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Golder Associates

DRAFT
REPORT ON

SUPPLEMENTAL DIFFUSION TESTING ON CORE SAMPLES CASMALIA, CALIFORNIA

Submitted to:

MACTEC ENGINEERING
1150 Sanctuary Parkway, Suite 300
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September 2007

06-1116-042

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September 26, 2007 **DRAFT** 06-1116-042

Mactec Engineering
1150 Sanctuary Parkway
Suite 300
Alpharetta, Georgia 30004
United States

Attention: Mr. Bill Feller

RE: SUPPLEMENTAL MATRIX DIFFUSION TESTING ON ROCK SAMPLES

Dear Mr. Feller:

Please find attached our draft report entitled "*Supplemental Diffusion Testing on Core Samples, Casmalia, California*".

Should you have any questions regarding the work, please do not hesitate to contact us.

Yours truly,

GOLDER ASSOCIATES LTD.

Frank S. Barone, Ph.D., P.Eng.
Principal

FSB/sa

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1.0 INTRODUCTION

This report presents the methodology and the results of diffusion tests carried out on two (2) rock core samples (approximately 6 cm diameter) to evaluate the matrix diffusion coefficient (D) for chloride and the corresponding matrix tortuosity factor (τ). The core samples were provided by Mactec Engineering, Inc. in November 2006. A description of the core samples is given in Table 1. Also presented in this report are the results of analyses for water content, specific gravity, total porosity and total organic carbon content.

The above testing was conducted between December 2006 and April 2007, at Golder Associates' laboratory in Mississauga, Ontario. All analyses for chloride concentration were carried out at ALS Laboratory Group in Mississauga, Ontario.

2.0 DEFINITION OF MATRIX DIFFUSION COEFFICIENT AND TORTUOSITY FACTOR

The diffusion coefficient (D) is a solute transport parameter, which relates the diffusive mass flux of a solute in a porous media to its concentration gradient via Fick's first law, i.e.:

$$f = -n' D \frac{\delta c}{\delta z} \qquad [1]$$

where:
- f = solute diffusive mass flux (mass of solute transported per unit area per unit time) [M/L^2/T],
- n' = porosity of the porous media which is available for diffusion (i.e. effective porosity),
- D = solute diffusion coefficient in the porous media [L^2/T],
- c = solute concentration in the porewater phase of the porous media [M/L^3], and
- z = distance in the direction of diffusion along the porous media [L]

The magnitude of the diffusion coefficient is influenced by temperature, characteristics of the solute itself and its co-diffusing species (e.g. size and concentration) and the fabric of the porous media (e.g. pore size and pore structure).

For a given temperature, the diffusion coefficient can be expressed as the product,

$$D = \tau D_o \qquad [2]$$

where: D_o = species diffusion coefficient in a purely aqueous solution at the given temperature [L^2/T], and

τ = tortuosity factor for the porous media

The porous media tortuosity factor (τ) is an empirical factor ($0 < \tau < 1.0$) which accounts for the fact that the rate of diffusion in a porous media is slower than that in aqueous solution due to diffusion pathways around solid particles being much longer and more "tortuous" than the direct pathways in aqueous solution. The tortuosity factor is considered to be independent of temperature and is assumed to be strictly a physical property of the porous media, dependant on the matrix fabric (i.e. pore structure and pore size) rather than on the nature of the solute species (e.g. Rowe, 1987).

The species aqueous diffusion coefficient (D_o) for a given temperature is dependant on properties of the porewater phase (e.g. viscosity) and properties of both the solute itself and its co-diffusing species (e.g. size and concentration). Aqueous diffusion coefficient values can be obtained from the literature (e.g. Li and Gregory, 1974, and Reid et. al., 1987).

3.0 THEORETICAL DESCRIPTION OF THE DIFFUSION TEST

A schematic drawing of the diffusion cell used for this study is presented in Figure 1. A source solution consisting of distilled water spiked with sodium chloride was placed in contact with one side of the core sample and a collector solution consisting of distilled water was placed on the opposite side.

The source solution constituents (i.e. sodium and chloride) were allowed to diffuse through the core sample and into the collector solution compartment over a period of 91 days. During this period, the source and collector solution compartments were periodically sampled in order to monitor the chloride concentration variation with time.

