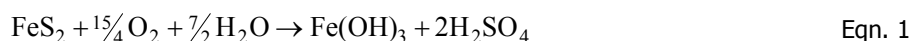

Theoretical Assessment of the Potential for Pyrite Oxidation Adjacent to the Proposed Cloverdale Minesite Following Groundwater Drawdown During Mining

Introduction

Iluka Resources Limited (Iluka) plan to mine the heavy mineral sand deposits at the Cloverdale Minesite. A detailed Acid Sulfate Soil (ASS) Survey was undertaken by Soil Water Consultants (SWC, 2006) to determine the presence or absence of ASS in this proposed minesite. Considerable Potential ASS (PASS) were identified both within and surrounding the proposed mine boundary (SWC, 2006), with the majority of the identified PASS occurring within the Yoganup Formation. This formation also hosts the heavy mineral sand deposit and the regional Yoganup aquifer, and consequently groundwater drawdown is required in order to access the heavy mineral deposit. The Department of Environment (DoE) has expressed concern that groundwater drawdown will result in oxidation of pyrite minerals surrounding the proposed minepit, resulting in the acidification of the aquifer and potential mobilisation of heavy metals into the surrounding environment. This theoretical assessment was therefore undertaken to determine the extent to which oxidation of PASS, adjacent to the proposed minepit, will occur in response to groundwater drawdown during mining.

The theoretical assessment applied an oxygen-diffusion modelling approach to determine whether PASS surrounding the proposed minepit will oxidise following groundwater drawdown. A similar approach has been successfully used by Cook *et al.* (2004) to determine pyrite oxidation based on oxygen fluxes into a soil profile following a declining watertable. The basis behind this approach is that oxygen (O₂) is required to oxidise the pyrite in soils¹ according to Equation 1:

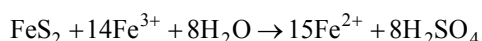


Based on this stoichiometric reaction, 3.75 moles of O₂ (120 g) is consumed during the oxidation of 1 mole of FeS₂ (120 g). Subsequently, considerable O₂ is required to drive the oxidation of pyrite, and if O₂ is limiting, as is the case below a watertable, then pyrite oxidation is prevented.

A schematic diagram showing the conditions of this assessment is provided in Figure 1.

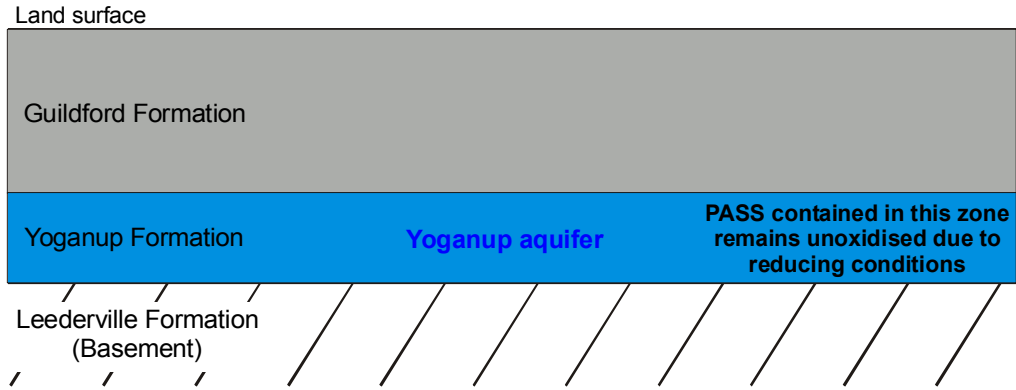
Prior to mining, the pyrite minerals contained within the Yoganup Formation exist in a unoxidised state, due to the anoxic, reducing conditions of the aquifer. Oxygen diffusion through water is extremely slow (oxygen diffusion rate (D_w) in water = 1.0 × 10⁻⁹ m²/s²), and consequently there is insufficient oxygen to facilitate oxidation of the pyrite minerals. When mining commences and groundwater drawdown occurs to access the heavy mineral deposit, the sediments of the Yoganup Formation come into direct contact with the atmosphere along the pit faces (Figure 1). There is a risk that oxygen diffusion into the Yoganup Formation sediments may be enhanced due to declining water table levels and greater contact with the atmosphere along the pit faces. It is therefore the objective of this theoretical assessment to determine whether groundwater drawdown may result in significant influx of oxygen into the exposed Yoganup Formation sediments resulting in the oxidation of pyrite in these sediments.

