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Determination of the Diffusion Coefficient of Oxygen for a Cover System Including a Pulp and Paper By-Product

ABSTRACT: Among the several solutions that have been proposed to curb the problem posed by the generation of acid rock drainage (ARD), the placement of covers with capillary barrier effect (CCBE) has received particular attention. With the creation of a capillary barrier, oxygen has to migrate through a nearly saturated layer, a much slower process than in air. As a consequence, its availability is drastically reduced, reducing ARD generation. An experimental procedure was developed to obtain the diffusion coefficient of oxygen through compacted deinking residues, an organic matter-rich by-product of paper recycling. With the oxygen concentrations obtained as a function of time, it was possible to deduce the diffusion coefficients based on the best reproductions of laboratory results, using the computer code POLLUTE v.6. As expected, it was found that the diffusion coefficient—and the associated flux—is highly influenced by the degree of saturation of the sample. Beyond a threshold in the vicinity of 85 %, a one order of magnitude drop in the diffusion coefficient was observed. A comparison of the results obtained with previously published data shows that deinking residues constitute a very effective oxygen barrier material due both to its ability to maintain a high degree of saturation and to rapidly consume oxygen. Given the latter, special care was needed in defining the most appropriate equipment design, sample preparation method, and testing procedure.

KEYWORDS: acid rock drainage, capillary barrier, oxygen diffusion, pulp and paper by-products

Introduction

Acid rock drainage (ARD) is a pervasive environmental problem throughout the world. It constitutes a major challenge to scientists and engineers, since the potential source of contaminants is generally very large and almost limitless within the time frame of a century. The environmental release of hazardous substances from mining wastes and abandoned mines is a result of biogeochemical conditions and processes: the weathering of metal sulfides and the activity of iron-oxidizing bacteria in the presence of water and oxygen. Due to acidity, bodies of water receiving ARD are contaminated with excessive amounts of heavy metals such as zinc, copper, and lead and high quantities of suspended solids (Gray 1997; Marcus 1997). As a consequence, ARD-contaminated surface waters constitute wasted resources as far as public water supply, irrigation, and aquatic ecosystems are concerned. This acidity is continuously generated from the exposure of sulfide-rich tailings, waste rock, and downstream riverine deposits to oxygen and water.

Among the several solutions that have been proposed to curb this problem, the placement of covers with capillary barrier effect (CCBE) has received particular attention from geoenvironmental engineers (Yanful and Aubé 1993; Aubertin et al. 1995, 1996a,b, 1997, 1999; Bussière et al. 2000a,b; Cabral et al. 1999, 2000a). When a capillary barrier is created, the moisture retaining layer (MRL), which is placed over a coarser material layer, remains at a

high degree of saturation. Given the fact that oxygen diffusion in the aqueous phase is four orders of magnitude slower than diffusion in air (Yanful 1993; Elberling et al. 1994; Rowe 2001), oxygen availability is drastically reduced, which in turn reduces the potential of ARD generation.

Several profiles for CCBEs have been proposed involving a variety of materials, such as non-reactive tailings (Aubertin et al. 1997, 1999; Ricard et al. 1997; Bussière and Aubertin 1999), fine-grained soils (Yanful 1993; Wilson et al. 1997), sands (Kämpf et al. 1999; Hude et al. 1999), and deinking residues (Cabral et al. 1999, 2000a). The latter is a by-product of paper recycling that is produced in great quantities by the pulp and paper industry and is still mostly disposed of in landfills at great cost.

In this paper, the authors describe the details of a laboratory procedure developed to obtain the diffusion coefficient of oxygen through compacted deinking residues and eventually quantify oxygen fluxes. The results of several tests are presented, analyzed, and compared to previously published data. Extensive recent literature is available on ARD production, oxygen migration through porous media (e.g., Collin 1987; Yanful 1993; Cabral et al. 2000a), and the hydraulic principles of capillary barriers (e.g., Nicholson et al. 1989; Morel-Seytoux 1993; Oldenburg and Pruess 1993); therefore, only a brief review of the basic principles needed to understand the boundary conditions of the problem in hand and interpret the results is presented.

Background

Acid Rock Drainage (ARD)

The oxidation of sulfide-rich mining residues results from a series of chemical reactions involving the presence of water and oxygen. If neither water nor oxygen is present in the system, ARD production

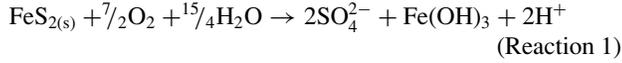
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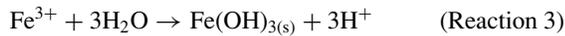
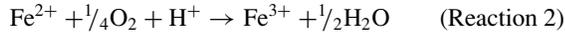
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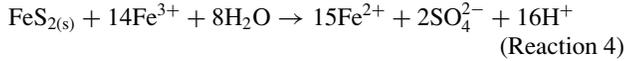
eventually stops. The reactions leading to the generation of acid rock drainage are well known (Ritcey 1989; Morin and Hunt 1997). In the case of pyrite oxidation, the following simplified (and idealized) reaction can be written (Reaction 1):



This reaction describes the slow oxidation of pyrite in an environment at near neutrality in the beginning. As the environment becomes acidified (production of H^+), ferrous iron (Fe^{2+}) is transformed into ferric iron (Fe^{3+} ; Reaction 2), which precipitates as hydroxide ($\text{Fe}(\text{OH})_3$). This precipitation leads to an important production of H^+ ions (Reaction 3), further acidifying the environment.



As the pH reaches a critical value (around 3.5), ferric iron remains in solution and directly oxidizes the metal sulfide (Reaction 4). A cyclical chain of reactions is triggered, as the Fe^{2+} produced by Reaction 4 feeds back Reaction 2, which, with the help of Thiobacillus ferrooxidans bacteria, greatly accelerates the production of acidity, even with low oxygen input.



Oxygen Migration

Migration of oxygen through porous media is the result of a diffusive phenomenon that takes place through air-filled as well as water-filled pores, which can be modeled according to Fick's laws. In the first law (Eq 1), the coefficient relating flux to concentration gradient (in the present case, oxygen concentration gradient) across a cover system is called the effective diffusion coefficient, D_e , defined in Eq 2.

$$f(t) = -\theta_a D_e \frac{\delta C(t)}{\delta z} \quad (1)$$

where $f(t)$ is the mass flux of oxygen ($\text{ML}^{-2}\text{T}^{-1}$); θ_a is the air-filled porosity (L^3/L^3), $C(t)$ is the concentration of oxygen at time t (ML^{-3}), and z is the depth of interest measured from the top of the barrier (L).

$$D_e = D_a^0 \tau (L^2 T^{-1}) \quad (2)$$

where D_a^0 is the diffusion coefficient of oxygen in air, and τ is the tortuosity of the medium. D_e can be back calculated by comparing the experimental data to values obtained using analytical, semi-analytical, or numerical solutions. One such semi-analytical solution (finite layer) is implemented in the computer code Pollute v.6.3 (Rowe et Booker 1985; Rowe et al. 1994), which was used in this paper.

Fick's second law describes the rate of change in the concentration across the cover, as follows:

$$\frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial z^2} - \lambda C \quad (3)$$

The term $-\lambda C$ relates to consumption of the species under study along the migration path (cover system). The parameter λ represents a reaction rate constant (T^{-1}) for a first-order decay equation of the type $C = C_0 e^{-\lambda t}$, where $\lambda = \ln 2/t_{1/2}$ and $t_{1/2}$ (T) is the half-life of the decaying (or consumed) species (in the present case, oxygen). In Pollute v.6, the half-life, rather than reaction rate, is used as an input parameter. As a consequence, any reference made herein to

consumption is translated into the parameter $t_{1/2}$: the lower its value, the faster the consumption rate (of oxygen, in this study).

Covers with Capillary Barrier Effect (CCBE)

The superposition of two materials with contrasting water-retention characteristics, with the material with higher retention capacity on top (moisture retaining layer), leads to the creation of a capillary barrier (Nicholson et al. 1989; Morel-Seytoux 1993; Aubertin et al. 1996). With proper design, the upper material can maintain a high degree of saturation irrespective of the conditions existing on the subjacent material (Nicholson et al. 1989). Since migration of oxygen in water ($D_w = 2.2 \times 10^{-9} \text{ m}^2/\text{s}$) is four orders of magnitude lower than migration in air ($1.8 \times 10^{-5} \text{ m}^2/\text{s}$), the presence of a highly saturated material constitutes a barrier to oxygen migration.

For partly saturated cover materials, which are most probably found in actual field conditions, diffusion occurs mainly through air-filled pores. The air-filled porosity is thus a parameter of concern. However, at a certain degree of saturation, migration through water eventually becomes significant (Aubertin and Mbonimpa 2001) and should be accounted for. Empirical models, such as the one proposed by Collin (1987), allow for the determination of the diffusion coefficient based on the degree of saturation and the porosity of the medium and accounts for migration in both phases (air and water). In the present study, migration of oxygen through water was neglected given the significant microbial activity existing inside deinking residues (Teixeira 2001; Cabral et al. 2000a; Panarotto et al. 1999), which consumes oxygen not only from air-filled pores, but also from the pore water.

Measurement of Oxygen Migration

Various experimental setups have been developed to measure diffusion coefficients of gases migrating across various types of materials (Aubertin et al. 2000; Yanful 1993; Mackay et al. 1999; Rahman et al. 2002). The basic principle is essentially the same, i.e., to evaluate the migration of the gas across a barrier on the basis of the concentration gradient applied. This is generally done by measuring the variations in gas concentration with time in the reservoirs situated at each end of a sample. In these closed systems, a decrease in the gas concentration in the source reservoir equals a similar increase in the receptor (bottom) reservoir. Any difference between the two is attributable to an accumulation of the element being studied in the pores of the sample.

