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OXYGENATION OF LAKE SEDIMENTS

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Abstract—The kinetics of oxygenation of Lake Mendota sediments have been studied using manometric techniques. Sediments from this lake contain 17,000-23,000 ppm iron, 1400-3300 ppm sulfide, and 260,000 ppm alkalinity as $CaCO_3$. A rapid uptake of O_2 was noted upon exposure of sediment to air. This rapid uptake was followed by a long period (over 45 days) of zero-order reaction in which the O_2 uptake was a linear function of time. Rate constants for the zero-order uptake were between 2.9-6.6 x 10^{-2} mg O_2/day/g of sediment dry weight. The rate was found to be dependent on temperature and iron content of sediment. These results indicate that appreciable amounts of the iron in the sediment are in the form of pyrite which is resistant to oxidation.

1. INTRODUCTION

THE deoxygenation of the hypolimnion of eutrophic lakes is generally thought to be due to the biochemical oxygen demand of dead planktonic organisms. However, ferrous iron and reduced sulfur species in the lake sediments may account for a significant part of the rate of deoxygenation of the hypolimnion of some lakes. This paper presents the results of a laboratory study on the oxygen uptake by sediment collected from Lake Mendota, a eutrophic lake in Madison, Wisconsin.

Previous studies on the oxidation of iron sulfide minerals by oxygen have shown that it is complicated by the numerous oxidation states of sulfur. SATO (1960) reports that the many possible combinations of these elements make it difficult to ascertain the rate-determining step and, therefore the mechanism of ferric iron and sulfate formation is poorly understood. ZOBELL (1963) and GARDNER (1964) have recently presented a review of the literature on the oxidation of iron sulfide minerals by oxygen. Some aspects of these reactions are discussed below.

It is generally agreed that the rate-controlling step appears to involve an interfacial mechanism in which a solid is one of the participating phases. The reaction rate is apparently directly related to the surface area of the solid reactant. The liquid-phase reactions which follow appear to be relatively rapid. Other factors reported to influence this reaction are partial pressure of the dissolved oxygen, ferric ion concentration, the presence of water, pH of the system, and possible catalytic agents and inhibitors. The composition and mineralogy of the iron sulfides involved are important. It is possible that physical factors, such as capillary limitation of chemical movement in the minerals, may influence the rate-controlling mechanism. Iron sulfides can be oxidized under sterile conditions, but the reaction may be significantly stimulated by bacterial action. TEMPLE and KOEHLER (1954), and SILVERMAN *et al.* (1961) report that the presence of some bacteria, including *Thiobacillus thiooxidans, Thiobacillus ferrooxidans,* and *Ferrobacillus ferrooxidans,* enhance the rate of oxidation in an acid environment, but the action of these bacteria is inhibited in basic solutions. The reviews of WOOD (1962) and ZOBELL (1963) should be examined for further discussion of the biochemical oxidation of reduced sulfur compounds. The oxidation of iron sulfide minerals is important from the water pollution standpoint because of the acid mine drainage problem. These investigations are discussed in greater detail by HANNA *et al.* (1961 and 1963) and BARNES and CLARKE (1964). The conditions for oxidation of the iron sulfides in this investigation differ from the conditions of the acid mine situation because the large quantity of carbonate present in Lake Mendota sediments cause the system to be highly buffered at a pH near 8.

The purpose of this investigation was to study the kinetics of the reactions between iron sulfide rich lake sediments and oxygen. It was hoped that the study would give further insight into the role that the sediments play in the deoxygenation of natural waters. Previous studies on the deoxygenation process (MORTIMER 1941 and 1942) were conducted under natural conditions or under experimental conditions where an attempt was made to approach natural conditions. A factor limiting the oxidation of the sediment in these studies was thought to be the rate of diffusion of oxygen to the sediments. Since the purpose of this study was to find the ultimate oxygenation rate of the sediments, it was desirable to study the oxygenation process under conditions wherein the oxygen diffusion would not be a rate-controlling factor. To accomplish this objective, the manometric procedure was selected for these investigations. Using this method, the sediments are constantly mixed intimately in an atmosphere of dissolved oxygen.

2. EXPERIMENTAL PROCEDURE

The sediment samples used for this investigation were collected from Lake Mendota with an Eckman dredge.

The total solids of the samples were determined by drying aliquots at 100°C.

