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Oxygen release kinetics from solid phase oxygen in Arctic Alaska

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Abstract

Child's Pad is a gravel construction surface that was contaminated with petroleum during oil-field service operations in Deadhorse, Alaska. As part of a remedial action plan, a buffer strip of uncontaminated sandy gravel was placed along sections of the pad boundary. A magnesium peroxide formulation manufactured by Regenesis, and sold as Oxygen Release Compound (ORC®), was placed in the buffer strips. The ORC was intended to supply oxygen to aerobic microorganisms capable of degrading petroleum. Studies were conducted in the laboratory to determine initial oxygen release kinetics from ORC in contact with barrier soil. Studies quantified the biotic and abiotic catalytic mechanisms for converting hydrogen peroxide (a possible MgO_2 intermediate) and ORC to oxygen and water, the effects of temperature on oxygen release from ORC, and the effect of field exposure on ORC viability. Barrier soil exhibited sufficient catalytic activity to convert hydrogen peroxide to oxygen faster than the expected biological demand. The oxygen evolution rate (OER) from ORC was lower at 7°C than 21°C by more than two times. The ORC recovered from Child's Pad after less than 1 year retained nearly all of the original available oxygen, although physical bridging was evident.

Keywords: Bioremediation; Oxygen supply; Barrier; Petroleum; Contamination

1. Introduction

Child's Pad is a gravel construction surface covering approximately 0.03 km^2 in Deadhorse, Alaska. The pad consists of silty, sandy gravel between 1 and 2 m thick

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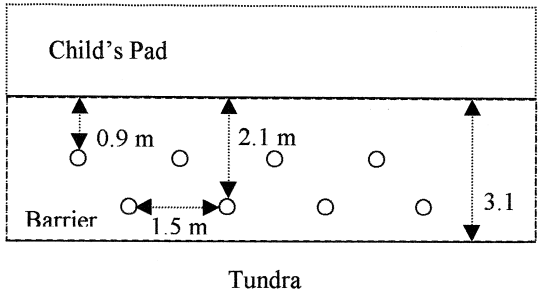

Fig. 1. Schematic of a section of one Child's Pad barrier. Open circles represent ORC socks. On one side of the barrier is Child's Pad and on the other is tundra. The first barrier is 81 m long and contains 100 ORC socks. The second barrier is 91 m long and contains 120 ORC socks.

overlying frozen tundra. Permafrost extends from approximately 1 m below the gravel surface to over 500 m under ground. During the summer the top 1 m of the pad thaws, allowing a perched water table to form in the unfrozen gravel. To prevent migration of petroleum contaminants, two migration barriers were designed to run along portions of the pad border. The first barrier is 3.1 m wide, 81 m long, 0.6 m deep and contains 100 Oxygen Release Compounds (ORC) socks. The second barrier is 3.1 m wide, 91 m long, 0.6 m deep and contains 120 ORC socks. Each ORC sock (0.3 m tall and 0.15 m diameter) was placed vertically in the barrier 0.3 m below grade. In each barrier, the socks were placed in two rows in a staggered arrangement (Fig. 1). This paper describes laboratory studies on oxygen evolution characteristics from ORC in contact with soil from the petroleum migration barrier at Child's Pad, AK.

2. Background

Solid phase oxygen (SPO) refers to a suite of solid compounds with the potential to release oxygen when in contact with moist soil. A number of companies manufacture a product containing SPO in the form of a simple peroxide or peroxyhydrate for use in bioremediation. Preliminary research on peroxyhydrates found that oxygen was released too quickly to be of practical benefit in bioremediation [1]. Additional work, however, demonstrated that oxygen was released less quickly from divalent metal peroxides than peroxyhydrates, and treatment of peroxides with phosphoric acid or phosphate salts could further slow the release of oxygen [2]. The SPO used in this research was a formulation of magnesium peroxide (MgO_2) and phosphate ions produced by Regenesis under the trade name ORC. Regenesis uses phosphate ions to produce ORC, in a patented intercolation process [3].