¹ Note: Oxidation of pyrite may also occur in the absence of oxygen at pH < 4 due to soluble Fe³⁺ which acts as the oxidant for pyrite according to (van Breemen, 1975; Ahern *et al.*, 2004; Cook *et al.*, 2004:

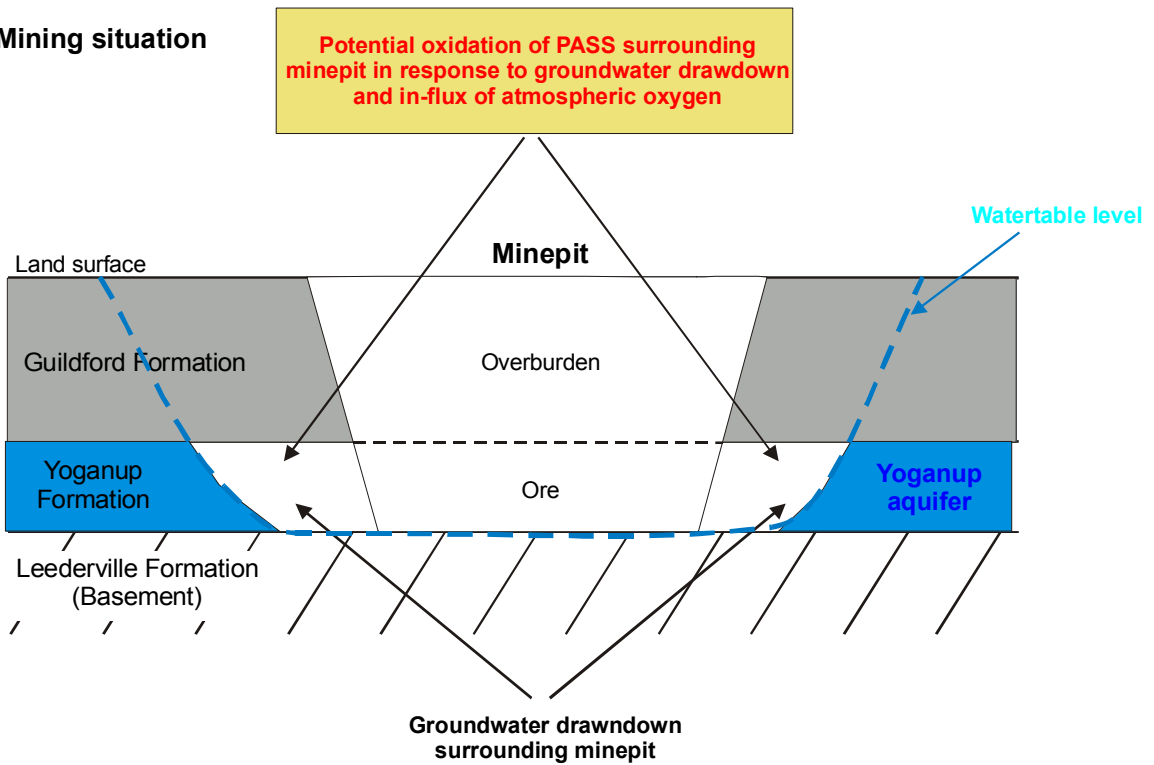


² This oxygen diffusivity in water is compared to an oxygen diffusion rate in air of 2.44 × 10⁻⁵ m²/s.


