EFFECTS OF KCl ON SOLUBILITY AND BIOAVAILABILITY OF Mn IN SOIL AND SOME REACTIONS OF BIRNESSITE IN THE PRESENCE OF SOME Mn COMPOUNDS

by

Shihua Tu

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A Thesis submitted to the Faculty of Graduate Studies of the University of Manitoba
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ABSTRACT

Laboratory and growth chamber experiments were conducted to examine different aspects of the solubility and bioavailability of Mn in soils as affected by KCl and some reactions of birnessite with Mn compounds. Extraction studies were conducted to compare KCl to several other K-salts such as, KBr, KI, K_2SO_4, KNO_3, KH_2PO_4, K_2HPO_4 and K_2CO_3 in their ability to extract Mn from soils and/or reduce Mn(IV) to Mn(II). Growth chamber experiments were conducted to determine if KCl application alone or in combination with Mn fertilizer would increase the solubility and bioavailability of indigenous and applied Mn in soil. KCl was also compared to NaCl, K_2SO_4, K_2CO_3 and $MnSO_4$ in its ability to enhance Mn uptake by crops. The mechanisms of KCl-enhanced Mn uptake by crops were investigated using ion exchange resins and relatively long term soil incubation studies. An adsorption study, using several clay minerals and oxides of Al, Fe and Mn, was carried out to determine which components of soil are responsible for retaining and releasing Mn that is readily available to plants. A desorption study was conducted to investigate the nature of Mn^{2+} after adsorption by birnessite. The effects of Mn^{2+} concentration and pH on the transformations of birnessite were studied.

The results of the extraction studies showed that the amount of Mn extracted by KCl was similar to K_2SO_4, KNO_3, and KBr. The K-salts, possessing a strong reducing power (eg. KI) or able to furnish H^+ and reduce solution pH to a substantial extent (eg. KH_2PO_4), extracted the highest amount of Mn from soils, whereas those tending to raise

solution pH such as K_2HPO_4 and K_2CO_3 extracted the least amounts of Mn. KCl was not able to reduce Mn oxides at ordinary soil pHs.

The growth chamber studies showed that KCl or NaCl, when applied in sufficient amounts, was as effective as $MnSO_4$ in increasing Mn uptake by wheat. When $MnSO_4$ was applied with KCl, the amount of Mn uptake by wheat was greater than either application of $MnSO_4$ or KCl alone. The order of different salts in increasing Mn uptake by wheat was KCl $> K_2SO_4 >> K_2CO_3$. The mechanism responsible for the improved bioavailability of Mn by KCl was due to its ability to solubilize native and/or added fertilizer Mn by forming anionic complexes of Mn and Cl.

Among the soil clay minerals and various sesquioxides of Al and Fe, the 2:1 clay minerals were the major adsorbent for Mn^{2+}. Birnessite (MnO_2), however, was shown to have the highest capacity for retaining Mn^{2+} from a $MnSO_4$ solution among the minerals tested. The reaction of Mn^{2+} with birnessite was not, as suggested by other workers, a simple specific adsorption or surface induced hydrolysis of Mn^{2+}, neither was it merely a surface-catalyzed oxidation of Mn^{2+}. The reaction was a combination of non-specific and specific adsorption followed by mineralogical transformation of the birnessite structures. The reaction completely transformed birnessite from a relatively unstable and poorly crystallized mineral into an array of more stable and highly crystallized minerals. The specific Mn minerals formed were governed by the pH of the reaction and the rate of the transformation reaction was determined by Mn^{2+} concentration.

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Application of KCl fertilizers to soils has been shown to increase Mn uptake by crops (York *et al.*, 1954; Foy, 1964; Jackson *et al.*, 1966; Westermann *et al.*, 1971; Cheng, 1982) and thus offers a way of improving Mn nutrition and depressing plant diseases related to Mn deficiency. The beneficial effect of Cl on Mn nutrition has drawn great interest from soil scientists and plant pathologists. On some Mn deficient soils, as soil scientists in China and elsewhere have observed in recent years, KCl application can, at least partly, overcome Mn deficiency. On Mn abundant soils, especially when acidic, Cl fertilization or irrigation with saline waters has been shown to increase Mn concentration to very high levels causing Mn toxicity (Khattak and Jarrell, 1989).