2.1. *Oxygen uptake studies*

For the oxygen uptake studies, manometric methods employing the Warburg apparatus were used. Standard manometric procedures, as described by UMBREIT *et al.* (1957), were followed. Four manometers were used with 125 ml sample flasks while the remaining two were used with flasks containing distilled water to serve as thermobarometers. The samples generally consisted of 5 ml aliquots of lake sediment on which total solids were determined. Distilled water was added to bring the volume up to 25 ml in each sample flask. Oxygen uptake values were obtained at selected time intervals during the run giving kinetic data for the oxygen uptake of the various samples.

2.2. *Chemical studies*

In addition to the manometric studies, chemical determinations were made of alkalinity, iron, and sulfides in the sediments.

The alkalinity of the sediments was determined by potentiometrically titrating the sediments with 0.05 N sulfuric acid. The alkalinity value obtained was 260,000 ppm as $CaCO_3$ in the total solids of the sediments.

For the determination of iron, the phenanthroline method for total iron given in STANDARD METHODS (1960) was followed with some modifications. Preliminary experiments showed that the digestion procedure called for in this method was not sufficient to extract all of the iron compounds from the sediments. For this reason a more vigorous digestion procedure, which involved boiling the samples in 6 M HCl, was adopted. This required the addition of sodium hydroxide after acid digestion to raise the pH to the level required for optimum color development.

The titrimetric method for sulfide, STANDARD METHODS (1960), was used for the initial sulfide determinations. This method involved stripping the sulfide as hydrogen sulfide by passing carbon dioxide through an acidified sample mixture and collecting the sulfide in zinc acetate solution. Because of difficulty experienced in obtaining reproducible results on known substances and because of the long time required to run the procedure, the carbon dioxide method of sulfide stripping was substituted with a steam distillation stripping method developed by TOMIYAMA and KANZAKI (1952).

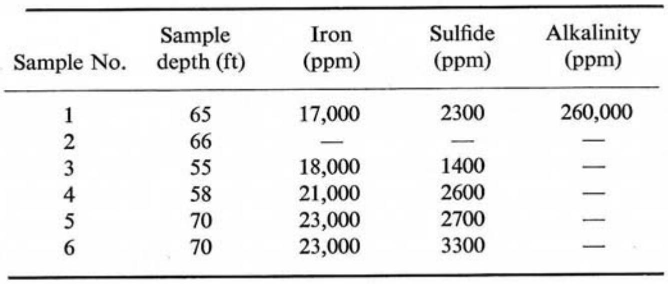
3. RESULTS

The experimental part of this investigation consists of a series of manometric studies on the factors that influence the rates of oxygen reduction by lake sediments.

3.1. *Chemical characteristics of lake sediments*

Lake sediment samples were analyzed for alkalinity, iron, and sulfide concentrations. The results for various samples are presented in TABLE 1. All analyses are reported in terms of total solids (dry weight) of sediments. These data show that the lake sediments are well buffered with large amounts of precipitated carbonates. In addition, these sediments have thousands of mg of iron and sulfide per kg of dry weight of sediments. The mole ratio of iron to sulfide is approximately four to one. From this ratio it is apparent that iron is in excess over sulfur and that some of the iron is present as a compound other than ferrous sulfide. It is reasonable to suggest that some of the iron may be present as ferrous carbonate.

TABLE 1. CHEMICAL ANALYSIS OF LAKE SEDIMENTS



Sample No.	Sample depth (ft)	Iron (ppm)	Sulfide (ppm)	Alkalinity (ppm)
1	65	17,000	2300	260,000
2	66	—	—	—
3	55	18,000	1400	—
4	58	21,000	2600	—
5	70	23,000	2700	—
6	70	23,000	3300	—

3.2. *Manometric studies*

In order to determine the kinetics of oxygenation of the lake sediments, samples of sediment were placed in respective Warburg flasks. After temperature equilibrium was reached (approximately 10 min), the manometers were closed and the gas pressure was read as a function of time.

3.2.1. *Long term oxygenation of sediments.* FIGURE 1 presents typical data obtained in the oxygenation of lake sediments. In this experiment four identical aliquots of Sample 1 (TABLE 1) of lake sediments (total solids: 0.82 g) were run in parallel at a temperature of 21°C. At approximately 21 days 5 ml of 10 per cent glucose solution was added to Flask 4. At approximately 30 days the contents of Flask 5 were removed and the run was terminated. The experiment was continued over a period of 45 days. The pH of the sediments increased from an initial value of 7.3 to a value of 9.6 when the run was terminated.