The stoichiometric conversion of a metal (M) peroxide to oxygen and a metal hydroxide is generally thought to occur by two reactions [4]:

$$2MO_2 + 4H_2O \rightarrow 2H_2O_2 + 2M(OH)_2 \quad (1)$$

$$2H_2O_2 + \text{catalyst} \rightarrow 2H_2O + O_2 + \text{catalyst} \quad (2)$$

Farone [5] postulates that for magnesium peroxide, however, the conversion occurs in the single reaction:

$$2MgO_2 + 2H_2O \rightarrow O_2 + 2Mg(OH)_2 \quad (3)$$

If the conversion of magnesium peroxide to oxygen occurred through a hydrogen peroxide intermediate, a possible rate-controlling step would be the conversion of hydrogen peroxide to oxygen and water. Hydrogen peroxide breaks down into oxygen and water in a reaction catalyzed by the microbial enzyme catalase, or elements such as iron and manganese. Two catalytic mechanisms using bivalent ions such as iron or manganese are the modified Haber–Weiss mechanism (i.e. Fenton's reaction) and the two-electron decomposition process [6]. Less common elemental catalysts include nickel, copper, zinc, and lead [7].

3. Materials and Methods

3.1. Catalytic activity of barrier soil

The catalytic activity of barrier soil was measured using a gas displacement test. The test was prepared by filling a 250 ml Erlenmeyer flask with the amounts of catalase and soil listed in Table 1. Sufficient distilled water was added to each flask to reach a 250 ml working volume. Each reactor was placed on a VWR magnetic stir-plate that provided continuous mixing. A clamped hose led from the top of the flask to a positive displacement vessel for quantifying the volume of gas released. A 30% hydrogen peroxide solution was added to the flask and a rubber stopper was placed in the top. The volume of gas evolved was recorded with time. Total iron and manganese content of the barrier soil was measured using atomic adsorption. Soil was prepared for atomic adsorption by drying at 100°C for 24 h and digesting in perchloric acid.

3.2. Kinetics of ORC

A series of studies were conducted to evaluate the initial oxygen evolution rate (OER) from ORC under different conditions. The OER was considered an 'initial' rate since each test lasted only 120 min. All studies used 250-ml Erlenmeyer flasks, a YSI dissolved oxygen probe and meter, a VWR stir plate, bovine liver catalase and/or barrier soil, distilled water, ORC, and parafilm. Each test was prepared by adding to a

Table 1
Contents of reactors for volumetric oxygen evolution study

Reactor	H_2O_2 solution (ml)	Catalase (mg)	Soil (g)	Soil treatment
Catalase alone	0.5	0.1	0	No soil
Barrier soil	1.0	0.0	45	Unautoclaved
Autoclaved barrier soil	1.0	0.0	45	Autoclaved

Table 2
Experimental matrix for ORC kinetic studies

Test	Water (ml)	SPO (g, condition)	Catalase (mg)	Soil (g)	Temperature (°C)	Treatment
A	250	15, fresh, powdered	none	none	21	Autoclaved
B	250	15, fresh, powdered	none	15	21	Autoclaved
C	250	15, fresh, powdered	none	15	21	none
D	250	15, fresh, powdered	12.5	none	21	none
E	250	15, fresh, powdered	none	15	21	none
F	250	15, fresh, powdered	none	15	7	none
G	250	15, fresh, powdered	12.5	none	7	none
H	250	1, fresh, powdered	12.5	none	21	none
I	250	1, June-field, sock-edge, powdered	12.5	none	21	none
J	250	1, June-field, sock-center, powdered	12.5	none	21	none
K	250	1, July-field, sock-edge, powdered	12.5	none	21	none
L	250	1, July-field, sock-edge, chipped	12.5	none	21	none
M	250	1, July-field, sock-center, powdered	12.5	none	21	none
N	250	1, July-field, sock-center, chipped	12.5	none	21	none

