

Cation Exchange Capacity in  
Composite Landfill Liners  
Worksheet v1.0: User Manual

National Groundwater & Contaminated  
Land Centre report NC/01/45



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March 2002

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National Groundwater & Contaminated Land Centre report  
NC/01/45

**Publishing Organisation:**

Environment Agency

Rio House

Waterside Drive

Aztec West

Almondsbury

Bristol BS32 4UD

Tel: 01454 624400

Fax: 01454 624409

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Product Code: SCHO0302BITL-E-P

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**Statement of use**

This document has been prepared to support risk assessors using the *Cation Exchange Capacity in Composite Landfill Liners Worksheet v1.0*, which was developed to aid calculation of flow through composite landfill liners, and the effects of cation exchange processes within those liners.

**Report author**

This report was produced under NGWCLC project NC/01/45 by:

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The Agency acknowledges the input of staff at CL Associates in developing the worksheet and user manual.

The worksheet and user manual have been independently reviewed by the Groundwater Protection and Restoration Group (GRPG) at Sheffield University. The Agency is grateful for comments from Professor D Lerner, Dr S Thornton and Dr I Watson.

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## **1. Introduction**

This User Manual has been prepared to assist users of the Environment Agency's Cation Exchange Capacity for Composite Landfill Liners Worksheet v1.0.

This document describes the functionality of the worksheet and gives guidance on its use. It is not intended to describe the technical basis underpinning environmental risk assessment, the regulatory and policy context within which risk assessments are undertaken, or the Environment Agency's approach to assessing risk assessment reports. The worksheet should only be used by suitably experienced risk assessors, who are conversant with the relevant UK legislation, policy and guidance.

The worksheet has been prepared in Microsoft Excel97™. The file comprises about 80KB, and should not require any significant additional computing capability beyond that needed to run Microsoft Excel97™. The worksheet has only been tested in MS Excel97, and can not be guaranteed to function in any other version of MS Excel, or any other spreadsheet package.

It is recommended that a blank copy of the worksheet is saved to a safe file and that each simulation is saved as a distinct file.

## **2. Overview**

The CEC in Composite Landfill Liner worksheet v1.0 calculates solutions to equations presented in *Geochemistry, Groundwater and Pollution* (Appelo & Postma, 1994), and Giroud *et al*, 1992.

The worksheet has been developed to help assessors determine the potential for attenuation of cations within the mineral layer of a composite landfill. Readers who are unfamiliar with the concepts of environmental risk assessment, cation exchange processes and the Agency's approach to protection of groundwater are directed to the following documents in the first instance:

- DETR *et al.*, 2000. *Guidelines for environmental risk assessment and management*. The Stationery Office.
- Environment Agency, 1999. *The EC Groundwater directive (80/68/EEC) and the Waste Management Licensing Regulations 1994. Internal Guidance on the Interpretation and Application of Regulation 15 of the Waste Management Licensing Regulations 1994 (The Protection of Groundwater) with respect to landfill*.
- Environment Agency, 2002 (*in preparation*). *Hydrogeological Risk Assessment for Landfills and the Derivation of Groundwater Control and Trigger Levels*.
- Environment Agency, 2000. *CEC and Kd determination in landfill performance evaluation; a review of methodologies and preparation of standard materials for laboratory analysis*. R&D Technical Report P340. Bristol
- Environment Agency, 1998. *Policy and practice for the protection of groundwater (2<sup>nd</sup>*

*Edition*). The Stationery Office.

- Environment Agency, 2001a. *LandSim Release 2 User Manual*. R&D Publication 120. Prepared by Golder Associates (UK) Ltd.
- Appelo, C.A.J. & Postma, D. 1994. *Geochemistry, groundwater and pollution*. A.A. Balkema, Rotterdam (2<sup>nd</sup> corrected print).

This worksheet has application for groundwater risk assessments performed for existing or proposed landfill sites using a composite landfill liner. It may be used in conjunction with a LandSim assessment, or in support of other groundwater risk assessments tools used at planning / waste licensing application stage. It may help to indicate whether a landfill can be engineered to comply with the EC Groundwater Directive (80/68/EEC), as implemented through Regulation 15 of the Waste Management Licensing Regulations, 1994 and the Groundwater Regulations 1998.

Before selecting this, or indeed any other assessment model or tool, assessors should have developed a sound conceptual model of the site. They should be satisfied that the tool they select to model the site is appropriate, both in respect of representing the conceptual model and in performing analyses to a level that is appropriate to the quality of the input data. Guidance on these issues is provided in:

- Environment Agency, 2001b. *Guide to good practice for the development of conceptual models and the selection and application of mathematical models of contaminant transport processes in the subsurface*. National Groundwater & Contaminated Land Centre Report NC/99/38/2. Solihull.

The development of a robust conceptual model is perhaps the most important aspect in the process of successfully estimating and evaluating environmental risks. The use of any mathematical modelling tool without first developing a robust conceptual model is likely to result in meaningless output. This worksheet should only be employed where a robust conceptual model has been developed, and the assessor is satisfied that the calculations performed by the worksheet are relevant to the processes described within that conceptual model.

Data quality is also a particular concern. Data used should be relevant, robust and derived from tests at the site, or be relevant to the site. The provenance and relevance of all data included in an assessment using the worksheet should be documented by the assessor and included in the report(s) submitted to the Environment Agency for consideration.

The basic conceptual model that is incorporated within the worksheet is illustrated in figure 2.1. It is important to note that the worksheet assumes that the landfill liner is a flat (horizontal) surface on which there is a uniform head of leachate, and that there is a hydraulic gradient out of the landfill. The worksheet can be used to calculate leakage through landfill side walls, but to perform this it will be necessary to run the simulation a number of times to simulate changing head of leachate on the liner.