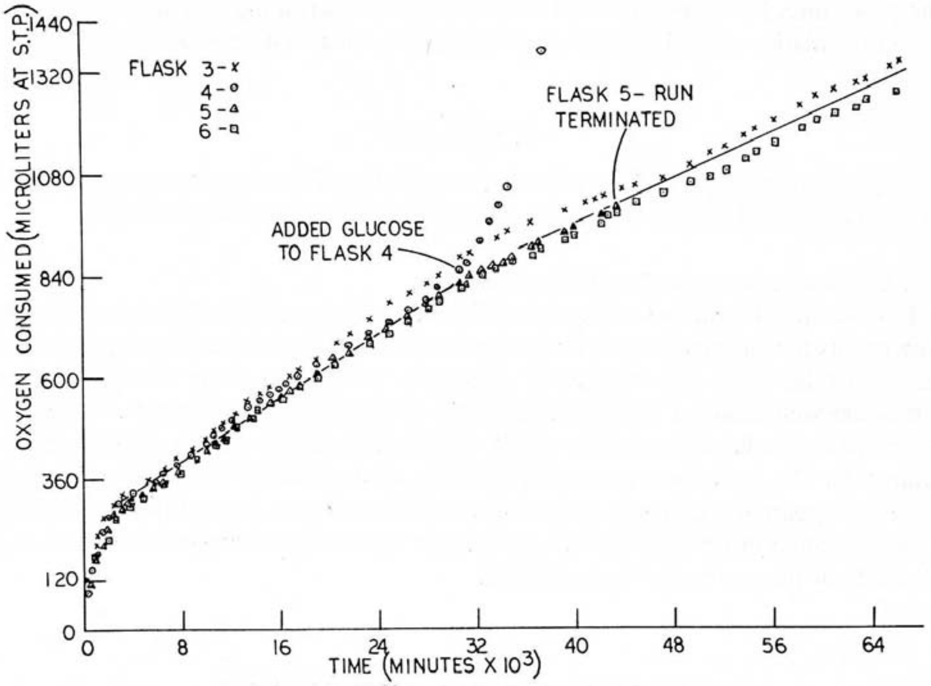


FIG. 1. Oxygenation of lake sediment at 21°C. Total solids per flask: 0.82 g, Sample 1.

Examination of FIG. 1 shows that there is a rapid uptake of oxygen during approximately the first 3 days. After this period the rate of oxygen uptake becomes an almost linear function of time for the rest of the run, decreasing only slightly over a long period. The immediate increase in the oxygen uptake of Flask 4 after the addition of glucose indicates a strong possibility of biological activity in the flasks. For the purpose of comparing reaction rates, the slope of the curve (between 3 and 22 days) was calculated from the slope of a straight line drawn through the points in this interval. The rate constant was calculated in terms of mg of oxygen taken up per day per g of total solids of sediments. The rate constant for this interval of the experiment was 6.6 x 10^{-2} mg O_2/day/g.

3.2.2. *Effect of temperature.* The purpose of this experiment was to investigate the effect of temperature on the rate of oxygen uptake. This run was extended over a period of 20 days at a temperature of 5°C. Sample 2 (TABLE 1) was used and the sample size was 0.67 g of total solids per flask. Four duplicate samples were run and the data is presented in FIG. 2. The slope was calculated by drawing a line through the points in the time interval of 3-20 days. The rate calculated in this case is 2.9 x 10^{-2} mg O_2/day/g. Thus the rate of oxidation at 5°C (after 3 days) is about one half of the rate obtained at 21°C. In other respects the curve shows the same general characteristics as the one at a higher temperature.