Assuming that the chloride concentration decreases with time in the source solution is due only to diffusion through the core sample (i.e. no short circuiting of chloride along the contact between the core and the latex membrane) the boundary condition representing the chloride concentration in the source solution can be written as (e.g. see Rowe and Booker, 1985):

$$c_s(t) = c_{os} - \frac{1}{H_s}\int_o^t f_s(t)\,dt \qquad [3]$$

where: $c_s(t)$ = chloride concentration in the source solution at time t [M/L^3],

c_{os} = initial chloride concentration in the source solution [M/L^3],
H_s = equivalent height of source solution, calculated as the source solution volume divided by the cross-sectional area of the core sample perpendicular to the direction of diffusion [L], and
$f_s(t)$ = mass flux across the core sample/source solution interface [M/L^2/T]

The mass flux across the sample/source solution interface, $f_s(t)$, can be further related to the chloride concentration gradient across this interface $(\delta c/\delta z)_s$ by Fick's first law, viz.:

$$f_s(t) = -n' D \left(\frac{\delta c}{\delta z}\right)_s \qquad [4]$$

where n' is the effective matrix porosity of the core sample.

The boundary condition representing the species concentration in the collector solution ($c_c(t)$) is given by:

$$c_c(t) = \frac{1}{H_c}\int_0^t f_c(t)\,dt - \frac{q_c}{V_c}\int_0^t c_c(t)\,dt \qquad [5]$$

where: $c_c(t)$ = chloride concentration in the collector solution at time t [M/L^3],
V_c = volume of the collector solution [L^3],
$f_c(t)$ = mass flux into the collector [M/L^2/T]
q_c = average rate of sampling of the collector solution [sample volume/average sampling frequency] [L^3/T], and
H_c = equivalent height of collector solution, calculated as the collector solution volume divided by the cross-sectional area of the core specimen, perpendicular to the direction of diffusion [L]

The mass flux into the collector $f_c(t)$ can be further expressed in terms of the concentration gradient across the sample/collector solution interface $(\delta c/\delta z)_c$, viz.:

$$f_c(t) = -n' D \left(\frac{\delta c}{\delta z}\right)_c \qquad [6]$$

For these flux controlled boundary conditions, a semi-analytical solution to the one-dimensional diffusion equation,

$$\frac{\delta c}{\delta t} = D\frac{\delta^2 c}{\delta z^2} \qquad [7]$$

has been implemented in the computer program POLLUTE (Rowe et. al., 1994). Using different values for the chloride diffusion coefficient, theoretical curves for the chloride concentration variation with time in the source solution and collector solution compartments were generated using POLLUTE and then compared to the experimental concentration data. The diffusion coefficient that gave the best fit "by eye" to the experimental data was chosen as the experimental value. For all samples, the effective porosity, n', was taken as the total porosity.

The diffusion test modelling using POLLUTE accounted for the initial chloride porewater concentration in the core sample at the start of the diffusion test. For one of the samples (RIMW11 (50 feet)), the initial porewater concentration was estimated based on actual groundwater concentrations obtained from a monitoring well screened at a similar depth/location as the sample. The other sample (RIMW11 (14 feet)) was from above the groundwater table and therefore there is no reference monitoring well for obtaining the initial porewater concentration. For this sample, the initial chloride porewater concentration was back-calculated based on analysis of the chloride concentration in the sample at the end of the diffusion test (units of µg/g) and consideration of mass balance knowing the initial and final concentrations in the source and collector solution compartments (refer to Appendix C for calculation). Table A.1 summarizes the initial porewater concentrations used for each diffusion test sample.

4.0 DIFFUSION TEST PROCEDURES

The following outlines the general procedures used in the set-up and monitoring of the diffusion tests for the measurement of matrix diffusion coefficient for chloride. Note that the diffusion tests were conducted at room temperature (~23°C).

(1) The core samples were cut to the lengths given in Table A. 1 (Appendix A).

(2) A thin layer of silicone vacuum grease was spread around the outer perimeter of each sample. A circular piece of non-woven geotextile, followed by a perforated plastic disc, were placed at each end of the sample. The sample and the end pieces were then surrounded by a latex membrane, which adhered to the vacuum grease surrounding the sample.

(3) The sample, capped at both ends by the geotextile and the perforated disc, was then placed between the two acrylic collars within the test apparatus. The latex membrane was secured to these collars by an "O" ring at each end. The positioning of the sample within the apparatus is shown in Figure 1.

(4) Following the securing of the sample, the chamber surrounding the sample was filled with water and pressurized to 50 kPa to apply a confining pressure on the outside of the sample, which in turn created a tight seal between the sample and the membrane.

(5) With the apparatus in a near horizontal position, distilled water was injected into the collector compartment through a injection/sampling port. The second injection port was left open to allow air to escape the compartment while it was being filled. The total volume of distilled water injected into the collector compartment ranged from 107 mL to 108 mL (refer to Table A.1).

(6) With the apparatus still in a horizontal position, the source solution consisting of distilled water spiked with 1.65 g/L sodium chloride was injected into the source reservoir. The second port was left open to allow air to escape the compartment while it was being filled. The total volume of sodium chloride source solution injected into the source compartment ranged from 333 mL to 356 mL (refer to Table A.1).