It is important that the results produced with this worksheet are correctly interpreted. Further

explanation is provided in section 5, however, it is useful to note at this point that:

- The worksheet calculates a duration for exhaustion of CEC in the liner. This does not imply that cations will be wholly retained within the liner until this duration has passed, rather that there will be a degree of attenuation within the clay liner for at least that duration; CEC is an equilibrium process and so only a portion of the leachate cations will be removed from solution by sorption. Furthermore, since cation exchange is a reversible process and a proportion of the cations will pass through the liner, it is likely that the period in which there is some attenuation by cation exchange will, in fact, exceed this estimated duration.
- The worksheet should only be used to assess the long-term potential for cation exchange to occur within a composite landfill liner. It is one method in the toolbox to aid decision-making – it does not make any decisions. You have to do that as the assessor!

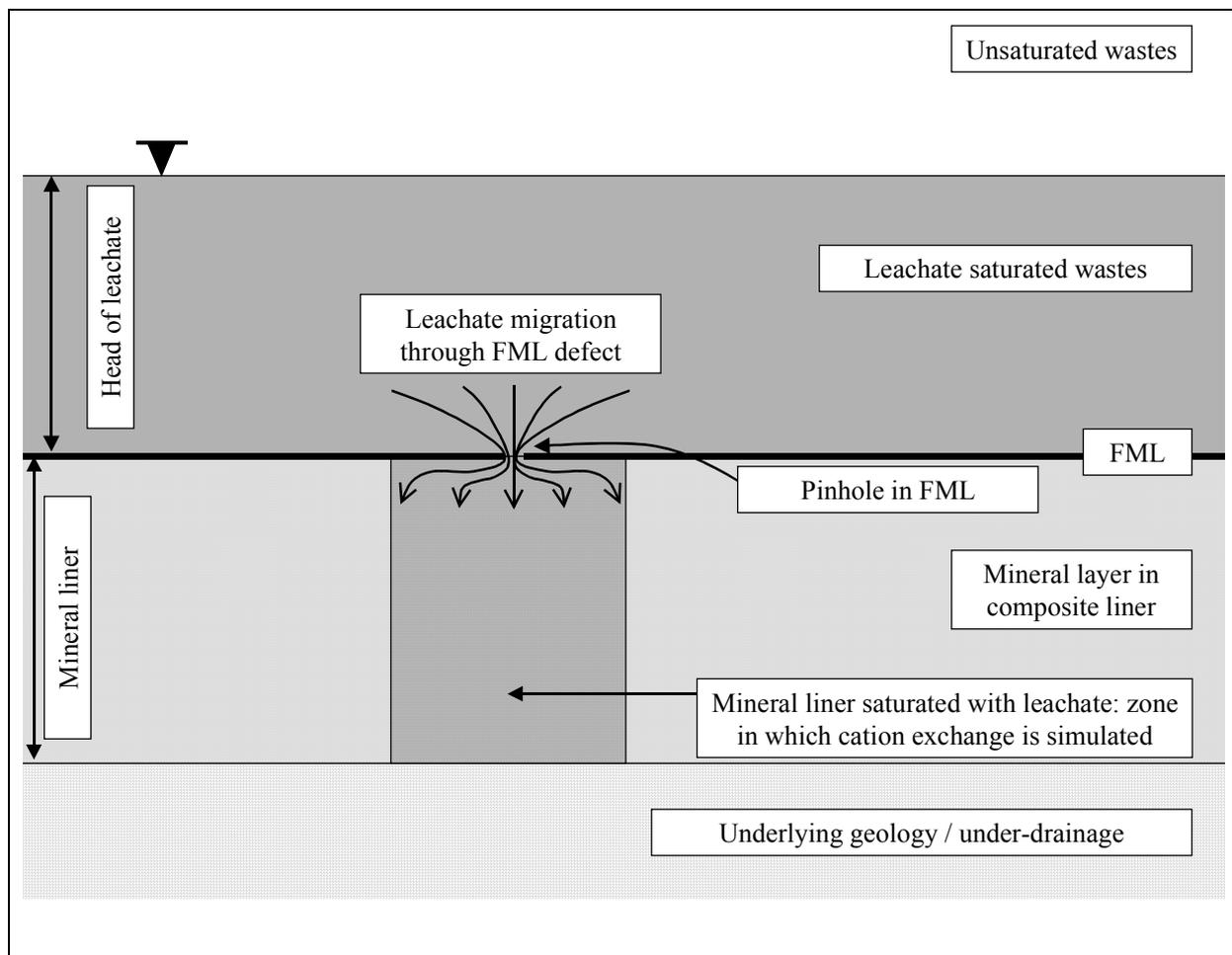


Figure 2.1 Conceptual model assumed within the CEC worksheet

### 3. Using the worksheet

The Cation Exchange Capacity in Composite Landfill Liner worksheet v1.0 incorporates 5 sheets, which have the following functions:

**Table 3.1 Function of worksheets**

<b>Title of worksheet</b>	<b>Function of sheet</b>
Introduction	Brief instructions; entry of site, contaminant and assessor details for transfer to subsequent sheets
Flow calculator	Calculates flow through a composite liner
CEC calculator	Calculates the wetted volume of mineral liner in which cation exchange can occur and presents results for ammonium transport
Cation properties	Models sorption of a range of cations between total CEC sites in the clay liner and calculates time to exhaust CEC capacity of the liner
Summary results	Presents the key results from the worksheet calculations in one place

Data entry takes three forms. Each of the worksheets is password protected and data may only be entered in specific cells, which are colour-coded blue, yellow or purple. Other cells are coloured grey or green and these are used to show interim and final calculation results respectively.