Premine situation



Mining situation



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PN	PN0060		Iluka Resources Limited CLOVERDALE MINESITE ASS SURVEY SCHEMATIC DIAGRAM SHOWING POTENTIAL PYRITE OXIDATION DURING DRAWDOWN	Figure 1
Prep. by	ASP	20/03/06		
Rev'd. by	AJH	20/03/06		
Revision No.	1			

Theoretical assessment

Oxygen diffusion in soils is strongly related to the water content of the soil, and the air-filled and total porosities of the material. Several relationships have been developed that relate the oxygen diffusivity of a soil to its air-filled porosity (Penman, 1940; Millington, 1959; Marshall, 1959; Gradwell, 1961; Papendick and Runkles, 1965). The most commonly used relationship is that developed by Millington (1959), which is described in Equation 2.

$$D_{\varepsilon} = D_o \times \varepsilon_g^{3.33} \times \varepsilon_o^{-2} \quad \text{Eqn. 2}$$

where,

D_{ε} = oxygen diffusion rate in soils (m^2/s);

D_o = oxygen diffusion rate in air (m^2/s);

ε_g = air-filled porosity (m^3);

ε_o = total porosity (m^3).

In this relationship, oxygen diffusion is directly related to the air-filled and total porosities of the soil. When the soil is completely saturated (i.e. when it is below a water table), the air-filled porosity is zero as all pores are completely filled water; hence the oxygen diffusion rate is extremely small. As the moisture content of the soil drops, as is the case of a declining water table, the air-filled porosity of the soil increases, as does the oxygen diffusion rate. The relationship between air-filled porosity and oxygen diffusion rate for a range of soils with differing total porosities is shown in Figure 2.

When the moisture content of an initially saturated soil begins to drop (i.e. the soil dries following groundwater drawdown) the increase in oxygen diffusion is much smaller than the corresponding increase in the air-filled porosity. This occurs in response to the poor connectivity of the air-filled pores, creating dead-end pores that act as 'oxygen-sinks', significantly slowing the rate of oxygen diffusion through the soil (Melhuish *et al.*, 1974; Figure 2).

In the situation of a declining water table, in response to groundwater pumping, water is only removed from those meso- and macro-pores (i.e. $> 30 \mu\text{m}$ pores) that drain freely under gravity (i.e. the sediments dry to field capacity) (Cresswell, 2002). Consequently, the aquifer sediments still contain appreciable soil moisture following groundwater removal, which significantly retards oxygen diffusion into and through the soil. The extent to which oxygen diffusion is impeded is based on the moisture content at field capacity, and hence on the texture of the soil. In clayey soils there are few pores $> 30 \mu\text{m}$, and consequently the moisture content at field capacity is reasonably high (i.e. $> 30\%$). In these soils the retention of considerable moisture at field capacity retards oxygen diffusion and oxygen diffusion rates of $< 8.0 \times 10^{-7} \text{m}^2/\text{s}$ occur. In contrast, for a sandy soil there is a dominance of meso- and macro-pores, and subsequently low moisture contents occur at field capacity (i.e. $< 10\%$), resulting in high oxygen diffusion rates into the soil. For sands, the oxygen diffusion rate at field capacity approaches $5.0 \times 10^{-6} \text{m}^2/\text{s}$.

Once the oxygen diffusion rate of a soil is known (i.e. from Figure 2), the oxygen flux (F ; $\text{g}/\text{m}^2/\text{s}$) through the soil can be determined using Equation 3 (Mbonimpa *et al.*, 2003; Moncayo, 2003).

$$F = -D_{\varepsilon} \frac{(C_z - C_o)}{L} \quad \text{Eqn. 3}$$

where,

D_{ε} = oxygen diffusion rate in soil (m^2/s);

C_z = oxygen concentration at depth z in the soil profile (g/m^3);

C_o = oxygen concentration at the soil surface (= atmospheric oxygen concentration – $252 \text{g}/\text{m}^3$);

L = depth in the soil profile ($z = L$) (m)

Using Equation 3 and oxygen diffusion rates of $8.0 \times 10^{-7} \text{ m}^2/\text{s}$ for clayey sediments and $5.0 \times 10^{-6} \text{ m}^2/\text{s}$ for sandy sediments (Figure 2), the oxygen flux at specific depths in the soil profile can be determined. These fluxes are provided in Table 1 and Figure 3, and show that oxygen flux decreases exponentially with depth in the soil profile.

Table 1: Oxygen flux required to achieve a soil oxygen concentration $\geq 120 \text{ g/m}^3$ for various distances away from the minepit face.