(7) Immediately after inserting the source solution, the injection ports were sealed using fitted rubber stoppers. The cell was then gently rotated in an attempt to remove any air from the interface between the source and/or collector solution and the sample. The apparatus was then placed in a horizontal position and the start time for diffusion (i.e. $t = 0$) was recorded.

(8) A 3 mL sample was taken from the collector compartment periodically (approximately once per 10 days an average) through the sampling port. Once each sample was taken, an equal volume of fresh collector solution (i.e. distilled water) was re-injected into the collector compartment.

(9) A 3 mL sample was taken from the source compartment periodically (approximately once per 20 days on average) through the sampling port, once each sample was taken, an equal volume of fresh source solution was re-injected into the source solution compartment.

(10) All source and collector solution samples were analyzed for chloride by ion chromatography at ALS Laboratory Group (Mississauga, Ontario).

Using the above procedure, a chloride diffusion test was carried out for each of the two core specimens. Specific details of the diffusion tests, such as the volumes of the source and collector solutions, initial chloride concentrations in the source and collector solutions and core specimen dimensions are presented in Table A.1.

5.0 RESULTS

The chloride diffusion test concentration data is presented in Figures 2 and 3 for the two core specimens. For each specimen, the data is presented in the form of source solution and collector solution concentration variation with time. The actual concentration data is provided in Appendix A, Tables A.2 and A.3.

The theoretical fitting of the diffusion test concentration data is presented in Figures 2 and 3. The best-fit (by eye) chloride diffusion coefficient values and corresponding core matrix tortuosity factors (calculated using Equation 2) are summarized in Table 2. The tests indicate chloride

diffusion coefficient (D) values of 0.3 x 10^{-6} cm^2/s for RIMW11(14 feet) and 0.5 x 10^{-6} cm^2/s for RIMW11 (50 feet) at 23°C.

As noted in Section 3.0, the theoretical fitting of the diffusion test data assumed that the effective porosity of the rock core matrix (i.e. n' in Equations 4 and 6) is equivalent to the total porosity (n). Values obtained for total porosity of the core specimens are presented in Table 2 and range from 46 % to 49 %.

The specific gravity and initial (as-received) water content values obtained for the core samples (see Table 2) are 2.61 and 23.8% for RIMW11(14feet) and 2.48 and 35.3% for RIMW (50 feet).

The total organic carbon content values obtained for the rock core specimens by the Walkley-Black wet oxidation method (Walkley, 1947) range from 0.27% for RIMW11 (14 feet) to 0.88% for RIMW11 (50 feet) on a dry weight basis (see Table 2).

GOLDER ASSOCIATES LTD.

DRAFT

Frank S. Barone, Ph.D, P.Eng.
Principal

FSB/sa

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TABLE 1

Description Of The Core Specimens Used For The Diffusion Tests

Golder Lab ID.	Sample No.	Sample Depth (ft)	Sample Description*
06-5631	RIMW11 (14')	14	Weathered Claystone
06-5632	RIMW11(50')	50	Unweathered Claystone