Blue cells are provided to record site details. Data takes the form of site details as text (on the 'Introduction' sheet), which are automatically transferred to all other sheets.

Yellow cells require data to be entered. Data should be site-specific, or literature data that are relevant to the site being considered. Field data and laboratory analyses should be obtained following a recognised good-practice method. Environment Agency R&D Technical Report P340 is particularly relevant in respect of cation exchange capacity test methods.

Purple cells require either a "1", "2" or "3" to be entered (as instructed on the sheets) and allow the assessor to define which analytical solution or treatment of a contaminant/aquifer property they wish to use. Interim results are presented in grey cells. These are hard-coded and cannot be modified by assessors. Final calculation results are presented in green cells.

#### 3.1 Introduction worksheet

The first sheet is the 'Introduction' worksheet. This contains brief instructions of data entry and three cells for entry of site information: site name; assessor's name and the date of the assessment. This data is automatically transferred to all subsequent worksheets and is printed on the final versions. The worksheet will function without this data being entered, however, it is considered good practice to record assessment details and the Agency will expect any submitted assessments to include this information.

### 3.2 Flow calculator worksheet

The ‘Flow calculator’ worksheet (Figure 3.2) allows assessors to determine the volume of leachate that will flow through a composite landfill liner.

Figure 3.2 ‘Flow calculator’ worksheet

	A	B	C	D	E	F	G	H
1	<b>Flow through a composite liner calculator</b>							
2								
3	Head of leachate on FML	m	1					
4	Quality of contact (FML to clay)	Constant, Cd	0.7					
5	Hydraulic conductivity of clay	m/s	1.00E-09					
6	Thickness of mineral liner	m	1.00					
7	Effective porosity of mineral liner	fraction	0.25					
8	Area of basal liner	ha	10					
9		defect density (ha <sup>-1</sup> )	X.S.Area (m <sup>2</sup> )					
10	pinholes	25	2.00E-06					
11	small holes	5	4.00E-05					
12	tears	2	0.004					
13		flow through hole	flow through site					
14		m <sup>3</sup> / hole / s	m <sup>3</sup> /s					
15	pinhole	4.12E-08	1.03E-05					
16	small holes	5.56E-08	2.78E-06					
17	tears	8.82E-08	1.76E-06					
18	<b>TOTAL</b>		1.49E-05	m <sup>3</sup> /s				
19								
20	<b>Leakage through composite liner</b>		1283.2	l/day	4.68E+05	l/year		
21	<b>Unretarded time to flow through clay liner</b>		2894	days	7.9	years		
22	<b>Site name</b>							
23	Enter site name here							
24								
25								

It solves the following equations, proposed by Giroud *et al* (1992). First, the flow through individual defects (pinholes, holes and tears) is calculated (cells B15:B17) as follows:

$$q = C_d \cdot i \cdot H^{0.9} \cdot a^{0.1} \cdot K^{0.74}$$

where:

- q = leachate flow rate per defect (m<sup>3</sup>/s)
- C<sub>d</sub> = constant describing quality of contact between FML and mineral liner
- i = vertical hydraulic gradient, assumed to equal 1
- H = head of leachate on the defect in FML (m)
- a = area of the defect (m<sup>2</sup>)
- K = hydraulic conductivity of the mineral liner directly beneath the FML (m/s)

Having calculated the flow through individual defects, the worksheet subsequently calculates the total flow through the landfill liner (cells C15:C17) using the following solution (after Giroud *et al*, 1992):

$$Q_c = A(\{q_p \cdot f_p\} + \{q_h \cdot f_h\} + \{q_t \cdot f_t\})$$

where:

- $Q_c$  = total leachate flow through liner (m<sup>3</sup>/s)  
 $A$  = area of composite liner on base of landfill (hectares)  
 $q$  = leachate flow rate per pinhole, hole or tear (m<sup>3</sup>/s)  
 $f$  = frequency of defects (pinholes/holes/tears) (defects per hectare of liner)

Data are required for the following parameters:

*Head of leachate on membrane, H:* the head of leachate acting on the flexible membrane liner (FML). This should be taken as the head of leachate present above the FML, but since this will vary across the site, the model should be run with maximum, mean and minimum heads in order to simulate the likely range of heads present.

*Quality of contact, C<sub>a</sub>:* An experimentally derived constant describing the quality of the contact between flexible membrane liner (FML) and underlying mineral liner (clay or BES). Giroud *et al* report values of C<sub>a</sub> varying between 0.21 where there is good contact, and 1.15 where there is poor contact. LandSim assumes that there is a uniform distribution between 0.1 and 2, to take account of system uncertainty (LandSim 2 Manual, p. 140). Alternative values or distributions should only be used where they can be justified on the basis of a construction quality assurance (CQA) scheme that addresses this issue.

*Hydraulic conductivity, K:* of the mineral liner that is directly beneath the membrane liner within the composite engineered liner.

*Thickness of mineral liner:* the design thickness of mineral component of the composite liner (perpendicular to FML/mineral liner contact).

*Porosity of mineral liner:* the fraction of volume of the mineral liner that is void space (either air or water filled). Expressed as a fraction between 0 and 1.

*Area of basal liner:* through which flow can take place.

*Defect density:* the density of defects within the membrane liner, expressed as a number per hectare of liner. Defects are split into three categories: pinholes, holes and tears.

*Defect area:* the area of a single defect within the membrane liner. Values are required for three defect types: pinholes, holes and tears.

