"NEW TECHNIQUES FOR DETERMINING THE STABILITY OF MANGANESE SLUDGES IN NEUTRALIZED ACID DRAINAGE"

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ABSTRACT

Differentiation and quantification of Mn-oxides species in soils and geologic systems is accomplished by selective dissolution in various solvents. The approach is lengthy and reveals little about the stability of the various Mn-oxide mineral species. In this study, dissolution kinetics and activation energies (Ea) of pure manganese oxide (reagent grade MnO₂), Ward's manganite (MnOOH) and Ward's pyrolusite (b-MnO₂) were determined through the use of an isothermal automanometric apparatus. This method is based on pseudo-first-order kinetics of oxygen gas (O₂) evolution by reducing the Mn⁴⁺and/or Mn³⁺to Mn²⁺ The manganese oxide reduction is carried out employing a solution mixture of 2.4% HO₂ and 9.7% concentrated H₂SO₄ on a volume basis. It is shown that the activation energies (Ea) are 8,702 cal/mole for MnO₂, 7,013 cal/mole for pyrolusite and 10,729 cal/molefor manganite. The most stable manganese oxide species is the Mn(III) (manganite). The study also demonstrates that the automanometric isothermal apparatus can be employed to quantify and differentiate various Mn-oxide species. The technique is also highly discriminatory to iron-oxides and organic components.

INTRODUCTION

The chemistry of manganese in soil and geologic systems is complex because three oxidation states are involved: Mn (II), Mn (III), and Mn (IV). Manganese forms hydrated oxides with mixed valency status. Qualitative and quantitative determination of manganese oxides in soils and geologic systems is essential in order to elucidate pedogenic processes and predict manganese release to natural water systems.

Work has been done to characterize the thermodynamics of manganese (Bricker, 1965) and to evaluate the presence and reactions of manganese in flooded soils (Ponnampenima et al., 1969; Patrick and Turner, 1968; Gotoh and Patrick, 1972) and in non-flooded soils (Redden and Porter, 1962; Taylor et al., 1964 Taylor and McKenzie, 1965; Taylor, 1968; McKenzie, 1970; Bohn, 1970; Lindsay, 1979; Taira et al., 1981; Uzochukwn and Dixon, 1986).

Additionally, research has been carried out to develop techniques that would allow one to quantify manganese in soils and sediments (Shuman, 1982; Chao 1972) as well as differentiate and quantify various manganese oxide species in geologic material (Tokashiki et al. 1986). These techniques are based on selective chemical dissolution.

Recently, Sajwan et al. (1988) have demonstrated the use of an automanometric isothermal apparatus for studying acid-dissolution of carbonates through the evolution of CO_2 gas. In this study we employed the same apparatus to evaluate reduction of Mn^{4+} and/or Mn^{3+} to Mn^{2+} through the evolution of oxygen gas (O_2).

THEORY

The manometric analysis of Mn-oxide minerals is based on two reactions. The first reaction involves the reduction of Mn^{4+} and/or Mn^{3+} to Mn^{2+} . The second reaction involves the oxidation of O^{2-} so that oxygen gas (O_2) is evolved. These reactions are shown below: In the case of Mn^{4+} such as manganese dioxide (MnO_2)

$Mn0_2$ (solid) = $Mn^{2+} + 0_2$ (gas) + 2e	[1]
$H_2O_2 + 2H + 2e^- = 2H_2O_1$	[2]
The overall reaction for reactions [1] and $MnO_2(solid) + H_2O_2 + 2H^+ = Mn^{2+} + O_2$ The AG* of reaction [3] is -28.01 kcal/mole.	[2] is (gas) ^{+ 2H} 2 ⁰ [3]
In the case of Mn^{3+} for a mineral such as $Mn00H = Mn^{2+} + 1/20_2 + 2e^{-+}$	manganite (Mn00H) 1/2H ₂ O ₂ [4]
and $H_2 0_2 + 2H^+ + 2e^- = 2H_2 0$	[5]
The overall reaction for reactions [4] and $Mn00H + 1/2H_2O_2 + 2H^+ = Mn^{2+} + 1/2O_2$	$_{2}^{[5] 1S}$ [6]

The AGO of reaction [6] is -19.84 kcal/mole. Reactions [3] and [6] exhibit negative AGO and therefore the release of oxygen gas (O_2) will be considered a spontaneous process. However, the kinetics of these two reactions would appear to differ possibly because the two manganese species (MnO₂ and MnOOH) are also expected to have different activations energies (Ea) (Daniels and Alberty, 1975).

The release of O_2 (gas) as shown in reactions [3] and [6] is expected to follow pseudo-first order kinetics when the quantity of H_2O_2 , and H^+ introduced in the reaction vessel is in excess of what is need to decompose the quantity of MnO_2 or MnOOH added (Evangelou, 1981; Evangelou et al., 1984). Limitations of such pseudo-first-order reactions have been discussed by Turner and Skinner (1959). The principal limitations are: 1) particle size cannot be greater than 0.5 mm in diameter and 2) reaction deviates from first-order when more than 50% of the particles have been decomposed. Both limitations have been considered in this study and appropriate measures have been taken (Sajwan et al. 1988).