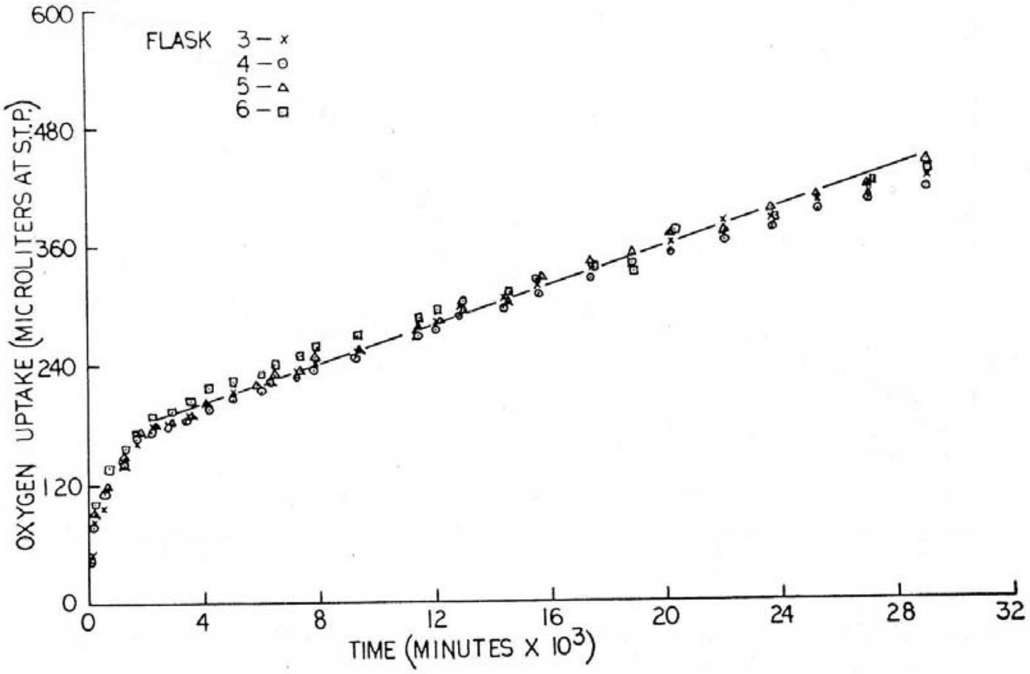


Fig. 2. Oxygenation of lake sediment at 5°C. Total solids per flask: 0.67 g, Sample 2.

3.2.3. Effect of sample size. This experiment has a two-fold purpose: (1) to observe the influence of sample size in the flasks, and (2) to investigate the influence of temperature change on the oxidation rate of a particular set of samples. Sample 2 (TABLE 1) was used for this experiment. Two of the sample aliquots consisted of 0.58 g of total solids per flask, while the remaining two aliquots consisted of 1.15 g of total solids per flask or twice as much. The run was begun at a temperature of 5°C; after continuing the run for 12.5 days, the temperature was raised to 21°C. The data are presented in FIG. 3. The rates of oxygen uptake, under these various conditions, were calculated over certain time intervals as had been done for the previous experiments. The rates calculated are presented in TABLE 2.

It should be noted that since the amount of sample is considered in the rate calculation, the final rates should have the same value for the different sample sizes if the rate of oxygen uptake is directly proportional to the sample size. From the data here considered, this appears to be the case for the comparison at 5°C, but does not hold true for the comparison at 21°C samples where the smaller sample has a significantly faster oxidation rate. It is observed that the long term rate of oxidation of the smaller sample approximately doubles with the increase in temperature. The long term rate of the larger sample increases also, but to a lesser extent. Another interesting observation is that although the temperature change took about 1 hr, the sample required approximately 4 days to achieve a linear oxygen uptake with time. The relatively slow adjustment of the rate of oxygen uptake upon a change in temperature possibly implicates microorganisms.