Several hypotheses have been proposed for increases in uptake of Mn by crops treated with chloride, including the salt effect on solubility of Mn compounds, salt-induced pH depressions, reduction of Mn oxides by Cl^-, and $MnCl^+$ complex formation. However, evidence for specific mechanisms is lacking in the literature and thus none of the reports to date have provided a complete explanation for the phenomenon. Moreover, it is unclear whether this Cl effect is caused chemically or biochemically, i.e., in soils or in plants. Therefore, further studies are needed to examine the mechanisms of Cl-Mn interaction.

Birnessite is a common soil Mn mineral and thus its reaction in the soil with solution Mn and Cl is important in understanding Mn bioavailability. Birnessite has a high capacity to adsorb Mn^{2+}. The exchangeability of the Mn after adsorption, however, is

reduced with time. It was not clear whether this Mn is specifically adsorbed or oxidized on the surface (Pankow and Morgan, 1981) or incorporated into the structure of the mineral (Krauskopf, 1972; McKenzie, 1989). It is therefore of great importance to understand the nature of the reaction and the fate of the Mn adsorbed on birnessite chemically, agronomically, and mineralogically.

Due to the agronomical importance of KCl fertilization on Mn nutrition, especially for those areas of Mn deficiency, I was chosen by the Soil and Fertilizer Institute, Sichuan Academy of Agricultural Sciences, China, to carry out this research project.

The objectives of this study were to: (1) examine the effect of pH, ionic strength and different cations and anions on the release of Mn from different soils; (2) determine if KCl application alone or in combination with Mn fertilizer would increase the bioavailability of indigenous and applied Mn in soil; (3) investigate the forms of complexes of Mn and Cl in aqueous solutions; (4) investigate soil components that are responsible for adsorption and release of Mn readily available to plants and the fate of Mn after adsorption by a Mn oxide, birnessite; and (5) study the effect of Mn concentration and pH on mineralogical transformations of birnessite.

1 LITERATURE REVIEW

1.1 INTRODUCTION

Manganese is an essential micronutrient in physiological functions of plants. Mn plays a unique role in plant nutrition by virtue of its redox sensitivity that involves it in a number of oxidation-reduction reactions and acts as an activator or a cofactor of enzymes that catalyze numerous biochemical reactions (Krauskopf, 1972). The chemistry of Mn is complicated due to its variable valences. Its oxidative states vary from Mn^{2-} to Mn^{7+} corresponding to its ability to accept electrons through empty $3d$ orbitals and to lose part or all of its $4s$ and $3d$ electrons. The common transitions in valence change can be observed as: $Mn^{2+} \rightleftarrows Mn^{3+} \rightleftarrows Mn^{4+} \rightleftarrows Mn^{5+} \rightleftarrows Mn^{6+} \rightleftarrows Mn^{7+}$, occurring in a wide variety of inorganic and metal-organo complexes. In nature, however, Mn exists only in the $2+$, $3+$ and $4+$ states (Bricker, 1965). In soils, the oxidized forms (Mn^{3+} and Mn^{4+}) predominate under aerobic conditions, whereas the reduced form (Mn^{2+}) predominates under anaerobic conditions. The Mn^{2+} can be present in solution, adsorbed on solid phases, precipitated in inorganic salts, and/or incorporated into the crystal structure of soil clay minerals and a number of oxides. The oxidized forms, especially Mn^{4+}, consist of a variety of Mn oxides and hydroxides. The solution and exchangeable Mn^{2+} are the major sources of Mn available to plants, whereas other forms of Mn are much less available under aerobic conditions.