Distance from minepit face (m)	Oxygen flux ($\text{g/m}^2/\text{s}$)
<i>Sandy sediments</i>	
5	1.32×10^{-4}
10	6.60×10^{-5}
20	3.30×10^{-5}
30	2.20×10^{-5}
100	6.60×10^{-6}
<i>Clayey sediments</i>	
5	2.64×10^{-5}
10	1.06×10^{-5}
20	5.28×10^{-6}
30	3.52×10^{-6}
100	1.06×10^{-6}

Graeme Campbell and Associates have conducted detailed kinetic studies to determine the oxidation rate of pyrite minerals in the Yoganup Formation (GCA, 2005). Through leaching trials with excess O_2 (i.e. O_2 non-limiting conditions³), they found that the maximum oxidation rate for these pyrite minerals was between $0.125 - 0.187 \text{ g FeS}_2/\text{kg/day}$ ($200 - 300 \text{ mg SO}_4^{2-}/\text{kg/day}$). These oxidation rates represent moderate reactivity's, and reflect the absence of more reactive FeS species, such as unstable iron monosulfides or marcasite (Ward *et al.*, 2004).

To achieve the above maximum FeS_2 oxidation rates (i.e. $0.125 - 0.187 \text{ g FeS}_2/\text{kg/day}$), the required O_2 flux must be in the order of $1.0 - 2.0 \times 10^{-3} \text{ g O}_2/\text{m}^2/\text{s}$. This represents a considerable O_2 flux, and when compared to Table 1 and Figure 3, it can be seen that such fluxes only occur within the first 1 m of the soil profile. The lower O_2 fluxes that likely occur in the Yoganup Formation, at distances $> 1 \text{ m}$ from the minepit, would significantly reduce the rate of pyrite oxidation. Pyrite oxidation rates at distances $> 1 \text{ m}$ from the minepit, based on the predicted oxygen fluxes listed in Table 1, are shown in Table 2.

In Table 2, the pyrite oxidation rate that could be supported by predicted oxygen fluxes at 5 m from the pit face would vary from $1.38 - 6.91 \times 10^{-3} \text{ g FeS}_2/\text{kg/day}$, depending on the texture of the sediments. This oxidation rate would release up to $2.30 \times 10^{-4} \text{ mol H}^+/\text{kg/day}$, which would result in a pH reduction of 1.87 units. At distances greater than 5 m, the rate of oxidation declines rapidly and the amount of acidity released is less than $1.0 \times 10^{-5} \text{ mol H}^+/\text{kg/day}$. This amount of acidity would result in a pH reduction of < 1.5 pH units.

³ O_2 non-limiting conditions were achieved by maintaining the water content in soil columns within the LLWR (Least Limiting Water Range), such that oxygen diffusion and the air-filled porosity of the soil was maximised (GCA, 2005).

Table 2: Rate of pyrite oxidation and release of acidity based on expected oxygen flux rates in Yoganup Formation sediments.

Distance from the minepit (m)	Oxygen flux (g/m ² /s)	Rate of pyrite oxidation (g FeS ₂ /kg/day)	Predicted acidity load (mol H ⁺ /kg/day)	Predicted pH change following H ⁺ release (pH units)
<i>Sandy soils</i>				
5	1.32×10^{-4}	6.91×10^{-3}	2.30×10^{-4}	1.87
10	6.60×10^{-5}	3.46×10^{-3}	1.15×10^{-4}	1.57
20	3.30×10^{-5}	1.73×10^{-3}	5.77×10^{-5}	1.28
30	2.20×10^{-5}	1.15×10^{-3}	3.83×10^{-5}	1.12
100	6.60×10^{-6}	3.46×10^{-4}	1.15×10^{-5}	0.76
<i>Clayey soils</i>				
5	2.64×10^{-5}	1.38×10^{-3}	4.60×10^{-5}	1.19
10	1.06×10^{-5}	5.55×10^{-4}	1.85×10^{-5}	0.84
20	5.28×10^{-6}	2.76×10^{-4}	9.20×10^{-6}	0.59
30	3.52×10^{-6}	1.84×10^{-4}	6.13×10^{-6}	0.47
100	1.06×10^{-6}	5.55×10^{-4}	1.85×10^{-6}	0.20