* Sample description provided by MACTEC

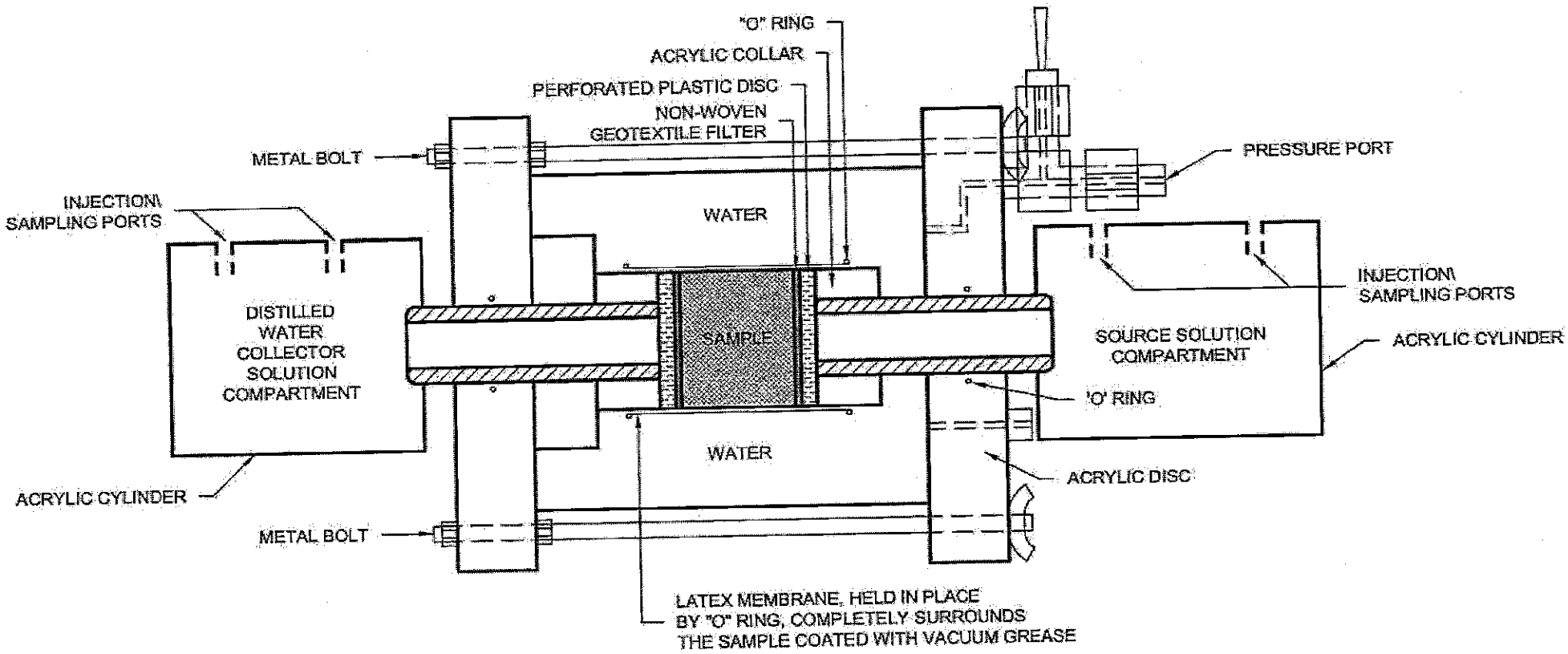
TABLE 2

SUMMARY OF TEST RESULTS

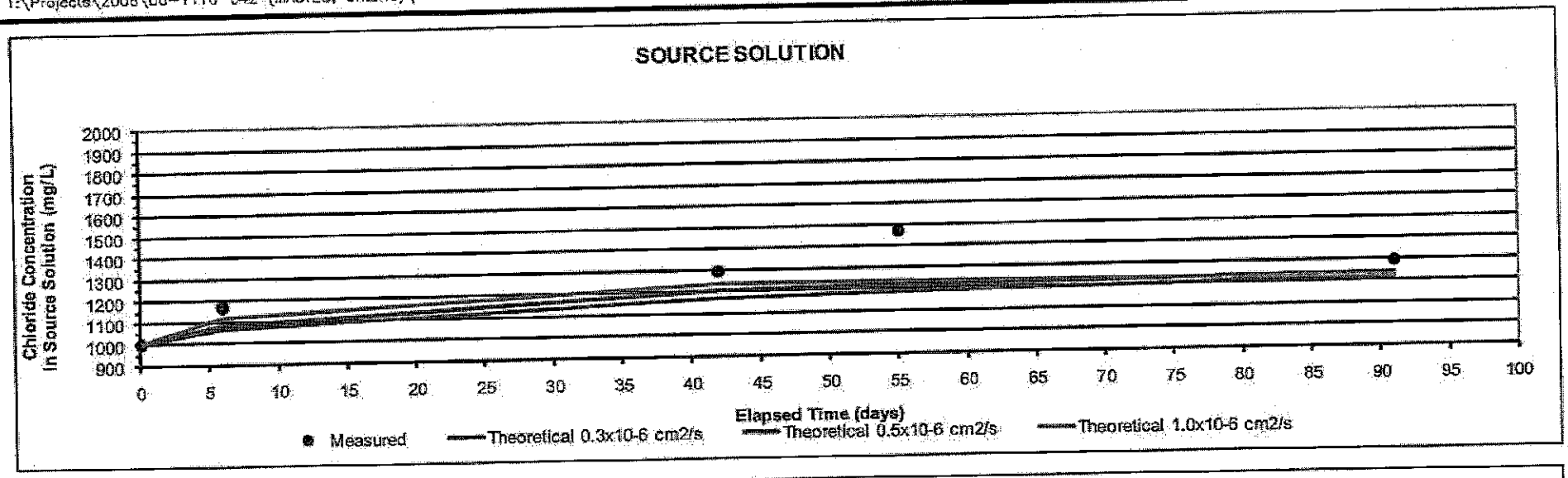
Lab ID	Sample No.	Sample Depth (ft)	Water Content[1] (%)	Dry Density[2] (Mg/m^3)	Specific Gravity[3]	Total Porosity[2] (%)	Total Organic Carbon Content[4] (%)	Chloride Matrix Diffusion Coefficient, D @ 23°C[5] (cm^2/s)	Matrix Tortuosity Factor, τ[6]
06-5631	RIM11(14')	14	23.8	1.41	2.61	46	0.27	0.3×10^{-6}	0.02
06-5632	RIM11(50')	50	35.3	1.27	2.48	49	0.80; 0.88	0.5×10^{-6}	0.03