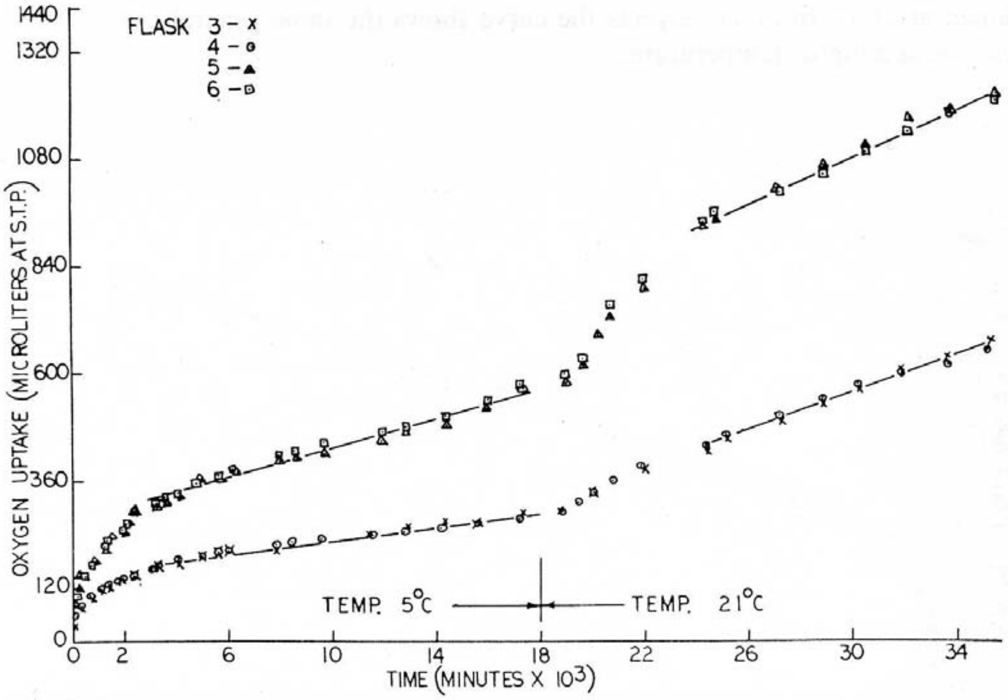


Fig. 3. Effect of temperature and sample size on the oxygenation of lake sediments. Temperature 5°C, 0–12.5 days; 21°C after 12.5 days. Total solids per flask, Sample 2. Flask 3 and 4: 0.58 g, and 5 and 6: 1.15g.

TABLE 2. EFFECT OF TEMPERATURE AND OF SAMPLE SIZE

Experimental conditions	Rate × 10^{-2} (mg O_2/day/g)
1.15 g sample at 5°C (interval of 2.5–12.5 days)	3.7
0.58 g sample at 5°C (interval of 2.5–12.5 days)	3.3
1.15 g sample at 21°C (interval of 17.5–24.5 days)	4.7
0.58 g sample at 21°C (interval of 17.5–24.5 days)	6.6

3.2.4. *Comparison of various sediment samples.* The purpose of this experiment was to make a comparison of the rate of oxygen uptake of sediments from different parts of Lake Mendota. Sediments were collected from four different locations in the lake. The runs were continued for a period of 7 days at a temperature of 22°C. Duplicates of each sample were run. The results are presented in FIGS. 4 and 5. The rates (after 2.5

days) were calculated as before from the slope of the line drawn through the points. Iron and sulfide determinations were also made on these samples. The data obtained in this experiment is summarized in TABLE 3. This data shows a tendency for the rate of oxygen uptake to be greater where the iron and sulfide concentrations are greater.

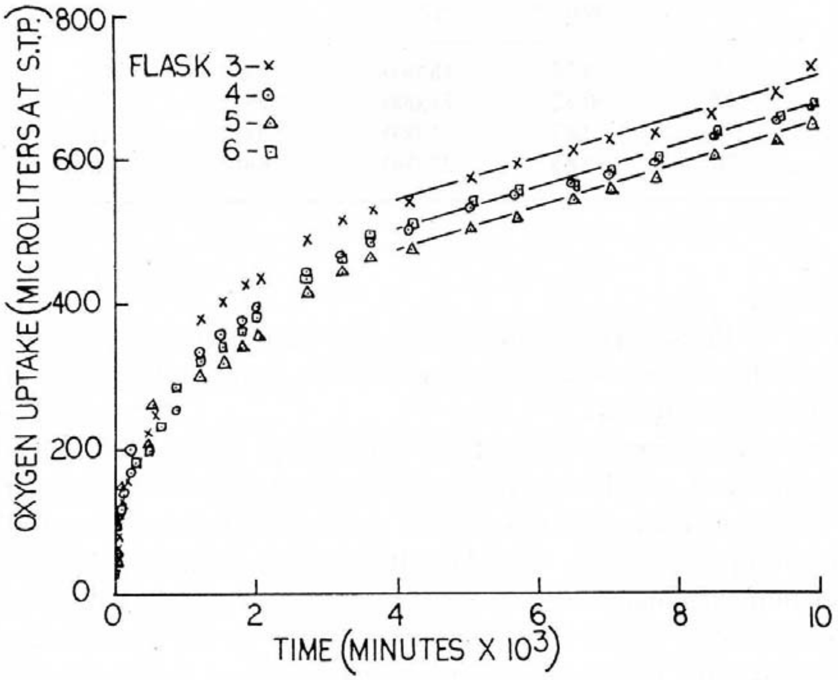


FIG. 4. Effect of various sediment samples on the rate of oxygenation at 22°C. Sample 4—Flasks 3 and 5, 0.82 g/flask. Sample 6—Flasks 4 and 6, 0.67 g/flask. Original depth of Sample 4, 58 ft and Sample 6, 70ft.