1.2 CHEMISTRY OF MANGANESE IN SOILS

1.2.1 Forms of Mn in soils

In soils the concentration of Mn is found over a wide range, from values < 20 mg

kg^{-1} to values >6,000 mg kg^{-1}, with an average of about 600 mg kg^{-1}. In aerated soils, Mn usually exists as exchangeable Mn, as water-soluble Mn, as both water-soluble and insoluble organically-bound Mn, as easily reducible Mn and as various oxides of Mn (Tisdale *et al.*, 1985). Divalent Mn in solution is in equilibrium with exchangeable Mn and both are important forms readily available to plants. The Mn present within the structural lattice of crystalline minerals is essentially unavailable except in terms of geochemical time as a sequence of natural mineral weathering. Between the availability extremes mentioned above are other potentially available forms of Mn (Gambrell and Patrick, 1982). Using a special sequential chemical fractionation procedure, Warden and Reisenauer (1991) divided soil Mn into readily soluble Mn, weakly adsorbed Mn, specifically-adsorbed Mn, carbonate-bound Mn, and oxide Mn. They further explained that readily soluble Mn includes that in solution and the easily exchangeable fraction; adsorbed forms of soil Mn are those held on soil surfaces by forces ranging from weak electrostatic to strong covalent bonds and, although not principal forms of soil Mn, they influence plant availability as they are in pseudoequilibrium with the readily soluble form; carbonate-bound Mn includes that chemisorbed or coprecipitated with calcite and related carbonate minerals; and oxide Mn consists of diverse Mn oxides. Unlike other methods, e.g. the methods developed by Gambrell and patrick (1982), the above fractionation scheme includes an evaluation of carbonate-bound Mn, avoids the use of extractants that reduce oxide-Mn and differentiates between weakly and specifically-adsorbed Mn.

1.2.2 Manganese minerals in soils

Among the wide variety of manganese minerals in soils, the oxides and hydroxides of Mn are by far the most significant. Extensive reviews on manganese oxides and hydroxides have been made by McKenzie (1980, 1989), Chukhrov et $al.$ (1980), Taylor (1987) and Waychunas (1991). The oxides and hydroxides of Mn are characterized by their poor crystallinity, structural defects, domain intergrowths, cation vacancies, and solid solutions (Davis and Kent, 1990). They are generally modifications of MnO_2 in which substitution of Mn(II) or Mn(III) for Mn(IV) can produce over 150 variations with compositions ranging from $MnO_{1.2}$ to MnO_2 (Dubois, 1963). Among them, only pyrolusite and ramsdellite are true modifications of MnO_2 (Giovanoli, 1969; Giovanoli and Staehli, 1970); all others are nonstoichiometric, and may cover a relatively large range of compositions from Mn(II) to Mn(IV). Another notable feature of Mn mineral chemistry is the striking tunnel and layer structures found in these minerals (McKenzie, 1989). The tunnel structures are formed from single, double, or wide chains of MnO_6 octahedra, which are linked by sharing corners into a framework that encloses tunnels through the structures. These tunnel structures are occupied by large foreign cations and water molecules. The common Mn minerals of these structures include pyrolusite, ramsdellite, nsutite, hollandite, cryptomelane, coronadite, romanechite and todorokite, and those of layer structures are birnessite, vernadite, ranieite, buserite and lithiorphorite. Birnessite, vernadite, lithiorphorite, and hollandite are the most common crystalline Mn-oxide minerals in soils. The Mn minerals commonly comprise < 1% of the soil and occur as coatings on other soil particles, as deposits in cracks and veins, and as

impurities in Fe oxides and other soil constituents in nodules (Ross *et al.*, 1976). The individual crystallites are small with large surface areas. For example, birnessite was reported to possess N_2 accessible specific surface areas of 50 to 300 m^2 g^{-1} (Healy *et al.*, 1966; McKenzie, 1980).

Due to their oxidative-reductive properties and large surface areas, manganese minerals have two important functions in soils. They act as a supply of Mn for nutrition and, through oxidation-reduction reactions, their availability to plants can be reduced to deficient levels or increased to high levels that are toxic to plants. They also act as very good adsorbents for a number of divalent heavy metal ions (McKenzie, 1989).

Besides manganese oxides and hydroxides, a number of other manganese minerals also exist in nature, such as manganese carbonates and silicates. Manganese carbonates are of importance in calcareous soils in regulating Mn supply to plants.

1.2.3 Adsorption

Adsorption is a term used to describe surface reaction phenomena in which solutes in solution are taken up by the solids without alteration of the solid (Parks, 1990). This reaction includes both non-specific and specific adsorption and is pH and ionic strength dependent.

