov & Rowe 1997). Second, there is the potential for internal erosion of the bentonite in the GCL when it rests on a gravel or geocomposite/geonet layer. Rowe & Orsini (2003) showed that different types of GCL had different susceptibility to internal erosion with GCLs having a scrim reinforced carrier performing better than those with either a woven or nonwoven carrier.

One design solution to these issues is to place the GCL on a well graded foundation layer that can act as a filter to prevent internal erosion and also provide a source of moisture for hydration of the GCL. An added benefit is that the layer provides at least partial insulation that could reduce the temperature on the secondary liner (Rowe & Hoor 2009) and hence reduce the many negative impacts of higher temperature (e.g., higher leakage, higher diffusion, reduced GMB service life, potential desiccation of the secondary clay liner – e.g., Rowe 2005). This will increase cost but improve long-term performance.

5 GMB/GCL INTERFACE TRANSMISSIVITY

Rowe (2012a) reviewed the published data relating to GMB/GCL interface transmissivity, θ . Considering permeation with water, published values fall in the range $6 \times 10^{-12} \text{ m}^2/\text{s} \le \theta \le 2 \times 10^{-10} \text{ m}^2/\text{s}$ with an average of about $4 \times 10^{-11} \text{ m}^2/\text{s}$ for reinforced GCLs over a range of stresses from 7–70 kPa. For GCLs containing sodium bentonite, the average θ was about $2 \times 10^{-11} \text{ m}^2/\text{s}$ (at 50 kPa). A study of the effect of applied stress in the range 25–200 kPa (Barroso et al. 2010) did not indicate a strong relationship between stress and θ for the cases considered. It also did not appear to matter greatly whether the GMB is smooth or textured in terms of θ for the conditions examined by Barroso et al. (2008).

Perhaps the most interesting recent finding is the lack of correlation between θ and k arising from the

work of Mendes et al. (2010) and Rowe & Abdelatty (2012b, 2013).

For otherwise similar conditions (50 kPa, smooth GMB, and permeation with water), Mendes et al. (2010) showed that two calcium bentonite GCLs had almost identical values of θ despite a two order of magnitude difference in k. Specifically, for the GCL with $k = 5.8 \times 10^{-8} \text{ m/s}$ ($M_A = 5730 \text{ g/m}^2$) θ was $3.0 \times 10^{-11} \text{ m}^2$ /s while for the GCL with $k = 6.9 \times 10^{-10} \text{ m/s} (M_A = 10590 \text{ g/m}^2) \theta \text{ was } 2.8 \times 10^{-10} \text{ m/s} (M_A = 10590 \text{ g/m}^2)$ $10^{-11} \text{ m}^2/\text{s}$. These values of θ were only slightly larger than two values obtained for two different sodium bentonite GCLs (viz: $\theta = 2.4 \times 10^{-11} \text{ m}^2/\text{s}$ for a GCL with $k = 1.6 \times 10^{-11} \text{ m/s} (M_A = 7400 \text{ g/m}^2)$ and $\theta' = 2.6 \times 10^{-11} \text{ m}^2/\text{s}$ for a GCL with $k = 3.2 \times 10^{-11} \text{ m}^2/\text{s}$ 10^{-11} m/s ($M_A = 5410$ g/m²) respectively). Comparing the extreme cases, a 360,000% increase in k of the GCL only corresponded to an increase in θ by 25%. Thus k and θ do not appear to be correlated suggesting that θ is controlled by factors other than k.

Rowe & Abdelatty (2012b, 2013) arrived at a similar general finding by a very different route. They performed four experiments to examine contaminant transport through a hole in a GMB overlying a GCL (at 100 kPa). These tests were of much larger diameter than previous GMB/GCL transmissivity tests. Rowe & Abdelatty (2012b) initially permeated the simulated barrier system with distilled water and from the measured flows at steady state Rowe & Abdelatty (2013) deduced $\theta \approx 2.3 \times 10^{-11} \text{ m}^2/\text{s}$. The permeant was changed to a NaCl solution and, at steady state, θ had decreased to 1.1×10^{-11} m²/s. Thus, despite the fact that the k of the GCL increased up to a factor of 8 from about 5×10^{-11} m/s when permeated with water to $2-4 \times 10^{-10}$ m/s when permeated with a 0.14 M NaCl solution, the value of θ decreased by a factor of 2; a totally opposite trend. This is attributed to an improvement in the interface characteristics of the GMB/GCL interface as the GCL consolidated in response to the chemical interaction that increased k. This also demonstrates that for the same GCL, the values of k and θ are uncoupled when the permeant is changed. This is good news for GCLs since Rowe & Abdelatty (2013) showed that for the conditions they examined an increase in k due to clay-leachate interaction did not significantly increase leakage through the composite liner and the GCL continued to fulfill its primary function of minimizing leakage though a hole in the GMB.

The available evidence suggests that even with good construction, the GMB/CCL interface transmissivity is several orders of magnitude higher than for a GMB/GCL (Rowe 2005, 2012a).

6 WRINKLES

Although design drawings show composite liners with GMBs directly and continuously on the underlying clay liner, in reality when it comes time to cover the GMB with the ballast or leachate collection layer, there will usually be wrinkles in the GMB (Figure 3). Although the presence of wrinkles in GMBs has long been recognised and Rowe (1998) developed an equation for calculating leakage through GMBs with wrinkles, it is only recently that the geometry and connectedness of wrinkles has been well documented (Take et al. 2007; Chappel et al. 2012a,b; Rowe et al. 2012a,b). Wrinkles arise from the thermal expansion of the GMB when heated (e.g., by the sun). They may align with geometrically regular features (e.g., creases arising from manufacture of blown film GMBs, seams which run parallel to the roll, or GCL panel overlaps), or they may occur at random locations (all of these are evident in Figure 3). The height and width of wrinkles as well as the percent area of a liner below wrinkles and length of connected wrinkles have been documented for a range of sites, times of day, and times of year in the references cited above.

The studies cited above were conducted in eastern Canada. For the conditions examined, it appears that if the GMB were to be covered by the leachate collection layer before 8:00 am or after 4:00 pm there would be about 6 to 7 connected wrinkles per hectare each with connected length $L \leq 200$ m. The length of connected wrinkle would increase with more solar radiation with the maximum connected wrinkle length often being observed (on a sunny day) at around 1:00 pm. For an unrestrained area of GMB of about 0.2 ha, there could be a connected wrinkle with a length of up to 2000 m at around 1:00 pm. Assuming a similar situation for each part of the GMB covered there could be five such connected wrinkles per hectare and a relatively high probability that at least one hole in the GMB will align with a the long connected wrinkle per hectare. As the restrained area that is covered at a given time increases so too does the length of the longest connected wrinkle. For example, Chappel et al. (2012b) reported the case of a GMB area of 0.61 ha where the longest connected wrinkle was 5330 m.

The studies cited above have indicated that, at least in eastern Canada, wrinkles in HDPE GMBs induced by thermal expansion may reach heights of 0.2 m, and occasionally more, but are typically about 0.06 m in height and wrinkle widths may reach up to 0.5 m but are usually in the 0.2–0.3 m range.

7 OVERLAPS

The potential for shrinkage of GCL panels causing a loss of overlap was discussed earlier. Any such gap would be problematic if it were beneath a hole in the GMB since the composite liner action would be lost at that location. However even more problematic would be the situation where there was a hole in a wrinkle that either ran directly above the overlap (as may happen in some cases; Figure 3) or if the wrinkle were to cross the point where there was a loss of overlap (which can be easily envisaged based on Figure 3). In this case the hole no longer needs to align directly with the



Figure 3. Wrinkles in GMB at QUELTS. In this photo GMB rolls run east-west (left to right) and GCL panels run north south (top to bottom) (modified from Rowe et al. 2012b and Rowe 2012a).

loss of overlap because fluid (leachate or gas) could easily migrate through a hole anywhere in the wrinkle and then laterally below the wrinkle to a point where the wrinkle intersects the place where overlap is lost and again composite liner action is lost. This further highlights the need to avoid loss of panel overlap.

Where significant wrinkles (i.e., with height >30 mm at the time they are covered) coincide with panel overlaps, the overlap below the wrinkle will be unloaded after the waste or cover soil is placed. Thus even if there is no loss of panel overlap, a significant reduction in panel overlap could represent a weak point for leakage as noted by Brachman et al. (2011). Current work at Queen's University is examining the potential for leakage through panel overlaps using unique equipment (geosynthetic landfill liner simulators with internal diameters up to 1 m). This equipment allows consideration of different overlaps, presence and absence of supplemental bentonite, heat tacking etc. on the hydraulic performance of overlaps both parallel and perpendicular to the wrinkle for applied stresses up to 250 kPa.

8 LEAKAGE THROUGH COMPOSITE LINERS

It has been well recognised for many years (e.g., Giroud & Bonaparte 1989; Rowe 1998) that leakage through a composite liner will depend on the head on the liner, the number and size of holes in the GMB, and the *k* of the clay component of the liner. Less well recognised has been the importance of the interface transmissivity, θ , between the GMB and the GCL and the role of wrinkles, although there have been some significant advances in understanding with respect to these two parameters over the last few years as discussed in previous sections. Rowe (2005, 2012a) examined the use of the Rowe (1998) equation for calculating leakage through the primary liner (allowing

for wrinkles) in double lined landfills and compared calculated and observed values. In 2005 there was a paucity of data on connected wrinkle length and the equation was used to infer what winkle length was required to explain the observed leakages. In 2012, the data on wrinkles discussed in an earlier section was available and Rowe (2012a) showed that the Rowe (1998) equation explains the observed leakage in landfills for heads and connected wrinkle lengths typical of those observed in construction provided the liner is not covered in the middle of a sunny day.

Rowe & Hosney (2010) and Rowe (2012a) have examined the effect of some of the key factors discussed above on the calculated leakage through composite landfill bottom liners. Some of their conclusions are summarized below assuming good liner construction and liner temperature less than 40°C. The justification for these comments is not repeated here and the interested reader is referred to the original papers for that information.

- An increase in liner temperature (Table 1) can greatly increase the calculated leakage, with the leakage at 60°C and 80°C being about double and triple that at 20°C respectively, other things being equal.
- Well-constructed composite liners substantially reduce leakage compared to a GMB, GCL or CCL alone.
- Leakage through a composite liner with a GMB/GCL is substantially less than through a GMB/CCL.
- Advection begins to dominate contaminant transport when leakage, Q, exceeds about 200 lphd and careful consideration must be given to the potential impact on groundwater for these situations.
- Assuming typical landfill design parameters (see Rowe 2012a), the calculated leakage through GMB/GCL composite was $Q \le 14$ lphd for $L \le 200$ m and $Q \le 50$ lphd for $L \le 700$ m. For a GMB/CCL (0.6 m thick), the corresponding leakage was $Q \le 83$ lphd for $L \le 200$ m and $Q \le 580$ lphd for $L \le 700$ m.
- Provided that the connected wrinkle length is kept relatively low ($L \le 125$ m), then a GMB/GCL composite liner can be expected to give Q < 50 lphd (Darcy flux <0.002 m/a) for leachate heads less than 3 m and hence remains modest. These leakages are considered small and usually of no practical consequence for MSW landfills. At these leakages, diffusion is likely to be the dominant contaminant transport mechanism for contaminants (e.g., volatile organic compounds) that can readily diffuse through a GMB.
- Provided that the connected wrinkle length is kept relatively low ($L \le 125$ m), then a GMB/CCL composite liner can be expected to give Q < 200 lphd for leachate head ≤ 1.5 m.
- Leakage through composite liners used in lagoons may be substantially larger than through landfill liners. This is because of the much lower stress on the liner and, typically, much higher heads. If the ballast

above the GMB is sufficient to ensure composite liner action, the leakage can be reduced by using a composite liner involving a GMB/GCL/CCL. In this case the GCL provides good interface properties thereby minimizing leachate flow at the GMB/GCL interface and the CCL controls the leakage where leachate can migrate between the GMB and GCL. Rowe (2012a) showed that the performance of the GMB/GCL/CCL system was substantially better than either a GMB/GCL or GMB/CCL system.

9 CONSTRUCTION ISSUES

Composite liner performance is highly related to construction issues (Rowe 2012a, b). With respect to the issues discussed in this paper, the performance of composite liners can be improved by considering the following.

- Ensure a suitably prepared CCL surface for placing the GMB (without stones, clods etc.) since this will influence the interface transmissivity and hence potential leakage.
- Ensure no linear features/irregularities in surface of CCL (e.g. tyre tracks).
- Keep the CCL surface sufficiently moist to avoid desiccation cracks before the GMB is placed.
- Ensure that the subgrade below the GCL is firm and unyielding (>90% standard Proctor density) with no abrupt changes in elevation (e.g., ruts). It should be proof rolled with a smooth drum roller immediately prior to placement of the panels. There should be no foreign matter or stones loose on the surface or penetrating out of the subgrade >10 mm.
- The subgrade upon which the GCL is to be placed should be at an appropriate water content to allow hydration of the GCL.
- Cover the composite liner with the protection layer and drainage or ballast layer quickly to avoid (a) desiccation cracking of a CCL which, as shown by Rowe (2012a) can substantially increase leakage, or (b) significant GCL shrinkage and opening of a gap between GCL panels. Of these the most critical is the need to cover a GMB over a CCL since severe desiccation can occur in a matter of hours on a hot sunny day when the GMB can heat to over 60°C and perhaps as much as 70°C.
- Minimize wrinkles by ensuring that the GMB is placed early in the morning or late in the day when the number of wrinkles is smallest (Chappel et al. 2012a,b; Rowe et al. 2012a,b; Take et al. 2012b).

To ensure the desired performance, good inspection is required during construction to check that the design conditions are actually achieved and factors such as those highlighted above (plus other issues not discussed here - e.g. see Rowe 2012b) are addressed. The old adage: "You get what you inspect, not what you expect" should always be kept in mind. Recent advances in the understanding of factors affecting the performance of liners in both bottom liner and capping systems for landfill and mining applications have been explored with respect to GCL and composite liner performance. Some of the implications for improving liner performance are highlighted below.

The available evidence suggests that both GCLs and composite liners have performed extremely well at controlling leakage in field applications for a couple of decades. However there have also been some problems and recent research has allowed us to have a much better understanding of the key design and construction factors affecting performance. There are also operational issues that can affect the performance of the system. Particular attention must be given to factors that could cause the liner temperature to exceed 40°C since they can have many negative effects on liner performance (e.g., higher leakage, higher diffusion, reduced GMB service life, and potential desiccation of the clay liner). Special design will be required for liners to be used in an environment where the liner temperature will exceed 35-40°C.

Factors that can affect the performance of a GCL include: (a) the type of bentonite, (b) the mass per unit area of bentonite, (c) the type and mass per unit area of the geotextiles used, (d) the amount of needlepunching, (e) whether or not the needle-punched fibres are thermally fused to the carrier geotextile. (f) the presence or absence of a geofilm bonded to the GCL, the nature of the geofilm, and how the geofilm is bonded to the carrier geotextile, (g) the characteristics of the GCL panel overlap, (h) whether or not the GCL is part of a composite liner, (i) the presence of wrinkles in the GMB, (j) the initial water content and particle size distribution of the soil above and/or below the GCL, (k) geochemical interactions between the bentonite and the pore water in the soil adjacent to the GCL, (1) interaction of the bentonite with the fluid to be retained, (m) the amount of cover soil over the GCL, (n) the level of exposure to thermal cycles, (o) thermal gradients, and (p) and the stress on the GCL.

A key parameter affecting GCL performance as a fluid barrier (to liquid or gas) is the degree of saturation. A GCL should have a high degree of saturation before it is required to restrict the migration of either gas or liquids (especially liquids that could chemically interact with the bentonite). The degree of saturation of the GCL will depend on the type of GCL (since they have different water retention curves) and the grain size distribution and initial water content of the subgrade (or cover soil if no GMB is present). As discussed, techniques have been developed that allow the estimation of a target water content required to achieve a desired degree of saturation of the GCL for a given subgrade.

GCLs should be covered with at least 0.3 m of ballast (e.g., leachate collection system or cover soil) shortly after GCL placement to minimize the risk of a number of problems including shrinkage of GCL panels that can occur when subjected to thermal cycles (e.g., when a composite liner is left exposed to heating by the sun). There are strategies that can be adopted to minimize the risk of panel separation in cases where the liner must be left exposed as discussed herein. Additional insights regarding issues arising from leaving composite liners exposed, and mitigation measures if they must be left exposed, will be provided when the findings from the studies at QUELTS are published.

GCLs used in covers are particularly prone to problems if not properly designed and constructed because of the combination of low stress and potential for wet-dry cycles. The risk of problems can be substantially reduced by (a) ensuring that the subgrade below the GCL has an adequate water content to allow reasonable hydration of the GCL, and (b) ensuring there is sufficient cover soil above the GCL, and (c) selecting the appropriate GCL for the application (some types of GCLs will perform much better than others).

Presently available evidence suggest that, under some circumstance, GCLs (or CCLs) used in a composite liner where the temperature may exceed 35°C could be desiccated by the thermal gradient. Although more research is required, it appears that the potential for desiccation can be reduced, and hence the performance of liner systems improved, by ensuring an adequate water content of subsoil, and one or more of the following: (a) limiting the temperature gradient (e.g., by avoiding leachate recirculation or disposing of waste such as combustion ash that would increase liner temperatures), or (b) by removing heat, or (c) by providing insulation to control the liner temperature.