flask 12.5 mg of pure catalase, 15 g of barrier soil, or neither, ORC, a magnetic stir-bar and sufficient distilled water to reach a working volume of 250 ml (see Table 2). A dissolved oxygen probe was placed in the solution, and the flask was either sealed or left open to the atmosphere. No headspace was allowed in sealed flasks. The concentration of dissolved oxygen was recorded for 120 min while a magnetic stir plate provided continuous mixing. Tests A through D were conducted to compare the organic and inorganic catalytic behavior of barrier soil with catalase. Test E was conducted to evaluate the oxygen evolution in an open system compared with the closed system in tests A through D. Tests F and G were conducted to evaluate the effect of decreased temperature on oxygen evolution from ORC. Tests H through N were used to compare the OER from fresh ORC to ORC that had been in the Child's Pad barrier for 9 to 10 months. Samples for tests I through N were removed from ORC socks retrieved from the Child's Pad barrier. When removed from the barrier, the ORC socks were very hard and non-friable, making it necessary to cut the ORC with a saw. Chips were removed from either the edge or center of the sock. OER tests were conducted using chipped ORC and ORC chips that were ground to a fine powder using a mortar and pestle (i.e., powdered).

4. Results

4.1. Catalytic activity of barrier soil

The initial OER when excess hydrogen peroxide was placed in contact with barrier soil was 0.7 ml O_2 min^{-1}, or 1.2 g O_2 kg $soil^{-1}$ h^{-1} (see Fig. 2). When the barrier soil was autoclaved, the OER decreased by a factor of 0.87. When catalase was added to the hydrogen peroxide solution, however, the OER increased by a factor of 9.4.

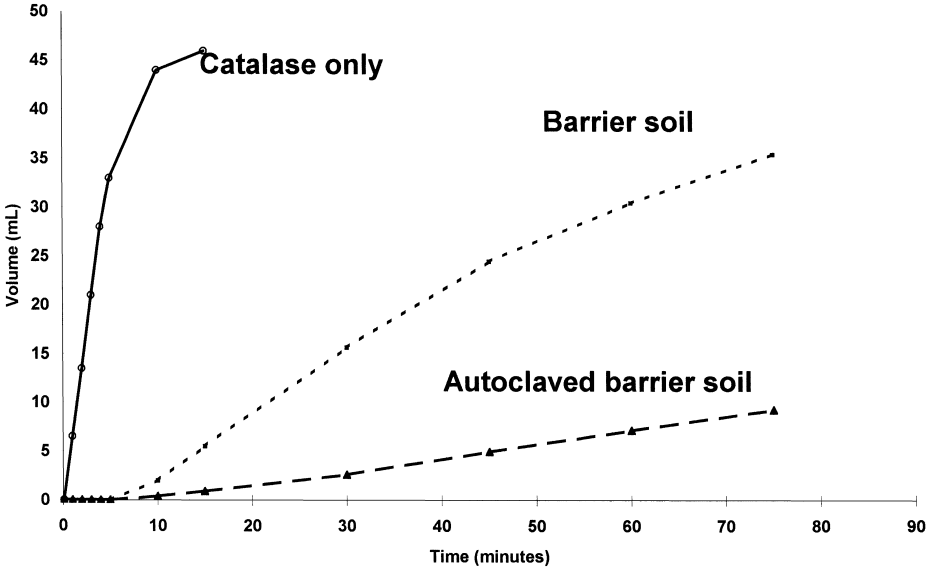

Fig. 2. This figure illustrates the conversion of hydrogen peroxide to oxygen as a measure of the catalytic activity of barrier soil. Values in the figure are the volume (ml) of oxygen released with time.