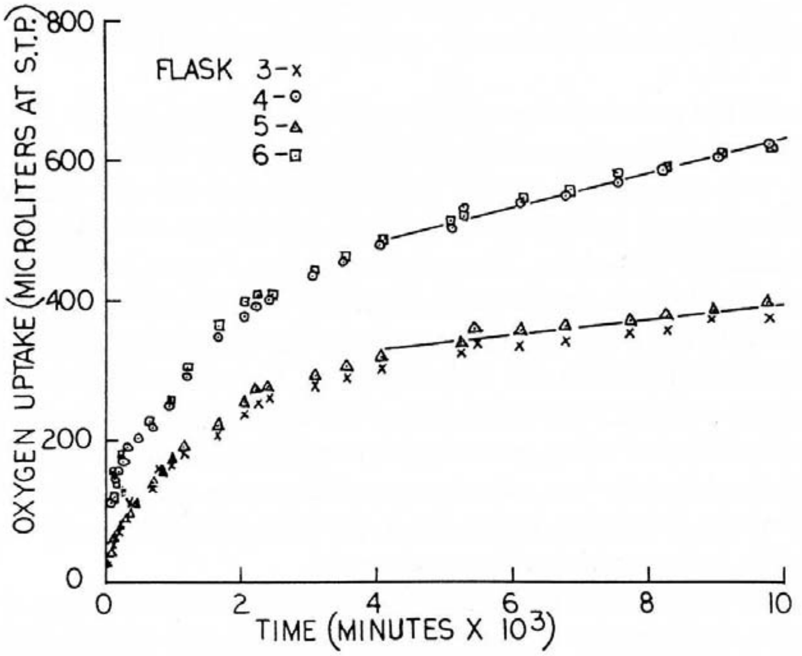


FIG. 5. Effect of various samples on the rate of oxygenation at 22°C. Sample 3, Flasks 3 and 5, 0.72 g/flask. Sample 5, Flasks 4 and 6, 0.66 g/flask. Original depth of Sample 3, 55 ft, and Sample 5, 70 ft.

TABLE 3. COMPARISON OF OXYGEN UPTAKE RATES OF VARIOUS SAMPLES

Initial depth of sediment sample (ft)	Sample size per flask (g total solids)	Iron (ppm)	Sulfide (ppm)	Rate of oxygen uptake × 10^2 after 2.5 days (mg/O_2/day/g)
55	0.72	18,000	1400	4.7
58	0.82	21,000	2600	7.6
70	0.67	23,000	2700	9.1
70	0.66	23,000	3300	8.0

3.3. *Other studies*

In addition to those reported above, studies were conducted on several related topics. The results of these studies are presented in detail by GARDNER (1964). These studies are summarized below.

Samples of lake sediment were acidified (10 ml conc. HC1 to 100 ml lake sediment) and boiled until lead sulfide was no longer detected on lead acetate test paper held above the boiling mixture. The sample was neutralized by NaOH and aliquots were used for oxygen uptake studies. The pH of the samples was maintained at 8.3 by adding solid calcium carbonate to the Warburg flasks. The oxygen uptake study showed that the same general shape of curve was obtained as for the untreated sediment samples. However, the linear oxygen uptake was obtained in one day and the rate of oxygen uptake in the linear part was about 10 times slower than the rates obtained for the untreated samples. The acid pretreatment of the sample would volatize all of the sulfide except that associated with pyritic minerals since pyrite is not soluble in HC1 (VALLENTYNE, 1963). The results of this experiment strongly point to the presence of pyritic minerals and that these minerals account for part of the oxygen demand of the sediments.