MATERIALS AND METHODS

Apparatus The apparatus employed for isothermal kinetic dissolution of oxides is that

designed by Sajwan et al. (1988) which is a further modification of the apparatus employed by Evangelou(1981) and Evangelou et al. (1984). A brief description of the overall apparatus will be given for convenience. An air-tight reaction vessel is connected through a 0.6 cm internal diameter pressure resistant rubber hose to a pressure transducer assembly (Dalec manometer model 280E-RHL S/N-Setra Systems, Inc., Action, Massachusetts 01720). The pressure transducer assembly is connected to a strip chart recorder. The major modification of the Evangelou (1981) and Evangelou et al. (1984) apparatus was in the reaction vessel which is shown in Fig. 1. It is made of Pyrex glass and consists of two chambers. The outer chamber serves as a water jacket for the inner chamber (reaction vessel). The outer chamber is connected through a water inlet and water outlet to a cooling-heating system (Tempryte RRS-0850-B-Bay Votrex, Fremont, California) by a 1-cm internal diameter tygon hose. The reaction vessel is closed by a bell shaped glass cap with two openings. one opening serves as a connection to the transducer and the second opening is equipped with a stopcock. It serves as a means to equalize the pressure in the inner chamber (reaction chamber) with the atmosphere. The bell shaped hollow glass cap is fastened to the lower portion of the reaction vessel with a horseshoe shaped 3-screw fastener. To make the system air-tight between the two reaction vessel components, a rubber ring of 0.5 cm thickness is inserted.

A magnetic stirring rod, cylindrical in shape (diameter, 0.9 cm; length, 3.5 cm) is placed inside at the center of the reaction vessel bottom. This particular stirring rod was selected by trial and error. The objective was to find a stirring rod that is effective in mixing and quickly degassing the solution in the reaction chamber. The entire reaction vessel is placed on top of a magnetic stirring motor (Nuova II stirrer, Model No. S18525 - Thermoloyne Corporation, Dubuque, Iowa). When in operation, the stirrer switch is set to the maximum (this is setting 10 on the switch dial).

In order to analyze a sample, a measured weight is placed in a parafilm cup which is placed in a metallic cup (diameter, 3 cm; height, 0.6 cm). The cup assembly is placed in the cap of the reaction vessel and held with a small horseshoe magnet. The magnet is secured with a rubber band. one hundred milliliters of 2.4% H_2O_2 +9.7% concentrated H_2SO_4 is placed in the reaction chamber and is given enough time (commonly 5 to 10 minutes) to reach the desired temperature. Then, the bell shaped hollow cap, with the sample attached, is fastened to the lower part of the reaction vessel. The stirrer is set to the maximum speed, the reaction chamber's pressure is equilibrated with the atmosphere and finally the magnet is rotated 1800 to release the parafilm cup and the sample into the acid. The pressure created by liberation of O_2 is recorded continuously by the strip chart recorder. When the pressure ceases to increase, the analysis is terminated. The apparatus is standardized by analysis of several known quantities of reagent grade MnO_2 , at temperatures of $14^{0}C$, $21^{0}C$, and $30^{0}C$. The composition of the manganese reducing solution introduced in the reacting chamber was selected through trial and error by fulfilling certain prerequisites. These prerequisites were: 1. The solution mixture should be insensitive to temperature (vapor pressure is kept to a minimum), 2. The solution mixture should be insensitive to rapid stirring in the presence of an innert solid (i.e. sand) with respect to any gas evolution and 3. The solution mixture must be able to discriminate between manganese-oxide minerals composed of Mn^{4+} and Mn^{3+} as well as to iron-oxides and any type of organic components.

Sample Preparation - - Oxide minerals consisting of manganese dioxide (Fisher Scientific Company), pyrolusite and manganite (Ward's Earth Science) were employed in this study. The

samples were ground and passed through a 140 mesh sieve (Turner and Skinner, 1959; Skinner et al., 1959). All the samples were run in duplicate at three different temperatures (14^0 , 21^0 and 30^0 C).

RESULTS AND DISCUSSION

Sample characterization -- Sample characterization was carried out by FT-IR spectroscopy (Nicolet 5SX) and x-ray diffaction (General Electric x-ray diffraction). The results of these analyses are shown in Figure 2 and Figure 3. Manganese content of these samples was also determined by first dissolving the samples in H_2O_2 and acids such as HNO_3 , H_2SO_4 , HF and $HC1O_4$ through the procedure described by Fiskell (1965). Manganese determination was then carried out by atomic absorption. The results are presented in Table 1.