At the proposed Cloverdale Minesite the Yoganup Formation sediments have a clayey sand – sandy loam texture (5 – 25 % clay fraction). These materials are therefore likely to retain considerable moisture following groundwater drawdown, which will significantly impede oxygen diffusion into these sediments. Low oxygen diffusion rates (i.e. between 5.0×10^{-6} – 8.0×10^{-7} m²/s) will limit the pyrite oxidation rate, and significant oxidation, which will cause the pH to drop by > 1.5 pH units, will likely be restricted to distances of 5 – 10 m from the exposed pit face.

It must be noted in interpreting this assessment, that this situation of groundwater drawdown and pyrite oxidation differs from those, more commonly investigated, conditions where pyrite occurs close to the land surface under a watertable (Blunden and Indraratna, 2000; Ward *et al.*, 2004). In these situations oxygen diffusion through the upper soil profile following groundwater drawdown will be much greater than those identified in this assessment. In the case of oxygen diffusion near the surface, evapotranspiration dries the soil to levels beyond field capacity and subsequently the air-filled porosity of the soil will be significantly increased. Oxygen diffusion into these soils will also be enhanced by the preferential movement of oxygen down old root channels, increasing oxygen levels at depth.

In the situation at Cloverdale, and other mineral sands minepits on the Swan Coastal Plain, the majority of the pyrite occurs at depth (i.e. > 10 m) beneath the massive, relatively homogeneous Guildford Clay Formation. Oxygen diffusion through such a thick clay layer from the soil surface is generally limited, and consequently oxygen diffusion and potential oxidation of pyrite occurs following excavation of the minepit and exposure of the soil profile along the minepit faces. These materials at depth do not experience evapotranspiration, and consequently draining of these soils can only occur to field capacity. This limited drying, results in considerable moisture remaining in the sediments, which severely reduces oxygen diffusion into and through this soil material, and retards pyrite oxidation. Consequently, pyrite oxidation rates following groundwater drawdown will be significantly lower than those observed in near-surface conditions.

Summary

Iluka Resources propose to mine the heavy mineral deposits at the Cloverdale Minesite. Mining of this deposit will significantly lower watertable levels surrounding the proposed minepit. Groundwater drawdown in response to pumping will only remove water stored within macro- and meso-pores (i.e. > 30 μm), and subsequently the moisture content of the soil following drawdown will remain relatively high (i.e. drain to field capacity only), given the clayey sand – sandy loam texture of these sediments.

This theoretical assessment has shown that oxygen diffusion rates in sediments with high moisture contents, and corresponding low air-filled porosities, will be low ($5.0 \times 10^{-6} - 8.0 \times 10^{-7} \text{ m}^2/\text{s}$) resulting in low oxygen fluxes into and through the soil. Low oxygen fluxes will significantly limit the extent to which pyrite will oxidise, and based on the oxidation kinetics of pyrite minerals within the Cloverdale area, it is expected that pyrite oxidation will be limited to < 10 m from the minepit face.