Since some of the iron sulfide minerals are ferromagnetic, a study was initiated on the oxygenation of magnetic particles collected from lake sediments. A large permanent magnet was attached to a rope and dragged through the sediments of Lake Mendota. The magnetic particles were washed and placed in a Warburg flask containing solid calcium carbonate. The oxygen uptake of these particles was found to proceed at a zero order rate similar to that obtained in the studies of the untreated lake samples. The relative rates of the oxygenation of the magnetic particles as compared to the untreated sediment in the linear part of the curve indicate that magnetic particles probably account for a small part of the oxygen demand of the sediment.

Studies on the effect of using pure oxygen in place of air in the Warburg flask and manometer showed that the rate of oxygen uptake was the same whether air or oxygen was used during the linear part of the curve. However, the initial rate of the first two days appeared to be faster when oxygen was used.

Studies on the oxygenation of $CaCO_3$ buffered sodium sulfide, and of freshly precipitated ferrous sulfide show that ferrous sulfide reacts with oxygen rapidly while the sodium sulfide reacts at a slower rate. Both of these compounds exert their oxygen demand in a relatively short time compared to the long term slow uptake of oxygen by the lake sediments.

4. DISCUSSION

The data obtained in this investigation show that oxygen uptake by Lake Mendota sediments is characterized by a one-to-three day period of rapid oxygen reduction followed by a period of several months of slow oxygen uptake. The long term oxygen uptake was found to be dependent on temperature and amount of sediment sample and independent of oxygen concentration.

In consideration of the total oxygen demand exerted by the sediments, it is of interest to calculate the stoichiometric amount of oxygen that would be theoretically consumed by the amounts of iron and sulfide determined analytically in the sediments. Sample 1 (Iron 17,000 ppm, sulfide 2300 ppm, sample size 0.56 g) would have a theoretical oxygen demand of 3.9 mg O_2. This calculation is based on the assumption that the iron exists in the sediment as Fe^{+II} and that the iron and sulfide are oxidized to Fe^{+III} and S^{+VI}. The experimental amount of oxygen uptake over the length of the run (45 days) was about 1.9 mg O_2 or about one-half of the theoretical value. At the time the run was stopped, the oxygen was still being taken up at a significant and steady rate. The theoretical demand from the iron and sulfide in the sediments could be greater or smaller than that calculated. Pyrite, thought to be one of the forms of iron sulfide in the sediments, tends to be insoluble in some acids. Since hydrochloric acid and sulfuric acid were the agents used to liberate the iron and sulfide in the respective chemical determinations, the quantitative values obtained for these elements were probably somewhat low. Another possibility for some error in the theoretical calculations is that the initial and final oxidation states assumed for sulfur may not be the actual oxidation states. Reduced sulfur possibly exists in the sediments in forms other than S^{-II}, such as polysulfides in which sulfur has an oxidation state of minus one. Likewise the sulfide may not be oxidized completely to sulfate, but may be stable as elemental sulfur (ZOBELL, 1963). The fact that all of the sulfide is not precipitated as iron sulfide is demonstrated by the sulfide concentration of 1.5 mg/l. which was found in the anaerobic water overlying the sediments.

The measured oxygen uptake may be low due to the 10-min temperature equilibration period prior to reading the manometer. Based on the shape of the oxygen uptake curve, the initial phase of the reaction shows a steep slope and, therefore, appreciable oxygen demand could be exerted in a short period of time. The studies on the oxidation of ferrous sulfide by dissolved oxygen show that the majority of the theoretical oxygen demand is exerted in the 10-min equilibration period. Therefore, an appreciable oxygen demand may be exerted by easily oxidizable compounds such as freshly precipitated ferrous sulfide and ferrous carbonate. However, the slope of the oxygen uptake curve shows that the lake sediments contain compounds that exert an appreciable oxygen demand over a long period of time.