Default values for defect size in membrane liners and density of defects from LandSim are summarised:

Defect type	Membrane defect rate			Defect area	
	PDF	Defect density with CQA (per hectare)	Defect density without CQA (per hectare)	PDF	Area of defect (m <sup>2</sup> )
Pinhole	Triangular	0, 25, 25	0, 750, 750	Log uniform	1.0E-8 – 5.0E-6
Hole	Triangular	0, 5, 5	0, 150, 150	Log uniform	5.0E-6 – 0.0001
Tear	Triangular	0, 0.1, 2	0, 0.5, 10	Log uniform	0.0001 – 0.01

It should be noted that the worksheet assumes that the defects are all circular. If long thin defects (e.g. tears) are likely, the assumption may not be valid. Tears are likely to result in greater leakage of leachate, a greater wetted area of clay, and consequently increased available CEC in the liner. If significant tears are likely, reference to Giroud *et al* 1992 should be made and alternative calculations may be more appropriate.

Once data has been entered in all of the yellow cells, click away on another cell and the flow through the landfill liner will be calculated (as litres/day) and presented in the green box at the bottom of the screen.

The time for migration of water or a conservative solute (e.g. chloride) through the composite liner (FML plus mineral sections) is also presented in days and years. This calculation is based on Darcian assumptions and is solved by the equation below. It is important to note that the equation only applies if the assumption that the strata directly beneath the clay liner is unsaturated is true, i.e. there is nil head of leachate at the base of the liner.

$$TT(days) = \frac{(L_{thickness} \cdot n)}{(K_{clay} \cdot 86400 \cdot i)}$$

where:

- TT = travel time for conservative solute through liner (days)
- L<sub>thickness</sub> = thickness of mineral liner (m)
- n = effective porosity of mineral liner (fraction)
- K<sub>clay</sub> = hydraulic conductivity of mineral liner (m/s)
- i = hydraulic gradient (assumed to equal 1)

### 3.3 CEC calculator worksheet

The CEC calculator worksheet (Figure 3.3) performs a number of calculations, primarily related to the hydraulics of the landfill liner system.

Firstly, the total CEC of the mineral liner is calculated. This requires the assessor to either input an experimentally or literature derived CEC value; the Agency recommends that site-

specific experiment values are used, following test methods described in R&D Technical Report P340 (EA, 2000). Alternatively, there is an option to estimate CEC from the following empirical relationship (after Appelo & Postma, 1994), where clay refers to the fraction  $<2\mu\text{m}$ . This approach should only be used as a screening tool and the Agency will expect site-specific CEC values to be determined by laboratory analysis where they are used as a significant part of the risk assessment. It should be noted that additional data on CEC for a range of UK lithologies has been published (Environment Agency, 2001c), and this may also be used for risk-screening purposes.

$$\text{CEC (meq/100g)} = (0.7 \times \% \text{clay}) + (3.5 \times \% \text{organic carbon})$$

The data on CEC is then combined with data entered in the 'Flow calculator' sheet to calculate the theoretical total CEC available within the clay layer of the entire composite liner.

In order to calculate the proportion of the total CEC that is actually available to attenuate pollutants, it is necessary to calculate how much of the clay liner is saturated by leachate as a result of leakage through defects in the overlying FML. The entire mineral liner will not be saturated with leachate.

Two options are presented for calculating the wetted volume of the mineral liner. Firstly, the wetted area may be calculated using the solution proposed by Giroud *et al.* (1992), or if alternative valid approaches are available, the value for the wetted volume may simply be entered. The Giroud *et al.* solution is given below for the wetted area below a single defect. It takes values for density and size of defects, and permeability of the mineral layer directly from the 'Flow calculator' worksheet, so that consistent values are used throughout.

$$w_a = \pi \left( C_d \cdot a^{0.05} \cdot H^{0.45} \cdot K^{-0.13} \right)^2$$

where:

- $w_a$  = wetted area beneath an individual defect ( $\text{m}^2$ )
- $C_d$  = constant describing quality of contact between FML and mineral liner
- $a$  = area of the defect ( $\text{m}^2$ )
- $H$  = head of leachate on the defect in FML (m)
- $K$  = hydraulic conductivity of the mineral liner directly beneath the FML (m/s)

The calculated wetted areas for each type of defect (pinhole, hole and tear) are then summed over the area of the site and multiplied by the thickness of the mineral liner to give an estimate of the total wetted volume of clay within the composite liner.

$$V_{\text{wetted}} = (\{W_{a(p)} \cdot f_p\} + \{W_{a(h)} \cdot f_h\} + \{W_{a(t)} \cdot f_t\}) \cdot A_{\text{base}} \cdot L_{\text{thickness}}$$

where:

$V_{\text{wetted}}$	= volume of mineral liner saturated with leachate (m <sup>3</sup> )
$W_a$	= wetted area beneath individual defects (pinholes, holes and tears) (m <sup>2</sup> )
$f$	= frequency of defects (pinholes, holes and tears) (defects per hectare)
$A_{\text{base}}$	= area of the base of the landfill liner (hectares)
$L_{\text{thickness}}$	= thickness of the mineral liner (m)

It is important to note that in calculating the wetted area beneath each defect a factor,  $C_d$ , is required that relates to the quality of contact between FML and mineral liner. It should be noted that this value of  $C_d$  is different to that used in the 'Flow calculator' sheet, although the relative goodness of contact must be the same in both cases. Experimental results (Giroud *et al.*, 1992) suggest that for this calculation, the value of  $C_d$  varies between 0.26 (for good contact) and 0.61 (for poor contact). It should be noted that LandSim models  $C_d$  between values of 0.2 and 0.7 to account for uncertainty in the derivation of this empirical relationship. The worksheet automatically calculates the value for  $C_d$  by scaling the input value entered in the 'Flow calculator' worksheet. No manipulation of  $C_d$  is required by the assessor.