When GCLs are used in primary liners as part of double liner systems, special consideration should be given to how the GCL will hydrate and the potential for internal erosion of the bentonite in the GCL if the GCL rests over a uniform gravel or geonet/geocomposite drainage layer. One design solution to these issues is to place a well graded foundation layer between the GCL and the leak detection system. This layer can act as a filter to prevent internal erosion and a source of moisture for hydration of the GCL. In addition, this layer will provide at least some insulation to reduce the temperature on the secondary liner.

For a well-constructed composite liner, the interface transmissivity, θ between the GMB and clay liner is at least as important as the hydraulic conductivity, kof the liner. Recent research suggests that k and θ are not correlated and hence that θ is controlled by factors other than k of the GCL (or CCL). One study showed that, for the conditions examined, permeation of a composite liner with a salt solution caused k to increase by almost an order of magnitude but θ decreased by a factor of two and there was negligible change in leakage through the hole in the GMB.

Well-constructed composite liners substantially reduce leakage compared to a GMB, GCL or CCL alone, however the leakage through composite liners

is highly dependent on the length of connected wrinkles that intersect a hole in the GMB. Wrinkles present at the time the GMB is covered with the ballast layer increase the area of the underlying clay liner in contact with leachate and hence leakage. Even more problematic would be the situation where there was a hole in a wrinkle intersecting a location where there has been loss of GCL panel overlap (e.g., due to panel shrinkage). In this case the hole in the GMB does not need to align directly with the loss of overlap because fluid (leachate or gas) could easily migrate through a hole anywhere in the wrinkle and then laterally below the wrinkle to a point where the wrinkle intersects the place where overlap is lost. In this case, composite liner action is lost. This further highlights the need to avoid loss of panel overlap.

When a composite liner involves a CCL, the performance is highly dependent on the interface transmissivity between the GMB and CCL and desiccation of the surface of the CCL either before or after the GMB is placed. The available evidence suggests that even with good construction the GMB/CCL interface transmissivity is orders of magnitude higher than for a GMB/GCL. As a consequence, leakage through a composite liner with a GMB/GCL is substantially less than through a GMB/CCL.

This paper has discussed a number of potential problems with liner performance. However all can be avoided by appropriate design, material selection, construction and operations. There are many examples where liners have exhibited excellent long-term performance.

11 NOTATION

CCL	Compacted clay liner	
GCL	Geosynthetic clay liner	
GMB	Geomembrane	
HDPE	High density polyethylene	
k	Hydraulic conductivity (m/s)	
L	Length of connected wrinkle (m)	
lphd	Litres per hectare per day	
M_A	Mass per unit area of GCL (g/m^2)	
MARV	Minimum average roll value	
MSW	Municipal solid waste	
Q	Leakage through a composite liner	
	(lphd)	
QUELTS	Queen's University Environmental	
	Liner Test Site	
SI	Swell index	
S_r	Degree of saturation	
W	Gravimetric water content of GCL	
W_f	Equilibrium gravimetric water content	
	of GCL	
W _{fdn}	Gravimetric water content of subgrade	
Wopt	Standard Proctor optimum water content	
	of subgrade	
WRC	Water retention curve	
θ	GMB/GCL interface transmissivity	
	(m^2/s)	

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Coupled modelling of barriers for radioactive waste disposal

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ABSTRACT: The paper first presents an overview of the issues associated with radioactive waste disposal and follows with a brief description of deep geological disposal for high level radioactive waste. The performance assessment of these underground repositories requires a good understanding of the basic phenomena that affect the succession of barriers separating the waste from the biosphere. A key safety element in the design of these facilities is an engineered barrier, made up of highly expansive clay, that surrounds the canister containing the waste. This barrier is subjected to a complex set of coupled thermo-hydro-mechanical (THM) phenomena that must be correctly modelled and understood. The paper presents a coupled THM formulation that incorporates the most relevant processes occurring in the barrier and their mutual interactions. The formulation is then applied to the modelling of an in situ test that simulates repository conditions at full scale. The tests involves heating and hydration of the engineered barrier. It is shown that the modelling results represent satisfactorily the observations from the test, including those obtained dafter a partial dismantling stage. This exercise demonstrates that the basic phenomena appear to be well understood and that the formulation and associated computer code are useful tools for the coupled analysis of this type of THM processes.

1 INTRODUCTION AND BACKGROUND

Radioactivity is a natural phenomenon that arises mainly from the disintegration of the unstable nuclei of some elements but there are some other natural sources like cosmic rays and their interaction with the atmosphere. However, the issue of nuclear waste is associated basically with human use of radioactivity for industrial, medical and military purposes as well as for energy production. These activities produce a wide variety of wastes that there are often classified in the following classes:

- Low Level Waste (LLW). Low activity waste is normally associated with radionuclides of short half-life and comprises the bulk of waste. All nuclear activitie generate amounts of LLW in significant quantities. Also, wastes resulting from mining and ore processing normally belong to this category. Worldwide they make up 90% of the waste volume but contain only 1% of the total radioactivity of all radioactive wastes.
- Medium or Intermediate Level Waste (MLW ILW). This is an intermediate class of waste that contains non-negligible amounts of radioactivity and normally requires shielding. They normally result from enrichment and fuel fabrication, reactor operation, reprocessing, and nuclear plant decommissioning. Heat emissions are low.
- High Level Waste (HLW). High activity wastes that, in addition to many short half-life radionuclides, also contain large amounts of long-lived radionuclides. They are also strong heat emitters. Although

they contain most of the radioactivity (over 95% of the total), the waste quantities are relatively low, of the order of 10,000 tonnes per year (Mc Combie et al. 2000). Generally, HLW waste is left to cool off before disposal for a number of years.

In this paper, attention will be focused on HLW where the performance of coupled modelling plays a key role in many aspects. They are practically exclusively the product of energy generation in nuclear power plants. They are mainly constituted by spent fuel rods or solidified high-level waste from reprocessing.

According to the recent IAEA (2012) data, there are at present 436 nuclear power plants in operation with a net installed capacity of about 371 GW (gigawatts). As shown in Figure 1, total nuclear power production has remained approximately steady (2518 terawatt-hour TWh in 2011) but the share of electricity production has dropped to 11% from a maximum of 17% in the early 1990's as the world electricity production has increased significantly since then.

Although 67 nuclear power reactors are officially listed as under construction (mainly in Eastern Europe and Asia), this figure is misleading because a number of projects are often cancelled or left uncompleted. Recent events in Japan have significantly affected the use and development of nuclear power and the subject remains hugely controversial. However, no matter what the future holds for nuclear energy production, the issue of the safe management of HLW must be addressed.

In this paper, the basic principles of deep geological repositories and its performance assessment are



Figure 1. Nuclear energy production and share of electricity production in the world, 1990–2011 (Schneider & Froggatt 2012).

summarily addressed first follows by a brief review of the basic thermo-hydro-mechanical (THM) behaviour of clay-based engineered barriers, a frequent component of the multi-barrier system of these facilities. A coupled formulation designed to encompass the THM phenomena involved and their interactions is then described. Finally, the performance of the formulation and associated computer code are applied to the analysis of a large scale test performed in an underground laboratory simulating actual repositories conditions. Although chemical processes interacting with THM phenomena also play a part in the evaluation of repository safety, they are not considered herein.

2 DEEP GEOLOGICAL REPOSITORIES

Any disposal system should in principle guarantee that the waste is removed from the human environment, the waste is isolated and contained over long periods of time (depending on waste type) and only small release rates will occur once the complete isolation period is over. A variety of procedures have been put forward to solve the problem of radioactive waste disposal: a) space disposal, b) ice sheet disposal, c) ocean bed disposal, d) disposal beneath the seabed, e) nuclear transmutation, and f) geological disposal.

Currently, only options e) and f) are the subject of significant research activity. Transmutation of the most harmful long-lived radionuclides does offer the possibility to reduce the requirements applied to a long-term disposal facility. This approach requires carrying out chemical separation of very radioactive materials, going well beyond present reprocessing activities. Whatever the result of this research, there will always remain significant quantities of HLW waste to be disposed of in some other fashion. Therefore, the construction of deep geological repositories remains the favoured option for practically all countries. The aim is to free future generation from the burden created by our present activities.

In fact, many countries have opted for the deep geological disposal not only of HLW but of non-heat emitting long-lived medium level waste (MLW) as well. Although shallow burial is the most common



Figure 2. Conceptual scheme of a deep geological repository for high-level nuclear waste.

method of low level waste (LLW) disposal, some countries are also considering deep geological disposal of all waste types, including LLW, because they consider the additional cost involved is compensated by the perceived enhanced safety of deep geological disposal.

All disposal designs for HLW resort to the multibarrier concept to achieve the required degree of waste isolation. If one considers the potential path of a radionuclide from inside the canister to the biosphere, it is clear that it will need to cross several barriers, the canister itself, the backfill (engineered barrier) and the host rock (geological barrier). Each one of those elements will provide a degree of safety to the overall disposal system. Originally it was thought that each barrier should be designed in such a way to provide sufficient isolation on its own, so that a simultaneous failure of all barriers would be required for significant radioactive releases to occur. In fact, this is too restrictive and, in cases involving long-lived wastes, possibly impossible to achieve. It is more realistic to consider all the barriers acting together in a unified disposal system.

A typical scheme for an underground mined repository involves the sinking of deep shafts down to a depth of several hundred meters (Figure 2), the depth is, of course, controlled by local geological conditions (Chapman & Mc Kinley 1987). The shafts provide access to a network of horizontal drifts that constitute the main repository area. Part of those drifts will be access tunnels and part will be devoted to nuclear waste disposal. A concrete plug often separates the disposal area from the access tunnel. The space between canisters and the host rock is generally (but not always) filled by a suitable material to constitute an engineered barrier. The material most usually considered is compacted swelling clay, normally some kind of bentonite on its own or mixed with other materials like sand although cement-based materials and crushed salt, for repositories located in salt rock, are also being considered for some specific applications.

The bentonite barrier fulfils several important functions. In the first instance, a very low hydraulic conductivity restricts water penetration and retards significantly solute transport due to its low diffusion coefficient and to additional sorption effects. It should also provide a favourable chemical environment and be able to self-heal if subjected to physical perturbation



Figure 3. Mean annual dose computed for the reference scenario of the Spanish reference concept for high level nuclear waste (Astudillo 2001).

such as cracking and fissuring events. The adjacent rock interacts with the barrier and it also plays a significant role in the safety performance of the repository by providing the next barrier of isolation and retardation.

3 PERFORMANCE ASSESSMENT

To ensure the adequacy of a design of an underground repository, it is necessary to undertake a thorough performance assessment exercise that allows the evaluation of safety in a comprehensive way. To this end, all the processes and phenomena that may affect the performance of the repository in a significant way must be considered in a systematic manner. This safety evaluation is a complex process due to the variety of materials and components of a repository and to the large number of interacting processes that potentially play a role.

The output of the performance assessment exercise may be expressed in different ways. A typical one is in terms of the computed individual dose that may be expected as a function of time. An example is given in Figure 3 for the reference scenario of the Spanish reference concept for high level nuclear waste (Astudillo 2001). It can be noted that not only the total dose is given but also the individual contributions of each radionuclide. Two immediate observations can be made: i) computations are extended to extremely long times, 10⁶ years in this case, and ii) the maximum doses obtained are very low compared with the natural radiation and are also well below the frequently specified limit value of 10^{-4} Sv/year. Naturally, the computed doses increase when considering the effect of external factors. Figure 3 is also useful to indicate that the central phenomenon to be examined is the transport of the radionuclides to the biosphere and that the analyses of the large variety of phenomena involved should be performed with this final aim in mind. Naturally, complexity and uncertainty in many areas prevent exact predictions. This difficulty, however, may be overcome (at least partially) by the use of



Figure 4. Example of performance assessment division into near field and far field.

conservative hypotheses and by the consideration of a sufficiently wide range of possible scenarios.

The contribution of geomechanical numerical analyses is pervasive in the study of the likely performance of a number of the various barriers. To carry out the assessment in an effective way, it is convenient to identify a number of subsystems that are analyzed separately. An example of a first-level subsystem classification is depicted in Figure 4. It can be observed that the output of a subsystem constitutes the input of the next one. A conceptual model is built for each subsystem that includes the most relevant processes, the main parameters and the interaction between phenomena. The subsystem is quantitatively analysed by means of appropriate numerical models. Finally the results of each subsystem are integrated in the description of the overall behaviour of the entire system. This division between different subsystems must be made considering what are the phenomena and time scales relevant to each particular component. Often there are large differences between the processes that operate in the various subsystems. A useful conceptual distinction refers to the division between near field and far field. In a rough way, the near field may be defined as the part of the disposal system that is directly affected by the presence of the waste. It usually includes the canister, the buffer or barrier and the adjacent rock. The far field extends from the boundary of the near field (not a precise location) to the region near the surface that may interact with the biosphere. In this context, the potential contribution of geotechnical numerical analysis is especially strong in the analyses affecting the near field, especially in the early-stage transient period.

From the geomechanical point of view attention is concentrated on the barrier and rock, canisters and waste matrices are the concern of materials science. A number of phenomena require specific numerical analysis; e.g. the coupled thermo-hydro-mechanical and chemical (THM and THMC) behaviour of the engineered barrier (Guimaraes et al. 2007, Sánchez et al. 2012), the identification of the magnitude and role of the Excavation Damaged Zone, EDZ, (Vaunat & Gens 2004), the thermohydraulic behaviour of the host rock (Gens et al. 2007) or the migration of gas through the barrier on to the rock (Olivella and Gens 2000, Olivella and Alonso 2008). Due to the importance of the problem, performance of large-scale tests in underground laboratories is also a characteristic feature of this field (Gens 2003). They are carried out to advance the understanding of the phenomena and to evaluate the validity of the models used. Again, the role of numerical analyses is a very prominent feature of this work (e.g. Gens et al. 1998; Gens et al. 2009; Thomas et al. 2009). In this paper, attention will be focused on the analysis of the THM behaviour of clay-based barriers and its interaction with the near field host rock. The barrier behaviour will be examined and numerically analysed with reference to a large-scale experiment carried out in the Grimsel Underground Laboratory (Switzerland).

4 ENGINEERED BARRIER BEHAVIOUR

The near field is an area of complex phenomena and interactions. The swelling clay making up the barrier is compacted so, initially, it is in an unsaturated state. After placing the canisters, the main actions that affect the bentonite barrier (at least in the short term) are the heating arising from the canisters and the hydration from the surrounding rock. At the inner boundary, the barrier receives a very strong heat flux from the canister. The dominant heat transfer mechanism is conduction that occurs through the three phases of the material. A temperature gradient will therefore develop in the near field and heat dissipation will be basically controlled by the thermal conductivity of the barrier and host rock. Maximum temperatures envisaged in repository design can be quite high. Some designs limit the maximum temperature to 100°C but other concepts allow significantly higher temperatures.

In the inner zone of the barrier, the heat supplied by the heater results in a temperature increase and in strong water evaporation that induces drying of the bentonite. Degree of saturation and water pressure will reduce significantly in this region. Vapour arising from bentonite drying will diffuse outwards until finding a cooler region where vapour will condense, causing a local increase in water saturation. Vapour diffusion is a significant mechanism of water transfer mechanism and, to a much lesser extent, of heat transport. Due to low water pressures existing initially in the unsaturated material that constitutes the backfill, hydration will take place with water moving from the host rock to the barrier. The distribution of water potential is also affected by the phenomena of bentonite drying and vapour transport described above. Hydration will eventually lead to saturation of the barrier, but saturation times can often be very long due to the low permeability of the bentonite and/or host rock. Figure 5 shows a scheme of the main thermohydraulic processes occurring in the bentonite barrier and rock in the near field. In the Figure, the rock has been assumed saturated but, in fact, it can desaturate in some circumstances.

In addition to the thermo-hydraulic behaviour, there are important mechanical phenomena also occurring.



Figure 5. Thermo-hydraulic processes occurring in the near field.

Drying of the bentonite will cause shrinking of the material whereas hydration will produce swelling that may be quite strong in bentonite barriers. Because the barrier is largely confined between canister and rock, the main result of hydration is the development of swelling pressures, in a process quite akin to a swelling pressure test. The magnitude of the stresses developed is critically dependent on the emplacement density of the bentonite and may reach values of several MPa.

The crucial feature of the THM behaviour described is that all those phenomena are strongly coupled, interacting with each other in a complex manner. As an example, consider the phenomenon of vapour transport. Evaporation and condensation depend on the value of suction (hydraulic variable) and temperature (thermal variable). Transport itself is a mixture of advection and diffusion that is influenced by temperature (thermal), degree of saturation (hydraulic) and porosity (mechanical). In fact vapour transport cannot be considered on its own, but as a branch of a cycle closed by the movement in opposite direction of liquid water. The flow of liquid water also depends on temperature (via water viscosity), degree of saturation and porosity. Another example of interaction is the main heat transfer mechanism, heat conduction. This is basically controlled by thermal conductivity that, in turn, depends on degree of saturation (hydraulic effect) and porosity (mechanical effect). Other coupling examples could be similarly discussed. The complexity of THM behaviour increases further when the interaction of the bentonite barrier with the host rock is taken into account (Gens et al. 2002).

Therefore, in order to encompass the processes outlined above, the THM formulation for saturated and unsaturated porous media should incorporate the following phenomena:

- i) Heat transport: Heat conduction, heat advection by liquid water, water vapour and gaseous air.
- ii) Water flow: Liquid advection and water vapour diffusion.
- iii) Air flow: Gas advection and dissolved air diffusion
- iv) Mechanical behaviour: behaviour of porous materials dependent on stresses, suction and temperature.