In the particular case of barriers with high organic matter contents, such as deinking residues, an additional parameter must be considered when developing an experimental setup intended to measure the oxygen diffusion coefficient: the consumption of oxygen. In fact, it was observed that, in the presence of oxygen (aerobic environment), this material is colonized by *Penicillium sp.* (Cabral et al. 2000a; Teixeira 2001). These fungi use oxygen as an electron receptor during degradation of the organic material, which significantly affects the migration of oxygen.

Materials and Methods

Deinking Residues, DR

Deinking residues (also known as fiber-clay) are composed mainly of wood fibers, grit, clay (from paper coating), calcite, and large amounts of water (45 to 70 % w/w) (Floess et al. 1995; Teixeira

TABLE 1—Typical composition of deinking residues.

Inorganics					Organics			
Calcite	Kaolinite (métakaolin)	Talc	Rutile	Other Inorganics	Cellulose	Hemicellulose	Lignine	Other Organics
29.2 %	3.9 %	1.4 %	1.9 %	3.3 %	34 %	9.2 %	6.6 %	10.5 %

2001). The amount and composition varies significantly with the type of wastepaper recycled and the efficiency of the deinking process employed (Latva-Somppi et al. 1994).

Over the years, several deinking residue samples have been collected from Industries Cascade's Kingsey Falls (Quebec, Canada) recycling plant and characterized for water content, volatile matter content (loss of weight upon burning at 550°C), specific gravity, mineral composition, and morphological structure. For the present study, one batch of material was obtained from this same plant and labeled KF 110298. While the water content of deinking residues generally varies from 100 to 190 %, the water content of the KF 110298 batch averaged 166 %. The organic matter content averaged 61.5 %, while the normal range for Kingsey Falls samples is 46 to 62 %. The specific gravity (G_s) was 1.94, which falls in the range of values found in recent literature (Moo-Young and Zimmie 1996; Kraus et al. 1997).

The mineral composition is determined by X-ray fluorescence, with a cross check normally done by differential thermogravimetric analysis (TG/DTA). A typical composition of DR from the Kingsey Falls plant is shown in Table 1 (Teixeira 2001). The volatile material consists mainly of cellulose, which acts as a carbon source for microorganisms. In aerobic conditions, spontaneous colonization of deinking residues by fungi occurs, which was verified by means of scanning electron microscope (SEM) photography. Two different morphological structures were identified by SEM: free cellulose fibers and cellulose fibers forming aggregates (crumbs) with mineral matter between the fibers (Cabral et al. 2000a).

Equipment Description

As pictured in Fig. 1, the cell consists of a Plexiglas cylinder with 6-mm-thick walls and an internal diameter of 10 cm. The cell is partitioned into three sections, A, B, and C. Between each section, an O-ring joint coated in silicone grease was placed in order to ensure the tightness of the cell. The three sections are held together with the help of four stud bolts connecting the base of the cell to its cover. Air enters the system through two holes placed in Section A, thereby maintaining a constant oxygen concentration of 20.9 % (approximate atmospheric concentration) on the top reservoir. Loss of moisture from the top of the cell is reduced by covering it with a plastic bag and placing a small water container inside section A (see Fig. 1). This proved an effective measure, as the variation of the degree of saturation was kept to a minimum (Cabral et al. 2000a; Tremblay 2000).

Samples up to 10 cm high can be compacted directly in Section B. In this study, practically all samples were compacted to a final height of 3 cm. This height was defined based on the time needed to test highly saturated samples. Once compacted, the residues are held in place with the help of two stainless steel perforated plates. The lower plate is inserted on the top of Section C (bottom reservoir), while the upper plate is secured to a piston that allows a charge representative of the stress conditions normally exerted by a top cover layer, i.e., 10 kPa to be transferred to the sample.

Oxygen migrates across the sample and accumulates in the bottom reservoir, which is connected to the gas measuring system. The

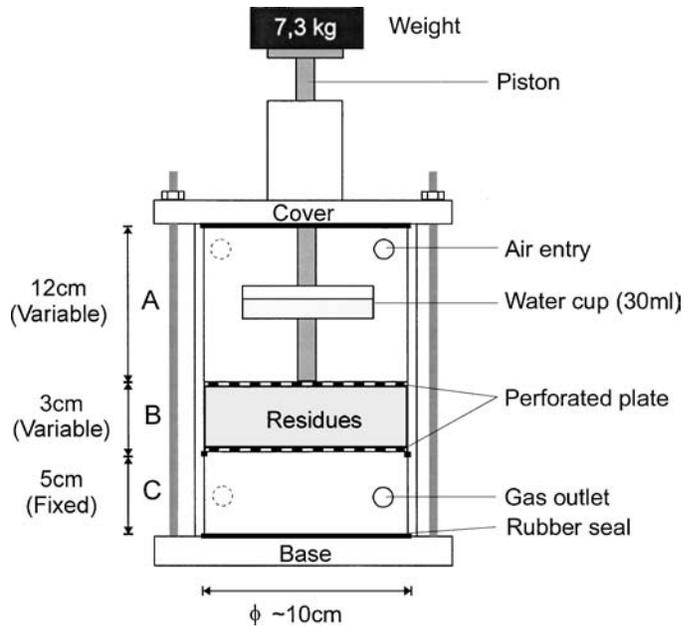


FIG. 1—Schematic drawing of the diffusion cell.

latter is divided in two parts, a closed loop and an open loop. The open loop allows the gas analyzer to be purged with nitrogen before each reading. The closed loop, presented in the schematic drawing in Fig. 2, allows oxygen, methane, and carbon dioxide concentrations to be measured in Section C. As shown in Fig. 2, a Masterflex peristaltic pump drives the gases from the bottom reservoir (Section C) to the gas-measuring system through Tygon lab L/S tubes. The gas first goes through a drierite (CaSO_4) tube in order to prevent humidity from entering the gas analyzer (Servomex LFG-20, with a precision of ± 0.1 % for oxygen). Any possible mass loss due to gas adsorption to the drierite was not evaluated. The outflow of the gas-measuring system returns to Section C, completing the loop. The peristaltic pump is turned on and left operating until two equal consecutive readings are obtained. The readings are taken at every minute. The pump is then turned off.

As suggested by Aubertin and Mbonimpa (2001), inducing gas circulation in the bottom reservoir for monitoring purposes can create a pressure gradient across the sample, which might lead to increased oxygen migration. However, circulation was induced just a few minutes at a time and at a relatively low flow rate (60 mL/min); thereby this procedure is not likely to cause any significant effect on the O_2 flux through the specimens.

In order to verify the air tightness of the bottom reservoir, preliminary tests were performed by isolating it from the rest of the cell. After saturating it with gaseous nitrogen, the concentration of oxygen was measured for an extended period of time. Adjustments were made until repetitive readings (in this case, zero oxygen readings) were obtained for at least 24 h.

It is important to note that this setup only allows oxygen concentration variations in the receptor reservoir to be measured.

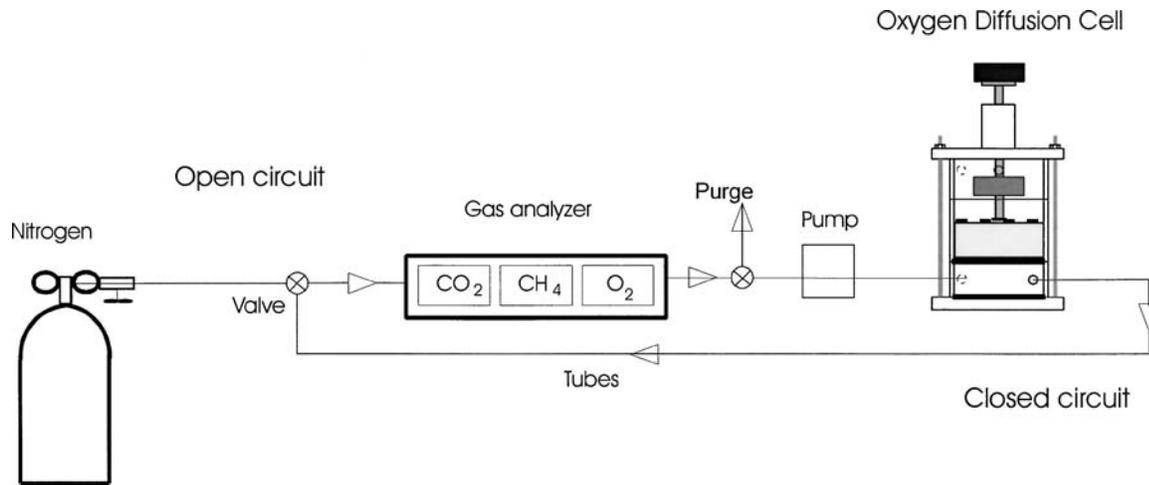


FIG. 2—Schematic drawing of the measuring system.

TABLE 2—Characteristics of the samples tested.

Test	W_i (%)	S_{ri} (%)	ρ_d (kg/m ³)	η_a	Thickness, cm
DC16b	117.0	80.9	509.5	0.1406	2.867
DC19	140.9	87.9	471.7	0.0915	3.023
DC21	126.8	84.3	494.6	0.1171	3.028
DC22	115.9	79.9	508.2	0.1483	3.010
DC24	177.5	93.1	412.5	0.0545	3.071
DC25	115.8	79.8	508.1	0.1488	3.002
DC26	126.9	85.7	500.8	0.1059	2.993

Technically, the measurement of oxygen concentration variations in both the receptor and source reservoirs, as conducted by Yanful (1993), Aubertin et al. (2000), or Rahman et al. (2002) proves problematic in the case of materials with high organic content. In fact, unless an oversized source reservoir is used, oxygen consumption by microorganisms occurs at such a rate that the oxygen concentration would quickly be brought to zero in the source reservoir, causing a zero gradient concentration and the premature end of the test. For these reasons, the measurement of oxygen concentration variation in the source reservoir has been abandoned and the source reservoir is kept open to the atmosphere throughout the tests.