The proportion of the mineral liner that is saturated by leachate, as a percentage, is shown (cell G25) and the actual CEC available for attenuation (based on the wetted volume of clay) is computed (cell C25).

In order to calculate time to exhaust the CEC of the liner, it is necessary to use the leakage rate through the liner. This can either use the value derived from the 'Flow calculator', or if other methods have been used may be entered in the relevant cell.

### 3.3.1 Surface Exposure Factor

Finally, a surface exposure factor term is needed. This term takes account of the fact that laboratory derived CEC values are determined from crushed, prepared samples. In the field there will be heterogeneity, agglomeration of grains etc. and as a result the exposure of mineral surfaces to infiltrating leachate will be less than under laboratory conditions. As a consequence the field CEC may be somewhat less than the reported laboratory result. The surface exposure factor should be used to take account of only this effect, and in that respect it is different from the reaction efficiency term required in LandSim.

The value of the surface exposure factor will vary between 0 and 1. In a compacted reworked

clay, or processed mineral (e.g. bentonite enriched sand, BES), this factor is likely to be greater than in consolidated strata where greater heterogeneity is likely to exist. Further work is needed to assess the likely ranges of relative surface exposure, although some work on clay liners (Richards & Bouazza, 1999) suggests the difference in mineral surface exposure can vary significantly between clay mineralogies. In the authors' opinion it is probably reasonable to assume that the surface exposure factor in an engineered clay liner will rarely be less than 0.5, or greater than 0.8. In consolidated strata, by contrast, ranges between 0.05 and 0.5 are more likely. Recent work on the migration of chlorinated solvents through Triassic Sandstones, for example, indicates that typically only about 10 – 15% of the sandstone pore space is exposed to solvents following a spillage from above, i.e. surface exposure factor of 0.1 to 0.15.

It should be noted that the reaction efficiency term is only required where CEC values are derived from laboratory experiment on crushed samples. Where CEC is derived from large-scale column or lysimeter experiments (for which the experimental design and results have been provided), no such factor is required: enter 1.

D14		A	B	C	D	E	F	G	H	I	J	K
1	<b>Cation Exchange Capacity worksheet</b>											
2						<b>Site name</b>						
3	<i>Select method to input CEC value</i>					Enter site name here						
4			Enter CEC value									
5	<b>User defined CEC value</b>					<b>Calculate total CEC of liner</b>						
6		CEC	meq/100g	5		Areal extent of landfill base	ha	10				
7	<b>Empirical calculation of CEC</b>					Thickness of mineral liner	m	1.00				
8		Clay content	%	0		Bulk density of clay	g/cm <sup>3</sup>	1.7				
9		Organic carbon content	%	0		Total volume of clay liner	m <sup>3</sup>	100000				
10		Calculated CEC	meq/100g	-		Total CEC of liner beneath site	meq	8.50E+09				
11												
12		CEC for rock mass used hereafter	meq/100g	5								
13												
14	<i>Select method of estimating volume of wetted clay in liner</i>											
15	Calculate wetted volume after Giroud et al 1992											
16	<b>User defined clay saturation by leachate</b>											
17		Wetted volume of clay in liner	m <sup>3</sup>	1.25E+03		Quality of contact	0.44	0.26=good; 0.61 = poor				
18												
19	<b>Calculate clay saturation</b>											
20			Defect density (ha <sup>-1</sup> )	X.S.Area (m <sup>2</sup> )		Wetted area/hole		<b>Wet zone of liner (Giroud, 1992)</b>				
21		Pinholes	25	0.000002		wa (pin)	36.22	9055.55	m <sup>3</sup>			
22		Small holes	5	0.00004		wa (hole)	48.87	2443.70	m <sup>3</sup>			
23		Tears	2	0.004		wa (tear)	77.46	1549.20	m <sup>3</sup>			
24						Total saturation of clay liner by leachate		13048.46	m <sup>3</sup>			
25		Clay liner saturation used hereafter	m <sup>3</sup>	13048.5								
26		Total CEC based on partial saturation	meq	1.11E+09		Percentage of clay liner saturated	%	13.05				
27	<i>Place "1" next to preferred option, "0" next to others</i>											
28		Estimated leakage through liner	l/day	0	0							
29		Calculated leakage using LandSim	l/day	0	0							
30		Calculated leakage from Flow Calc	l/day	1283.2	1	Leakage rate used	1.28E+03	l/day				
31	<b>Surface Exposure Factor in clay liner</b>											
32		Relative surface exposure of clay	fraction	0.50		Time for NH <sub>4</sub> <sup>+</sup> to exhaust liner capacity	7.0	yrs				
33						Time for unretarded flow through clay li	7.9	yrs				
34						Time for retarded flow through liner (NH	15.9	yrs				
35						Leachate flow through liner	1283.2	litres/day				
36						Total NH <sub>4</sub> <sup>+</sup> load through liner	468.4	kg/yr				
37												

Figure 3.3 CEC Calculator worksheet

The specific data required in this worksheet are summarised below:

*CEC*: the cation exchange capacity of the mineral liner forming part of the composite liner system. Laboratory results should normally be derived using test methods described in Environment Agency R&D Technical Report P340.

*Clay content (particles <2 $\mu$ m)*: of the mineral liner as a percentage (i.e. between 0 and 100).

*Organic carbon content*: of the mineral liner as a percentage (i.e. between 0 and 100).

*Bulk density*: of the mineral liner material.