In the next section a thermo-hydro-mechanical (THM) formulation incorporating all those phenomena in a coupled manner is outlined. More details are given in Gens & Olivella (2000).

5 COUPLED THM FORMULATION

5.1 General

Several THM formulations have been described in the literature, e.g. Olivella et al. (1994), Gawin et al. (1995), Thomas & He (1995, 1997), Khalili & Loret (2001) and Gatmiri & Arson (2008). The equations that govern this problem can be classified into three main groups: balance equations, constitutive equations and equilibrium relationships (Gens 2010). Equations for mass balance are established following the compositional approach. That is, mass balance is established for water, air and mineral species instead of using solid, liquid and gas phases. Equation for balance of energy is established for the medium as a whole.

The following convention is established for writing the equations defining the formulation: superscripts refer to species (w for water and a for air) and subscripts refer to phases (s for solid, l for liquid and gfor gas). The notation used is as follows:

 ϕ : porosity

- i: non-advective mass flux
- σ : stress tensor
- θ : mass content per unit volume of phase, i.e., $\theta = \omega \rho$ E: specific internal energy
- ρ : density
- **q**: advective flux
- **b**: body forces vector
- S_l : degree of saturation of liquid phase
- j: total mass flux
- u: solid displacement vector
- ω : mass fraction
- S_g : degree of saturation of gas phase
- \mathbf{j}_E : energy fluxes due to mass motion

Volumetric mass of a species in a phase (e.g. water in gas phase θ_g^w) is the product of the mass fraction of that species, ω_g^w , and the bulk density of the phase, ρ_g , i.e. $\theta_g^w = \omega_g^w \rho_g$.

The total mass flux of a species in a phase (e.g. flux of air present in gas phase jgw) is, in general, the sum of three terms:

- the nonadvective flux: i^w_g, i.e. diffusive/dispersive, flux
- the advective flux caused by fluid motion: $\theta_g^w \mathbf{q}_g$, where \mathbf{q}_g is the Darcy's flux,
- the advective flux caused by solid motion: $\phi S_g \partial_g^w \mathbf{u}/dt$ where $d \mathbf{u}/dt$ is the vector of solid velocities, S_g is the volumetric fraction of pores occupied by the gas phase and ϕ is porosity.

The sum of the nonadvective and fluid motion advective fluxes is separated from the total flux in order to simplify the algebraic equations. This flux is relative to the solid phase and is denoted by \mathbf{j}_g^{w} . It corresponds to the total flux minus the advective part caused by solid motion. When solid deformation is negligible, then $\mathbf{j'} = \mathbf{j}$.

5.2 Balance equations

Mass balance of solid present in the medium is written as:

$$\frac{\partial}{\partial t} \left(\theta_s \left(1 - \phi \right) \right) + \nabla \cdot \left(\mathbf{j}_s \right) = 0 \tag{1}$$

where θ_s is the mass of solid per unit volume of solid and **j**_s is the flux of solid. From this equation, an expression for porosity variation is obtained as:

$$\frac{D_s \phi}{Dt} = \frac{1}{\theta_s} \left[(1 - \phi) \frac{D_s \theta_s}{Dt} \right] + (1 - \phi) \nabla \cdot \frac{d\mathbf{u}}{dt}$$
(2)

Equation (2) expresses the variation of porosity caused by volumetric deformation and solid density variation. To obtain it, the material derivative with respect to the solid

$$\frac{D_s(\bullet)}{Dt} = \frac{\partial}{\partial t} + \frac{d\mathbf{u}}{dt} \cdot \nabla(\bullet)$$
(3)

has been used.

Water is present in liquid and gas phases. The total mass balance of water is expressed as:

$$\frac{\partial}{\partial t} \left(\theta_l^w S_l \phi + \theta_g^w S_g \phi \right) + \nabla \cdot \left(\mathbf{j}_l^w + \mathbf{j}_g^w \right) = f^w \tag{4}$$

where f^w is an external supply of water. An internal production term is not included because the total water mass balance is considered. The use of the material derivative leads to:

$$\varphi \frac{D_{s}\left(\theta_{l}^{w}S_{l}+\theta_{g}^{w}S_{g}\right)}{Dt}+\left(\theta_{l}^{w}S_{l}+\theta_{g}^{w}S_{g}\right)\frac{D_{s}\varphi}{Dt}+\left(\left(\theta_{l}^{w}S_{l}+\theta_{g}^{w}S_{g}\right)\varphi\right)\nabla \cdot \frac{d\mathbf{u}}{dt}+\nabla \cdot \left(\mathbf{j}_{l}^{v}+\mathbf{j}_{g}^{v}\right)=f^{w}$$
(5)

The final objective is to find the unknowns from the governing equations. Therefore, the dependent variables will have to be related to the state variables in some way. For example, degree of saturation will be computed using a retention curve that should be expressed in terms of temperature, liquid pressure and gas pressure.

Porosity appears in this equation of water mass balance not only as a coefficient, but also in a term involving its variation caused by a variety of processes. It is also implicit in variables that depend on porosity (e.g. intrinsic permeability). The way of expressing the derivative term as a function of the state variables is via the solid mass balance equation. This allows taking correctly into account the influence of porosity variation in the balance equation for water. It should be noted that in equation (5) the material derivatives can be approximated as eulerian if the assumption of small strain rate is adopted while the volumetric change is not neglected. This is consistent with the classical way of deriving the coupled flow-deformation equations.

Following the same approach, it is straightforward to obtain the mass balance of air taking into account that air is the main component of the gas phase and that it may also be present in the liquid phase as dissolved air.

$$\varphi \frac{D_s \left(\theta_l^a S_l + \theta_g^a S_g\right)}{Dt} + \left(\theta_l^a S_l + \theta_g^a S_g\right) \frac{D_s \varphi}{Dt} + \left(\left(\theta_l^a S_l + \theta_g^a S_g\right) \varphi\right) \nabla \cdot \frac{d\mathbf{u}}{dt} + \nabla \cdot \left(\mathbf{j}_l^a + \mathbf{j}_g^a\right) = f^a$$
(6)

The momentum balance reduces to the equilibrium of stresses if inertial terms are neglected:

$$\nabla \cdot \mathbf{\sigma} + \mathbf{b} = \mathbf{0} \tag{7}$$

where σ is the stress tensor and **b** is the vector of body forces.

The equation for internal energy balance for the porous medium is established taking into account the internal energy in each phase (E_s, E_l, E_g) :

$$\frac{\partial}{\partial t} \left(E_s \rho_s \left(1 - \varphi \right) + E_l \rho_l S_l \varphi + E_g \rho_g S_g \varphi \right) + \nabla \cdot \left(\mathbf{i}_c + \mathbf{j}_{Es} + \mathbf{j}_{El} + \mathbf{j}_{Eg} \right) = f^{\mathcal{Q}}$$
(8)

where \mathbf{i}_c is energy flux due to conduction through the porous medium, the other fluxes $(\mathbf{j}_{Es}, \mathbf{j}_{El}, \mathbf{j}_{Eg})$ are advective fluxes of energy caused by mass motions and f^Q is an internal/external energy supply. The use of the material derivative leads to an equation formally similar to the mass balance of water.

Only one equation is therefore required to express the balance of internal energy in the porous medium as a whole. The fluxes in the divergence term include conduction of heat and advection of heat caused by the motion of each species in the medium. A non-advective mass flux causes an advective heat flux because a species inside a phase moves and transports energy. In contrast to the case of the movement of a contaminant in a groundwater system, the diffusive term for heat transport (conduction of heat) is much larger than the term concerning hydromechanical dispersion (non-advective flux caused by the velocity of fluids). For this reason, this term is usually neglected.

5.3 Constitutive equations

A fundamental part of the formulation is constituted by the set of constitutive laws and equilibrium restrictions. The constitutive equations establish the link between the state variables (or unknowns) and the dependent variables. The global unknowns in this formulation are liquid pressure, gas pressure, displacements and temperatures. The governing equations are finally written in terms of the unknowns when the constitutive equations are substituted in the balance equations.

Another series of relationships that relates dependent variables with unknowns are the equilibrium restrictions. They are obtained assuming chemical equilibrium for dissolution of a particular species in a phase. This assumption is appropriate because those processes are fast compared to the transport phenomena that take place in porous media and, therefore, they are not rate controlling. The concentration of vapour in the gas phase and the amount of air dissolved in the liquid phase are governed by expressions of this type.

The constitutive equations and equilibrium restrictions adopted are given in detail in Gens & Olivella (2000) and Gens et al. (2009). Only some aspects are highlighted here:

- Balance of momentum for fluid phases and dissolved species are reduced to constitutive laws: Darcy's law and Fick's law.
- Fourier's law. Thermal conductivity depends on porosity and state of hydration of the material through a geometric mean expression.
- Darcy's law. Hydraulic conductivity depends on porosity, on degree of saturation and, via water viscosity, on temperature.
- Fick's law is adopted for vapour diffusion. A tortuosity coefficient, τ, is included to take into account the effect of a porous medium on the diffusion coefficient.
- The mechanical constitutive law explicitly considers the effects of strains, suction and temperature changes.

5.4 Numerical implementation and computer code

The formulation outlined above has been discretized in space (finite elements) and time (finite differences) in order that it can be used for numerical analysis. The basic formulation and numerical discretization constitute the bases of a computer code, CODE_BRIGHT that has been used to perform the analysis reported below (Olivella et al. 1996).

6 DESCRIPTION OF THE LARGE-SCALE IN SITU TEST

The large-scale in situ test (named FEBEX) simulates, at full scale, the Spanish repository concept for HLW that envisages placing the waste-containing canisters in horizontal drifts surrounded by an engineered barrier made up of compacted bentonite. The test has been performed in the Grimsel Test Site located in the Swiss Alps. To install the experiment, a 2.28 m diameter circular tunnel was excavated in the GTS underground laboratory using a TBM machine. The tunnel is 70.4 m long and the final 17.4 m section was selected for the



Figure 6. Heater placed in the axis of the excavated tunnel and surrounded by an engineered barrier made up of compacted bentonite blocks.



Figure 7. Layout of the large-scale in situ test. Instrumented sections are indicated.

performance of the test. In the test area, two 4,300 W heaters were placed in the axis of the horizontal drift. The heaters were 4.54 m long and 0.90 m in diameter and were intended to simulate the release of heat by HLW. The space between the rock surface and the heaters was backfilled using blocks of compacted bentonite (Fig. 6). Finally, the test area was sealed by a 2.7 m long concrete plug. Figure 7 shows a schematic layout of the test.

The host rock is good quality Central Aare granite crossed, in the test zone, by a lamprophyre dyke. The clay is a bentonite ($w_L = 98-106$, $w_P = 50-56$) with a high smectite content, in the range of 88%–96%, with small and variable quantities of accessory minerals such as quartz, calcite and feldspars. The cation exchange capacity is 100–102 meq/100 g (42% Ca, 33% Mg, 23% Na, 2% K). The bentonite blocks were compacted to a dry density of 1.7 g/cm³ at an average water content of 14.4%. Because there were small gaps between blocks and between the clay barrier and the rock, the overall dry density of the emplaced barrier was 1.6 g/cm³.

The test is heavily instrumented, a total of 632 sensors were installed in the engineered barrier and in the rock. The instrumented bentonite sections are indicated in Figure 7. The following parameters were measured: temperatures, relative humidity (total suction),



Figure 8. Location of boreholes for installing instrumentation in the rock.

pore water pressures, total pressures and displacements. Of special importance were the observations of hydraulic variables: relative humidity and pore pressures. Relative humidity was determined using PCT-55 Wescor psychrometers and capacitive transducers manufactured by Vaisala. In some places, they were supplemented by vibrating wire transducers to observe positive pore water pressures. Capacitive sensors proved to be much more robust and reliable than psychrometers. It should be noted that there is a direct relationship between relative humidity and total suction given by Kelvin's equation (shown later). Therefore, measuring relative humidity (and temperature) is equivalent to measuring total suction. In addition, a number of boreholes were drilled into the rock prior to the emplacement of the heaters and bentonite blocks in order to install monitoring devices (Fig. 8). Temperature, pore pressures, total stresses and displacements were observed in the rock.

After the installation of the test, four months were allowed to elapse before switching the heaters on to achieve equilibrium conditions in the monitoring system. During this time there was some hydration of the barrier from the rock but, obviously, no thermal loading. During the heating stage, the test was temperature-controlled with a prescribed maximum temperature of 100°C at the contact between liner and bentonite. To achieve this, the sequence of operations was as follows: i) the heaters were switched at a constant power of 1200 W each during 20 days. The aim was to identify the thermal response of the system and to adjust the power control algorithm, ii) afterwards, the power of each heater was increased to 2000 W and kept constant until a temperature of 100°C at the contact between liner and bentonite was reached (this occurred after 33 days), and iii) subsequently, the system operated under temperature control, i.e. power was adjusted to keep a constant 100°C maximum temperature on the liner/barrier contact

The heating stage under this temperature controlled conditions lasted for exactly five years. Afterwards, the



Figure 9. a) Bentonite retention curve. b) Relationship between thermal conductivity and degree of saturation.

heaters were switched off and, after a cooling period, the experiment was partially dismantled. The dismantling phase is considered in more detail in the final part of the paper. Additional information on the test is given in Huertas et al. (2006).

7 MODELLING RESULTS

Here only some typical results of the modelling compared with test observations over the five years of the heating stage are presented. The analyses require a significant number of parameters that, for the most part, were determined independently from laboratory and in situ tests. For illustration purposes the retention curve of the bentonite and the relationship between thermal conductivity and degree of saturation together with laboratory experimental results are depicted in Figure 9. More information on the analyses carried out and the material parameters adopted are given in and in Sánchez & Gens (2006) and Gens et al. (2009).



Figure 10. Variation of temperatures with time in the engineered barrier: observations and computed results. a) section D1, b) section I.

7.1 Bentonite barrier

Thermal. Figure 10 shows the evolution of the temperature in two sections of the test. In each section, temperatures at different radial distances from the axis of the tunnel are plotted. More than one set of observations for a particular radial distance and section are shown because temperature sensors were sometimes placed along several radial lines. The repeatability of results indicates the degree of approximation to thermal axisymmetric conditions and, indirectly, the reliability of the observations.

It can be noted that, after the initial stage, temperatures generally rise very slowly throughout the barrier. The analysis reproduces quite well the observations, although this is helped by the fact that it is a temperature-controlled test. Because practically all energy is transported by conduction, the good agreement at different radial distances indicates that the value of thermal conductivity is well captured, even when the barrier is subjected to changes in water content and degree of saturation.

Hydraulic. Of more interest and more challenging are the observations and predictions of the hydraulic changes inside the barrier. Figure 11 shows the variation with time of relative humidity, measured with capacitive sensors, in two sections, a cool one away from the heater (C) and a hot one between the two heaters (H). Relative humidity is plotted because it is the actual parameter measured by the capacitive transducers. It is recalled that total suction, ψ , is related to relative humidity, RH, via the psychrometric (Kelvin's) equation:

$$RH = \exp\left(\frac{\Psi M_w}{R(273+T)\rho_l}\right)$$
(9)

where M_w is the molecular weight of water.

It can be observed that in the cool section C there is a monotonic increase of relative humidity corresponding to the progress of hydration caused by water drawn from the host rock. The inner region, however, is far from being saturated after five years. The hydraulic behaviour is more complex in the hot section close to the heaters. In the zone near the rock and in the middle of the barrier, there is a monotonic increase of relative humidity reflecting again the process of hydration induced by the rock water. However, in the region closer to the tunnel axis, it can be observed that there is first an increase of relative humidity immediately followed by drying and, finally, a gentle increase of relative humidity occurs.

Assisted by the examination of the numerical analysis' results, it is possible to identify the processes underlying this behaviour. The first relative humidity increase is due to a vapour front (driven by heating) passing through the observation point. Afterwards, temperature increase causes evaporation and, therefore, drying of the material. After approximately one year, general hydration takes over causing the final gradual increase of relative humidity. It can be noted that vapour movement plays an important role in the evolution of the hydraulic state of the barrier in the hot zone; indeed, a significant part of the early hydration of the middle and outer barrier zones is due to the condensation of vapour coming from the inner region. Naturally, those hydraulic changes cause variations in thermal conductivity that, in turn, affects heat conduction. It is interesting to note that the analysis is able to reproduce very satisfactorily the thermo-hydraulic observations; even from a quantitative point of view, predictions agree quite well with observations.



Figure 11. Variation of relative humidity with time in the engineered barrier: observations and computed results. a) section C (cool zone), b) section H (between heaters).

Mechanical. Because of the very limited movements that the confined bentonite barrier can undergo, the main mechanical parameter considered is total stress. It would be expected that stresses in the barrier will increase very significantly during hydration because of the high swelling potential of a heavily compacted bentonite. As Figure 12 demonstrates, such an increase is indeed observed reaching quite high values of total stresses at the end of the test, of the order of 2–4 MPa. Unfortunately, it is not easy to measure reliably total stresses as the scatter of observations clearly indicates. It is difficult, therefore, to check in detail the agreement with the results from the analysis.



Figure 12. Variation of total radial stress with time in the engineered barrier: observations and computed results. Section E1.

It is however possible that the slower development of the measured swelling stresses as compared to the predictions from the analysis may be due, at least in part, to the initial liner/barrier and rock/barrier gaps, not accounted for in the modelling. In any case, it can be noted that the predicted final total stress in the barrier is similar to that measured in quite a number of total stress cells.

7.2 Host rock (granite)

The host rock, granite, is subjected to more limited heat loading and, therefore, the observed effects are bound to be more muted. However, to complete the picture of near field behaviour, it is necessary to examine the behaviour of the rock mass during the test.