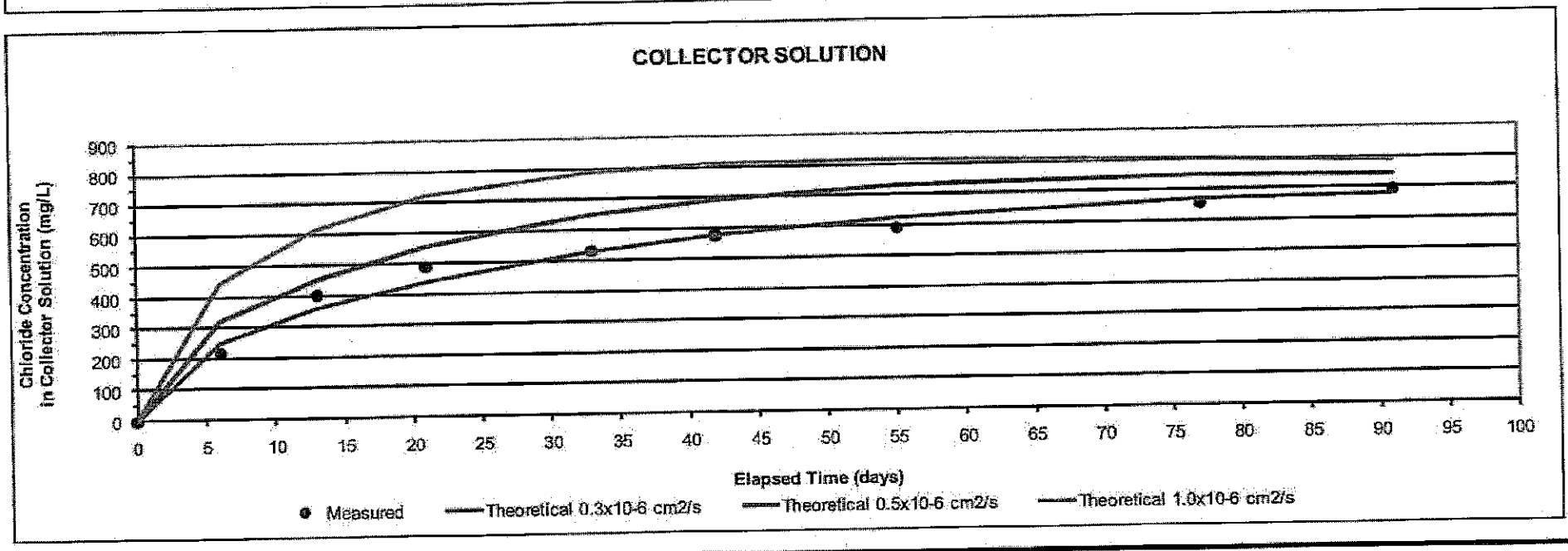
n/a - not applicable, solid plastic core

1. ASTM Method D2216-98 measured on rock sample as -received.
2. ASTM Method D4531-86(1992), Method B.
3. ASTM Method D854-00
4. Walkley and Black Wet Oxidation Method (Walkley, 1947).
5. Chloride matrix diffusion coefficient (D) obtained at 23°C using the test method described in this report (see Figures 2 and 3).
6. Matrix tortuosity factor (τ) calculated as D_{Cl^-}/D_{eCl^-} where D_{eCl^-} is the aqueous diffusion coefficient for chloride when diffusing together with sodium from a source solution containing 0.03 Molar NaCl at 23°C. The value used for D_{eCl^-} is 16.8×10^{-6} cm^2/s (American Institute of Physics Handbook, 1972).