*Wetted volume of clay*: optional input for the wetted clay volume. If this input cell is used over the provided calculation based on Giroud *et al*, a full explanation of methods must be provided.

*Estimated leakage through liner*: optional input for the leakage through the liner. If this cell is used over the other methods provided, full explanation of the methods must be provided.

*LandSim leakage*: calculated leakage, using LandSim (The confidence limit for the value should also be provided in project documentation).

*Surface exposure factor*: (between 0 and 1) takes account of the fact that laboratory tests for CEC are performed on crushed prepared samples. Field exposure of mineral surfaces to leachate is likely to be significantly less, and a surface exposure factor equal to the exposed mineral surface area divided by the total surface area of crushed samples, should be inserted. In an engineered clay liner the surface exposure factor is likely to be larger than in consolidated rock.

### 3.4 Cation Properties worksheet

The ‘Cation properties’ worksheet (Figure 4.4) is the final worksheet included. It calculates the relative proportion of cation exchange sites within the mineral liner that will be taken by the various monovalent and divalent cations present within the landfill leachate.

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T
1																	Site name			
2	Cation	Conc	Conc	Mol. weight	Conc	Conc	Valency	$K'_{Na}$	$\beta_{cation}$	$\beta_{cation} * CE$	Daily load	Exhaustion	Exhaustion	Kd	cation flow	Enter site name here				
3		mg/l	g/l		meq/l	mol/l				meq	meq/d	Years	Days	l/kg	relative H <sub>2</sub> O					
4																				
5	Na <sup>+</sup>	2000	2.0E+00	23	86.96	0.087	1	1	0.129	1.43E+08	1.12E+05	1.76	641	3.7E-02	0.80	To calculate a: 23.399 To calculate b: 4.73216				
6	NH <sub>4</sub> <sup>+</sup>	1000	1.0E+00	18	55.56	0.056	1	0.25	0.330	3.66E+08	7.13E+04	7.03	2565	1.5E-01	0.50					
7	K <sup>+</sup>	800	8.0E-01	39.1	20.46	0.020	1	0.2	0.152	1.68E+08	2.63E+04	8.78	3206	1.9E-01	0.44	To solve for $\beta_{Na}$				
8	Rb <sup>+</sup>	0.1	1.0E-04	85.5	0.00	0.000	1	0.1	0.000	1.92E+04	1.50E+00	17.57	6412	3.7E-01	0.28	0.129				
9	Fe <sup>3+</sup>	350	3.5E-01	55.8	12.54	0.006	2	0.6	0.038	4.25E+07	1.61E+04	3.62	1321	3.1E-01	0.32					
10	Mn <sup>2+</sup>	15	1.5E-02	54.9	0.55	0.000	2	0.55	0.002	2.21E+06	7.01E+02	4.31	1572	3.6E-01	0.29					
11	Mg <sup>2+</sup>	250	2.5E-01	24.3	20.58	0.010	2	0.5	0.091	1.00E+08	2.64E+04	5.21	1903	4.4E-01	0.25					
12	Ni <sup>2+</sup>	0.2	2.0E-04	58.7	0.01	0.000	2	0.5	0.000	3.33E+04	8.74E+00	5.21	1903	4.4E-01	0.25					
13	Cu <sup>2+</sup>	0.1	1.0E-04	63.5	0.00	0.000	2	0.5	0.000	1.54E+04	4.04E+00	5.21	1903	4.4E-01	0.25					
14	Ca <sup>2+</sup>	750	7.5E-01	40.1	37.41	0.019	2	0.4	0.257	2.85E+08	4.80E+04	8.15	2973	6.9E-01	0.18					
15	Cd <sup>2+</sup>	0.02	2.0E-05	112.4	0.00	0.000	2	0.4	0.000	2.72E+03	4.57E-01	8.15	2973	6.9E-01	0.18					
16	Zn <sup>2+</sup>	3.5	3.5E-03	65.4	0.11	0.000	2	0.4	0.001	8.17E+05	1.37E+02	8.15	2973	6.9E-01	0.18					
17	Sr <sup>2+</sup>	2	2.0E-03	87.6	0.05	0.000	2	0.35	0.000	4.55E+05	5.88E+01	10.64	3883	9.0E-01	0.14					
18	Pb <sup>2+</sup>	0.2	2.0E-04	207.2	0.00	0.000	2	0.3	0.000	2.62E+04	2.48E+00	14.48	5285	#####	0.11					
19																				
20									Total:	1.000										
21																				
22																NOTE: THIS SPREADSHEET IS ONLY APPLICABLE TO MONO AND DI-VALENT CATIONS				
23																				

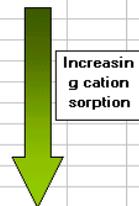


Figure 3.4 Cation properties worksheet

Data must be entered in the yellow cells (B5:B18) for leachate chemistry (in mg/l) for those monovalent and divalent cations that are present. The worksheet is restricted to common monovalent and divalent cations in order to simplify the mathematics, and because the concentrations of trivalent, tetravalent (and above) cations are generally so small that they would not make a significant difference to the overall results to the main pollutants of concern, i.e. ammonium. If highly charged cations (3+ or greater) are present in significant concentrations in the landfill leachate, assessors should consider whether this model adequately simulates the conceptual model and whether an alternative assessment is warranted.