Thermal. Figure 13 shows, as an example, the evolution of the temperature measured in borehole SF21. Four temperature sensors at different distances from the tunnel axis were installed in the borehole. A rapid increase of temperature is again observed at the start of the test followed by a constant but gentle rise. Observed temperatures in the rock reached a maximum value of about 40°C. The values and evolution of the temperatures are well predicted in practically all observation points, indicating again that the thermal conductivity estimate was quite accurate.

Hydraulic. The initial pore pressure field in the granite was determined in a comprehensive hydrogeological investigation performed before the test that provided the initial hydraulic conditions for the analysis (Ortuño et al. 2005). Those pore pressures were subsequently affected by the excavation of the tunnel for the installation of the experiment. By modelling this excavation, the new pore pressure distribution was



Figure 13. Variation of temperatures with time in the host rock: observations and computed results. Borehole SF21.



Figure 14. Variation of pore pressures with time in the host rock: observations and computed results. Borehole SF24.

largely reproduced. During the thermal test, it was observed that the pore pressures in the granitic rock were little affected by heating. What Figure 14 shows is basically the recovery of pore pressures after excavation. The same process is in fact predicted by the numerical analysis. This is quite different from the very strong hydrothermal response of argillaceous rocks in similar circumstances (Gens et al. 2007).

Mechanical. Both displacements and total stresses have been measured in the rock. The measured radial displacements are shown in Figure 15; they are quite



Figure 15. Variation of radial displacements with time in the host rock: observations and computed results. Borehole SI1.



Figure 16. Variation of total stresses with time in the host rock: observations and computed results. Borehole SG2.

small (of the order of 0.1 mm) and they develop in response to the increase of temperature. The predicted radial displacements are also small but larger than the observed ones. It is likely, therefore, that the thermal expansion of the rock was overestimated in laboratory tests performed to determine thermal dilation.

Measured normal stresses in borehole SG2 are plotted in Figure 16. Again, the difficulty of measuring stresses is reflected in the rather erratic nature of the observations. It is clear, though, that the magnitude of stress increase reduce as the distance to the tunnel becomes larger. Although the development of



Figure 17. Layout of the experiment after dismantling.

swelling pressure in the bentonite contributes to the rock stress increase, the major factor in rock stress development is the rise of temperature. Stresses computed in the numerical analysis appear to provide a good estimate of the magnitude of the observed stress increase although it is difficult to judge the accuracy of the predicted evolution.

8 OBSERVATIONS DURING THE DISMANTLING OF THE EXPERIMENT

Exactly after five years of heating, Heater 1 (the one closest to the concrete plug) was switched off. After allowing 33 days for cooling, the bentonite was carefully removed up to the end section of Heater 1, leaving the rest of the barrier in place. At the same time, Heater 1 was removed from the experiment. Those operations lasted for an additional 75-days period. Subsequently, a new shotcrete plug was constructed and the test on the remaining part of the experiment continued (Fig. 17). A detailed description of the procedures during dismantling is presented in Bárcena et al. (2003).

This partial test dismantling allowed the direct and detailed observation of the state of the barrier after five years of heating and hydration. In addition, large amounts of quantitative data could be obtained; this information provides an opportunity to check the performance and reliability of the numerical model in a completely predictive mode. At selected sections, a large number of specimens were cored out from the barrier and dry density and water content were determined immediately in a field laboratory in order to minimize disturbance and humidity loss. This comprehensive set of values of dry density and water content helped to provide a complete picture of the state of the bentonite barrier. Thanks to the high density of determinations, contours of dry density and water content can be plotted in the sampled sections. An example is presented in Figure 18 where it can be observed that the process of hydration and associated density changes is basically axisymmetric.



Figure 18. Contours of (a) water content and (b) dry density measured during dismantling. Hot section near the middle of Heater 1.

Figure 19 shows the all measured values of water content and dry density as a function of distance to the tunnel axis for a section near the middle of Heater 1; it is therefore representative of a hot region of the test. It can be observed that, as expected, water content increases as the rock is approached, consistent with the process of natural hydration from the rock. It is also interesting to observe that the part of the barrier close to the heater is still below its initial value of water content, a consequence of the strong drying that has occurred in this area. In spite that a certain amount of water has already reached the inner region, it is still insufficient, after five years, to compensate for the initial drying. It is also noticeable that the barrier as a whole is very far from full saturation at the end of the heating stage.

The distribution of dry density also shows the expected patterns. Close to the rock the clay has expanded, exhibiting values of dry density well below its initial value. In contrast, in the zone near the heater the dry density has increased. Because of the confined nature of the test, the variation of dry density in the



Figure 19. Dismantling observations and computed results: a) dry density, b) water content. Hot section near the middle of Heater 1.

inner part is compensated by the reduction of dry density in the outer part. It should be noted that the change of dry density (i.e. porosity) is the combined effect of expansion due to temperature increase (thermal effect), suction changes (hydraulic effect) and stress increase due to the development of swelling pressure (mechanical effect).

Water content and dry density values are also plotted for a cool section (Fig. 20) where the temperature increase is very limited. There are some differences in the patterns of observations. Water content again increases as the rock is approached but, now, there is also a net (but small) gain of water content near the



Figure 20. Dismantling observations and computed results: a) dry density, b) water content. Cool section.

centre of the tunnel. There has been no drying in this region but the amount of hydration is very small, even after five years, because of the larger thickness of the barrier in this section. The dry density also shows a significant reduction close to the rock but a somewhat smaller increase in the inner part where the change appears to be more uniform. Again, the net volume change of the section is quite small.

It is interesting to observe that the results of the numerical analysis show a very good agreement with the measurements. The patterns of the hot and cool sections are reproduced very well and the quantitative agreement between observations and predictions is quite close. It should be noted that to obtain those predictions, the numerical analysis has simulated the cooling stage and the excavation performed prior to sampling operations. Dismantling operations lasted for two months; the time required to reach each particular sampling section has also been incorporated in the analysis.

9 CONCLUDING REMARKS

Nuclear energy production generates high level radioactive waste that must be isolated for very long periods. At present, the most widely adopted method for disposal is the construction of deep underground repositories in suitable geological media. The performance and safety assessment of these facilities require a good understanding and adequate modelling facilities for all components of the system. Often, one of these components is an engineered barrier composed of compacted expansive clay that fills the space between the canisters containing the waste and the host rock. Understanding the complex THM phenomena occurring in the barrier in the early life for the repository require adequate modelling. The paper has presented a formulation that encompasses, in a coupled manner, all the relevant THM processes and their interactions. It has been shown that the formulation and computer code has enabled quite a successful modelling a large scale test that simulates the THM behaviour of the clay barrier under full scale conditions. Consequently, it can be stated that formulation and computer code constitute a useful numerical tool for tackling this type of THM problems.

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Application of solid potassium permanganate to oxidize VOC vapours: Batch and column experiments

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ABSTRACT: Volatile organic compounds (VOCs) may cause major contamination problems in groundwater and soil. Their presence in air can create a hazard to public health. However, limited remedial options exist in controlling the vapour transport of these compounds in the unsaturated zone. In this study, batch and column experiments were carried out to investigate the oxidation of TCE, ethanol, and toluene vapour in air by solid potassium permanganate under different condition. The kinetic of chemical oxidation has been investigated widely for dissolved VOCs in the saturated zone. But, so far there have been few studies on the use of in-situ chemical oxidation (ISCO) of vapour phase contaminants. Results of batch experiments revealed that solid potassium permanganate is able to transform the vapour of these compounds into harmless oxidation products. The oxidation rates for TCE and ethanol were higher than for toluene. The oxidation process was modeled using a kinetic model, linear in the gas concentration of VOC [ML⁻³] and relative surface area of potassium permanganate grains (surface area of potassium permanganate divided by gas volume) $[L^{-1}]$. The second-order reaction rate constants (cm s⁻¹) for TCE, ethanol, and toluene were found to be equal to 2.0×10^{-6} , 1.7×10^{-7} , and 7.0×10^{-8} , respectively. Column experiments were carried out to study the impact of water saturations on the removal efficiency and longevity of potassium permanganate. Results of column experiments showed that the efficiency and longevity of potassium permanganate increased with water saturations. Results also showed that the efficiency of potassium permanganate depends on the solubility of target compound in water.

1 INTRODUCTION

Volatile organic compounds (VOCs) are defined as organic compounds with boiling points (at 1 amt) below 260°C (De Nevers, 2000). VOCs have high vapour pressures under normal conditions, so they can easily vaporize into the atmosphere or form vapour plumes in the soil (Kim et al., 2007). VOCs are present in some household products and automobile liquids (Berscheid et al., 2010).

Releases of VOCs to the environment have occurred through surface spills, leaking underground storage tanks, and inadequate disposal practices (Berscheid et al., 2010). Small quantities of VOCs may contaminate large volumes of water. When released as free product, VOCs may migrate downward to significant depths through the soil. In addition, VOC vapours can migrate upwards to the surface through diffusion and produce elevated concentrations within indoor air spaces (Berscheid et al., 2010). Exposure to some VOCs might affect central nervous system and internal organs, and might cause symptoms such as headache, respiratory tract irritation, dizziness and nausea, known as the Sick Building Syndrome (SBS) (Yu, and Lee, 2007).

We have chosen TCE, ethanol, and toluene, as model VOCs (target compounds) for chlorinated solvents, biofuel, and mineral oil, respectively, for the reasons explained below.

TCE is one of the most common man-made chemicals found in soil (Albergaria et al., 2012). It has been widely used as a dry cleaning solvent, degreasing agent, and chemical extraction agent. Since TCE is carcinogenic, its movement from contaminated groundwater and soil into the indoor air of overlying buildings is of serious concern (EPA, 2011).

Ethanol is being increasingly used in (renewable) fuel alternatives and as replacement for methyl tertiary-butyl ether (MTBE), which, despite helping to accomplish Clean Air Act goals, has caused widespread water contamination problems (Johnson et al., 2000; Capiro et al., 2007). Ethanol can reduce the biodegradation rate of light non-aqueous phase liquid (LNAPL) such as benzene, toluene, ethylbenzene, and xylene isomers (BTEX) in groundwater and soil (Mackay et al., 2007; Freitas et al., 2010).

Toluene is found frequently in indoor environments. Toluene is mainly used as an additive to improve the octane number of gasoline (Yu and Lee, 2007).

One of most common treatment techniques for unsaturated zone polluted with VOCs is soil vapour extraction (SVE). This is a long-term operation and does not convert a contaminant to less toxic compounds. A promising alternative is in-situ oxidation of VOC that can lead to favourable results in less time. Oxidation of VOCs may convert hazardous contaminants to harmless compounds. The oxidizing agents most commonly used for the treatment of hazardous contaminants are potassium permanganate, ultraviolet radiation, ozone, chlorine dioxide, hydrogen peroxide, sodium persulfate, and Fenton's reagent (H₂O₂ oxidation in the presence of ferrous iron, Fe²⁺).

Among these oxidants, potassium permanganate has been receiving increased attention for the treatment of liquids, slurry soils, and sludges polluted with VOCs (Kao et al., 2008). Early laboratory studies have indicated that dissolved potassium permanganate can remediate a variety of organic compounds, chlorinated alkanes (Waldemer, and Tratnyek, 2006), chlorinated ethylenes (Huang et al., 1999; Hood et al., 2000; Yan and Schwartz, 2000; Waldemer and Tratnyek, 2006; Kao et al., 2008; Urynowicz, 2008), oxygenates (Jaky et al., 2000; Damm et al., 2002; Waldemer, and Tratnyek, 2006), BTEX (Gardner, 1996; Rudakov and Lobachev, 2000; Waldemer, and Tratnyek, 2006), substituted phenols (Jin et al., 2003; Waldemer, and Tratnyek, 2006) and PAHs (Forsey, 2004), in aqueous phase. However, the potential of solid potassium permanganate to oxidize VOC vapours in unsaturated zone is currently unknown.

In this study, we demonstrate the ability of solid potassium permanganate to oxidize VOC vapours. Currently, the literature lacks data on the reaction between solid oxidants such as permanganate and vapour phase of contaminants. Therefore, we planned a series of batch and column experiments with four objectives: (1) to evaluate the ability of solid potassium permanganate to oxidize vapour phase contaminants, (2) to determine kinetic parameters for TCE, ethanol, and toluene oxidation by solid potassium permanganate, (3) to evaluate the ability of solid potassium permanganate as a horizontal permeable reactive layer to oxidize the vapour of three VOCs under saturated conditions, and (4) to investigate the impact of water



Figure 1. A schematic view of the column.

saturation on the removal efficiency and longevity of potassium permanganate.

2 MATERIALS AND METHOD

2.1 Materials

The contaminants used in this study were TCE, ethanol, and toluene (from Sigma-Aldrich, Merck and ACROS companies, respectively). Solid potassium permanganate of 99% purity was obtained from Sigma-Aldrich. The sand used in this study was extracted from river bed in Papendrecht (Filcom Company, Netherlands) and sieved $\sim 0.5-1$ mm.

The deionized (DI) water was used to provide the different saturations for the combination of solid potassium permanganate and sand in column experiments.

Since TCE reaction experiment produces proton (Equation 1), we used NaHCO₃ and CaCO₃ (Merck) as basic salts to control pH during the experiment.

A 10-mL transparent glass vial (Headspace-vial, Grace), which was capped with a magnetic cap (Tin plate magnetic crimp cap, Chromacol) and hard septum (DK GRY, Agilent) was used as batch.

A cylindrical column glass of 5 cm length and 2 cm internal diameter and a steel stainless lid was employed to perform experiments involving the vapour intrusion and a horizontal reactive barrier (Figure 1). The column was divided into two parts by a glass filter. Column was equipped with three valves for injecting pure phase of VOC, adding air, and taking samples.

2.2 Experimental procedure

2.2.1 Batch experiment

We used 4.8×10^{-6} , 3.5×10^{-6} , 2.3×10^{-6} moles of TCE, ethanol, and toluene vapours, respectively.

These chemical were calculated in 1.5 mL of gas samples (under normal conditions). Oxidation reactions for TCE, ethanol, and toluene vapours, respectively, by solid potassium permanganate are as follows:

$$\begin{split} & C_{2}HCl_{3}+2KMnO_{4}\rightarrow 2K^{+}+3Cl^{-}+2MnO_{2(s)}+H^{+}+2CO_{2(g)} \quad (1) \\ & C_{2}H_{5}OH+4KMnO_{4}+4H^{+}\rightarrow 4K^{+}+4MnO_{2(s)}+2CO_{2(g)}+5H_{2}O \quad (2) \\ & C_{6}H_{5}CH_{3}+12KMnO_{4}+12H^{+}\rightarrow 12K^{+}+12MnO_{2(s)}+10H_{2}O+7CO_{2(g)} \quad (3) \end{split}$$

The required amount of potassium permanganate for oxidizing above-mentioned amount of TCE, ethanol, and toluene were estimated to be 1.25, 2.22, and 4.44 mg, respectively. These were calculated based on reactions in an aqueous environment, assuming a full dissolution of crystals. In dissolved form, potassium permanganate may be fully available for oxidation. But, in the solid form only the surface of potassium permanganate grains is in contact with the gas phase. Accordingly, more potassium permanganate is needed to avoid limitation in the degradation rate. Hence, excess amount of potassium permanganate (namely, 2.703 g) was used for each batch.

Potassium permanganate grains were put inside 12-mL transparent glass vials, which were capped with a hard septum to prevent any leakage. VOC vapour was injected using a gas tight syringe (2.5 mL Hamilton, SGE) and 16 mm disposable needles (Φ 0.5 mm, Terumo).

In order to get kinetic parameters, three batch experiments at three different initial amounts of vapour and potassium permanganate were performed for all compounds (Table 1). All experiments were carried out in duplicate. For each experiment, we prepared several identical batches and each batch was allocated to a given sampling time.

A control experiment was also performed in duplicate for each compound to ensure that the loss of target compound due to leakage was negligible over the course of the experiments. To prepare a control batch, a 12-ml transparent glass vial was capped with a hard septum. Then VOC vapour was injected into the vial. All experiments were carried out in a vertical rotary shaker, at room temperature, $20 \pm 2^{\circ}$ C, and air humidity of $37 \pm 2\%$, which is also the initial humidity inside the vials.

2.2.2 Column experiment

Different combinations of mass of solid potassium permanganate grains (20 g), dry sand (10 g), and various water saturations (0, 20, 40, and 60%) were placed on the glass filter.

To provide the desired saturation, both solid potassium permanganate and sand were put into a small plastic container. This mixture was moisted with the required amount of DI water. To prepare a well mixed

Table 1. Initial experimental conditions for batch experiment.

VOC	Exp.	*[C] _o (mol)	M _{KMnO4} (g)	**V _{gas} (cm ³)	A (cm ²)	***S _o (cm ⁻¹)
TCE	1 2 3	$\begin{array}{c} 6 \times 10^{-5} \\ 3 \times 10^{-5} \\ 6 \times 10^{-5} \end{array}$	2.703 2.703 1.351	10.5 10.5 10.5	2703 2703 1351.5	257.43 257.43 128.71
Ethanol	1 2 3	6×10^{-5} 3×10^{-5} 6×10^{-5}	2.703 2.703 1.351	10.5 10.5 10.5	2703 2703 1351.5	257.43 257.43 128.71
Toluene	1 2 3	$\begin{array}{c} 6 \times 10^{-5} \\ 3 \times 10^{-5} \\ 6 \times 10^{-5} \end{array}$	2.703 2.703 1.351	10.5 10.5 10.5	2703 2703 1351.5	257.43 257.43 128.71

*[C]_o: Initial concentration of compound, ** V_{gas} : Volume of the gas in batch, *** S_o : Initial relative surface area

combination of required materials, the mixture was packed and shaked for 20 min. Finally, the mixture was place on the glass filter and the column was immediately capped by a steel stainless lid.