Sample Preparation and Test Startup

Samples from the batch identified as KF 110298 were used in this study. A total of seven tests are presented in this paper. The main characteristics of the samples are presented in Table 2. The material was brought to the desired water content and then left to rest for 24 h. A known inoculum—in this study a solution containing microscopic fungi (*Penicillium sp.*)—was added to help accelerate the development of the fungi strain so that oxygen consumption could be observed from the beginning of the test.

The hammer normally used in Standard Proctor tests (ASTM D 698) is used to compact the samples in two lifts directly into the cell. To avoid oxygen migration between the cell wall and the sample, the inside of the cell is coated—before compaction—with a thin layer of petroleum jelly along the thickness of the sample. Previous experiments have shown that samples of deinking residues compacted using this procedure achieve dry densities and water

contents very close to the Proctor curves (Cabral et al. 2000a). Figure 3 presents the Standard Proctor compaction curve obtained for the DR sample used in the present experimental study. The approximate optimum moisture content is in the vicinity of 67 % at a dry density of 527 kg/m³. The compacted water contents of the samples varied from 115.8 to 177.5 % (Table 2).

Given that the densities, dimensions, and water content of the samples can be controlled, it is also possible to prepare samples at the target degrees of saturation. The experimental program foresaw the study of the coefficient of diffusion under several degrees of saturation, including the 80 to 95 % range. Based on several field measurements from different sites where DR was used as cover material (Cabral et al. 1999, 2000a,b; Burnotte et al. 2000), degrees of saturation superior to 85 % are quite often achieved during compaction of DR barriers. Also, continuous monitoring of several sites (Cabral et al. 1999; Burnotte et al. 2000) has shown that this high degree of saturation has been maintained with time.

After compaction and assembly of the cell, the sample is left in contact with atmospheric oxygen for 72 h. This time period allows for sufficient growth of the fungi, so that oxygen consumption can be observed from the beginning of the test. The receptor reservoir is purged several times during this period. Nitrogen is circulated in the receptor reservoir until the measured oxygen concentration is below the detectable limits of the gas analyzer.

Following the last purge, the actual test starts. The oxygen, which is at a constant concentration of 20.9 % in the upper reservoir, migrates by diffusion from the source reservoir towards the receptor reservoir by crossing the deinking residues sample. The oxygen concentration is periodically controlled in the receptor reservoir as it increases with time. When it reaches between 1 and 3 % (or slightly higher if migration occurs too fast), the receptor reservoir is purged and the test repeated two or three times. This procedure allows the reproducibility of the method to be verified. Also, by flushing the CO₂ from the receptor reservoir, an increasing counter-gradient across the sample is avoided.

At the end of each test, the cell is disassembled, the sample is weighed, its dimensions are measured, and a sub-sample is taken in order to obtain its water content. The latter is done as a means of determining the variation in the degree of saturation during the test. The oxygen concentrations recorded during the tests are used to plot the variation of oxygen concentration with time (Fig. 4, discussed in the following).

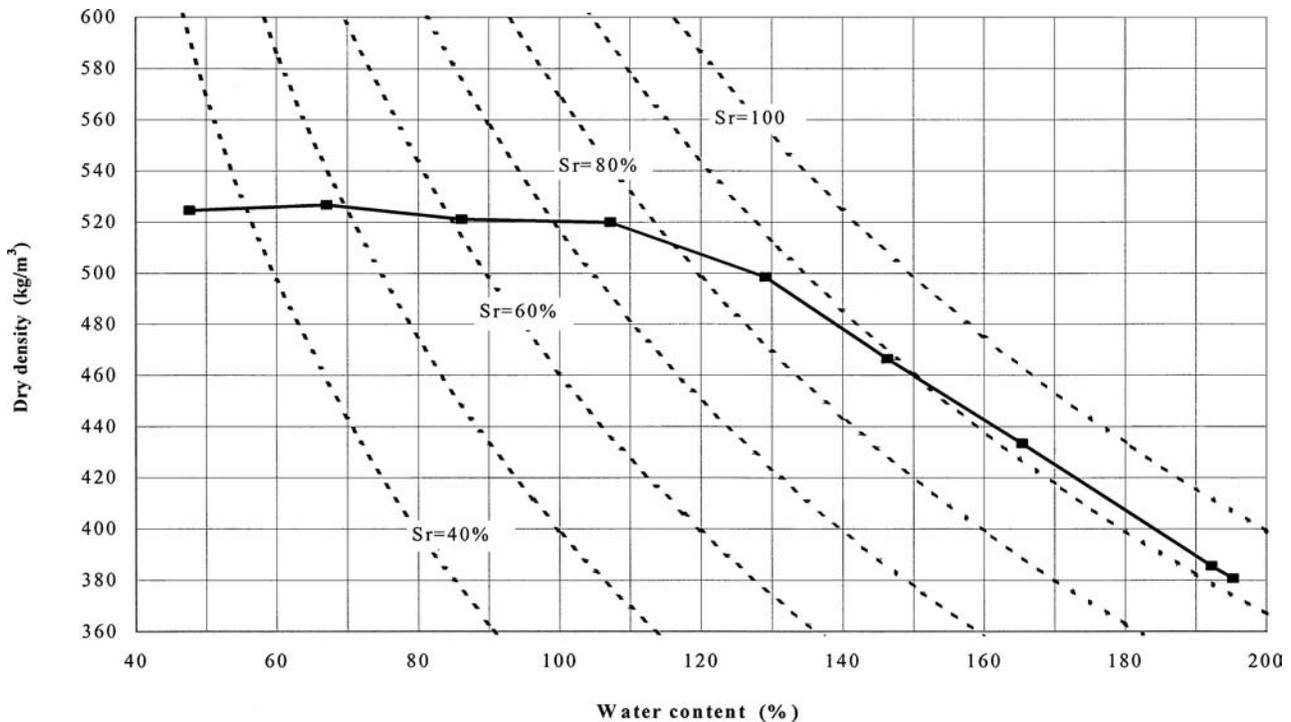


FIG. 3—Standard Proctor curve for a sample of deinking residue.

Results and Discussion

Figures 4a to 4f present the results of six diffusion tests performed on samples having different initial degrees of saturation. It can be observed that as the degree of saturation increases from 78.8 % (Test DC25; Fig. 4a) to 87.9 % (Test DC19; Fig. 4f), the time needed for the O_2 concentration to reach a similar level in the receptor reservoir (for example, 1 %), increases. In all tests, the increase in O_2 concentration with time follows an almost linear path, which was also observed by Cabral et al. (2000a) in a series of tests performed using a different procedure.

Based on quite similar slopes obtained from the linear regression analyses using laboratory data for each individual subtest (or segment) in Fig. 4, it is clear that the testing procedure yields very consistent and repeatable results. The only exception is the third subtest of Test DC26 (Fig. 4c), for which the rapid increase in O_2 concentration following the first reading is most possibly due to experimental errors.

The results of Test DC22 (Fig. 4b; $Sr_i = 79.9\%$) are presented in order to compare them to those of Test DC25 (Fig. 4a), which has a similar initial degree of saturation (Sr_i DC25 = 79.8 %). Indeed, quite similar slopes were found, ensuring that the entire procedure can be repeated not only from one subtest to another, but also from one test to another.

In the case of Test DC19 (Fig. 4f), only one segment was obtained, since no O_2 was measured after more than 200 h. The results obtained for Sample DC19 (Fig. 4f) are also representative of those obtained for Sample DC24 (and of other tests performed at degrees of saturation higher than 85 %). As a consequence, the results obtained for Test DC24 are not presented.

It can also be noted that as the degree of saturation increases from 84.3 % in Test DC21 (Fig. 4d) to 85.7 % in Test DC26 (Fig. 4e), the slope of the curve obtained by regression analysis of laboratory data drops from 1.61 (1st segment in Fig. 4d) to 0.19 (1st segment in Fig. 4e), i.e., a one order of magnitude decrease. A similar

threshold degree of saturation (i.e., $Sr \approx 85\%$) was obtained in other studies dealing with oxygen diffusion through different materials (Rahman et al. 2002). Indeed, beyond a certain degree of saturation, the air-filled voids are no longer interconnected, forcing O_2 to diffuse mainly as dissolved species in the liquid phase (Corey 1957). The segments that procured the best correlation for each of the tests presented in Fig. 4 was chosen as representative of the test and was later used for further interpretation of the results.

Determination of D_e and $t_{1/2}$ by Data Fitting

With the help of the computer code Pollute v.6.3 (Rowe et al. 1994), it is possible to deduce the one-dimensional diffusion coefficient, D_e , and the half-life, $t_{1/2}$, for each individual segment in each test. Pollute handles the parameter D_e as it is defined in Eq 2, i.e., as an independent parameter from the consumption rate (λ) or the associated half-life ($t_{1/2}$).

A constant oxygen concentration of 20.9 %—typical atmospheric concentration—was assumed for the top boundary (Section A in Fig. 1), whereas a zero outflow velocity condition was imposed in the receptor reservoir (Section C). The latter reflects the situation whereby O_2 cannot flow out of the cell. The initial O_2 concentration inside the sample was considered equal to zero, which reflects actual O_2 consumption that starts quite rapidly in the case of deinking residues. In order to select the best fit to the experimental data, several sets of D_e and $t_{1/2}$ were used as input to Pollute. The best fitting for each segment of each test was determined based on the minimum average differential from the experimental data.