4.2. Kinetics of ORC

Test A was conducted in a sterile system with no catalase and no barrier soil. No change in dissolved oxygen concentration was observed in the system for the duration of the 120-min test (see Fig. 3). In a closed system with ORC and barrier soil (test C), the dissolved oxygen concentration increased from 7.5 mg l^{-1} to 12.2 mg l^{-1} in 120 min for a total release of 1.2 mg of oxygen. When the closed system test was repeated with autoclaved soil (test B), a total of 1.7 mg O_2 were released from the ORC with a maximum oxygen concentration of 11.7 mg l^{-1} (from 5.1 mg l^{-1}). When the closed system test was run with pure catalase instead of barrier soil (test D), the oxygen concentration in the reactor increased to over 18 mg l^{-1}, the maximum recordable concentration (see Fig. 3).

During a 120-min test, the oxygen concentration in an open system (test E) containing ORC and barrier soil increased by only 0.6 mg. Compared to the closed system with the same contents, the open system appeared to lose roughly half the oxygen released to the atmosphere. The maximum concentration of oxygen observed in the open system, 9.3 mg l^{-1}, was still greater than the saturation concentration of 8.9 mg l^{-1}.

When the closed system containing barrier soil was tested at 7°C (test F), 0.7 mg l^{-1} of oxygen were released. This represented an OER of slightly less than half when compared to the same test run at 21°C. When the closed system containing catalase was tested at 7°C (test G), 3.3 mg of oxygen were released in the first 20 min. This represented an OER of roughly one third compared to the test run at 21°C.

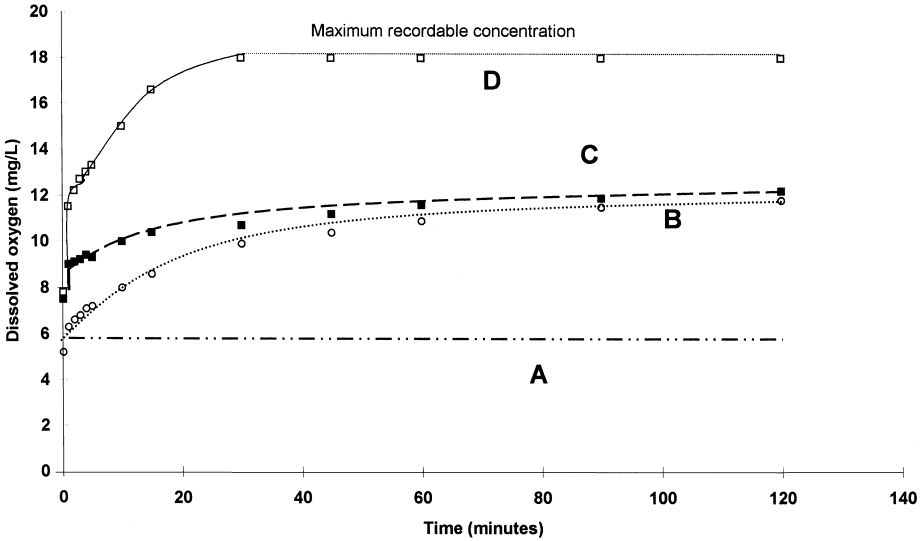

Fig. 3. Kinetics of oxygen evolution from ORC. Test A contains only ORC in water. Test B contains ORC and water and barrier soil. Test C contains ORC, water, and barrier soil. Test D contains ORC, catalase and water.

4.3. SPO retrieved from the field

Test H was conducted with ORC taken from a sock that had never been installed in the field. As shown in Fig. 4, the dissolved oxygen concentration increased from 7.0 mg l^{-1} to 9.3 mg l^{-1} in 100 min, for a release of 0.6 mg O_2, or 0.7% of the total oxygen