To provide the vapour of target compounds, 2.5 ml pure phase of target compounds was injected into the bottom part of column. Control columns with 30 g sand and same saturation conditions were carried out for all compounds.

To prevent the photodecomposition of potassium permanganate, all columns were wrapped by aluminum foil. The columns were kept at room temperature $(22 \pm 1^{\circ}C)$.

2.3 Sampling and measurements

2.3.1 Batch experiment

Reaction and control batches were periodically sampled using a gas tight syringe until no detectable concentration was found in the reaction vial. To eliminate the effect of pressure drop due to sampling, each vial was used only once.

The concentrations of target compounds, TCE, ethanol, and toluene were measured by a gas chromatograph (GC). Gas samples of 2 mL were taken using the headspace syringe of the GC from each vial. Then, samples were injected into the GC. The GC (Agilent Technologies 6850) equipped with a capillary column (0.25 mm \times 60 m), a flame ionization detector, and a purge and trap.

Specific surface area of potassium permanganate was measured using 10-point Brunauer-Emmett-Teller (BET) method by a Nova 3000 from Quantachrome. Performance of this machine was controlled using reference 173 from Community Bureau of Reference. Samples were degassed at 120°C overnight before measurements. The relative surface area was calculated as the surface area per volume of gas (Table 1).

To calculate the amount of the potassium permanganate consumption, at the end of each experiment, potassium permanganate grains were dissolved in DI water and its concentration was measured using a UV-Spectrophotometer (UV-1800, Shimadzu) at a wavelength of 525 nm.

2.3.2 Column experiment

At various times 1.5 ml sample from headspace of reaction and control columns were taken using a 2.5 ml gas tight syringe (SGE Analytical Science, Australia). At the same time, in order to eliminate the effect of pressure drop due to sampling, the same volume of air (1.5 ml) was injected in upper part of the column. Then, the gas sample was injected to a 10-ml transparent glass vial which was capped with a magnetic cap and hard septum (Magnetic Bitemall; Red lacquered, 8mm center hole; Pharma-Fix-Septa, Silicone blue/PTFE grey; Grace Alltech). Sampling vials were immediately put into the tray of a gas chromatograph (GC). Then, the concentrations of target compounds were measured by the GC. In the GC, the headspace method was used to determine the concentration of target compounds.

Total organic carbon content (TOC) of the dried and sieved (grain diameter $<250 \,\mu$ m) soil sample were measured in an elemental analyzer (Fisons Instruments NA 1500 NCS). We also measured dissolved organic carbon using Geolab GL-WV-014 method (Shimadzu TOC-5050A).

3 RESULTS AND DISCUSSION

3.1 Target compound oxidation in batch system

Figure 2 depicts the normalized concentration (C/C_0) of the target compounds as a function of time, where C denotes the observed concentration of the target compound for a given time and C_0 is the initial concentration of the target compound. Oxidation of target compounds shows an exponential trend, as indicated by the fitted formula in the graph (Figure 2). These results also show that solid potassium permanganate was able to rapidly oxidize the vapour phase of TCE and ethanol. Toluene was also degraded but less rapidly. No VOC intermediates or by-products were found in vapour samples. During the experiment, potassium permanganate crystals turned into dark color, which is the color of a coating layer of produced manganese dioxide (MnO₂). Moreover, we compared results of oxidation of VOCs in vapour phase with the oxidation of VOCs in aqueous phase that we have performed and also reported in the literature (Waldemer, and Tratnyek, 2006). We found that the oxidation process in aqueous phase takes place in shorter time. Otherwise the oxidation in both phases is similar. So, for example, the oxidation rate for TCE was much higher than for the other two compounds. However it takes place in short time.

3.2 Kinetic analysis of batch data

Since the degradation of three reactants showed an exponential trend (Figure 2), we assumed that the kinetics followed a first-order reaction rate. We also assumed that only surface of solid potassium permanganate reacts with compounds. So, to a proper calculation of the reaction rate coefficient, we should have an equation that involves the physical properties of



Figure 2. Degradation date for TCE, ethanol, and toluene vs. time using from batch Experiment 1 (Exp. x-y: x denotes number of experiment and y is the experiment repetition).

potassium permanganate, such as the surface area and mass of potassium permanganate. Such an equation may be written as:

$$\frac{dC}{dt} = -k C S \tag{4}$$

where k denotes the reaction rate constant, C is the vapour concentration of compound $[ML^{-3}]$, t is time [T], and S is the relative surface area of solid potassium permanganate $[L^{-1}]$, which is defined as:

$$S = \frac{A}{V}$$
(5)

where A is the surface area of the potassium permanganate $[L^2]$ and V is the volume of the gas phase $[L^3]$.

First, we assumed the relative surface area not to alter significantly during the course of the reaction.

Table 2. Reaction rate constants for oxidation of TCE, ethanol, and toluene in vapour phase at 20° C.

Compound	$K (cm s^{-1})$	R ²
TCE Ethanol Toluene	$\begin{array}{c} 2.0\times 10^{-6} \\ 1.7\times 10^{-7} \\ 7.0\times 10^{-8} \end{array}$	9.6×10^{-1} 9.8×10^{-1} 9.9×10^{-1}

 R^2 = The square of the correlation coefficient.

To validate this assumption, we determined the amount of potassium permanganate that was consumed, at the end of the experiment. This was done by dissolving potassium permanganate grains which were used in the experiments in DI water and then using a spectrophotometer to determine its mass. We compared this to the initial mass and the result showed that there was no significant consumption of solid potassium permanganate during our experiments.

With S set equal to S_0 Equation 4 can be solved to obtain:

$$\frac{1}{S_0} \operatorname{Ln} \frac{C}{C_0} = -kt \tag{6}$$

where S_0 denotes the initial relative surface area of potassium permanganate $[L^{-1}]$. According to Equation 6, plot of $1/S_0 LnC/C_0$ versus time should yields a straight line. Then, the reaction rate constant k can be obtained from the slope of this line. We used all data from Experiments 1, 2, and 3 to estimate k for each compound. Figure 3 shows that the plots of $1/S_0$ LnC/C_0 versus time for all compounds. The square of linear correlation coefficients (R²) obtained for TCE, ethanol, and toluene were 9.6×10^{-1} , 9.9×10^{-1} , and 9.9×10^{-1} , respectively. Results suggest that the oxidation of the target compounds can be modelled by Equation 6 as long as sufficient relative surface area of potassium permanganate is available. These results also show the accuracy of reaction rate constants which are given in Table 2.

We compared results of our experiments with the oxidation of VOCs in aqueous phase reported in the literature (Waldemer, and Tratnyek, 2006). We found that the oxidation process in both phases follows a first-order model. This comparison also revealed that the oxidation rates for VOCs in vapour phase are much smaller than for aqueous phase. However, in both phases, the reaction rate for TCE is higher than for ethanol and toluene. As mentioned above, as a result of oxidation, MnO₂ is produced and coats the grains. This may affect the efficiency of oxidation process. To analyze the effect of surface coating, we accounted for the reduction of the relative surface area during the experiment. This was done by supplementing Equation 4 with an equation relating the relative surface area to the MnO₂ concentration. This resulted in the following equation:

$$\frac{\mathrm{dC}}{\mathrm{dt}} = -\mathrm{kC}[\mathrm{S}_{\mathrm{o}} - \frac{\omega}{\gamma}(\mathrm{C}_{\mathrm{o}} - \mathrm{C})] \tag{7}$$



Figure 3. Plot of $1/S_0 LnC/C_0$ (denoted by y) vs. time (denoted by x) for evaluating k following Equation 6. Data are from batch experiments.

where ω is the number of moles of MnO₂ produced per mole of target compound (based on stoichiometry reaction) and γ is the coating factor (number of moles of produced MnO₂ per area of potassium permanganate grains) [ML⁻²].

3.3 Impact of water saturation on the removal efficiency and longevity of potassium permanganate

Figures 4–6 depict the normalized concentration (C/C_0) of the target compounds as a function of time for different saturation values. Oxidation of a target compound gradually increases with time. The concentration of VOC vapours reaches to the concentration of control experiment due to the coating effect of produced MnO₂ during the experiment. The results for different water saturations showed that the efficiency and longevity of potassium permanganate increased with saturation, so that, at the highest saturation ($S_w = 60\%$), we observed a high removal efficiency for all target compounds. Results also showed that the efficiency of potassium permanganate depends on the solubility of the target compound in water. Dissolution



Figure 4. Oxidation of TCE vapour under different water saturations in column experiments.

of VOC vapours into water around and between grains can increase the residual time of VOC in the reactive layer (combination of potassium permanganate, sand, and water). Since potassium permanganate is soluble in water (6.38 g/100 mL; 20°C), it also gives a chance to the dissolved potassium permanganate to remove VOC from water. As shown in Figures 4–6, the removal efficiency of potassium permanganate for ethanol is much higher than for TCE and toluene.



Figure 5. Oxidation of ethanol vapour under different water saturations in column experiments.

Since ethanol is fully miscible in water, it is expected that more ethanol vapour (mass of ethanol) can be removed during the vapour migration.

3.4 Intermediate products in column experiments

We found intermediates products during TCE and ethanol oxidation in column. At high saturation conditions ($S_w = 0.6$) for TCE experiment, an inorganic



Figure 6. Oxidation of toluene vapour under different water saturations in column experiments.

compound, with the formula manganese heptoxide (Mn_2O_7) was observed after one hour. Manganese heptoxide is produced as dark-green oil by the addition of concentrated sulfuric acid to potassium permanganate (Equation 8). The reaction initially produces permanganic acid, HMnO₄ (structurally, HOMnO₃), which is dehydrated by sulfuric acid to form its anhydride, Mn₂O₇.

$$2KMnO_4 + 2H_2SO_4 \rightarrow Mn_2O_7 + H_2O + 2H_2SO_4 \qquad (8)$$

$$2MnO_4^- + 2H^- \longrightarrow Mn_2O_7 + H_2O$$
⁽⁹⁾

To control pH during the oxidation of TCE vapour $(S_w = 0.6)$, we used sodium bicarbonate $(NaHCO_3)$ and calcium carbonate $(CaCO_3)$ as basic salts. Both salts could control pH in TCE oxidation and prevent Equation 9 to take place. However, results showed that sodium bicarbonate can increase the removal efficiency potassium permanganate more that calcium carbonate.

We also measured two unknown peaks (compounds) in the GC results for ethanol experiment ($S_w = 0.6$). To determine these compounds, three gas samples were analyzed by Chromatography-Mass Spectrometry (GC-MS).

Results showed that first peak belongs to ethyl acetate and second one to 1,1-diethoxyethane. We also found that ethanol can react with potassium permanganate and produces ethanoic acid based on the following two reactions:

$$3C_2H_5OH + 4KMnO_4 + 4H^+ \rightarrow 4K^+ + 4MnO_2 + 3CH_3COOH + 5H_2O$$
 (10)

or

 $3C_2H_5OH + 4KMnO_4 \rightarrow 4K^+ + 4MnO_2 + 3CH_3COOH + H^+ + 5OH^-$ (11)

Above Equations show that reaction can occur in both neutral and acidic conditions. Equation 10 may produce water but Equation 11 gives H^+ and decreases pH. Ethanoic acid, by-product of Equation 10 and 11, again might react with ethanol. If reaction take places based on the equation 10, ethyl acetate (C₄H₈O₂) can be produced otherwise 1,1-diethoxyethane (C₆H₁₄O₂) will be formed.

$$C_2H_5OH + C_2H_4O_2 \longrightarrow C_4H_8O_2 + H_2O$$
(12)

$$5C_2H_5OH + C_2H_4O_2 \xrightarrow{H^+} 2C_2H_{14}O_2 + 3H_2O$$
 (13)

We found that they observed only in high saturation conditions ($S_w = 0.6$). During experiment, first these peaks became larger and then disappeared. It seems that the concentration of these two peaks positively correlated to concentration of ethanol and water saturations.

4 CONCLUSION

In this study, we investigated the oxidation of both chlorinated and non-chlorinated hydrocarbon vapours by solid potassium permanganate under room temperature and humidity conditions. Results showed that potassium permanganate is able to oxidize the vapour of TCE, ethanol, and toluene. This study also shows that TCE and ethanol in vapour phase can be rapidly oxidized by solid potassium permanganate. Toluene, however, is degraded much slower.

A linear kinetic oxidation model, based on the concentration of VOC in gas and a constant relative surface area, effectively predicted the rate of TCE, ethanol, and toluene degradation. Results revealed that the reaction rate constants (cm s⁻¹) for TCE, ethanol, and toluene are 2.0×10^{-6} , 1.7×10^{-7} , and 7.0×10^{-8} , respectively. Results also showed that the amount of used potassium permanganate for all three compounds was only a small fraction of initial amount (around 4%).

Results of column experiments showed that the efficiency and longevity of potassium permanganate increased with water saturations and solubility of target compound.

These findings will be helpful in designing a horizontal permeable reactive barrier with solid potassium permanganate in unsaturated zone for vapour intrusion. The performance of such methodology may be affected by temperature of the soil matrix. Also, one has to consider the health effects of by-product gases such as ethane (Pant and Pant, 2010) and methane (Freitas et al., 2010) that can be produced under anaerobic biodegradation of TCE and ethanol, respectively.

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General reports

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Membrane behavior in engineered bentonite-based containment barriers: State of the art

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ABSTRACT: Membrane behavior in clays is a coupled phenomenon that results in solute restriction and chemico-osmosis. Thus, the containment function of engineered clay-based barriers used for geoenvironmental applications (e.g., landfills, waste impoundments, contaminated groundwater control) can be enhanced if such barriers exhibit membrane behavior. In particular, membrane behavior has been shown to be potentially significant in bentonite, such that engineered barriers comprised wholly or partly of bentonite (e.g., geosynthetic clay liners [GCLs], compacted clay liners [CCLs], and soil-bentonite [SB] cutoff wall backfills) may offer improved containment performance relative to the expected performance based on conventional contaminant transport analyses that neglect membrane behavior. Thus, the purpose of this paper is to provide a state-of-the-art review of the available information pertaining to the existence and magnitude of semipermeable membrane behavior in engineered, bentonite-based containment barriers. After illustrating conceptually the reduction in contaminant concentration emanating from engineered containment barriers that exhibit membrane behavior, a brief description of the expressions governing liquid and chemical mass fluxes through clay membranes is provided. This brief description is followed by a detailed description of the experimental considerations required for measuring membrane behavior in the laboratory. Of particular note is the distinction between the use of open and closed systems for performing such experiments, with emphasis on the relative advantages of closed systems, followed by a detailed description of the closed-system approach for conducting membrane testing. Example results from different studies involving closed-system membrane testing of a GCL, two SB backfills, and a bentonite-amended CCL then are presented to illustrate the types of data typically obtained from such testing. The effects of four independent variables then are illustrated, including salt concentration, bentonite content, salt cation valence, and effective confining stress. Although the data are limited and exceptions do exist, membrane behavior in bentonite-based barriers is shown to increase with decreasing concentration of simple monovalent salt solutions (e.g., KCl) and with increasing bentonite content and/or effective confining stress. However, the use of salt solutions containing multivalent cations (e.g., Ca²⁺) has been shown to adversely affect the existence and magnitude of membrane behavior. Finally, recommendations are given for further research and relevant conclusions are drawn.

1 INTRODUCTION

The primary objective of clay barriers used for geoenvironmental containment applications, such as the containment of solid wastes and liquids (e.g., landfills, liquid impoundments, etc.) and the containment or control of contaminated groundwater, is to minimize the migration of contaminants into the surrounding environment. With respect to this objective, the existence of semipermeable membrane behavior, whereby solutes are restricted from migration through the clay barrier, represents a potentially significant beneficial aspect that presently is not considered in practical applications. In this regard, the potential existence and magnitude of such membrane behavior in clay barriers has been the subject of significant research over the past 15 years (Keijzer et al. 1999, Keijzer 2000, Malusis 2001, Malusis & Shackelford 2001, 2002a,b,c, 2004a,b, Malusis et al. 2001a,b, 2003,

2012, 2013, Shackelford et al. 2001, 2003, Shackelford & Malusis 2002, Van Impe 2002, Dominijanni & Manassero 2003, 2005a,b, 2008, 2012a,b, Manassero & Dominijanni 2003, Mazzieri et al. 2003, 2005, 2010, Shackelford & Lee 2003, Van Impe et al. 2003, 2005, Yeo 2003, Henning 2004, Lu et al. 2004. Domimijanni 2005, Garavito 2005, Yeo et al. 2005, Dominijanni et al. 2006, 2013, Henning et al. 2006, Evans et al. 2008, Kang 2008, Kang & Shackelford 2009, 2010, 2011, Whitworth & Ghazifard 2009, Di Emidio 2010, Shackelford 2011, 2012, Bohnhoff 2012). The results indicate that membrane behavior can exist in clay containment barriers, but this behavior is likely to be significant only in clay barriers that contain high swelling smectite minerals (e.g., montmorillonite), such as sodium bentonite (Shackelford et al. 2003).