Adsorption of Mn^{2+} by layer silicates and humic substances

The amount of metal ion adsorbed by soil constituents is dependent on the type of soil components and whether or not it carries a fixed charge or consists of variable charge constituents (Schmitt and Sticher, 1991). Oxides of Fe, Al and Ti, aluminosilicate minerals without permanent charge, and soil organic matter possess *proton-bearing*

surface functional groups. Consequently, adsorption onto these solid phases is pH dependent (Davis and Kent, 1990). Several clay minerals and most Mn oxides develop a negative charge as a result of lattice substitutions and thus have *ion-bearing exchange sites* in addition to *proton-bearing surface functional groups.*

Like other cations, aqueous Mn^{2+} participates in ordinary ion exchange with cations held by electrostatic attraction near negatively charged surfaces of layer silicate minerals (Norvell, 1988). Mn^{2+} held by electrostatic force is in equilibrium with solution Mn^{2+} and readily available to plants. Though permanent charges do not change with pH, increased pH usually favors metal hydrolysis and leads to strong adsorption of some polyvalent metals. In the case of Mn, however, this mechanism is not likely to be of much importance because it hydrolyzes extensively only at pH values above 9 (Lindsay, 1979).

The adsorption of Mn^{2+} by soil organic matter appears to be of relatively low specificity (Norvell, 1988). Mn and many other cations are held by soil organic matter in exchangeable form. Kerrndorff and Schnitzer (1980) showed that Mn^{2+} was unable to compete effectively with several other metals (Co, Ni, Zn, Cd, Cu, Pb and Hg) for the binding sites on the surface of humic acids. Passioura and Leeper (1963) found little preference for Mn^{2+} over Ca^{2+} on colloidal organic materials when the cations were present at similar concentrations. Based on these observations Norvell (1988) attributed adsorption of Mn^{2+} by humic surfaces to electrostatic and weak outer sphere complexing. Thus, the amount of Mn held by organic colloidal matter is likely to be very small except in soils with appreciable amounts of organic matter.

Adsorption of Mn on carbonates

The mechanisms of Mn^{2+} adsorption on carbonates are uncertain. Specific adsorption of Mn^{2+} on calcite or coprecipitation with Ca^{2+} to form $(Mn,Ca)CO_3$ solid solutions has been proposed by McBride (1979) and Norvell (1988). At low concentrations, adsorption of Mn^{2+} is favored and can decrease Mn^{2+} concentrations below the solubility of $MnCO_3$ (McBride, 1979; Stumm and Morgan, 1981).

Adsorption of Mn^{2+} on oxides

Adsorption of Mn^{2+} and other polyvalent metal ions on oxide surfaces shows evidence of specific bonding or chemisorption and simple electrostatic attraction (Norvell, 1988). The specific adsorption of Mn^{2+} often occurs at pH values well below the point of zero charge (PZC) of the oxide surface in opposition to coulombic forces for which adsorption usually takes place at pH values above the PZC. The extent of nonspecific adsorption is mainly determined by the variable charges developed with increasing pH on the oxide surfaces, whereas specific adsorption correlates with the tendency of the metal to hydrolyze or form hydroxides (Kinniburgh and Jackson, 1981). However, if hydrolysis or hydroxide formation is directly involved, the reaction must be surface-promoted because metal adsorption often occurs well below the pH range where hydrolysis or hydroxide precipitation would occur in solution (James and Healy, 1972; Kinniburgh and Jackson, 1981). Although adsorption of Mn^{2+} by goethite and other oxides may occur below the PZC of the surface, Mn^{2+} is generally not adsorbed extensively at low pH and it is bound with lower preference than other divalent transition metals (Kinniburgh and Jackson, 1981; McKenzie, 1981), as was noted for humic substances. The relatively low

preference of the surfaces for Mn^{2+} correlates with its low tendency to hydrolyze and form hydroxides.

Adsorption of metal ions on Mn oxides

As has already been mentioned, the known oxides and hydroxides of Mn are numerous and diverse. Among them birnessite and a few other hydrous oxides such as vernadite appear to be the most abundant forms identified in soils. Mn oxides often have large specific surface areas because they have very fine particle size and may be present as coatings on other particles. Furthermore, Mn(IV) vacancies and substitution of Mn(II) and Mn(III) for Mn(IV) in the structure give rise to a permanent structural negative charge which is compensated by loosely bound cations that occupy a range of interstitial positions (Davis and Kent, 1990). These cations are exchangeable, as are some of the Mn(II) ions in the structure. It is clear that Mn oxides can exhibit a variety of types of adsorption sites.