A summary of the trial fits and input parameters for the representative segment of each test is presented in Table 3. Selected trial fits are also presented in graphic form in Fig. 5.

FIG. 5a (DC25), Fig. 5b (DC21), and Fig. 5c (DC26). As a starting point to the fitting trials, degradation was neglected by assigning to $t_{1/2}$ a much higher value than the duration of the test (Table 3).

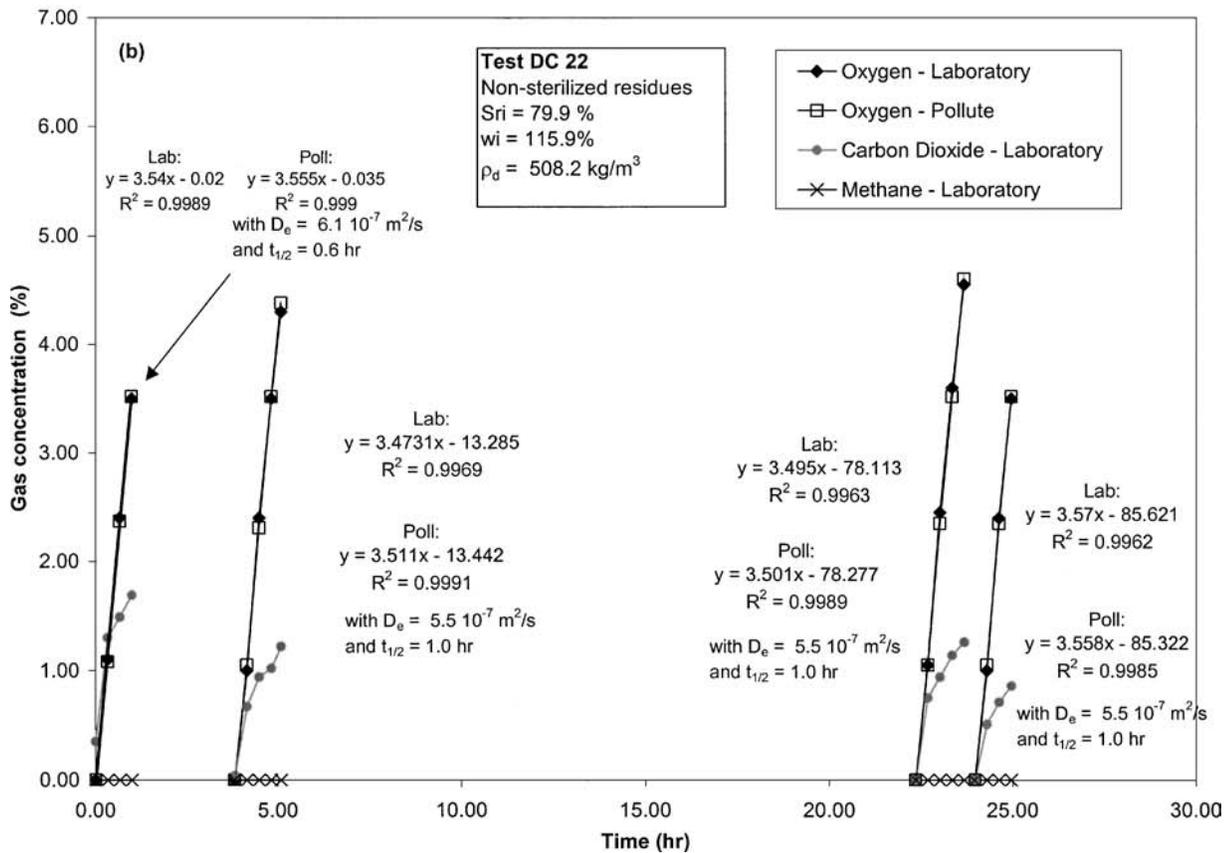
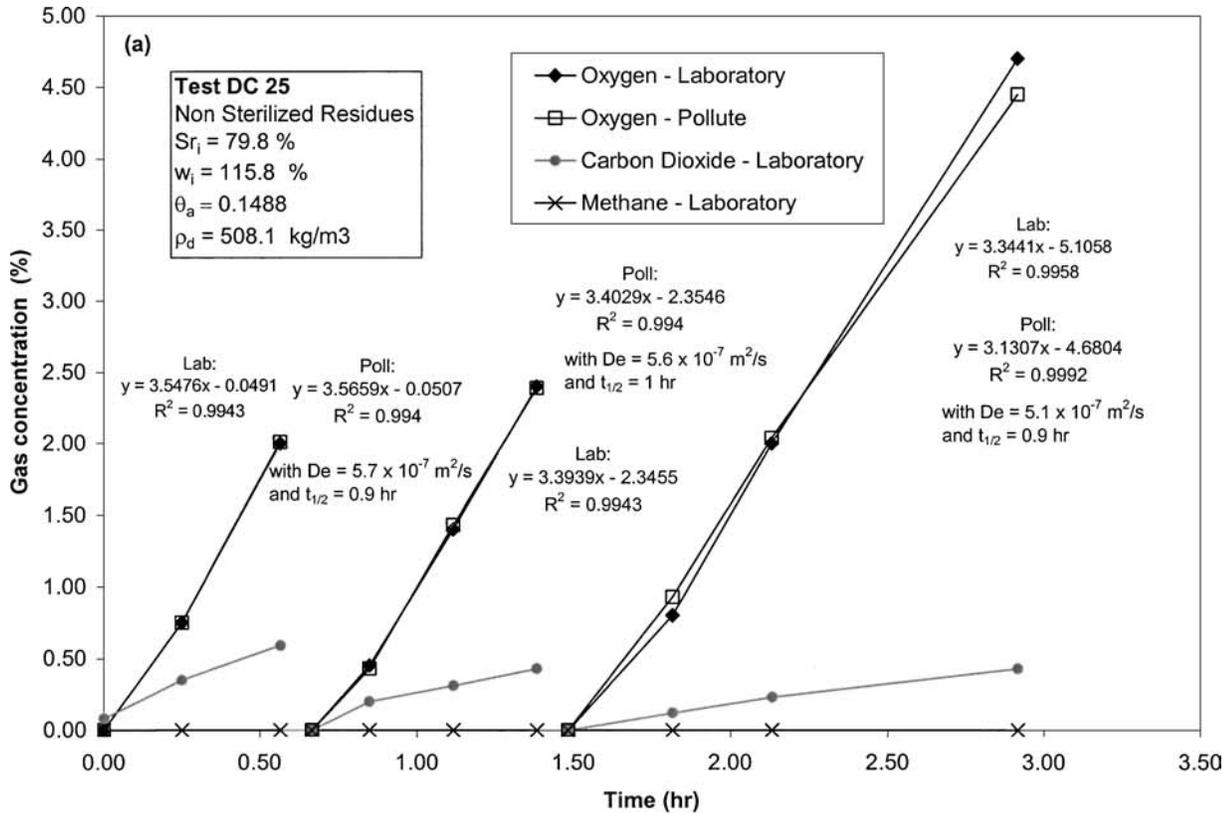


FIG. 4—Variation of the O_2 concentration in the bottom reservoir (Section c) for four selected tests: laboratory and modeling results.