Accordingly, the objective of this paper is to provide a state-of-the-art review with respect to the existence and magnitude of membrane behavior in the various types of bentonite-based barriers commonly used for geoenvironmental containment applications. The focus of the review is on barriers that are comprised wholly or partially of sodium bentonites, and more specifically on those bentonite-based barriers that are engineered for containment applications as opposed to natural smectitic clay formations (aquitards, aquicludes) that may behave as semipermeable membranes (e.g., Greenberg et al. 1973). These engineered barriers generally include geosynthetic clay liners (GCLs), soil-bentonite (SB) backfills for vertical cutoff walls, and bentonite amended natural clays that are used as compacted clay liners (CCLs) (Shackelford 2012).

2 DEFINITIONS & MOTIVATION

2.1 Definitions & terminology

Membrane behavior in clays represents the ability of clays to exclude dissolved (aqueous miscible) chemical species, or solutes, from entering the pores of the clays, thereby restricting the migration of the solutes through the clays. In the case of charged inorganic solutes (i.e., anions and cations), this restriction occurs when the pore sizes between individual clay particles are sufficiently small such that electrostatic repulsion of the ions results from the interaction of electric fields associated with adjacent clay particles (e.g., Fritz 1986). Such solute restriction also leads to the process known as chemico-osmosis, whereby water (H₂O) migrates from a location of lower solute concentration (higher water activity) to a location of higher solute concentration (lower water activity) (Fritz 1986, Shackelford et al. 2003). Neutral (uncharged) solutes also may be restricted from migrating through clays if the solute exhibits polar charge character despite being neutral (e.g., carbon tetrachloride), or if the physical structure of the chemical molecule is simply too large to fit through the pores. This latter mechanism of solute restriction is referred to as steric hindrance, and is expected to be more prevalent in the case of large-chain organic molecules.

Clay membrane behavior is quantified in terms of a "membrane efficiency coefficient" that represents the relative extent of solute restriction. In the geotechnical engineering literature, this efficiency coefficient is designated by the symbol ω and commonly referred to as the "chemico-osmotic efficiency coefficient," or simply the "osmotic efficiency coefficient." In the science literature, the membrane efficiency coefficient often is referred to as the "reflection coefficient" and designated by the symbol, σ . The symbol ω is preferred in the engineering literature because the symbol σ commonly represents applied or total stress in the engineering literature, and the terminology for ω of "chemico-osmotic efficiency coefficient" is preferred because other osmotic phenomena can exist in clays, including "electro-osmosis" and "thermo-osmosis" (e.g., Mitchell & Soga 2005, Medved & Černý 2013). The writer prefers using the term "membrane

efficiency coefficient" for ω , and the term "membrane efficiency" to refer to the value of ω expressed in percent.

Although negative values of ω (or σ) have been reported in some cases due to atypical circumstances resulting from processes such as "diffusion-osmosis" (e.g., Olsen et al. 1990), the vast majority of ω (or σ) values typically range from zero for clays exhibiting no membrane behavior to unity (100%) for "perfect" or "ideal" membranes that prohibit passage of all solutes. Membranes with efficiencies less than 100 % (i.e., $\omega < 1$) are referred to as "imperfect" or "nonideal." Imperfect membranes also have been referred to as "semipermeable," "selectively permeable," "partially permeable," or "differentially permeable" (Shackelford 2011). These other terms result because perfect membranes are still permeable to the solvent water molecules (H₂O), whereas imperfect membranes also allow some solutes to migrate through the larger pores of the clay. Clays that exhibit membrane behavior generally are non-ideal, because the variation in pore sizes inherent in most clays results in only some of the pores within the clay being restrictive.

2.2 Motivation

In terms of motivation for understanding the extent and magnitude of semipermeable membrane behavior in engineered bentonite-based containment barriers, consider the simplified horizontal and vertical barrier containment scenarios illustrated in Figs. 1a and 1b, respectively. The two barrier scenarios assume a constant source concentration of a given contaminant, C_o , at the upgradient side of the barrier (point A), and initial concentrations of the same contaminant of zero both within and downgradient of the barrier. Also, for the sake of simplicity, the hydraulic liquid flux through the barrier, q_h , is assumed to be constant at times greater than zero with respect to solute transport, and also equal to the product of the hydraulic conductivity, k_h , and hydraulic gradient, i_h , in accordance with Darcy's law (i.e., $q_h = k_h i_h$). As will be shown subsequently in this paper, such a simple expression for the hydraulic liquid flux actually is not accurate in the case where the barrier behaves as a membrane. Finally, the contaminant may be subjected to sorption onto the surface of the clay particles, e.g., via cation exchange for metals or hydrophobic partitioning for nonpolar organic compounds, but otherwise is assumed to be conservative (e.g., not subject to mass transformation or degradation due to biological activity). Under these conditions, the possible breakthrough curves (BTCs) representing the ratio of the concentration of the contaminant at the downgradient side of the barrier (point B) as a function of time, C(L,t), relative to C_o are shown schematically in Fig. 1c as a function of k_h and ω .

In the case of a barrier with a relatively high k_h and no evidence of membrane behavior (i.e., $\omega = 0$), the BTC reflects advective (hydraulic) dominated transport conditions with some solute dispersion due to mechanical processes (e.g., variations in pore water velocity through the barrier), such that solute breakthrough as defined by the center of solute mass, or $C(L, t)/C_o = 0.5$, occurs at time t_1 (see Fig. 1c). However, as the k_h of the barrier is reduced, solute transport through the barrier becomes increasingly dominated by diffusion, resulting in an overall greater degree of solute dispersion and an increase in the time required to achieve breakthrough, such as reflected by time t_2 in Fig. 1c. This increase in containment time from t_1 to t_2 is the primary reason for using clays with low k_h as engineered containment barriers. Furthermore, if the low- k_h barrier also exhibits semipermeable membrane behavior (i.e., $0 < \omega \le 1$), then solute restriction will reduce the maximum possible value of C(L, t) at steady-state transport relative to the case where $\omega = 0$, such that $C(L, t)/C_o \rightarrow 0$ as $\omega \rightarrow 1$. Thus, as illustrated schematically in Fig. 1, the primary reason for considering engineered clay containment barriers with membrane behavior is that the containment function of the barrier can be improved significantly if the barrier exhibits membrane behavior.

Although no direct correlation between k_h and ω has been found, there is a general expectation that ω will be greater than zero only in the case where k_h of a soil is low, primarily because small pore sizes are required for both low k_h and $\omega > 0$. This is the reason why membrane behavior generally is relevant only in the case of clays. Furthermore, for the pore sizes to be sufficiently small to restrict the migration of dissolved chemical species, the clay particle sizes must be relatively small, which is a reason why membrane behavior generally is substantially greater in bentonites with smaller particle sizes relative to other clays, such as kaolin (Shackelford et al. 2003).

3 LIQUID & CHEMICAL FLUXES

3.1 Liquid fluxes

The total liquid flux through a barrier that behaves as a semipermeable membrane, q, at steady state includes a hydraulic component of liquid flux, q_h , in response to the difference in hydraulic head, and a chemico-osmotic component of liquid flux, q_{π} , in response to a difference in solute concentration (e.g., Barbour & Fredlund 1989, Malusis et al. 2001a, 2003, Shackelford et al. 2001), or

$$q = q_h + q_\pi = k_h i_h + k_\pi i_\pi$$

$$= k_h \left(\frac{-\Delta h}{L} \right) + \omega k_h \left(\frac{\Delta \pi}{\rho_w gL} \right)$$
(1)

where k_{π} = the chemico-osmotic permeability (= ωk_h), i_{π} = the chemico-osmotic gradient, Δh = the head loss across the barrier, L = the thickness of the barrier, ρ_w = the density of water (~1,000 kg/m³), i.e., assuming dilute solutions, g = acceleration due to gravity (9.81 m/s²), and $\Delta \pi$ = the theoretical difference in chemico-osmotic pressure resulting from the difference in solute concentrations across the barrier. With respect to Fig. 1, q_h is directed in the positive-x



Figure 1. Engineered barrier containment scenarios: (a) horizontal barrier; (b) vertical barrier; (c) barrier solute breakthrough curves $[k_h =$ hydraulic conductivity; $\omega =$ membrane efficiency coefficient].

direction or outward (i.e., from A to B), whereas q_{π} is directed in the negative-x direction or inward (i.e., from B to A). For this reason, q_{π} often is referred to as the chemico-osmotic counter flow (e.g., Malusis & Shackelford 2001, Malusis et al. 2001a, 2003, Shackelford et al. 2001). Note that, for the containment scenarios depicted in Fig. 1, the direction of q_{π} always will be inward, whereas the direction of q_h can change depending on the direction of the hydraulic gradient. For example, drawing the contaminated groundwater level behind the vertical cutoff wall in Fig. 1b down via pumping to a level lower than that outside the wall will reverse the hydraulic gradient such that both q_h and q_π will be directed inward, i.e., from B to A (e.g., see Kang & Shackelford 2011 and Yeo et al. 2005 for examples pertaining to Figs. 1a and 1b, respectively). Also, note that $q \rightarrow q_h$ as $\omega \rightarrow 0$, such that Eq. 1 reduces to Darcy's law in the limit when $\omega = 0.$

3.2 Chemical fluxes

In general, for low- k_h containment barriers, the total chemical or solute mass flux, J [units of ML⁻²T⁻¹,

where M = mass, L = length, and T = time] across the barrier will be the sum of three components, *viz.*,

$$J = J_a + J_\pi + J_d \tag{2}$$

where J_a = the advective (hydraulic) mass flux, J_{π} = the chemico-osmotic mass flux, and J_d = the diffusive mass flux. Note that Eq. 2 excludes any component of mass flux due to mechanical dispersion, which is the common assumption in the case of transport across containment barriers due to the low k_h and the typically short distances of transport for such barriers (e.g., ≤ 1 m) (e.g., Sleep et al. 2006).

The first term in Eq. 2, J_a , is the traditional advective transport term that results from the presence of the applied hydraulic gradient. As a result, J_a will occur in the same direction as q_h , i.e., in the positive-x direction or outward (from A to B) for the containment scenarios depicted in Fig. 1. However, in the case where the barrier behaves as a semipermeable membrane ($0 < \omega \le 1$), this traditional component of solute mass flux is reduced by a factor of $(1 - \omega)$, such that $J_a \rightarrow 0$ as $\omega \rightarrow 1$ (e.g., see Manassero & Dominijanni 2003, Malusis et al. 2012). In physical terms, the factor $(1-\omega)$ is considered to represent the process of hyperfiltration, whereby solutes are filtered out of chemical solution as the solution passes through the membrane under an applied hydraulic gradient. For this reason, J_a also has been referred to as the hyperfiltrated advective flux (e.g., Malusis et al. 2001a, 2003, Shackelford et al. 2001).

The second term in Eq. 2, J_{π} , represents the advective transport of solutes due to chemico-osmotic liquid flux, q_{π} . Thus, J_{π} is directed in the same direction as q_{π} , i.e., in the negative-x direction or inward (from B to A) for the containment scenarios depicted in Fig. 1. For this reason, J_{π} also has been referred to as the counter advective component of solute transport (e.g., Malusis et al. 2001a, 2003, Shackelford et al. 2001). The form of J_{π} has been shown to differ depending on the assumptions inherent within the theoretical development of the chemical flux terms associated with semipermeable membranes (Malusis et al. 2012). However, for the assumption of salt (mutual) diffusion, whereby all chemical species are diffusing in the same direction, such as depicted in Fig. 1, Manassero & Dominijanni (2003) proposed including the term $(1-\omega)$ in the formulation of J_{π} , such that the sum of the two terms J_a and J_{π} (i.e., $J_a + J_{\pi}$) in Eq. 2 represents the net advective flux resulting from the sum of liquid fluxes q_h and q_π in Eq. 1 (i.e., $q_h + q_\pi$). Of course, for the scenario where q_h is directed outward (i.e., from A to B in Figs. 1a,b), the effect of q_{π} is to reduce the outward mass flux of chemical species relative to that which would occur in the absence of q_{π} (i.e., $J_a + J_{\pi} < J_a$).

The third term in Eq. 2, J_d , represents solute diffusion through soil in the form of Fick's first law. In general, diffusion occurs in the direction from higher solute concentration to lower solute concentration, such that J_d will always occur in the direction opposite to J_{π} (and q_{π}) and, for any containment scenario, will always be directed outward (i.e., the positive-*x* direction in Fig. 1). In addition, J_d also is a function of the term $(1 - \omega)$, such that $J_d \rightarrow 0$ as $\omega \rightarrow 1$ (Malusis & Shackelford 2002b, Manassero & Dominijanni 2003, Malusis et al. 2013, Shackelford & Moore 2013). Thus, the general breakthrough curves scenarios shown in Fig. 1c are consistent with the fact that all three chemical flux terms comprising *J* in Eq. 2 are functions of the term $(1-\omega)$, i.e., $J (=J_a + J_\pi + J_d) \rightarrow 0$ as $\omega \rightarrow 1$.

4 EXPERIMENTAL CONSIDERATIONS

4.1 Type of system

Membrane behavior in clays has been measured using both open and closed hydraulic control systems (Shackelford & Lee 2003, Shackelford 2011). The difference between these two systems is illustrated schematically in Fig. 2. In an open system (Fig. 2a), the clay specimen to be tested is bounded by two reservoirs, both of which are open to the atmosphere and there is no applied hydraulic gradient (liquid levels in both reservoirs are the same). However, the reservoirs are chemical solutions with different concentrations of the same solutes in order to establish the requisite concentration difference, ΔC , across the specimen. Although not necessarily required, the typical experimental setup is as indicated in Fig. 2a, whereby one reservoir contains a chemical solution with solutes at concentrations greater than zero (C > 0), and the other reservoir contains de-ionized water (DIW) such that $C \approx 0$. If the clay behaves as a semipermeable membrane, then this established ΔC will result in q_{π} occurring across the specimen, from lower solute concentration (right reservoir) to the higher solute concentration (left reservoir). In general, the migration of liquid from the right to the left reservoirs would cause overflow of liquid from the left reservoir, such that right reservoir would require replenishment of fresh DIW to maintain the same liquid levels in each reservoir. However, replenishment of DIW may not be required in cases where the reservoir volumes are much larger than the size of the specimen and/or the testing durations are relatively short, as the magnitudes of q_{π} typically are low, such that the decrease in the liquid level in the right reservoir in Fig. 2a may be imperceptible.

In the case where the clay specimen behaves as a perfect membrane (i.e., $\omega = 1$), the aforementioned process would continue indefinitely, i.e., as long as DIW was replenished in the right reservoir. However, in the case where the clay specimen behaves as an imperfect membrane such that $0 < \omega < 1$, then some solute diffusion (J_d) also will occur simultaneously, from higher solute concentration (left reservoir) to lower solute concentration (right reservoir), or in the direction opposite to q_{π} . In this case, diffusion of the solute from left to right will cause a decrease in the solute concentration in the left reservoir (i.e., dilution) and an increase in the solute is added to the left



Figure 2. Open versus closed systems for clay membrane testing: (a) open system with replenishment; (b) open system without replenishment; (c) closed system; (d) relative difference in concentration profiles within clay membrane at equilibrium or steady state (i.e., t_{ss} = time at steady state).

reservoir and removed from the right reservoir to maintain the initially established value of ΔC , this diffusion eventually will equilibrate the solute concentrations in the two reservoirs, such that the concentration difference will be destroyed and the flow of liquid and diffusion of solute will cease to exist (i.e., $q_{\pi} \& J_d \to 0$ as $\Delta C \to 0$).

As shown in Fig. 2b, if the left reservoir is reconfigured with a standpipe, such that any liquid flowing into the left reservoir would rise in the standpipe instead of overflowing the reservoir, and the right reservoir is not replenished with DIW, then the height of rise of the liquid in the standpipe would represent the equilibrium value of the chemico-osmotic pressure head, h_{π} , which is equivalent to the value of the chemicoosmotic pressure, P_{π} , expressed in terms of pressure head (i.e., $h_{\pi} = P_{\pi}/\rho_w g$). As will be shown subsequently, the magnitude of P_{π} and, therefore, h_{π} , is directly proportion to the magnitudes of ω and ΔC , with the maximum values of P_{π} or h_{π} for a given ΔC corresponding to the case of a perfect membrane ($\omega = 1$). Of course, liquid will not rise above the standpipe (i.e., overflow) as long as the standpipe is of sufficient height to accommodate h_{π} (i.e., $H > h_{\pi}$ in Fig. 2b).

In the closed system illustrated in Fig. 2c, q_{π} is prevented, such that P_{π} develops across the specimen to counteract the tendency for q_{π} . This development of P_{π} can be measured using a pressure transducer (e.g., Malusis et al. 2001b). However, since solute diffusion is independent of q_{π} , solute diffusion through the clay specimen still will occur, i.e., provided $\omega < 1$.

As illustrated in Fig. 2d, the occurrence of q_{π} in an open system can affect the steady-state solute concentration profile across the specimen relative to that in a closed system where q_{π} is absent. In an open system, the effect of q_{π} on the solutes within the pores of the clay membrane is counter to that of J_d , such that the actual steady-state concentration profile within the clay membrane is nonlinear (e.g., see Dutt & Low 1962, Quigley et al. 1987, Manassero & Dominijanni 2003). In contrast, in a closed system, the solute concentration profile within the clay membrane at steady state will be linear, since there is no effect of q_{π} on the diffusion of the solutes (e.g., Malusis et al. 2012). Note that, for simplicity, the comparison shown in Fig. 2d assumes the concentrations at each end of the clav membrane are the same, whereas this situation may not be the case in reality. Also, any potential discontinuity in concentrations across the reservoir-clay boundaries at each end of the specimen due to ion exclusion are not explicitly illustrated in Fig. 2d (e.g., see Dutt & Low 1962. Ouiglev et al. 1987).