The data in Table 2 show regression equations relating milligrams of reagent grade MnO_2 to arbitrary units of pressure generated by the evolution of O_2 gas during manganese dioxide (MnO_2) decomposition. Note that the regression equation changes as the temperature changes due to the expandability of the O_2 gas as the temperature increases. These regression equations were employed to change arbitrary units of pressure to MnO_2 equivalent weight of pyrolusite (b $-MnO_2$) and manganite (MnOOH). All the data involving O_2 gas evolution with respect to time were plotted as first-order plots. The data employed for these plots were limited to 50% of sample's decomposition (Turner, 1959; Turner and Skinner, 1959). The slope of the linear regression was taken to represent the first-order rate constant (k). Examples of these type of plots are shown in Figure 4.

The data in Figure 4 show that there is small difference in the and pyrolusitekinetics of decomposition between reagent grade $MnO_2(b - MnO_2)$. Both of these minerals are composed of Mn^{4+} The major difference in these kinetic decompositions shown in Figure 4 is that between manganite (MnOOH), which is composed of Mn^{3+} and the two other oxide species which are composed of Mn^{4+} . Thus, this technique appears to effectively discriminate manganese-oxide species composed of Mn^{4+} from those composed of Mn^{3+}

In order to test further the validity of the observations made from the data in Figure 4 a number of iron oxides (hematite, goethite, magnetite) were tested. None of these oxides appear to be involved in any form of gas (O_2) evolution. Additionally, we tested various types of organics for the purpose of testing their potential to oxidize and release CO_2 gas. These organics included peat, glycine, albumin, dextrose and sucrose. No gas evolution was observed.

The values of the first-order rate constant (k) at the three different temperatures 14^{0} C, 21^{0} C and 30^{0} C (for example fig. 5) were plotted as lnk versus 1/T (T is in unit Kelvin). From these plots the Arrhenius activation energy Ea is calculated from the equation (Daniels and Alberty, 1975)

lnk = (-Ea/1.987)(I/T) + ln A,

where A is the pre-exponential factor. Regression equations and Ea values are shown in Table 3. In order to verify that the Ea values shown in Table 3 are not influenced by the size of the sample, we generated Ea values by running three different size samples (200 mg, 150 mg and 100 mg). The deviation from the mean Ea value for the three sample weights was in the range of 9% to 12%.

The data in Table 3 clearly show that activation energies for manganite (MnOOH) are the highest (10,729 cal/mole) while those of repent grade MnO_2 and pyrolusite are the lowest. Thus, reduction of Mn^{3+} contained in the mineral manganite to Mn^{2+} is more temperature dependent that reduction of Mn^{4+} contained in the reagent grade MnO_2 and pyrolusite (b- MnO_2) to Mn^{2+} . This information signifies that the technique quickly establishes that Mn^{3+} - oxide species are more stable in nature than Mn^{4+} -oxide species. This is consistent with what has previously been reported in the literature (Garrels and Christ, 1965).

The information presented in this paper and the technique and apparatus employed to generate this information have important practical utility. The technique can be used to rapidly, effectively and cheaply establish the type of Mn-oxide species in a geologic setting. Such information can be used to delineate pedogenic processes in soils rich in manganese. Recently manganese has become a big environmental issue in coal mining environments where it is part of 2 the geologic strata that upon exposure to the atmosphere releases Mn + in water. The technique reported here allows one to establish the quantity of manganese-oxides as well as their chemical stability and consequently the possible release of this manganese to natural water systems.

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	Mn content based on chemical formula	Recovered Mn	
sample I.D.	8	8	
Manganese			
dioxide (MnO ₂)	63.19	63.10	
Pyrolūsite (<u>\$</u> MnO ₂)	63.19	44.96	
Manganite (MnOOH)	62.47	46.33	

Table 1. Manganese content of various manganese oxide samples.

Table 2. Regression equations relating milligrams of pure MnO2 to arbitrary units of pressure at various temperatures.

°c	MnO2(mg) vs. Arbitrary press	sure r ²
30	Y = 2.34x - 4.58	0.999
21	Y = 2.45x + 3.79	0.999
14	Y = 2.50x + 8.71	0.999

 $Y = mg \text{ of } MnO_2$ x = arbitrary strip-chart paper units denoting pressure.

Table 3.	Regression equations of 1/T versus Lnk, correlation
	coefficient and activation energies (Ea) of acid dissolution
	of manganese dioxide, pyrolusite and manganite.

sample I.D.	Regression equation	r ²	Activation Energies (Ea)cal/mole
Manganese dioxide (MnO ₂)	Y = -4379x + 14.53	0.979	8,702
(<u>BMnO</u> 2)	Y = -3529x + 12.53	0.999	7,013
(MnOOH)	Y = -5400x + 13.64	0.999	10,729



Figure 1. Schematic of the isothermal automanometric apparatus.



Figure 2. Infrared spectra of the three manganese-oxide species.



Degrees 20

3. 1

Figure 3. X-ray diffractograms of the three manganese-oxide species.



Pseudo-first-order plots of dissolution of three

manganese oxide species at 21°C employing $H_2SO_4-H_2O_2$ solution.



5. Pseudo-first order plot of dissolution of manganite at

three different temperatures employing $H_2SO_4-H_2O_2$ solution.