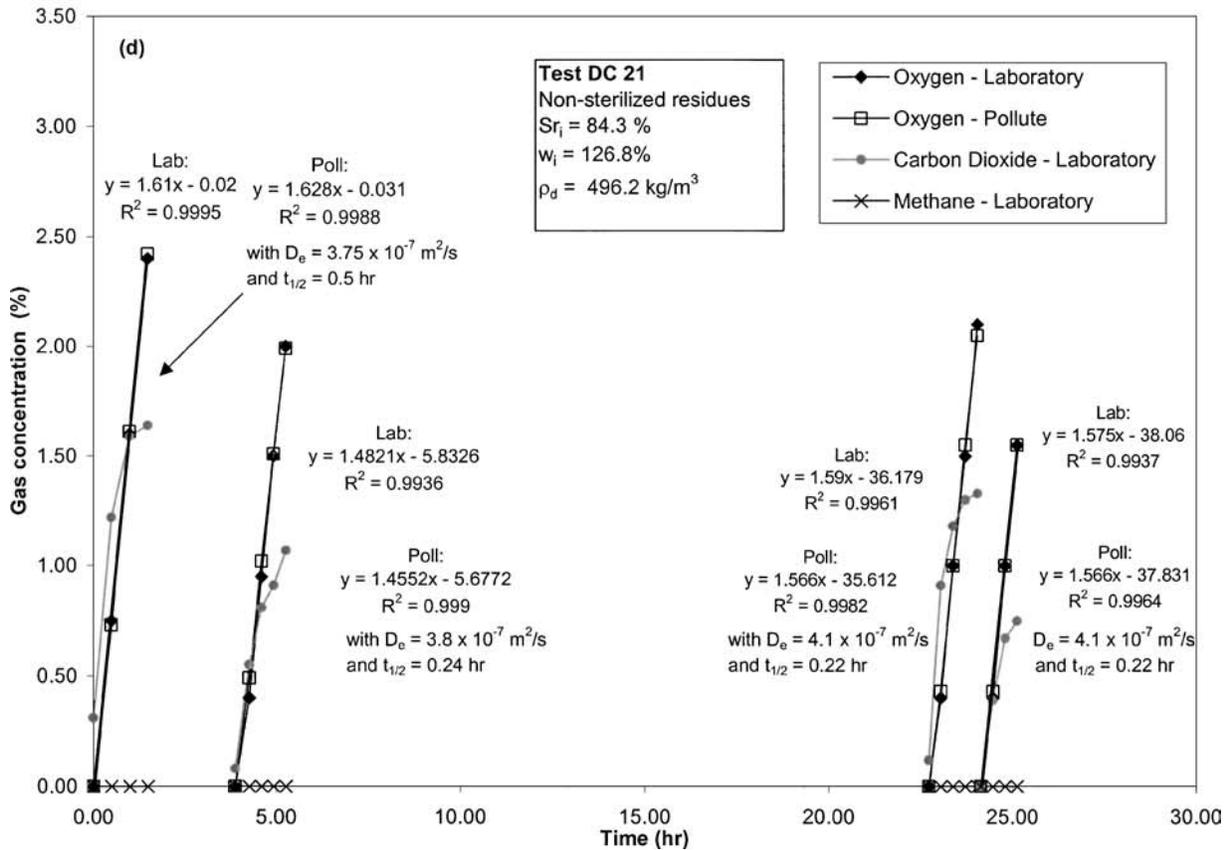
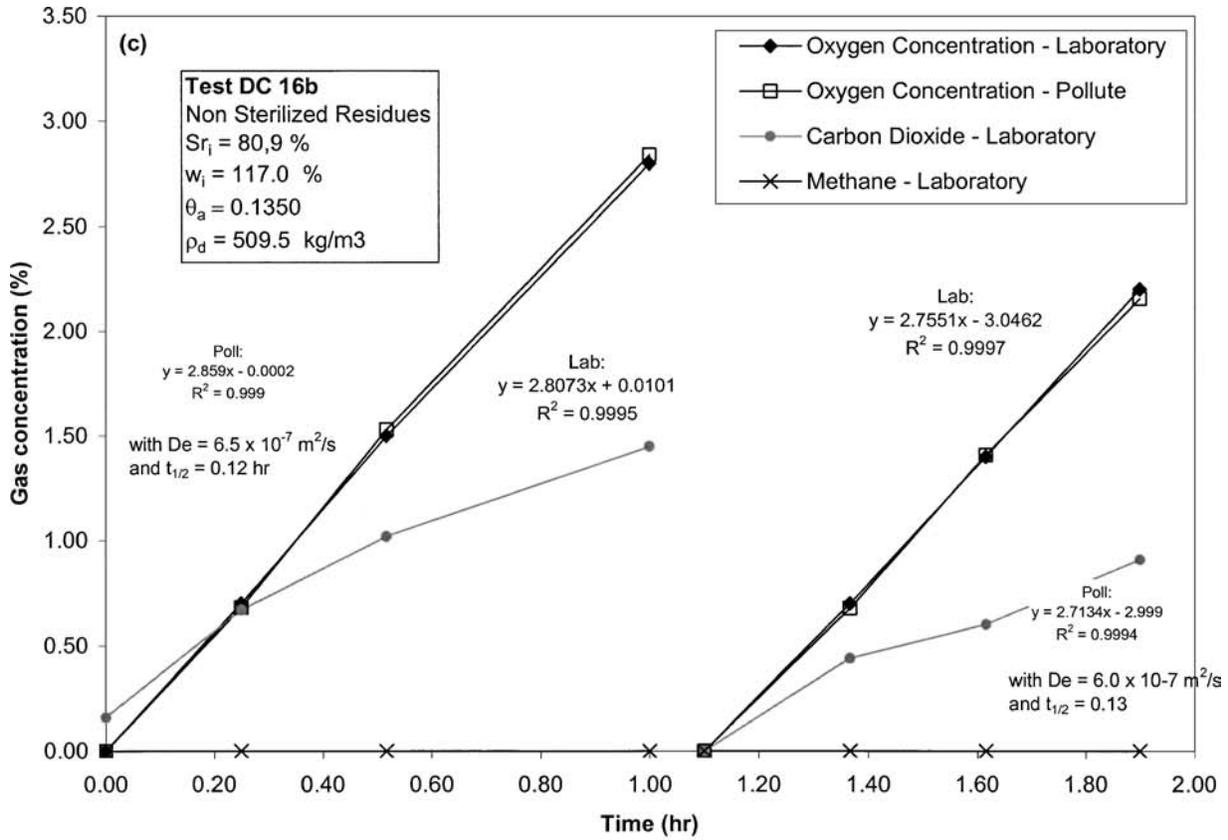


FIG. 4—(Continued).

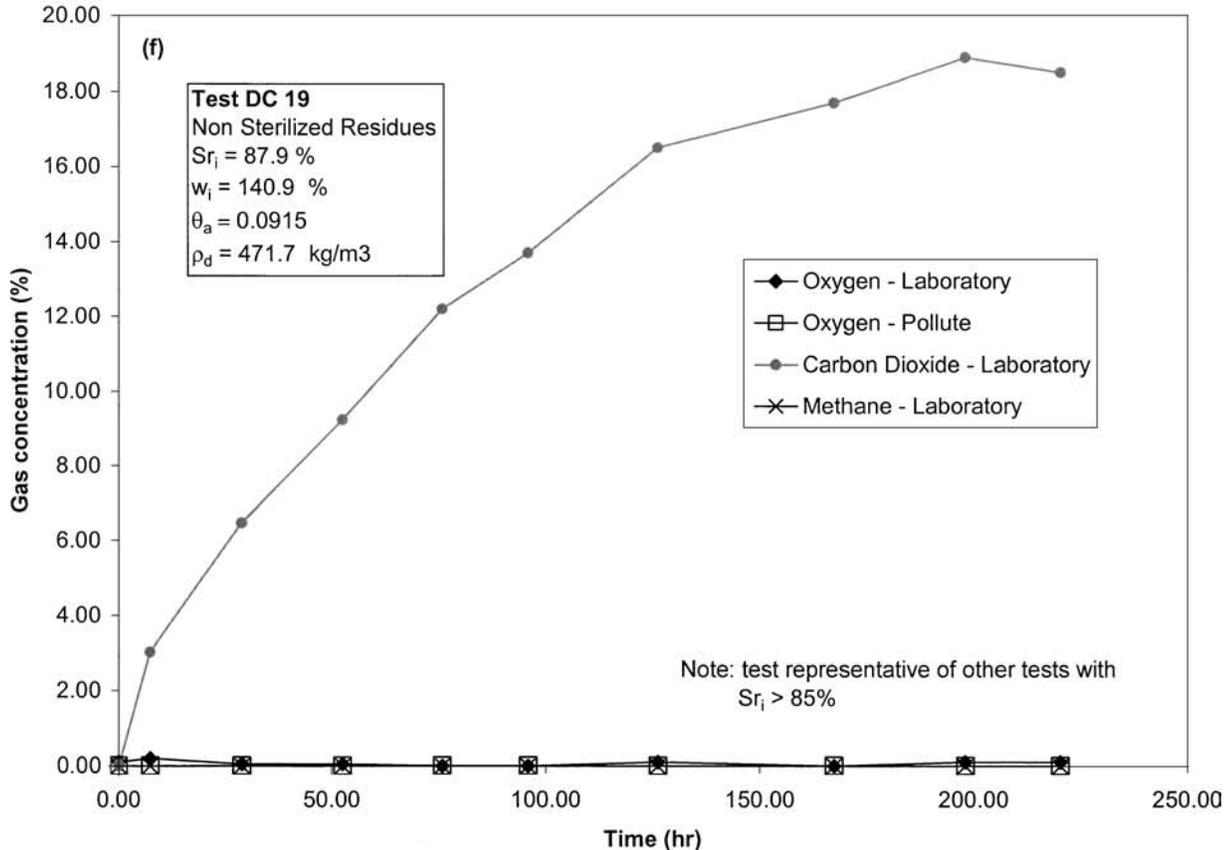
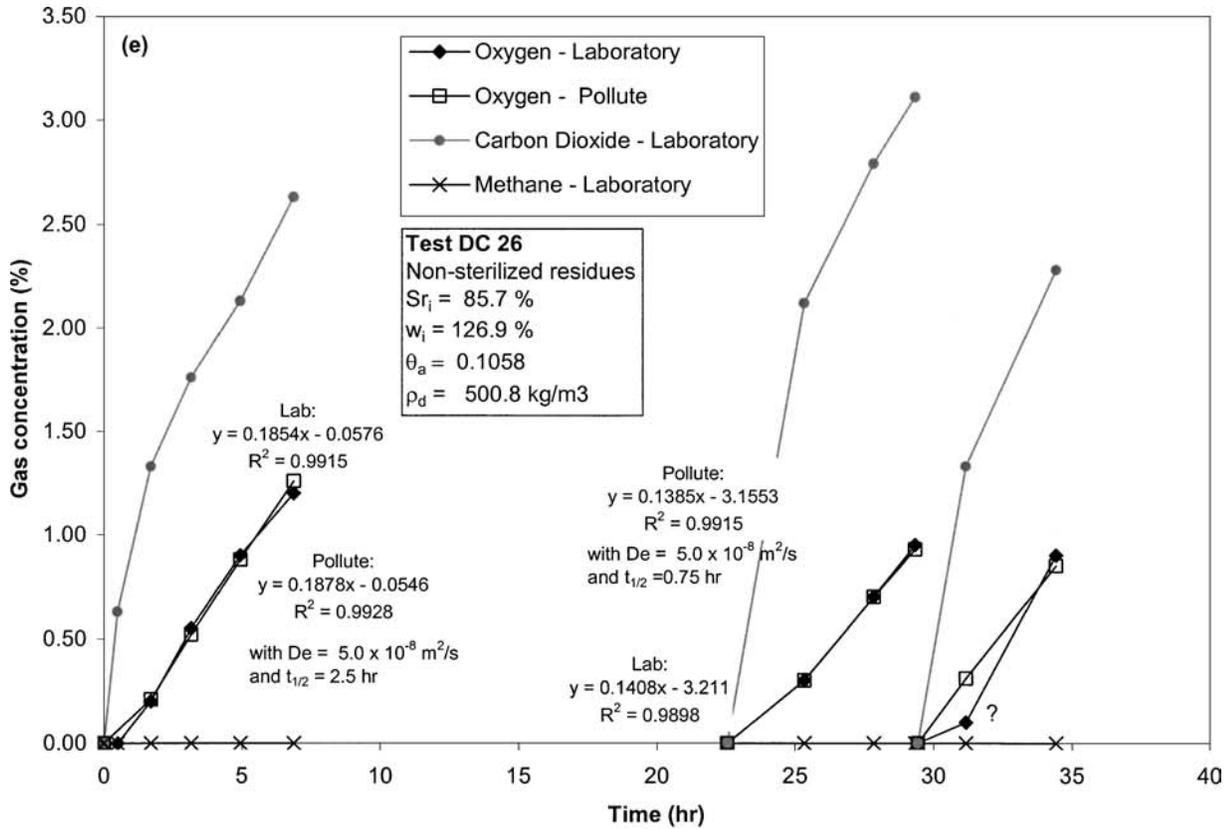


FIG. 4—(Continued).