There are at least three advantages for measurement of membrane behavior using a closed system relative to an open system (e.g., Shackelford & Lee 2003). First, measurement of P_{π} using a digital transducer is vastly less complicated and far more accurate than measuring the small quantities of liquid flux resulting from q_{π} in an open system. Second, control of the boundary conditions in open systems is far more difficult than control of boundary conditions in closed systems. Third, the simplicity of the resulting linear concentration profile at steady state in a closed system greatly reduces the complexity associated with evaluating diffusion coefficients relative to the analysis that would be required in an open system with a nonlinear concentration profile (Malusis et al. 2012).

As an example of this third advantage of closed systems, Dutt & Low (1962) noted that their bentonite specimens tested in open systems restricted solute migration, but interpreted their measured nonlinear

concentration profiles at steady state, which required 182 d for 70-mm-length specimens, only on the basis of Fick's first law for J_d to indicate that concentrationdependent diffusion coefficients existed. However, Manassero & Dominijanni (2003) have shown that such nonlinear concentration profiles can result from a single, concentration-independent diffusion coefficient provided that all the chemical flux processes occurring in the system (e.g., both J_d and J_{π}) are taken into account in the analysis. Thus, the diffusion coefficients determined by Dutt & Low (1962) may not be correct, but rather may have resulted from the use of an open system and failure to recognize that J_{π} also was operative in their system. Of course, the analysis conducted by Dutt & Low (1962) would have been appropriate had they conducted their experiments in a closed system, in which case they likely would have measured a linear concentration profile at steady state. The study by Dutt & Low (1962) also illustrates that failure to recognize all of the processes involved in a test system (i.e., q_{π} and J_{π} in the case of Dutt & Low 1962) may result in a misinterpretation of test results (i.e., concentration-dependent diffusion coefficients).

4.2 Type of cell

Either rigid-wall or flexible-wall cells can be used to measure membrane behavior, although the vast majority of membrane testing of clays has involved the use of rigid-wall cells, whereby the volume of the specimen is maintained constant. A detailed example of a rigid-wall cell is given in Malusis et al. (2001b).

In some studies, flexible-wall cells that provide control of the state of stress in the specimen have been used, including both open-systems where volume change is allowed during the test (e.g., Keijzer et al. 1999), and closed systems where volume change is prevented during the membrane measurement stage of the test, but can occur between successive testing stages of a single membrane test (e.g., Kang and Shackelford 2009).

4.3 Definitions of concentrations

Given the advantages of closed systems relative to open systems, the remaining discussion on experimental considerations will be limited to those existing for closed systems. A detailed description of such a closed-system testing apparatus is presented in Malusis et al. (2001b). A more general description based on the simplified schematic scenario shown in Fig. 3 is given herein.

In a closed system, membrane testing commences once chemical (source) solutions containing the same solute or solutes are circulated across both the top and bottom boundaries. The circulation rates are controlled to be the same via a flow-pump hydraulic system, and both the top and bottom circulation systems are closed loops, such that there is no volume change in either circulation system during circulation (see Malusis et al. 2001b for details on how this is accomplished). The volume of the specimen also is maintained constant



Figure 3. Circulation boundary concentrations (C) and pressures (P) for a clay membrane specimen contained in a rigid-wall cell between two porous disks in a closed system.

during this circulation stage of the test. As a result, there is no volume change in the system during this circulation stage, i.e., the system is closed, such that q_{π} is zero. In order to establish the requisite concentration difference, ΔC , the concentration(s) of the solute(s) in the solution being circulated across the top boundary, or C_{ot} , must be different than that (those) being circulated across the bottom boundary, or C_{ob} . Typically, $C_{ot} > C_{ob}$, and DIW is circulated across the bottom boundary (i.e., $C_{ob} = 0$), such that ΔC based on the source solutions, or ΔC_o , is represented as $C_{ob} - C_{ot} = C_{ot} < 0$. For this case, and assuming the specimen is not a perfect membrane (i.e., $0 < \omega < 1$), some solute diffusion (J_d) will occur from the top circulation boundary into the specimen and eventually all the way through the specimen, emanating from the bottom of the specimen into the bottom circulation system (e.g., see Malusis & Shackelford 2002b). As a result, the concentration(s) of the solute(s) in the circulation outflow across the top, C_t , will be lower than that (those) in the circulation inflow across the top (i.e., $C_t < C_{ot}$), whereas the concentration(s) of the solute(s) in the circulation outflow across the bottom, C_b , will be greater than that (those) in the circulation inflow across the bottom (i.e., $C_t < C_{ot}$).

As previously noted, if the specimen behaves as a semipermeable membrane, then a chemico-osmotic pressure, P_{π} , will be generated in the top reservoir to counteract the tendency to develop q_{π} from bottom to top. This P_{π} is designated P_t in Fig. 3. Also, since $C_b > C_{ob}$, the concentration(s) of solute (s) in the bottom porous disk cannot be assumed to be zero, and the actual ΔC across the specimen will less than ΔC_o . Thus, the pressure at the bottom of the specimen, P_b , also is measured as a reference pressure, such that the actual chemico-osmotic pressure across the specimen is represented by $\Delta P = P_b - P_t < 0$.

Given the testing scenario illustrated in Fig. 3 and the associated testing procedure and conditions, several different characteristic concentrations have been defined for the purpose of analyzing and presenting the results of the experiments. In general, three average concentrations (C_{ave}) have been identified, including the average of the source concentrations being circulated across the bottom and the top of the specimen, $C_{o,ave}$, and the individual averages of the concentrations in the top and bottom circulating liquids, or $C_{t,ave}$ and $C_{b,ave}$, respectively, as follows (e.g., Malusis et al. 2001, Malusis & Shackelford 2002a, Kang & Shackelford 2009):

$$C_{o,ave} = \frac{C_{ot} + C_{ob}}{2} = \frac{C_{ot}}{2} \Big|_{C_{ob} = 0}$$
(3)

$$C_{t,ave} = \frac{C_{ot} + C_t}{2}$$

$$C_{b,ave} = \frac{C_{ob} + C_b}{2} = \frac{C_b}{2} \Big|_{C_{ob} = 0}$$

$$(4)$$

Three differences in concentrations (ΔC) also have been defined as follows (e.g., Malusis et al. 2001, Malusis & Shackelford 2002a, Kang & Shackelford 2009):

$$\Delta C_o = C_{ob} - C_{ot} = -C_{ot} \big|_{C_{ob=0}}$$
⁽⁵⁾

$$\Delta C_{o,ave} = \frac{C_{ob} - C_{ot}}{2} = -\frac{C_{ot}}{2} \Big|_{C_{ob=0}}$$
(6)

$$\Delta C_{ave} = C_{b,ave} - C_{t,ave} \tag{7}$$

Note that, for the sign convention defined in Fig. 3, the magnitudes of all definitions of ΔC given by Eqs. 5–7 will be negative (<0).

4.4 Preconditioning of specimens and circulation of liquids

In several studies (e.g., Malusis & Shackelford 2002a, Shackelford & Lee 2003, Yeo et al. 2005, Kang & Shackelford 2009, 2010, 2011), the specimens have been permeated prior to membrane testing with DIW to leach or flush soluble salts from the pores of the specimen for the purpose of enhancing the likelihood of observing significant membrane behavior. The durations of this preconditioning by permeation can be quite lengthy, e.g., on the order of several months, even using relatively high hydraulic gradients $(i_h > 100)$, primarily because of the low values of k_h for bentonites based on permeation with DIW, e.g., $k_h < 2 \times 10^{-11}$ m/s (Daniel et al. 1997). More importantly, since the bentonite used in the actual barriers in the field is unlikely to be preconditioned in a similar manner, the results of studies involving such preconditioned specimens probably cannot be extrapolated directly to field applications. In this case, some assessment of the effect of this specimen preconditioning on field performance should be undertaken.

Following preconditioning, the membrane testing stage begins, typically by circulating DIW across both the top and bottom boundaries of the specimen under a closed condition to establish a baseline or reference value of ΔP with respect to DIW, or ΔP_{DIW} , if any. Conceptually, if DIW is circulated simultaneously at the same rate through both the top and bottom

porous disks, and the disks have identical hydraulic properties, then ΔP_{DIW} should be zero. However, in most cases, some small, nonzero value of ΔP_{DIW} has been observed. This nonzero ΔP_{DIW} generally has been attributed to three possible causes (e.g., Malusis et al. 2001b): (1) the existence of remnant or residual salts or other chemical species stored within the porous disks or system plumbing, e.g., if the disks and system plumbing previously have been used and not completely cleaned prior to reuse; (2) slightly different circulation rates between the top and bottom resulting in minor imperfections in the machining of the actuators and plungers used to displace the circulation liquids; and/or (3) slightly different hydraulic properties of the porous disks.

After establishing the steady-state magnitude of ΔP_{DIW} , ΔC is established across the specimen by changing the circulation liquid across the top of the specimen from DIW to some chemical solution, typically a salt solution, while maintaining DIW as the circulation liquid across the bottom of the specimen. This circulation proceeds until a new steady-state value of ΔP , or ΔP_{Sol} , has been established and measured. If desired, this process can be repeated sequentially using chemical solutions with progressively higher concentrations of the specified solutes to establish increasingly higher values of ΔC and, therefore, measurement of different values of ω as a function of ΔC for the same specimen. Tests that involve this sequential circulation of chemical solutions with increasingly higher concentrations of the specified solutes are referred to as multi-stage tests, with the results from each different chemical solution representing a separate stage of the testing procedure (e.g., see Malusis & Shackelford 2002a). An alternative type of multi-stage test involving circulating the same chemical solution during all stages, but doing so on a single specimen that was progressively compressed or consolidated to achieve progressively lower values of the specimen void ratio, e, also has been conducted (Yeo et al. 2005).

4.5 Calculating membrane efficiency coefficients

For closed systems, ω is defined as follows (Groenevelt & Elrick 1976, Olsen et al. 2000, Malusis et al. 2001a):

$$\omega = \frac{\Delta P}{\Delta \pi} \tag{8}$$

where $\Delta \pi (<0)$ is the theoretical maximum value of ΔP that would result across a perfect semipermeable membrane (i.e., if $\omega = 1$). The actual value of ΔP to be used with Eq. 8 is the effective or net pressure difference, ΔP_e , which is equal to the difference between ΔP_{sol} and ΔP_{DIW} (i.e., $\Delta P_e = \Delta P_{sol} - \Delta P_{DIW}$). The value of $\Delta \pi$ in Eq. 8 is calculated on the basis of the difference in solute concentration, ΔC , across the specimen in accordance with the van't Hoff expression as follows (e.g., Malusis et al. 2001b):

$$\Delta \pi = \nu R T \Delta C \tag{9}$$

Ζ

where ν is the number of ions per molecule of the salt, *R* is the universal gas constant [8.314 J mol⁻¹K⁻¹], *T* is the absolute temperature (K), and *C* is the solute concentration (M). For example, for 1:1 electrolyte solutions (e.g., NaCl, KCl), $\nu = 2$, whereas for 2:1 electrolyte solutions (e.g., CaCl₂), $\nu = 3$. Use of Eq. 9 assumes dilute chemical solutions and fully dissociating chemical compounds.

In general, ω can be calculated on the basis of the difference in the source solute concentrations of the circulating liquids, designated as ω_{o} , as follows:

$$\omega_o = \frac{\Delta P_e}{\Delta \pi} \bigg|_o = \frac{\Delta P_e}{\Delta \pi_o} = \frac{\Delta P_e}{\nu RT \Delta C_o}$$
(10)

where ΔC_o is given by Eq. 5. Alternatively, ω can be calculated on the basis of the difference in the average solute concentrations across the top and bottom, designated as ω_{ave} , as follows:

$$\omega_{ave} = \frac{\Delta P_e}{\Delta \pi} \bigg|_{ave} = \frac{\Delta P_e}{\Delta \pi_{ave}} = \frac{\Delta P_e}{\nu R T \Delta C_{ave}}$$
(11)

where ΔC_{ave} is given by Eqs. 4 and 7. Since $C_{t,ave} < C_{ot}$ and $C_{b,ave} \ge C_{ob}$, the magnitude of $\Delta \pi_o$ will be greater than that of $\Delta \pi_{ave}$, such that $\omega_o < \omega_{ave}$ for the same measured value of ΔP_e . Thus, values of ω_o are more conservative (lower) than values of ω_{ave} (Malusis et al. 2001b, Kang & Shackelford 2009). However, in the limit as the membrane efficiency approaches 100 percent, solutes can neither enter nor exit the specimen, such that $C_{t,ave} \rightarrow C_{ot}$, $C_{b,ave} \rightarrow C_{ob}$, and $\omega_{ave} \rightarrow \omega_o$ (Malusis et al. 2001b, Kang & Shackelford 2009).

4.6 Typical results for closed systems

Examples of chemico-osmotic pressure responses (i.e., $-\Delta P > 0$) resulting from membrane testing under closed-system conditions for specimens of different types of bentonite-based barriers are shown in Fig. 4. The pressure responses from Malusis & Shackelford (2002a) for both single-stage and multistage tests conducted on specimens of the same GCL tested in a rigid-wall cell are shown in Figs. 4a and 4b, respectively. For the single-stage test (Fig. 4a), simultaneous circulation of DIW across both the top and bottom boundaries of the specimen resulted in a baseline pressure difference, $-\Delta P_{DIW}$ (>0), of ~4.0 kPa. Upon replacing the DIW circulating across the top boundary of the specimen with 47 mM KCl (= $C_{ot} = -\Delta C_o$), the pressure difference increased relatively rapidly to a peak value of 41.4 kPa before diminishing to a final steady-state value of 32.0 kPa. This post-peak degradation of $-\Delta P$ commonly occurs at higher solute concentrations in the case of imperfect clay membranes $(0 < \omega < 1)$, and is attributed to diffusion of the solutes into the pores of the specimen resulting in progressively greater compression of the adsorbed layers of cations, or diffuse double layers (DDLs), surrounding individual clay particles with a concomitant increase in the sizes of pore channels available to solute migration and, therefore, a decrease in the solute restrictive capability of the specimen (e.g., Malusis & Shackelford 2002a). This effect of the higher solute concentrations on the post-peak degradation of $-\Delta P$ also is clearly evident from the results of the multi-stage test shown for the same GCL in Fig. 4b, where increases in C_{ot} (= $-\Delta C_o$) from 3.9 mM KCl to 47 mM KCl resulted in not only progressively higher peak values of $-\Delta P$, but also progressively greater magnitudes in post-peak degradation of $-\Delta P$.

The results shown in Fig. 4c pertain to a membrane test conducted in a rigid-wall cell on a specimen of a sand-bentonite backfill representative of that for a vertical cutoff (slurry) wall as reported by Yeo et al. (2005). The test was a multi-stage test conducted in a rigid-wall cell, except each stage was represented by a difference in the void ratio, e, of the specimen instead of a difference in C_{ot} (= $-\Delta C_o$), which was maintained constant at 3.88 mM KCl. Relative to the test results for the GCL shown in Figs. 4a & 4b, the results for the backfill in Fig. 4c illustrate much lower peak and steady-state values of $-\Delta P$. This difference was attributed by Yeo et al. (2005) primarily to the difference in bentonite contents in the two different types of barrier materials, with the GCL essentially containing 100% bentonite as the hydraulic/transport resistance component of the barrier, and the sandbentonite backfill containing only 7.2% bentonite. Also, the fact that the sand-bentonite backfill exhibited the same trend in post-peak degradation in $-\Delta P$ as that for the GCL, but at a much lower concentration than for the GCL, also was attributed to the significantly lower bentonite content of the backfill. That is, the much higher bentonite content of the GCL relative to the sand-bentonite backfill resulted in the GCL being more resistant to physico-chemical interactions due to diffusion of invading salt cations (K⁺) at the lower concentration of these salt cations. Finally, despite the relatively low magnitudes of $-\Delta P$ associated with the sand-bentonite backfill, there is a distinct, albeit slight, increase in the peak and steady-state values of $-\Delta P$ with decreasing e, as expected.

The results shown in Fig. 4d are from Kang & Shackelford (2010) for a single-stage membrane test conducted on a compacted specimen of a local, natural clay known as Nelson Farm Clay (NFC) containing 89% fines but no high activity clay minerals amended with 5% (dry weight) sodium bentonite.

The bentonite addition was deemed necessary because a separate specimen of the NFC without such bentonite amendment did not exhibit any significant membrane behavior, despite measurement of a suitably low k_h (i.e., $<10^{-9}$ m/s). The k_h of the compacted specimen of bentonite amended clay was lower than that of the unamended specimen and, therefore, also suitably low. The membrane test was conducted in a flexible-wall cell on the compacted specimen that had been back-pressure saturated, consolidated to an initial



Figure 4. Chemico-osmotic pressure responses $(-\Delta P)$ under closed-system conditions: (a) & (b) single-stage and multi-stage tests for a GCL; (c) multi-stage test for a sand-bentonite backfill; (d) single-stage test for bentonite amended compacted clay (data from Malusis & Shackelford 2002a, Yeo et al. 2005, and Kang & Shackelford 2010).

effective stress, σ' , of 34.5 kPa, and then permeated with DIW to flush soluble salts prior to membrane testing under closed-system conditions. Unlike the responses shown in Figs. 4a–c, the response in Fig. 4d represents a continuous record of $-\Delta P$, and the daily decreases and increases in the pressure response resulting from refilling the circulating liquids within the system are shown. The pressure response record shown in Fig. 4d is otherwise similar to those shown in Figs. 4a-c, except the response during the period from about 21 to 38 d is relatively erratic. This erratic response behavior was attributed, in part, to a less uniform consistency in the natural clay-bentonite mixture and the likely more complex nature of the network of pores, both of which can be expected when non-processed natural clays with varied mineralogy are evaluated for membrane behavior.