Golder Associates, Mississauga, Ontario, Canada	SCALE: AS SHOWN	TITLE	**SCHEMATIC DRAWING OF THE CHLORIDE DIFFUSION CELL**
	DATE: Sep. 26, 2007		
	DESIGN: FSB		
	CAD: FC		
FILE No. 061116042AA001.dwg	CHECK: FSB		DIFFUSION TEST RESULTS
PROJECT No. 06-1116-042 REV. A	REVIEW: FSB		FIGURE 1





Golder Associates
Mississauga, Ontario, Canada

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DATE	Sep. 26, 2007
DESIGN	FSB
CAD	FC
CHECK	FSB
REVIEW	FSB

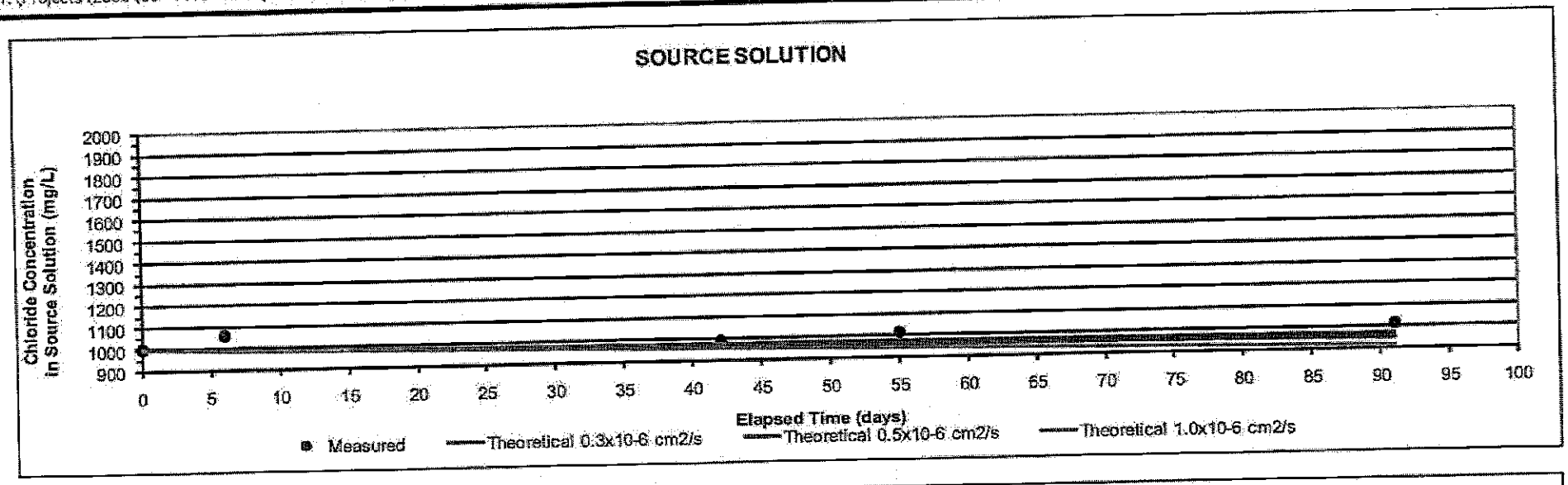
TITLE

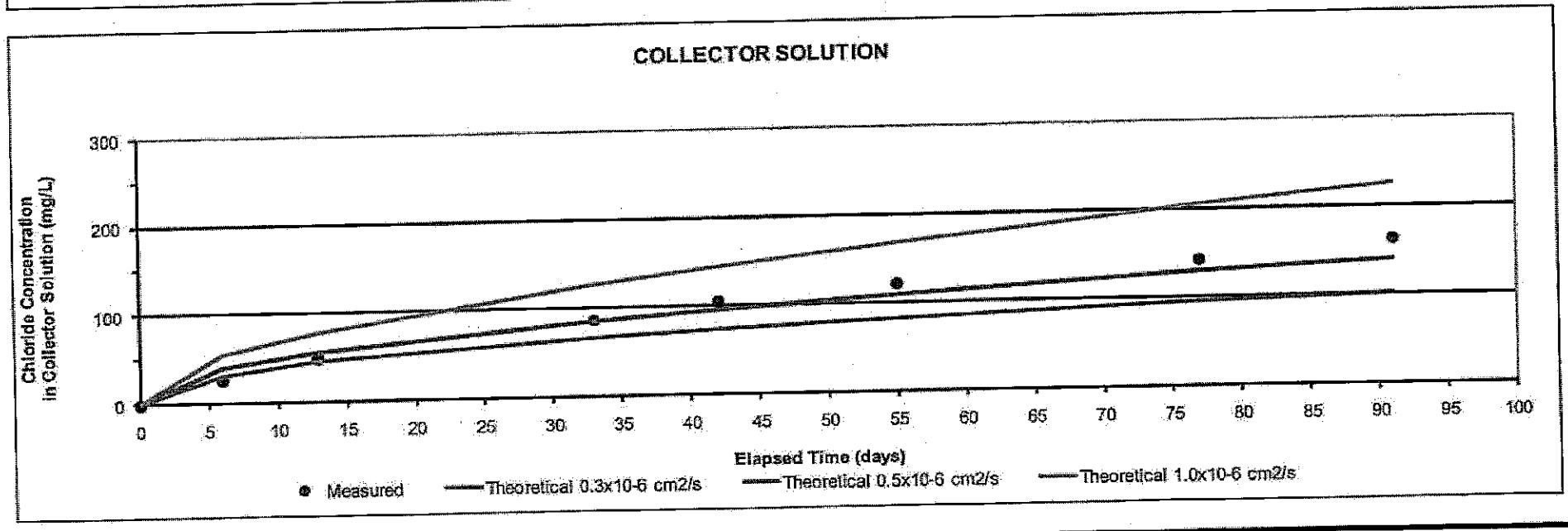
SAMPLE RIMW11 (14 ft)