The results of this investigation do not yield definitive information of the mechanism of oxygen reduction by lake sediments. However, this study does point to several mechanisms that deserve further investigation. The oxygen consumed during the first few days is most probably due to the reaction of oxygen with easily oxidizable species such as ferrous carbonate, ferrous sulfide and other unidentified components. However, studies on the rate of oxidation of ferrous sulfide under similar conditions have shown that the reaction is completed in a few minutes. Therefore, the unidentified compounds most probably account for the oxygen demand in the first phase of the reaction. It is impossible to rule out biochemical reactions since the reaction system was not sterile. However, since the sediments were stored in the absence of oxygen at 1°C prior to study, it is reasonable to expect that a considerable lag should be evident under the conditions of this investigation. The oxygen uptake during the initial phase of the reaction shows no evidence of a lag phase, and, therefore, biochemical reactions are probably of minor significance during this period. However, the slow uptake following the first two-to-three days of the run may be due to chemical and/or biochemical reactions. There is no doubt that some of the oxygen consumed is due to the biochemical oxidation of organic matter present in the sediment. It is impossible to estimate the relative role of biochemical and chemical reactions without further study. Previous studies (ZOBELL, 1963; BERNER, 1964) have shown that the aqueous environmental chemistry of sulfur compounds is an extremely complex system that will require much additional study before it is understood. However, it is generally accepted that the formation of sulfide in the hypolimnion of lakes results in the precipitation of ferrous sulfide. The ferrous sulfide will through diagenetic aging form pyritic compounds, some of which are resistant to oxidation in an oxic environment. It is reasonable to propose that the slow uptake of oxygen found in this study is the result of the oxidation of pyritic compounds.

TEAL and KANWISHER (1961) found that well-stirred anaerobic mud from a salt marsh consumed oxygen at a rate of 60-1000 mm^3/hr/ml. They characterized the reaction as initially rapid, followed by gradually declining rate. They proposed that O_2 consumption during the initial phase was predominantly chemical while the slower reaction was due in part to biochemical mechanism. These studies were restricted to a few hours and, therefore, it is not known whether or not these muds would show the same long term slow uptake found in this investigation.

4.1. *Limnological implications*

The results of this study present some interesting implications concerning the deoxygenation of the hypolimnion of some lakes. The deoxygenation of the hypolimnion of a lake can result from the biochemical oxygen demand of the dead planktonic organisms and other organic matter as it settles through the water and accumulates in the sediments, and from chemical-biochemical oxygen demand of reduced inorganic compounds in the sediments. The relative importance of each of these processes has been discussed for several lakes by HUTCHINSON (1957). In the case of Lake Mendota, previous studies on the physical-chemical characteristics of the sediments, lake currents, and geology yield further insight on the relative importance of each of these processes. LEE (1962) summarized these studies, and reported that the sediments of Lake Mendota are composed of 1-14 in. of a flocculant black sludge. This sludge overlies a grey marl. Wind induced circulation of the epilimnion results in hypolimnetic currents of sufficient magnitude to cause movement and mixing of the sludge. The flocculant nature of the iron-sulfide rich sediment is further demonstrated by scuba divers who have found that swimming over the sludge results in the formation of large amounts of highly turbid water. There can be little doubt that the amounts of reduced iron and sulfur compounds in the sediment result in a greater rate of deoxygenation of the hypolimnion than would be predicted based on the productivity of Lake Mendota.

The results of this study raise questions about the relationship between lake photosynthetic productivity and deoxygenation of the hypolimnion. ANDERSON (1961) has shown that Lake Washington is becoming eutrophic as an apparent result of discharge of sewage effluent to the lake. An increasing rate of deoxygenation of the hypolimnion was one of the criteria of an increasing degree of eutrophication. The relationship between the photosynthetic productivity and rate of deoxygenation of the hypolimnion will depend on the chemical composition and physical characteristics of the sediments.

Those lakes that have reduced iron-sulfur rich sediments, such as Lake Mendota, would tend to lose hypolimnetic oxygen at a greater rate than those lakes that are poor in these compounds even though they both have the same photosynthetic productivity. This study has shown that this relationship is dependent not only on the amount of ferrous iron and sulfide species, but also on their types of mineralogy since an appreciable part of the theoretical oxygen demand due to these compounds may be exerted at a very slow rate.

5. SUMMARY AND CONCLUSIONS

This study has shown Lake Mendota surface sediments to have an oxygen demand in excess of 8 mg O_2/g of dry sediment. Approximately one-half of the oxygen demand is exerted in a 3-day period, while the remaining oxygen demand is exerted at essentially a constant rate over a period of months. The rate and amount of oxygen demand appear to be related to the oxidation of reduced iron and sulfur. However, appreciable amounts of the ferrous iron and sulfide are resistant to oxidation, which suggests that these elements may be present as pyritic compounds. This and other studies have shown that an appreciable part of the deoxygenation of hypolimnetic waters in Lake Mendota may be due to the iron-sulfide rich flocculant sediment. Further chemical and biochemical studies on various iron sulfide compounds will be necessary to elucidate the mechanism of oxygen reduction by lake sediments.

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