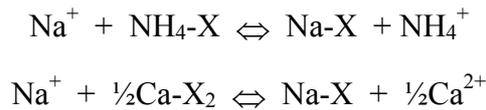
The worksheet performs a series of functions on the entered leachate chemistry data, as follows:

1. Leachate chemistry is converted from a concentration (mg/l) into milli-equivalents (meq/l) and molar concentrations (mol/l), where:

$$\text{Concentration (meq/l)} = \frac{\text{concentration (mg/l)} \times \text{ion valency}}{\text{Molecular weight}}$$

$$\text{Concentration (mol/l)} = \frac{\text{concentration (mg/l)}}{\text{Molecular weight} \times 1000}$$

2. The relative proportion of each cation sorbing onto CEC sites in the mineral,  $\beta_{\text{cation}}$ , is calculated. This calculation is based on that presented in example 5.4 of Appelo & Postma, 1994, using data for exchange co-efficients presented in table 5.5 and assuming that activity is numerically equal to concentration in mol/l. The cation exchange reactions involving the exchange of monovalent cations (e.g.  $\text{Na}^+$ ,  $\text{NH}_4^+$ ) and divalent cations (e.g.  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) are illustrated below:



where:

$\text{NH}_4^+$  = dissolved ammonium ions

$\text{NH}_4\text{-X}$  = ammonium ions sorbed to an exchange site (-X) on the clay surface.

The equilibrium cation exchange coefficients for monovalent cation exchange (e.g.  $\text{NH}_4^+$ ) are then given by:

$$K_{\text{Na}/\text{NH}_4} = \left( \frac{[\text{Na-X}][\text{NH}_4^+]}{[\text{NH}_4\text{-X}][\text{Na}^+]} \right) = \left( \frac{\beta_{\text{Na}}[\text{NH}_4^+]}{\beta_{\text{NH}_4}[\text{Na}^+]} \right)$$

$$\therefore \beta_{\text{NH}_4} = \left( \frac{\beta_{\text{Na}}[\text{NH}_4^+]}{K_{\text{Na}/\text{NH}_4}[\text{Na}^+]} \right)$$

and for divalent cation exchange (e.g.  $\text{Ca}^{2+}$ ):

$$K_{\text{Na}/\text{Ca}} = \left( \frac{[\text{Na-X}][\text{Ca}^{2+}]^{0.5}}{[\text{Na}^+][\text{Ca-X}_2]^{0.5}} \right) = \left( \frac{\beta_{\text{Na}}[\text{Ca}^{2+}]^{0.5}}{\beta_{\text{Ca}}^{0.5}[\text{Na}^+]} \right)$$

$$\therefore \beta_{\text{Ca}} = \left( \frac{\beta_{\text{Na}}^2[\text{Ca}^{2+}]}{K_{\text{Na}/\text{Ca}}^2[\text{Na}^+]^2} \right)$$

The sum of all  $\beta_{\text{cations}}$  must equal 1, that is to say the sum of each of the relative proportions of cations sorbed (cell I20) must be 1 (e.g.  $\beta_{\text{Ca}} + \beta_{\text{NH}_4} + \beta_{\text{Na}} = 1$ ). Reactions involving mono- and divalent cations can be arranged to give a quadratic equation after substitution of the above terms for  $\beta_{\text{cation}}$ :

$$\beta_{\text{Na}}^2 \left\{ \sum \frac{[\text{cation}^{2+}]}{K_{\text{Na}/\text{cation}^{2+}}^2 [\text{Na}^+]^2} \right\} + \beta_{\text{Na}} \left\{ 1 + \sum \frac{[\text{cation}^+]}{K_{\text{Na}/\text{cation}^+} [\text{Na}^+]} \right\} = 1$$

where:

$\beta_{\text{Na}}$  = proportion of CEC sites that are taken by sodium under equilibrium conditions  
[cation] = concentration of cation in leachate (mmol/l)  
 $K_{\text{Na/cation}}$  = cation exchange coefficients with respect to sodium  
[Na<sup>+</sup>] = concentration of sodium in leachate (mmol/l)  
cation<sup>+</sup> = monovalent cations  
cation<sup>2+</sup> = divalent cations

This equation can then be solved simply for  $\beta_{\text{Na}}$  as it is a quadratic equation using the data for  $K_{\text{Na/cation}}$  presented in Table 5.5 of Appelo & Postma (1994) and analytically measured values for dissolved cation concentrations (e.g. [Na<sup>+</sup>]); back substitution allows  $\beta_{\text{cation}}$  to be calculated for all the other monovalent and divalent cations present. If trivalent cations (or above) are present, the relationship can no longer be solved by a simple quadratic equation and more complex mathematics is needed.

3. The calculated values of  $\beta_{\text{cation}}$  are each multiplied by the calculated total CEC for the liner through which leakage occurs, to give “ $\beta_{\text{cation}} * \text{CEC}$ ”, which is the total amount of each cation (in meq) that are predicted to be removed from solution (by cation exchange) during leakage through the clay.

4. The daily cation load (meq/d) is calculated by multiplying the calculated leakage rate (from the ‘Flow calculator’ worksheet) by the concentration of cations in the leachate (meq/l).

5. A calculation for the time to exhaust the CEC of the mineral liner is calculated by dividing the total CEC available within the liner (meq) by the daily load (meq/d). The results are presented as time to exhaustion of the CEC in both days and years.

6. The retardation co-efficient,  $K_d$ , is calculated using the following expression after Appelo & Postma (1994):

$$K_d = \frac{\text{CEC}}{100 \cdot z} \cdot \frac{\beta_{\text{cation}}}{[\text{cation}^{z+}]}$$

where:

$z$  = cation charge  
[cation<sup>z+</sup>] = aqueous concentration (mol/l)

It should be noted that the laboratory-derived value of CEC is multiplied by a reaction efficiency factor that relates to the fact that laboratory results are taken on crushed, prepared samples. In the field exposure of mineral surfaces to leachate will be some factor less due to heterogeneity within the stratum (see section 3.3.1).