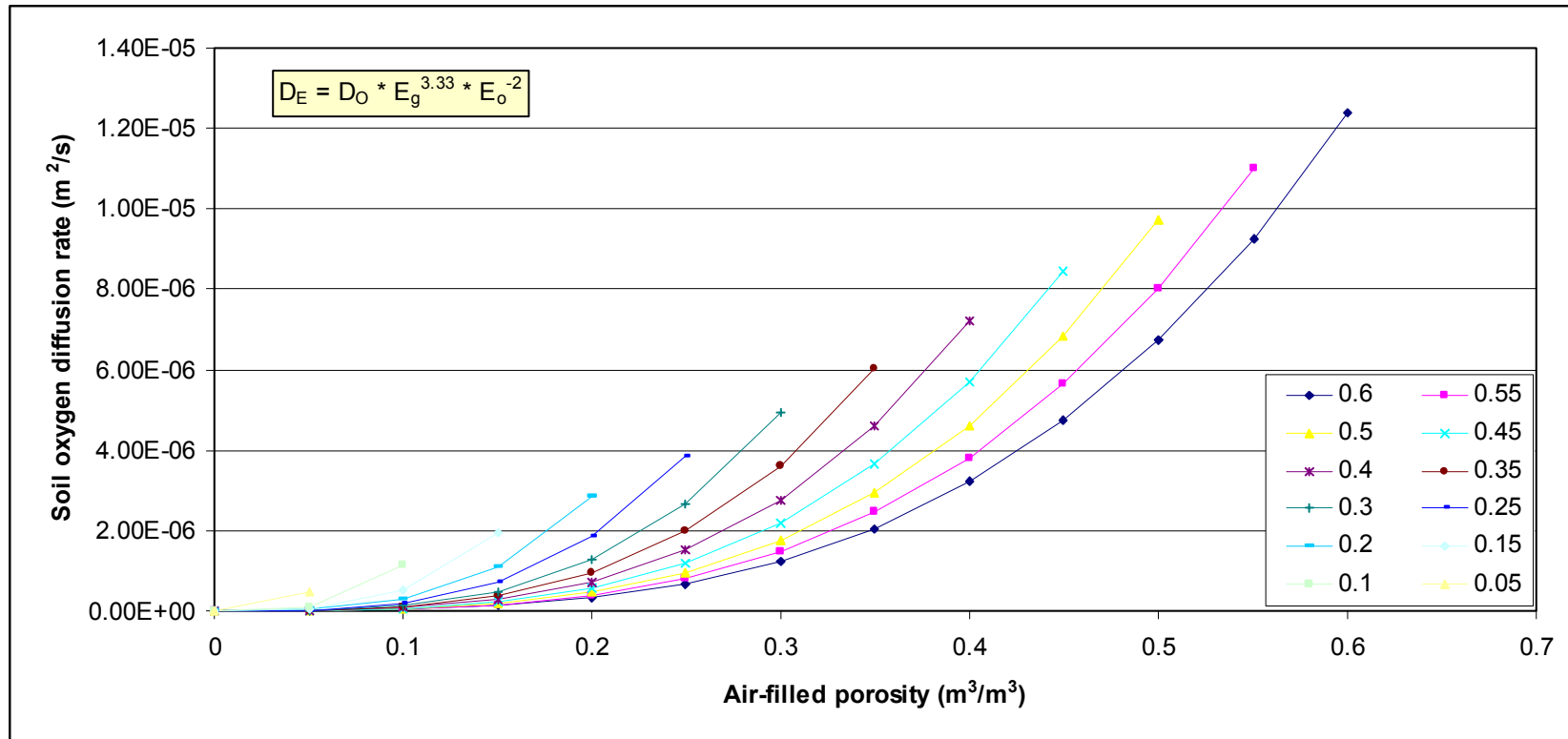
Based on predicted oxygen fluxes a maximum pyrite oxidation rate of $3.5 - 7.0 \times 10^{-3} \text{ g FeS}_2/\text{kg/day}$ will occur immediately adjacent the minepit face (i.e. to a maximum depth of 10 m), resulting in a drop in pH by 1.6 – 1.9 pH units. Given the field pH of these soils is between 5.5 and 6.5, this will result in soil pH values of 3.6 – 4.9, if all available pyrite oxidises. These relatively low soil pH values will be restricted to areas immediately adjacent the minepit, and are unlikely to cause any environmental impact. Limited pyrite oxidation at distances > 10 m from the minepit face, will result in soil pH drop of < 1.5 pH units, with soil pH values remaining above 4.5 – 5.0.

This theoretical assessment clearly shows that pyrite oxidation, in response to groundwater drawdown during mining at the proposed Cloverdale Minesite, will be restricted to within 10 m of the minepit face. At distances greater than 10 m, low oxygen fluxes will become rate-limiting, and minimal pyrite is expected to oxidise. Given these findings, no specific management plan is required at the proposed Cloverdale Minesite, to manage or control groundwater levels during mining so as to minimise pyrite oxidation.