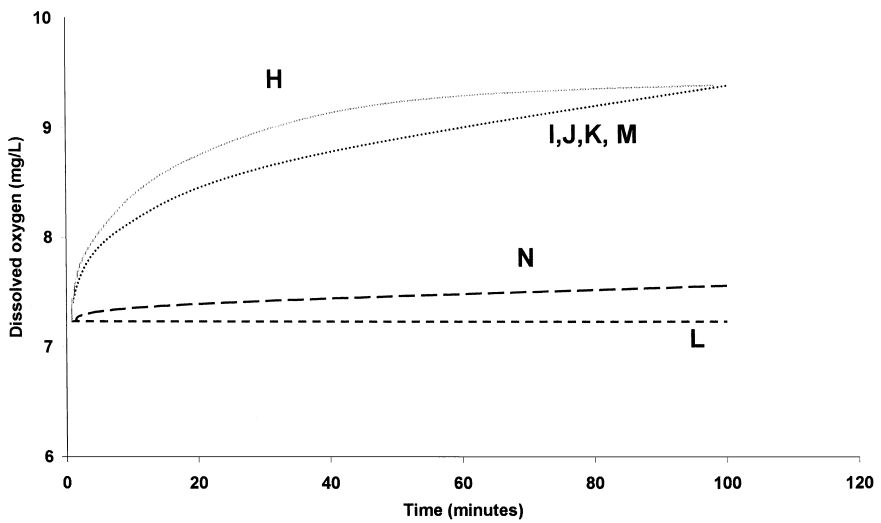

Fig. 4. Oxygen evolution profiles from ORC retrieved from Child's Pad. Tests I through N all contain water, ORC, and catalase. The ORC used in tests I and J is powdered ORC from the edge and center, respectively, of a sock retrieved in June. The ORC used in tests K and L is powdered and chipped ORC, respectively, from the edge of a sock retrieved in July.

available. All tests in which the ORC from the field was ground to a powder responded similarly; that is tests I and J (June samples) and K and M (July samples). When the ORC samples were left in chips (tests L and N), the cumulative oxygen released after 100 min was less than 0.1 mg for both samples.

5. Discussion

5.1. Catalytic activity of barrier soil

Results show that the barrier soil's catalytic activity was equivalent to 200 μg catalase kg soil^{-1}. This equivalent concentration of catalase is approximately 100 times lower than observed in some top soils, but was expected for the sandy gravel of the Child's Pad barrier [8]. Although only trace manganese (2 ppm) was measured in the barrier soil, iron was abundant (4134 ppm). Iron was most likely responsible for the observed catalytic activity that could not be attributed to catalase (i.e. in autoclaved soil). The results from this test show that naturally occurring catalysts in the barrier soil can breakdown excess hydrogen peroxide at the rate of 1.2 g O_2 kg soil^{-1} h^{-1} at standard temperature and pressure. A high biological oxygen demand at a contaminated site could be 2 mg O_2 kg soil^{-1} h^{-1}.

5.2. Kinetics of ORC

The OER curves for ORC in contact with autoclaved and unautoclaved barrier soil were similar. Since the only difference between the autoclaved and unautoclaved soil was the activity of the organic catalysts, the OER was either independent of organic soil catalysts or was governed by non-enzymatic breakdown of the ORC complex. The maximum OER for tests A and C was 60 mg O_2 kg soil^{-1} h^{-1}. This is only 5% of the rate oxygen was released from hydrogen peroxide in contact with barrier soil (i.e. 1.2 g O_2 kg^{-1} soil^{-1}). Conversion of a hydrogen peroxide intermediate, if it exists, did not appear to limit oxygen release from the ORC. Oxygen release from ORC did, however, depend on the presence of a catalyst. In test A, with no catalysts, no oxygen was produced during the 120-min test. However, oxygen was produced from ORC in tests with barrier soil and to the greatest extent in tests with catalase. As such, the rate of oxygen release from ORC was limited by both the type of catalyst in the system and the breakdown of magnesium peroxide in ORC. Farone [9] postulated that the catalyst directly causes the breakdown of ORC rather than a hydrogen peroxide intermediate. These results are consistent with Farone's hypothesis but were not corroborated.