The time-dependent values of the membrane efficiency coefficients based on the difference in source KCl concentrations across the specimens, ω_o , for the chemico-osmotic pressure records in Fig. 4 are shown in Fig. 5. All of the values for ω_o shown in Fig. 5 are based on the effective pressure differences, ΔP_e .

The results for both the single-stage and the multistage tests (Figs. 4a and 4b, respectively) are shown together in Fig. 5a for the sake of comparison. At least two observations are readily apparent. First, in contrast to the values of $-\Delta P$ in Fig. 4b, which increased with increasing C_{ot} (= $-\Delta C_o$) from 3.9 mM KCl to 47 mM KCl, the corresponding values of ω_o in Fig. 5a (closed data symbols) decrease with increasing C_{ot} $(=-\Delta C_o)$ from 3.9 mM KCl to 47 mM KCl. This trend may seem counterintuitive, given the basic definition for ω represented by Eq. 8, where ω is shown to be directly proportional to ΔP . However, the reason for decreasing ω_o with increasing $C_{ot} (= -\Delta C_o)$ is related to the $\Delta \pi$ term in the denominator of Eq. 8 (or $\Delta \pi_o$ in Eq. 10), which is directly proportional to C_{ot} (= $-\Delta C_o$), as shown in Fig. 6 for KCl. Thus, the increase in $-\Delta P$ with increasing $C_{ot} (= -\Delta C_o)$ is offset by a greater increase in $\Delta \pi$ (or $\Delta \pi_o$) with increasing C_{ot} (= $-\Delta C_o$), such that the overall effect from increasing C_{ot} (= $-\Delta C_o$) is a decrease in ω_o . Second, the temporal trends in ω_o and ultimately the steady-state value of ω_o for the single-stage test based on C_{ot} (= $-\Delta C_o$) of 47 mM KCl (open data symbols) are similar to those for last stage of the multi-stage test also corresponding to C_{ot} (= $-\Delta C_o$) of 47 mM KCl. This similarity in ω_o trends and values suggests that the results were affected little by the type of test (single stage or multi-stage), i.e., all other factors being the same.

The temporal trend in ω_o corresponding to the values of $-\Delta P$ for the sand-bentonte backfill specimen in Fig. 4c are shown in Fig. 5b. Three observations are apparent. First, the range in the vast majority of ω_o values for the sand-bentonite backfill specimen in Fig. 5b of $0.19 \le \omega_o \le 0.36$ is significantly narrower than that for the GCL specimen shown in Fig. 5a of $0 \le \omega_o \le 0.67$ for similar values of $C_{ot} (= -\Delta C_o)$ (i.e., 3.88 mM KCl in Fig. 5b vs. 3.9 mM KCl in Fig. 5a). This difference again can be attributed, in part, to the different amounts of bentonite in the two types of barriers (i.e., 100% for the GCL vs. 7.2% for the sand-bentonite backfill). Second, despite the relatively



Figure 5. Time-dependent measured membrane efficiency coefficients, ω_o , based on results from Fig. 4: (a) single-stage (Fig. 4a) and multi-stage (Fig. 4b) results for a GCL; (b) multi-stage results for a sand-bentonite backfill (Fig. 4c); (c) single-stage results for a bentonite amended compacted clay (Fig. 4d).

low bentonite content for the sand-bentonite backfill, these values of ω_o still may be considered as substantial. Third, there is a slight trend of increasing ω_o with decreasing *e*, as expected. For example, the steadystate values of ω_o for void ratios of 1.212, 1.012, and 0.812 were 0.12, 0.14, and 0.16, respectively.

Finally, the temporal trend in ω_o for the compacted clay specimen amended with 5 % bentonite corresponding with the values of $-\Delta P$ in Fig. 4d are shown in Fig. 5c. For this test (i.e., $C_{ot} = -\Delta C_o = 3.9$ mM KCl), Kang & Shackelford (2010) reported a steadystate value of ω_o of 0.76, which is significantly higher than the steady-state value of ω_o of 0.01 reported for the unamended compacted clay subjected to the same $C_{ot} (= -\Delta C_o)$ of 3.9 mM KCl, and higher than that for either the GCL in Fig. 5a subjected to C_{ot}



Figure 6. Correlation between maximum chemico-osmotic pressure difference, $-\Delta \pi_o$, and source KCl concentration based on the van't Hoff expression (Eq. 9).

 $(= -\Delta C_o)$ of 3.9 mM KCl or the sand-bentonite backfill in Fig. 5c subjected to C_{ot} $(= -\Delta C_o)$ of 3.88 mM KCl, despite the latter two specimens having greater bentonite contents. This comparison illustrates the ability of bentonite to impart a significant membrane behavior to a soil that would otherwise exhibit little or no membrane behavior, especially when the soil being amended is predominantly fine-grained soil (i.e., clay) as opposed to a coarse-grained soil (i.e., sand).

4.7 Limitation in calculated ω values

Neuzil & Prost (2009) noted that Eq. 8 is obtained by assuming ω does not vary across the specimen, which is not accurate as ω is known to be strongly affected by solute concentration, which varies across the specimen as depicted in Fig. 2d. Thus, in reality, ω generally also will vary spatially within the membrane, such that values of ω calculated in accordance with Eq. 8 are actually apparent values that lie somewhere between the maximum and minimum ω in the specimen during the experiment. For this reason, Neuzil & Prost (2009) indicate that, although ω based on Eq. 8 has a simple physical interpretation and is easily calculated, accurate predictions of chemico-osmotic pressures or fluxes under conditions differing from those of the test generally are not possible using such ω values. Thus, prediction of field performance using values of ω based on Eq. 8 for systems unlike those upon which the ω values were determined should be interpreted with caution and, at best, should be assumed to provide only approximate results.

5 EFFECTS OF INDEPENDENT VARIABLES

5.1 Effect of salt concentration

As previously noted, membrane behavior in clays is known to be a function of salt concentration. For example, consider the results from Malusis & Shackelford (2002a) and Kang & Shackelford (2010) shown in Fig. 7, where the measured values of ω_o at steady state for the aforementioned GCL and bentonite amended compacted clay are plotted as a function of the $C_{o,ave}$ (Eq. 3) for KCl solutions. Also, the results from a test conducted on a specimen of the unamended compacted clay are included in Fig. 7 for comparison.

In general, ω_o decreases approximately semi-log linearly with increasing $C_{o,ave}$, although the slope of the decrease in ω_o with increasing logarithm of $C_{o,ave}$ varies as a function of the barrier material. As previously noted, the decrease in ω_o with increasing $C_{o,ave}$ is attributed to physico-chemical interactions, whereby an increase in salt concentration in the pores of the soil decreases the thicknesses of the adsorbed layers of cations (or DDLs) surrounding individual bentonite particles, resulting in progressively larger pore spaces available for ion migration (Shackelford 2011, 2012). The maximum values of $C_{o,ave}$ above which membrane behavior no longer exists ($\omega_o = 0$) are referred to as "threshold concentrations" (e.g., Shackelford et al. 2003). Conservative (low) estimates of these threshold concentrations can be obtained by extrapolating the semi-log linear trends.

As indicated in Fig. 7, the membrane behavior of the unamended compacted clay was negligible over the entire range of $C_{o,ave}$ (1.95 $\leq C_{o,ave} \leq$ 23.5 mM). However, significant membrane behavior was evident in both the bentonite amended compacted clay and the GCL for values of $C_{o,ave}$ less than about 9.5 and 47 mM KCl, respectively. In addition, the slope of the regressed relationship between ω_o and log $C_{o,ave}$ for the bentonite amended compacted clay was about 2.7 times greater than that for the GCL. Thus, ω_o for the GCL is greater than ω_o for the bentonite amended compacted clay for $3.7 \le C_{o,ave} \le 47$ mM KCl, whereas ω_o for the GCL is less than ω_0 for the bentonite amended compacted clay for $C_{o,ave} \leq 3.7 \text{ mM}$ KCl. This difference has been attributed, in part, to the difference in bentonite contents of the bentonite amended compacted clay versus the GCL, i.e., 5% vs. 100% (Kang & Shackelford 2010, Shackelford 2012). That is, the membrane efficiency of a barrier with a lower bentonite content generally will be more sensitive to an increase in salt concentration than that with a higher bentonite content, as the greater the amount of bentonite, the more resilient the barrier against chemical attack.

5.2 Effect of bentonite content

The overall effect of the amount of bentonite on the magnitude of the membrane behavior existing in various containment barriers is illustrated in Fig. 8. In addition to the aforementioned barrier materials, the results from Yeo et al. (2005) for a soil-bentonite backfill consisting of the aforementioned NFC natural clay and mixed with 5% bentonite slurry to achieve a slump of 100 mm prior to testing (i.e., a total bentonite content of 2.12% by dry weight) are shown. In general, all of the results in Fig. 8 pertain to steadystate ω_o values resulting from tests conducted using $C_{ot} (= -\Delta C_o)$ of 3.9 mM KCl (3.88 mM KCl for the backfill specimens), and all of the specimens were permeated with DIW prior to membrane testing to flush



Figure 7. Membrane efficiency coefficients for bentonite-based containment barriers as a function of the average of the source KCl concentration across the barrier (replotted after Shackelford 2012).

(leach) soluble salts from the materials for the purpose of enhancing the likelihood of significant membrane behavior. Finally, the tests for the GCL specimens and the backfill specimens were conducted using rigidwall cells, with variations in ω_o at a given bentonite content resulting primarily from different initial void ratios of the specimens (e_o) and some variability resulting from conducting single-stage versus multistage tests, whereas the tests for the unamended and bentonite amended compacted clay specimens were conducted in flexible-wall cells at an initial effective stress, σ ', of 34.5 kPa.

As indicated by Fig. 8, except for the bentonite amended compacted clay, there is a general trend of increasing membrane behavior with increasing bentonite content, with the steady-state values of ω_o increasing from virtually nil ($\omega_o = 0.01$) for the unamended compacted clay to $0.48 \le \omega_o \le 0.68$ for the GCL containing 100% sodium bentonite. The paucity of data for bentonite contents between 7.2% and 100% can be attributed to bentonite contents for containment barrier materials greater than about 10% generally being considered cost prohibitive, except in the case of manufactured GCLs (Shackelford 2012).

Shackelford (2012) also noted two additional interesting aspects of the results for the bentonite amended compacted clay shown in Fig. 8. First, since the k_h values of both the unamended compacted clay and the bentonite amended compacted clay were less than 10^{-9} m/s, low k_h apparently is a necessary but not sufficient condition for the existence of significant membrane behavior. Second, the membrane behavior of the bentonite amended compacted clay (i.e., $0.73 \le \omega_o \le 0.76$) was greater than that of the GCL, which contained 100 % bentonite. Although the reasons for this apparent discrepancy are not entirely


Figure 8. Correlation between bentonite content and membrane efficiency coefficient for various bentonite-based containment barriers subjected to 3.9 mM KCl (replotted after Shackelford 2012, Shackelford & Moore 2013).

clear, one factor likely contributing to this difference is the relatively high fines content of the natural clay (i.e., \sim 89% fines), which likely enhanced the ability of the clay upon bentonite amendment to exhibit significant membrane behavior. Another possible factor contributing to the difference is that the tests with the GCL specimens were conducted using rigid-wall cells where the stress conditions in the specimens were unknown, whereas the tests with the specimens of bentonite amended compacted clay was conducted using a flexible-wall cell at an initial average effective stress of 34.5 kPa. Thus, the different stress conditions in these two types of cells may have contributed, in part, to the difference in the test results for the two types of bentonite-based containment barriers.

5.3 Effect of valence of salt cation

The use of salt solutions containing multivalent cations (e.g., Ca^{2+}) versus those containing monovalent cations (e.g., K^+) is known to result in more compressed DDLs, larger pores, and increased k_h of bentonite based materials (e.g., Shackelford 1994, Gleason et al. 1997, Petrov & Rowe 1997, Petrov et al. 1997a,b, Stern & Shackelford 1997, Shackelford et al. 2000, Kolstad et al. 2004, Jo et al. 2005). Given that larger pores should correlate with lower solute restriction, an increase in salt cation valence also should be expected to result in a decrease in membrane behavior.

For example, consider the results in Fig. 9 showing the temporal membrane behavior of two specimens of a GCL using KCl solutions as reported by reported by Malusis & Shackelford (2002a) versus the temporal behavior for a specimen of the same GCL using a 5 mM CaCl₂ solution as reported by Shackelford & Lee (2003). All the tests were conducted using rigidwall cells where the thickness of the specimen was



Figure 9. Effect of valence of salt cation on the temporal membrane efficiency of a GCL (replotted after Shackelford 2012).

maintained constant during the test, and the GCLs were permeated with DIW prior to membrane testing to reduce the soluble salts contents within the bentonite of the GCL.

As shown in Fig. 9, steady-state values for ω_o of 0.55 and 0.28 resulted for the tests using 3.9-mM and 20-mM KCl solutions, respectively, with the lower ω_o for the higher KCl solution being consistent with the aforementioned effect of increasing salt concentration on clay ω_o . However, for the test involving the 5 mM CaCl₂ solution, complete destruction of the initially observed membrane behavior eventually occurred despite this test specimen being only half the thickness of the specimens tested using KCl solutions (i.e., denser). This destruction of membrane behavior upon exposure to Ca²⁺ has been attributed to progressive collapse of DDLs and the possibility of particle aggregation resulting from diffusion of Ca²⁺ (Shackelford & Lee 2003, Di Emidio 2010, Mazzieri et al. 2010, Shackelford 2012). These results suggest that the effect of containment of liquids comprised of multivalent cations on the membrane behavior of a bentonite-based containment barrier should be evaluated prior to relying on any such membrane behavior in design of the containment system.

5.4 Effect of effective confining stress

An increase in effective confining stress, σ' , of clay is known to result in lower k_h values based on permeation with water. This effect generally is attributed to consolidation of the clay, resulting in a lower void ratio, e, with increasing σ' , which in turn results in smaller pores and lower k_h . This same effect should be evident with respect to membrane behavior, i.e., since smaller pores should be more restrictive to solute migration.

For example, consider the results shown in Fig. 10 from Shackelford (2012) illustrating the trends in ω_{ρ}



Figure 10. Effect of initial void ratio on the membrane efficiency of three bentonite-based barriers (replotted after Shackelford 2012).



Figure 11. Ratio of the membrane efficiency coefficient, ω_o , at 241 kPa versus that at 34.5 kPa as a function of the average KCl concentration for specimens of a geosynthetic clay liner (replotted after Shackelford 2012).

with the initial void ratio, e_o , for three of the bentonite based barriers previously considered. As expected, ω_o generally decreases with increasing e_o , although the trends for the two, less compressible bentonite-based backfills are not nearly as evident as the trend for the more compressible GCL.

An increase in σ' also is known to provide increased resistance of clays to the detrimental effects on k_h resulting from permeation with liquids other than water (e.g. Fernandez & Quigley 1991, Shackelford et al. 2000). This same beneficial effect recently has been shown with respect to the membrane behavior of a GCL (Kang & Shackelford 2011).

For example, consider the results in Fig. 11 where the ratio of ω_o at σ' of 241 kPa (35 psi) relative to that at σ' of 34.5 kPa (5 psi), R_{ω} , increased from 1.6 at $C_{o,ave}$ of 1.95 mM KCl (i.e., $C_{ot} = 3.9$ mM KCl) to 7.9 at $C_{o,ave}$ of 23.5 KCl (i.e., $C_{ot} = 47$ mM KCl) for the same GCL as previously described and tested in a flexiblewall cell. Although these results are limited to a single GCL and a simple salt solution, the results illustrate the potentially beneficial effects of increasing σ' on the membrane behavior. However, additional results for different bentonite-based containment barriers and more complex chemical solutions clearly are required before more general conclusions can be drawn in this regard.

6 FUTURE DIRECTIONS

As documented in this state-of-the-art review, significant research pertaining to the existence and magnitude of membrane behavior in bentonite-based containment barriers has been conducted in the past approximate decade. Although the results of this research have answered many questions regarding such behavior and, therefore, have advanced the state of the art, the research also has resulted in raising questions that still need to be answered.

In particular, future research should focus at evaluating ways to overcome or control the deleterious impact of more realistic and more aggressive chemical solutions on the existence and magnitude of membrane behavior in bentonite-based containment barriers than has heretofore been used. Some research along these lines recently has been conducted in terms of evaluating the potential of polymer modified bentonites for resisting the deleterious impacts resulting from chemical attack (e.g., Di Emidio 2010, Scalia et al. 2011, Bohnhoff 2012, Scalia 2012, Bohnhoff et al. 2013), but given the number of potential independent variables affecting such behavior, including the myriad of possible polymer and other chemical amendments to bentonites, considerable additional research is needed. Also, given the results of previous research indicating that the deleterious impacts of chemical attack on the hydraulic conductivity of bentonites can be mitigated to some extent via increases in effective stress, and the potential benefit of increased effective confining stress on the membrane behavior (Fig. 11), more research should be conducted to evaluate the potential benefit gained from consolidating bentonite-based containment barriers to higher effective stress in the presence of more aggressive chemical solutions.

Finally, all of the experimental studies to date have focused on the membrane behavior of bentonites under fully or nearly fully saturated conditions. Given that some applications may involve the use of bentonite-based containment barriers under unsaturated conditions, such as those used in cover systems or as buffers for deep, underground disposal of high-level radioactive wastes located above the