7. Finally, the retarded leachate flow rate is calculated as a velocity relative to water, using the following expression:

$$v_R = \frac{1}{\left(1 + \left(\frac{\rho \cdot K_d}{n}\right)\right)}$$

where:

- $v_R$  = retarded velocity of leachate, relative to water (fraction)  
 $\rho$  = bulk density of mineral liner material (g/cm<sup>3</sup>)  
 $K_d$  = partition co-efficient of pollutant between mineral surface and pore water (ml/g)  
 $n$  = porosity of mineral liner

## 4 Summary results

The final worksheet, 'Summary results' provides all of the results in one place. No data entry is required on this sheet and it is provided only to allow easy viewing of the results produced by the various calculations.

Figure 4.1 'Summary results' worksheet

	A	B	C	D	E	F	G	H	I
1	<b>Summary of results</b>		Site name:	Enter site name here					
2									
3		<b>Leakage through composite liner</b>	1283.2	l/day	4.68E+05	l/year			
4		<b>Time for a conservative solute to flow through clay liner</b>	2894	days	7.9	years			
5									
6									
7									
			<b>Time to exhaust liner CEC (yrs)</b>			<b>Time to flow through liner (yrs) (retarded travel)</b>			
8		Na <sup>+</sup>	1.8			9.9			
9		NH <sub>4</sub> <sup>+</sup>	7.0			15.9			
10		K <sup>+</sup>	8.8			17.9			
11		Rb <sup>+</sup>	17.6			27.9			
12		Fe <sup>2+</sup>	3.6			24.4			
13		Mn <sup>2+</sup>	4.3			27.5			
14		Mg <sup>2+</sup>	5.2			31.7			
15		Ni <sup>2+</sup>	5.2			31.7			
16		Cu <sup>2+</sup>	5.2			31.7			
17		Ca <sup>2+</sup>	8.1			45.0			
18		Cd <sup>2+</sup>	8.1			45.0			
19		Zn <sup>2+</sup>	8.1			45.0			
20		Sr <sup>2+</sup>	10.6			56.4			
21		Pb <sup>2+</sup>	14.5			73.9			
22									
23									
24									
25									

## 5. Interpreting the results

The worksheets described perform a number of calculations that are presented on each of the worksheets and summarised on the 'Summary results' sheet. Each of the results presented is described below, together with an interpretation of their implications:

- Leakage through composite liner

The calculated flow-rate of liquid through the composite landfill liner. The calculation assumes that the fluid has the properties of water. If the landfill leachate has physical properties (e.g. viscosity, density) significantly different from water, that will affect its rate of migration. These can be taken into account, if necessary, by calculating a hydraulic conductivity for the liner to the landfill leachate. It is considered unlikely, in the majority of cases, that this issue will make a significant difference to the results.

- Unretarded time to flow through clay liner

The estimated time for water or a conservative species, such as chloride, to pass through the clay liner under Darcian conditions. The calculation ignores the effect of longitudinal dispersion, so in fact slightly over-estimates the time taken for break-through of the contaminant.

- Time for retarded flow through liner

The estimated time for a retarded cation to pass through the clay liner under Darcian conditions. The calculation ignores the effect of longitudinal dispersion, so in fact slightly over-estimates the time taken for break-through of the contaminant.

The concentration of the cation passing out of the base of the clay liner will be less than the concentration entering the top of the liner (due to sorption within the liner), but is not calculated by this worksheet. The interpretation of the results should be limited to the following:

- Leachate will enter the top of the clay liner at the concentrations input to the worksheet;
- Leachate will pass through the liner, but most cations will be retarded relative to a conservative tracer;
- Cationic pollutants will migrate through the liner (and reach the base) in a period somewhat longer than the time taken for water to pass through the liner;
- Contaminant concentrations in the leachate as it reaches the base of the liner will be less than the concentrations entering the top of the liner, by a factor determined by the reaction kinetics, and selectivity coefficient (e.g.  $K_{Na/Ca}$ ) of the sorption process;
- Cations will continue to sorb (from leachate onto mineral surfaces) within the liner for a duration at least equal to the calculated time taken to exhaust the liner CEC (see below). After this period there may not be any further sorption and leachate chemistry leaving the base of the liner will be the same as that entering the top.

- Time to exhaust cation exchange capacity (CEC) of liner

The estimated time in which there will be some CEC available within the mineral liner to sorb cations migrating from the landfill above. It should not be implied that cation exchange processes would remove all the cations from the leachate during this period – they will not, it is an equilibrium process and so only a portion of the leachate cations will be removed from solution by sorption. Some cations will remain dissolved in the leachate and will therefore be transported through the liner. However, cation exchange processes will act to reduce the cation concentrations passing through the liner for the duration of the calculated period.

- Displacement of cations already present in the clay mineralogy

The spreadsheet implicitly assumes that all cation exchange site in the clay liner are vacant at the point at which leachate enters the liner. In reality this is a false assumption, since those sites will be filled with naturally occurring cations, such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$ . As leachate enters the liner, the more strongly sorbed cations in the leachate will displace the existing cations with lower affinity for clay minerals. As such, the sorption of  $\text{NH}_4^+$  and other cations from the leachate onto the clay minerals is likely to result in the release of  $\text{Na}^+$  in particular. The input of leachate may cause an increase in the concentration of displaced cations, such as sodium and potassium, exiting the base of the liner. In most circumstances the benefits of sorption of ammonium and other potentially polluting cations within the liner is likely to greatly outweigh the possible environmental damage that could be caused by the release of those naturally occurring cations.

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