DIFFUSION TEST RESULTS

FILE No. 061116042AA002.dwg
PROJECT No. 06-1116-042 REV. A

FIGURE 2





Golder Associates
Mississauga, Ontario, Canada

SCALE	AS SHOWN
DATE	Sep. 26, 2007
DESIGN	FSB
CAD	FC
CHECK	FSB
REVIEW	FSB

TITLE

SAMPLE RIMW11 (50 ft)

DIFFUSION TEST RESULTS

FIGURE 3

FILE No. 061116042AA003.dwg
PROJECT No. 06-1116-042 REV. A

APPENDIX A

DIFFUSION TEST DATA

TABLE A. 1

Specific Details of the Chloride Diffusion Tests

Parameter	Golder Lab ID. [Sample No.]	
	06-5631 [RIMW11 (14')]	06-5632 [RIMW11 (50')]
Initial Concentration of Chloride in the Source Solution Compartment (mg/L)	1000	1000
Source Solution Volume (mL)	333	356
Equivalent Height of Source Solution, H_s (cm)	11.4	12.4
Initial Concentration of Chloride in the Collector Solution Compartment (mg/L)	<2	<2
Collector Solution Volume (mL)	107	108
Equivalent Height of Collector Solution, H_c (cm)	3.7	3.8
Cross-Sectional Area of Sample (cm^2) (perpendicular to direction of diffusion)	29.2	28.7
Rock Specimen Thickness (cm)	3.57	3.47
Rock Specimen Diameter (cm)	6.10	6.05
Initial Chloride Concentration in Rock Specimen Porewater at Start of Test (mg/L)	4,822‡	580 ‡‡
Rock Matrix Total Porosity	0.46	0.49
Average Rate of Sampling of the Collector Solution, q_c** (cm^3/day)	0.3	0.30

* Assumed value for rock core specimen

** Average rate of sampling of the collector solution (q_c, refer to Eqn. 5) was calculated as the volume of each sample (~3mL) divided by the average frequency of sampling (~10 days).

‡ Sample is from above the water table, therefore, monitoring well data was not available for defining the intial chloride concentration in the porewater phase of the rock matrix. The chloride concentration was therefore back-calculated based on analysis of the chloride concentration in the sample at the end of the diffusion test (units of µg/g) and consideration of mass balance knowing the inital and final chloride concentrations in the source and collector solution compartments (refer to Appendix Cfor calculation)

‡‡ Initial chloride concentration in porewater phase was based on data from monitoring well RIMW11 which has a screen interval of 30 to 55 feet (data provided by MACTEC)

TABLE A.2

Diffusion Test Data
Lab ID. 06-5631 Sample No. RIMW11 (14')

Sampling Date	Elapsed Time (days)	Chloride Concentration in the Source Solution (mg/L)	Chloride Concentration in the Collector Solution (mg/L)
December 1, 2006	0	1000	<2
December 7, 2006	6	1170	221
December 14, 2006	13	n/a	400
December 22, 2006	21	n/a	491
January 3, 2006	33	n/a	534
January 12, 2006	42	1380	573
January 25, 2006	55	1470	593
February 16, 2006	77	n/a	655
March 2, 2006	91	1300	695

n/a = not analyzed

TABLE A.3

Diffusion Test Data
Lab ID. 06-5632 Sample No. RIMW11(50')

Sampling Date	Elapsed Time (days)	Chloride Concentration in the Source Solution (mg/L)	Chloride Concentration in the Collector Solution (mg/L)
December 1, 2006	0	1000	<2
December 7, 2006	6	1060	27
December 14, 2006	13	n/a	48
December 22, 2006	21	n/a	473*
January 3, 2007	33	n/a	87
January 12, 2007	42	987	104
January 25, 2007	55	1020	122
February 16, 2007	77	n/a	143
March 2, 2007	91	1020	164

n/a = not analyzed

* - inadvertantly sampled collector compartment from RIMW11(14')

APPENDIX B

ADDITIONAL TEST RECORDS

SUMMARY OF WATER CONTENT DETERMINATIONS

ASTM D 2216-98

PROJECT NUMBER	06-1116-042
PROJECT NAME	Mactec / Lab Testing / 4098042051
DATE TESTED	December, 2006