TABLE 3—Summary of input parameters and data fitting obtained by modeling with the Pollute model.

DC 25 (Sr _i = 79.8%)		Pollute Model							
Laboratory	O ₂ (%)	D _e (m ² /s) = 5.4 E-07	5.40E-07	5.60E-07	5.80E-07	6.00E-07	7.00E-07	8.00E-07	
		t _{1/2} (hr) = 500	2	1	0.7	0.4	0.15	0.09	
Time (hr)	O ₂ (%)	O ₂ (%)							
0.18	0.45	0.42	0.42	0.43	0.45	0.46	0.50	0.55	
0.45	1.40	1.47	1.43	1.43	1.48	1.47	1.50	1.53	
0.71	2.40	2.42	2.36	2.39	2.42	2.38	2.37	2.37	

DC 22 (Sr _i = 79.9%)		Pollute Model								
Laboratory	O ₂ (%)	D _e (m ² /s) = 5.7 E-07	5.70E-07	5.80E-07	6.00E-07	0.00	6.40E-07	6.80E-07	7.00E-07	7.20E-07
		t _{1/2} (hr) = 500	5	2	0.75	0.60	0.4	0.25	0.2	0.15
Time (hr)	O ₂ (%)	O ₂ (%)								
0.33	1.10	1.07	1.06	1.07	1.07	1.08	1.11	1.13	1.13	1.10
0.67	2.40	2.40	2.37	2.38	2.37	2.37	2.40	2.41	2.39	2.31
1.00	3.50	3.61	3.56	3.57	3.52	3.52	3.55	3.52	3.47	3.33

DC 16b (Sr _i = 80.9%)		Pollute Model						
Laboratory	O ₂ (%)	D _e (m ² /s) = 4.5 E-7	4.50E-07	4.80E-07	5.10E-07	0.00	8.10E-07	1.00E-06
		t _{1/2} (hr) = 500	5	1.3	0.5	0.12	0.06	0.035
Time (hr)	O ₂ (%)	O ₂ (%)						
0.25	0.70	0.55	0.55	0.59	0.61	0.68	0.74	0.78
0.52	1.50	1.42	1.40	1.46	1.48	1.53	1.57	1.58
1.00	2.80	2.87	2.83	2.92	2.90	2.84	2.77	2.63

DC 21 (Sr _i = 84.3%)		Pollute Model							
Laboratory	O ₂ (%)	D _e (m ² /s) = 3.25e-7	3.25E-07	3.50E-07	0.00	0.00	0.00	4.40E+00	4.60E-07
		t _{1/2} (hr) = 500	5	0.9	0.50	0.30	0.25	0.2	0.18
Time (hr)	O ₂ (%)	O ₂ (%)							
0.50	0.75	0.70	0.69	0.71	0.73	0.73	0.75	0.76	0.79
1.00	1.60	1.61	1.58	1.59	1.61	1.58	1.60	1.60	1.64
1.50	2.40	2.48	2.43	2.42	2.42	2.36	2.38	2.35	2.40

DC 26 (Sr _i = 85.7%)		Pollute Model					
Laboratory	O ₂ (%)	D _e (m ² /s) = 4.0 E-08	4.00E-08	0.00	6.00E-08	8.00E-08	1.00E-07
		t _{1/2} (hr) = 500	15	2.50	1	0.45	0.27
Time (hr)	O ₂ (%)	O ₂ (%)					
1.72	0.20	0.17	0.16	0.21	0.24	0.28	0.30
3.18	0.55	0.46	0.45	0.52	0.53	0.57	0.58
4.95	0.90	0.83	0.80	0.88	0.87	0.90	0.89
6.88	1.20	1.23	1.18	1.26	1.22	1.21	1.18

	Good fitting
	Best fitting

As the value assigned to $t_{1/2}$ approaches the actual duration of the test, better fittings are obtained. The assigned D_e values were then slightly increased, requiring $t_{1/2}$ to be lowered in order to maintain a good fit. Table 3 shows that various sets of D_e and $t_{1/2}$ fit the experimental data rather well and that D_e values fall into a relatively narrow range. If D_e values higher than this range are assigned, fittings are no longer as good, no matter what values are given to $t_{1/2}$ (not all trial fits presented).

The results of Tests DC21 ($Sr_i = 84.3\%$; Table 4d) and DC26 ($Sr_i = 85.7\%$; Fig. 4e) clearly show that, as the degree of saturation reaches the $Sr \approx 85\%$ threshold, the diffusion coefficient decreases from $3.75 \times 10^{-7} \text{ m}^2/\text{s}$ (DC21) to $5.0 \times 10^{-8} \text{ m}^2/\text{s}$ (DC26), i.e., by one order of magnitude. The half-lives vary between 0.12 h (test DC16b) and 2.5 h (DC 26), which is a relatively narrow range that lies within the same order of magnitude as the duration of the tests. Such low half-lives are associated with oxygen being readily consumed, i.e., high reaction rates. They were expected due to the addition of the inoculum and to the fact that the actual measurements started only 72 h following compaction, which allowed the *Penicillium sp.* colonies to develop.

As shown in Table 3, several half-life values within the narrow range mentioned above could be attributed and still maintain good fitting. As a result, a relationship does not seem to exist between

half-life and other relevant parameters, such as the degree of saturation. A clear relationship between half-life and CO₂ production could not be established for the same reason. What needs to be emphasized is the fact that the best fittings are clearly those in which low half-life values are attributed.

Effective Diffusion Coefficient and Oxygen Fluxes as a Function of the Degree of Saturation

As diffusion coefficients drop with increasing degrees of saturation, it is expected that the gas fluxes reaching the base of the sample diminish. As a result, the production of acidity resulting from reactions involving the presence of O₂ is reduced. In the case of deinking residues, this tendency is clearly observed in Fig. 6, where the effective oxygen diffusion coefficients (Fig. 6a) and oxygen fluxes reaching the base (Fig. 6b) are plotted against their respective degrees of saturation. The results in Fig. 6 (also summarized in Table 4) corroborate the previously provided explanation referring to the threshold degree of saturation: as Sr reaches approximately 85%, the flux of oxygen reaching the base of the 3-cm-thick deinking residue sample drop by an order of magnitude from 11.3 kg O₂/m² · year to 1.3 kg O₂/m² · year (Table 4). For samples with