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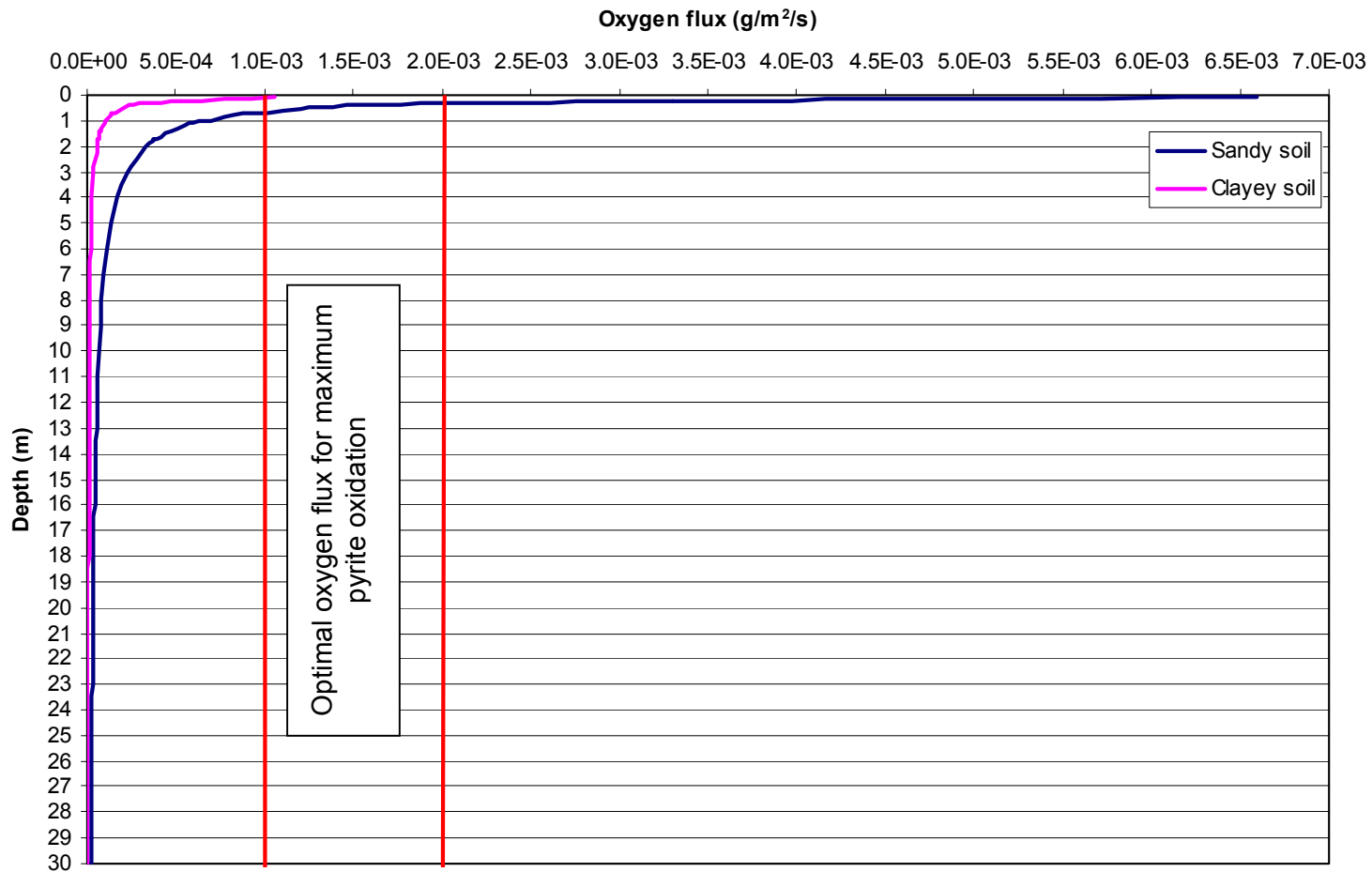


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**RELATIONSHIP BETWEEN OXYGEN
DIFFUSION AND SOIL POROSITY**

Figure 2





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TYPICAL OXYGEN FLUX WITH DEPTH

Figure 3