Sample No.	Water Content (%)	Atterberg Limits LL, PL, PI
RIMW11-14	23.8%	
RIMW11-50	35.3%	

Checked by

Golder Associates

SPECIFIC GRAVITY TEST RESULTS

ASTM D 854-00 TEST METHOD A

PROJECT NUMBER	06-1116-042
PROJECT NAME	Mactec / Lab Testing / 4098042051
DATE TESTED	December, 2006

Borehole No.	Sample No.	Specific Gravity
-	RIMW11-14	2.61
-	RIMW11-50	2.48

Note: Test carried out on soil particles <4.75mm using distilled water.

DENSITY AND POROSITY DETERMINATIONS OF IRREGULAR SHAPE SAMPLES

ASTM D 4531-86 TEST METHOD B

Sample Number	RIMW11-14	RIMW11-50
Wet Mass of Rock in Air, g	295.80	539.48
Wet Mass of Rock + Wax in Air, g	314.62	571.11
Wet Mass of Rock + Wax in Water, g	123.96	222.08
Weight of Wax, g	18.82	31.63
Displaced Volume, cm^3	190.66	349.03
Displaced Wax, cm^3	20.73	34.83
Volume of Rock, cm^3	169.93	314.20
Specific Gravity, measured	2.61	2.48
Volume of Solids, cm^3	91.55	160.78
Volume of Voids, cm^3	78.39	153.42
Porosity	0.46	0.49
Water Content, %	23.80	35.30
Unit Weight, kN/m^3	17.07	16.84
Dry Unit Weight, kN/m^3	13.79	12.45

Project Number 06-1116-042 Tested By Angela

Date Tested 12/1/2006 Checked By

TOTAL ORGANIC CARBON CONTENT (TOC)

PROJECT NUMBER 06-1116-042

PROJECT NAME Mactec / Lab Testing / 4098042061

DATE TESTED January, 2007

Sample No.	Soil Passing 0.6mm (%)	Grain Size Distribution Gravel (%)	Passing Sand (%)	Silt (%)	Clay (%)	TOC <0.6mm (%)
RIMW11-14	-	-	-	-	-	0.27
RIMW11-50	-	-	-	-	-	0.80
RIMW11-50 (repeat)	-	-	-	-	-	0.88

Notes:

1. Samples dried at 110 degree centigrade prior to testing.
2. Test performed on rock crushed to minus 600 micron, using the method of Walkley and Black (Walk
3. Grain size distribution of sand, silt and clay based on Unified Soil Classification.

APPENDIX C

CALCULATION OF INITIAL CHLORIDE POREWATER CONCENTRATION

[SAMPLE RIMW11 (14')]

APPENDIX C

1. Initial Cl^- mass in diffusion cell @ start of test

   - Source Solution Compartment

$$333ml \times 1{,}000mg/l \times \frac{1L}{1000ml} = 333mg$$

   - Collector Solution Compartment

$$107ml \times < 2mg/l \cong 0mg$$

   - Sample Porewater Phase (where $C_{op.w}$ = initial porewater phase concentration)

$$C_{o\,p.w} \times \left[3.5cm \times \frac{\pi(6cm)^2}{4} \times 0.46\right] \frac{1}{1000} \frac{L}{cm^3} = 0.045C_{o\,p.w.}$$

   - Total Initial Cl^- Mass

$$=333\text{ mg} + 0\text{ mg} + 0.045C_{op.w.}$$

$$=333\text{mg} + 0.045C_{op.w}$$

2. Cl^- Mass in diffusion cell @ end of test

   - Source Solution Compartment

$$333mL \times 1{,}300mg/L \times \frac{1}{1000} \frac{L}{mL} = 433mg$$

   - Collector Solution Compartment

$$107mL \times 695mg/L \times \frac{1}{1000} \frac{L}{mL} = 74mg$$

   - Sample Porewater Phase

$$310mg/kg \times \frac{\pi(6cm)^2}{4} \times 3.5cm \times 1.14gm/cm^3 \times \frac{1}{1000} \frac{kg}{gm} = 43mg$$

   - Total End of Test Cl^- Mass

$$=433\text{mg}+74\text{mg}+43\text{mg}$$
$$=550\text{mg}$$

3. From conservation of Cl^- mass, the initial Cl^- mass in the diffusion cell at the start of the test must equal the Cl^- mass in the cell at the end of test.

$\therefore$ 333mg+0.045$C_{op.w.}$=550mg

$\therefore$ $C_{op.w}$ =4,822mg/L (initial Cl^- concentration in porewater phase of test sample)