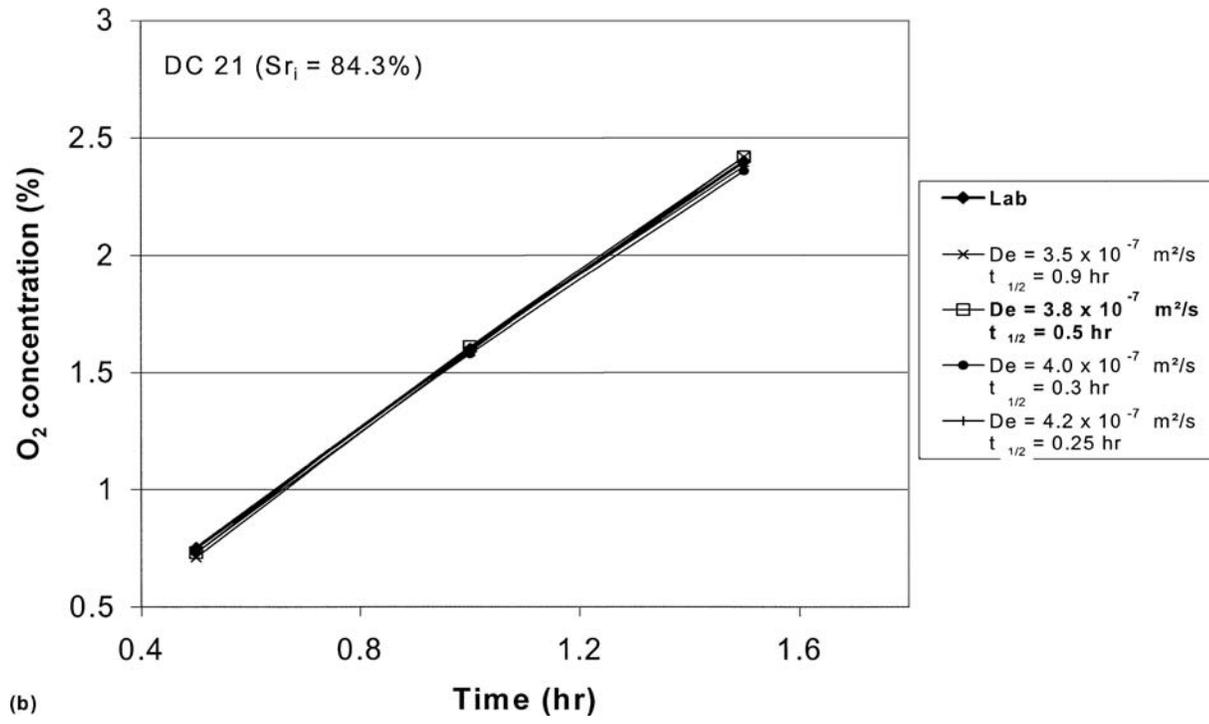
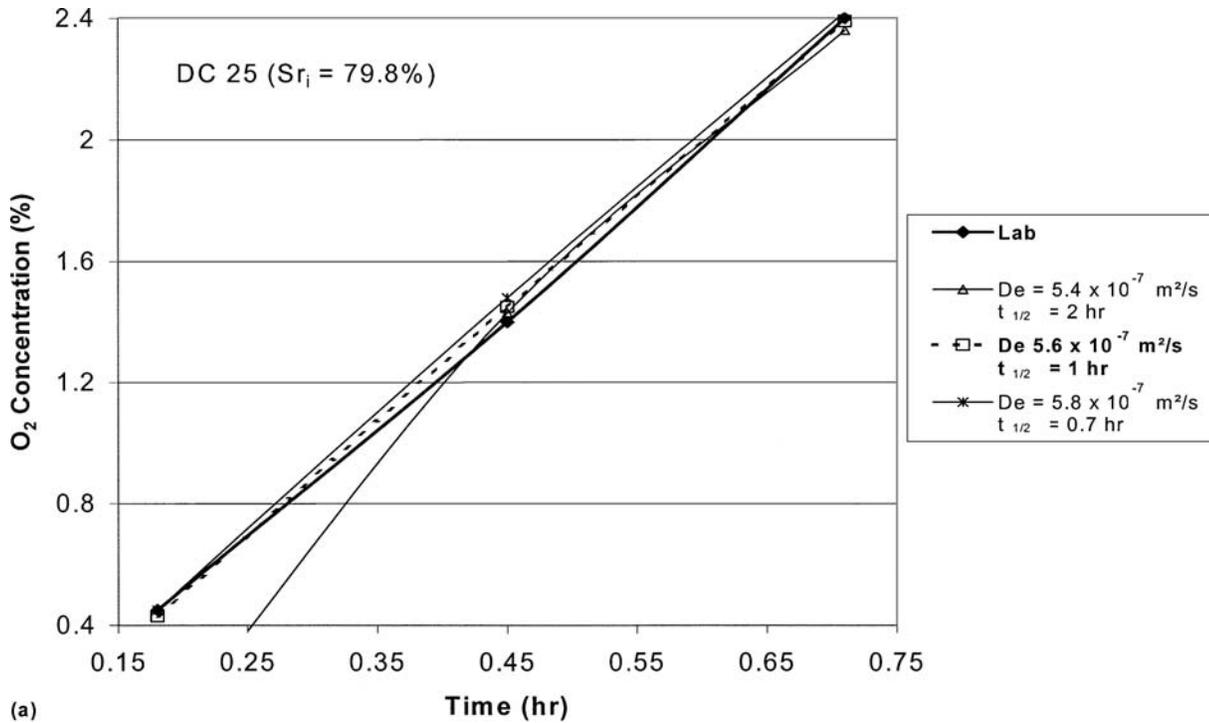


FIG. 5—Data reduction by fitting modeling results with experimental data.

degrees of saturation higher than 85 % (DC19 or DC24), a condition that is commonly achieved in the field (Cabral et al. 1999, 2000a,b; Burnotte et al. 2000), O_2 was not detected in the receptor reservoir after hundreds of hours, which equates to a zero flux situation.

Considering, for example, that the flux of O_2 reported by Tibble and Nicholson (1997) for highly reactive tailings is in the order of $110 \text{ kg } O_2/m^2 \cdot \text{year}$, the efficiency ratio of a 3-cm-thick deinking residue cover would be approximately 100. The efficiency ratio

equals the ratio between the flux through uncovered tailings near the surface and the flux reaching the bottom of the oxygen barrier. For the purpose of comparing cover systems, Yanful (1993) reports an O_2 flux of $0.022 \text{ kg } O_2/m^2 \cdot \text{year}$ that reaches the base of a 60-cm-thick multi-layer cover system. For a 60-cm-thick deinking residue barrier with the same characteristics of the specimen in test DC26, the flux of O_2 obtained is in the order of $10 - 10 \text{ kg } O_2/m^2 \cdot \text{year}$, i.e., virtually zero. This corroborates the results of simulations made by Cabral et al. (2000a), who showed that in an actual 1-m-thick

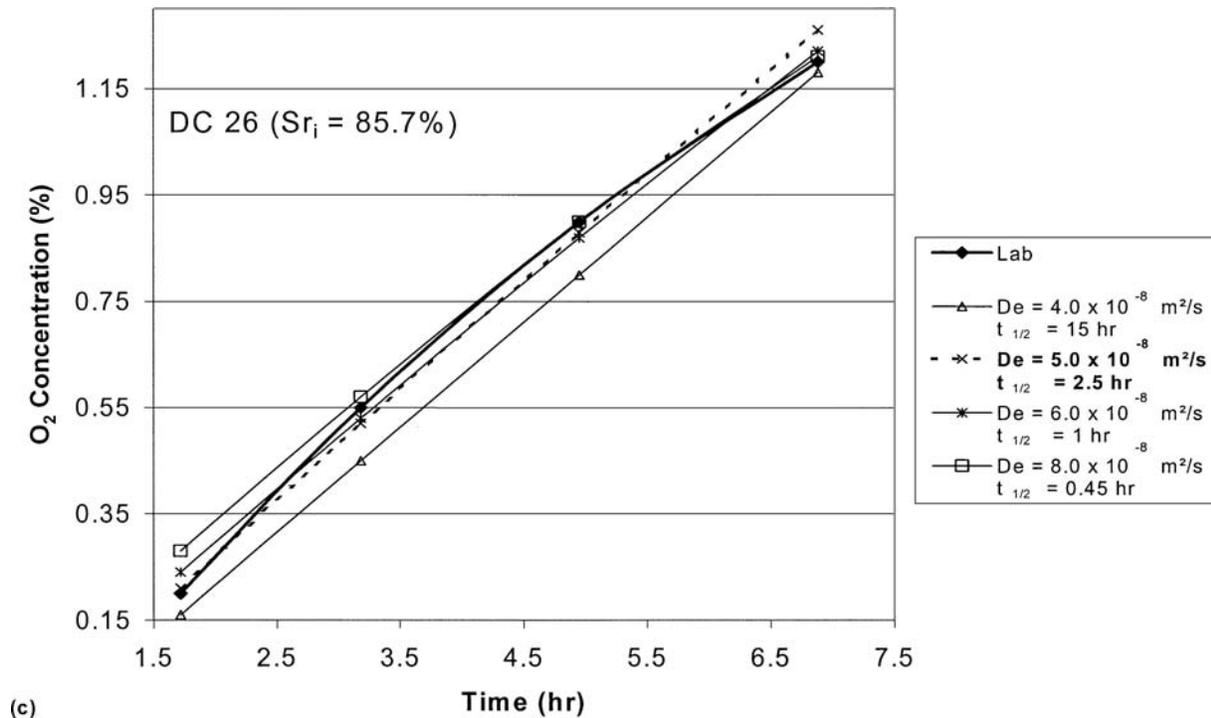


FIG. 5—(Continued).

TABLE 4—Effective diffusion coefficients and fluxes associated with several tests.

Test	Sr_i^a (%)	r_d (kg/m ³)	Duration of Test Segment (h)	$t_{1/2}$ (h)	D_e Poll (m ² /s)	Flux Reaching Base of 3-cm Sample (kg O ₂ /m ² · y)	Equivalent Acidity Production ^b (kg H ₂ SO ₄ /m ² · yr)
DC25	79.8	508.1	0.7	1	5.60E-07	23.0	37.8
DC22	79.9	508.2	1.0	0.6	6.10E-07	26.4	43.3
DC16b	80.9	509.5	1.0	0.12	6.50E-07	20.3	33.3
DC21	84.3	494.6	1.5	0.5	3.75E-07	11.3	18.5
DC26	85.7	500.8	6.9	2.5	5.00E-08	1.3	2.2
DC19	87.9	471.7	225.0	Not obtained	Not obtained	0 (after 225 h)	0 (after 225 h)
DC24	93.1	412.5	530.0	Not obtained	Not obtained	0 (after 500 h)	0 (after 225 h)
6-cm multi-layer cover (Data from Yanful 1993)						≈ 0.022 ^c	0.036
Uncovered high-sulfide tailings (Data from Tibble and Nicholson, 1997)						≈ 110.0 ^c	181.5

^a Degree of saturation in the beginning of the test. Variation from the beginning to the end is less than 1 % for all tests.

^b 3.75 moles of O₂ oxidize 1 mole of pyrite (FeS₂), thus producing 2 moles of H₂SO₄.

^c Not related to 3-cm samples.

barrier with $Sr > 85\%$, the flux of O₂ reaching its base is, for all practical purposes, nil.

Another relevant observation that can be made about the efficiency of deinking residue barriers refers to the intense microbial activity that takes place inside the DR barrier. Given this activity, any O₂ in the water phase is rapidly consumed. Moreover, evidence has been collected from field measurements that the concentration of O₂ at the bottom of the DR layer remains below detectable limits (Cabral et al. 2000a) even near the crest of a slope where the DR cover is in extension and not as saturated (thus creating the conditions for a more important O₂ diffusive flux). As a consequence of the above comments and results, acidity production can be effectively prevented by the placement of a deinking residue cover.