The OER in tests B and C appeared to reach approximately 17 mg O_2 kg soil^{-1} h^{-1} in the second hour of the test. The microbial and inorganic oxygen uptake rate (measured during subsequent studies) for petroleum in barrier soil was 1 mg O_2 kg soil^{-1} h^{-1}. Since tests B and C were conducted with a ratio of 1:1 ORC to soil, this ratio could be decreased to 1:17 ORC to soil while still theoretically meeting the soil's oxygen demand. To construct a mass balance on oxygen in a barrier system, however,

other oxygen sources and sinks should be considered, such as gain or loss of oxygen from/to the atmosphere and inorganic oxygen consumption (e.g. by reduced iron).

When compared to the closed system tests, the mass of oxygen lost to the atmosphere in the open system was approximately 50% of the total oxygen released. This was expected since the oxygen concentration in the water quickly exceeded saturation. Since ORC is placed in the field (i.e. an open system), loss to the atmosphere should be considered when calculating the total oxygen needed in the system. A loss of 50% of the total oxygen should not always be expected, however, since microorganisms could consume much of the oxygen before it is lost to the atmosphere.

Two times more oxygen was released at 21°C than 7°C in the test systems with barrier soil and ORC. Three times more oxygen was released at 21°C than 7°C in test systems with catalase and ORC. The catalase system was effected more by a change in temperature than the soil system because enzyme activity decreases with temperature to a greater extent than the catalytic activity of elements such as iron and manganese. This should be considered when placing ORC in cold environments. At the Child's Pad barrier, the ORC is frozen at least 9 months of the year. Even during the unfrozen months, temperatures near freezing will affect oxygen release rates. During periods when the ground is frozen, no leachate is expected to pass through the barrier and so no oxygen would be required.

5.3. SPO retrieved from the field

Although June and July samples had been exposed to the environment since the previous October, the samples retained much of the original capacity to release oxygen. The soil was probably frozen for at least 7 of the 9 months the ORC was in the barrier. At the end of a 100-min test, powdered samples released approximately the same amount of oxygen as ORC that had not been in the field. When the ORC was left in the chipped form, however, very little oxygen was detected in the OER test. This result suggests that the encrusting, or bridging, of the ORC decreased oxygen *availability*. While oxygen still permeated the encrusted ORC, the rate appeared significantly reduced.

6. Conclusions

The first set of studies demonstrated that barrier soil at Child's Pad had enough catalytic activity to convert hydrogen peroxide to oxygen much faster than the probable microbial demand. However, hydrogen peroxide is not a proven intermediate in the conversion of ORC to oxygen and water. Nonetheless, the absence of known catalysts for the conversion of hydrogen peroxide to oxygen and water proved to limit the breakdown of ORC. In tests with no catalyst present, no oxygen was released from ORC. The same set of tests, however, indicated that ORC released oxygen much more slowly than hydrogen peroxide. These tests demonstrate that both the initial breakdown of ORC and catalyst concentration are limiting factors in oxygen release. As long as the soil is not sterile and devoid of catalysts, it appears that ORC breakdown will likely

govern the rate of oxygen release. The initial rate of oxygen release in all tests conducted using fresh ORC, except the system containing ORC and sterile distilled water, would meet the probable oxygen demand of contaminated soil. These studies did not address the long-term release of oxygen from ORC.

In determining the amount of ORC-oxygen needed in a system, the amount lost to the atmosphere should be considered. Roughly half the oxygen from ORC was lost to the atmosphere in an open, stirred system. If the oxygen demand by microorganisms and inorganic catalysts prevents the oxygen concentration in the groundwater from exceeding saturation, loss to the atmosphere will be minimized. An oxygen mass balance should also include the effects of temperature on both the oxygen release from ORC and the inorganic and microbial demand.

The focus of this study was on the initial release rates of oxygen from ORC. Preliminary tests of ORC retrieved from the field, however, indicated that much of the original oxygen remained in the socks after 9 months. The availability of this oxygen is complicated by a bridging phenomenon that did not eliminate further oxygen release but appreciably reduced the rate under the test conditions. Whether the oxygen release rate from ORC socks affected by bridging would satisfy the microbial demand could not be determined. Additional studies of the bridging affect are needed to determine the true field effectiveness of ORC.

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