In the case of the tests performed in this study, the appearance of CO₂ almost right from the start is a clear consequence of oxygen consumption resulting from microbial activity. The results presented in Fig. 4 show that in the case of tests with $Sr_i < 85\%$

(DC25, DC22, and DC16b), O₂ concentrations increase faster than CO₂ concentrations. As the degree of saturation nears 85 % (Test DC21), the CO₂ concentration starts to dominate over O₂ and eventually increases at a faster pace than that of O₂ (DC26). Eventually, O₂ migration is brought to a halt (case of Test DC19 and others with $Sr > 85\%$), while the CO₂ concentration continues to increase. This once again shows that the $Sr \approx 85\%$ threshold is an important one in the design of O₂ barriers with high organic matter contents, such as deinking residues. Methane concentrations were always below the detectable limits, an indication that methanogenesis was not taking place.

Conclusions

This paper described the details of an experimental procedure developed to obtain the diffusion coefficient of oxygen through deinking residues (DR). Given the fact that this alternative construction

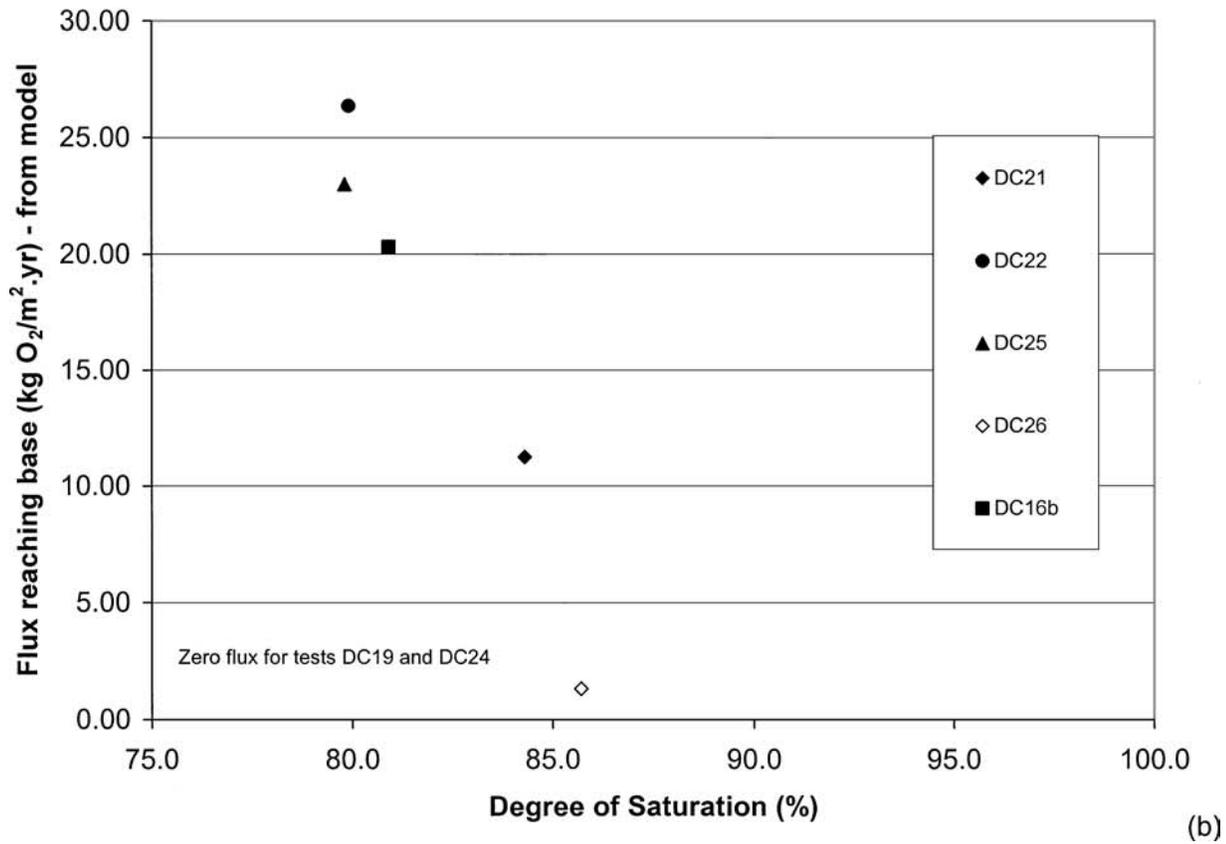
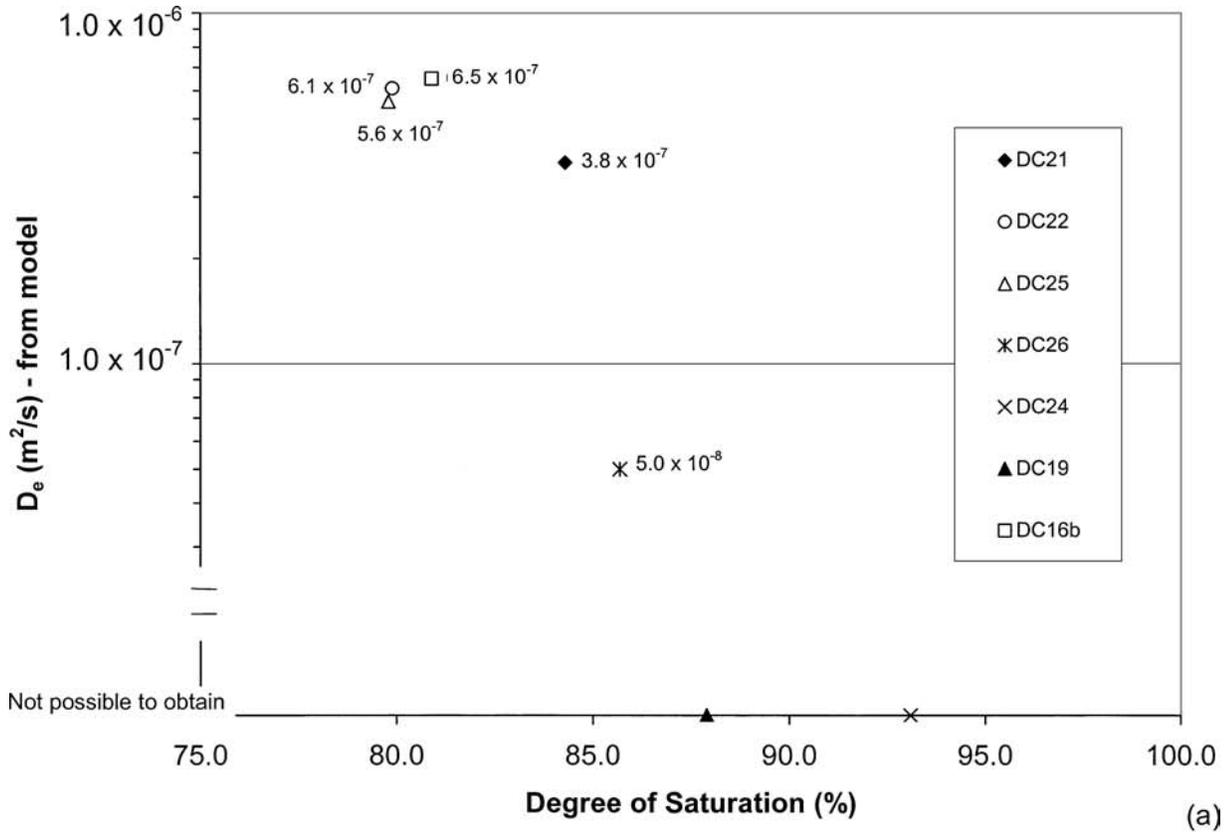


FIG. 6— D_e and flux reaching the base of the samples as a function of S_r .

material has a high organic matter content, significant oxygen consumption occurs, which required special care in defining the most appropriate equipment design, sample preparation method, and testing procedure.

Several tests were performed with samples at varying degrees of saturation. Each test was repeated several times in order to verify the consistency of the procedure adopted. Some tests with similar characteristics were also preformed in order to verify the consistency of the procedure from one test to another. With the oxygen concentrations obtained as a function of time, it was possible to deduce the oxygen diffusion coefficients and associated fluxes. This was done by using the computer code POLLUTE v.6 (Rowe et al. 1994), which provides numerical solutions to Fick's laws. Pairs of diffusion coefficients and half-lives ($t_{1/2}$) of the consumed species (in the present case, oxygen), as well as the density, thickness, and air-filled porosity of the samples were the main input parameters to Pollute. The diffusion coefficients and associated fluxes were determined based on the best reproductions of laboratory results.

As expected, the results showed that diffusion coefficients are highly influenced by the degree of saturation of the sample: as the latter increases, the former decreases. Beyond a threshold in the vicinity of 85 %, a one order of magnitude drop in the diffusion coefficient was observed. Accordingly, the fluxes reaching the base of the sample also decreased by one order of magnitude. For even higher degrees of saturation (which is commonly achieved in the field), the concentration of O₂ at the base of the sample is virtually zero (which also corroborates field measurements). A simulation made with Pollute for a hypothetical 60-cm-thick deinking residue barrier showed that the O₂ flux reaching the base of the barrier is several orders of magnitude lower than the flux obtained for a 60-cm multi-layer cover constructed with soils.

The half-lives varied between 0.12 and 2.5 h. This relatively narrow range of $t_{1/2}$ is in the same order of magnitude as the duration of the tests, i.e., O₂ consumption by microorganisms occurred within the testing period. The latter is confirmed by the increase in CO₂ concentrations.

For degrees of saturation higher than 85 %, the air-filled voids are no longer connected and migration could only occur through the liquid phase. However, given the intense microbial activity, oxygen concentrations remained below the detectable limit of the measuring system for more than 200 h (as CO₂ concentration increased steadily). This advocates for the effectiveness of DR as barrier material for the prevention of acid rock drainage.

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