Most work done to date on Mn oxides has concentrated on birnessite. Minerals in the birnessite group have a N_2 accessible interlayer surface with total specific areas of 50 to 300 m^2 g^{-1} (Healy *et al.*, 1966; McKenzie, 1980). The structural variability of the Mn oxides is reflected in the variation of PZC. Birnessite was shown to have PZC values of pH 1.5 to 2.5, cryptomelane of pH 2 to 4.5, and pyrolusite of pH 6 to 7. Because of their low PZC, oxides of birnessite and cryptomelane groups develop high surface charge and large CEC as pH rises (McKenzie, 1981). A CEC of 240 cmol(+) kg^{-1} for a relatively well-crystallized birnessite at pH 5.5 (Golden *et al.*, 1986) and CECs of 63, 167, 64, and 121 cmol(+) kg^{-1} at pH 7 for two birnessites and two cryptomelanes,

respectively, have been reported (McKenzie, 1981).

The adsorption of metal ions by birnessite occurs extensively even at low pHs and increases with pH (Norvell, 1988). During the process of adsorption, protons are usually released. A number of metal ions adsorbed on birnessite have been examined by several workers (Golden *et al.*, 1986; McKenzie, 1980; Posselt *et al.*, 1968; Triana and Doner, 1985) and their affinity series is given as:

$$Mg < Ca < Ni < Zn < Mn \leq Co < Cu < Pb$$
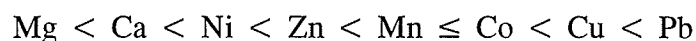
Divalent Mn and Co are bound by birnessite with unusual preference. For Co the affinity is due to oxidation of the adsorbed metal in addition to specific interaction between Co^{2+} and the oxide surface. Oxidation may also be involved in the preference for Mn^{2+} and the very strong binding of Pb^{2+}. Anion retention on Mn oxides has not been found (McKenzie, 1979), a fact probably related to the low PZC on these oxides.

Mechanisms of Mn^{2+} adsorption by Mn oxides

The mechanism of adsorption of Mn^{2+} onto MnO_2 is not clear. Murray (1975) reported that the adsorption capacity of Mn oxides for Mn^{2+} was considerably greater than for several other divalent cations studied. The high affinity of manganese oxides for Mn^{2+} has been attributed to specific adsorption or autocatalytic oxidation mechanisms (Pankow and Morgan, 1981). Ritchie (1989) compared Mn^{2+} to other more hydrolysable metals and suggested that the high affinity of Mn oxides for Mn cannot be readily explained by just specific adsorption of Mn^{2+} alone or specific adsorption combined with surface induced hydrolysis. She attributed the high affinity of birnessite for Mn^{2+} to oxidation of Mn(II) to Mn(IV) catalyzed by the oxide surface at which the Mn^{2+} and OH

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accumulated. An alternative explanation for the strong affinity of birnessite for Mn^{2+}, proposed by Krauskopf (1972) and McKenzie (1989), is worth mentioning. They considered that, in practice, the differentiation between ions adsorbed on the surface and those in the structure sites is often difficult. The mineralogy of manganese is complicated by the large number of oxides and hydroxides formed, in which substitution of Mn^{2+} or Mn^{3+} for Mn^{4+} occurs extensively. The reversible substitutions of Mn^{2+} or Mn^{3+} for Mn^{4+} may be achieved by a topochemical reduction or oxidation without a change in position of the Mn ions in a structure (Feitknecht, 1960). These substitutions result in changes in the average Mn-O bond lengths, with consequent changes in unit cell size, and are accompanied by the substitution of some O^{2-} by OH to maintain electrical neutrality. Consequently, the ions initially adsorbed on the surface may later become incorporated into these structural sites.

1.2.4 Mn complex formation

Formation of inorganic Mn complexes

Fully hydrated Mn^{2+} appears to be the dominant inorganic species in the soil solution and natural waters (Norvell, 1988). The main inorganic complexes are formed with SO_4^{2-}, HCO_3^- and Cl^- (Lindsay, 1979; Mattigod and Sposito, 1977). The proportion and importance of inorganic Mn^{2+} complexes vary with pH and other soil conditions. According to Florence (1977) and Sposito (1983), the species of Mn complexes include $MnSO_4^0$ and organo-Mn in acid soil; $MnSO_4^0$ (K=204), $MnCl_2^0$ (K=0.04) and $MnCl^+$ (K=5.5) (Lindsay, 1979) in saline soil; and $MnCO_3^0$, $MnHCO_3^+$(K=89), $Mn(OH)^+$(K=2570) (Mattigod and Sposito, 1977) in alkaline conditions. The H_2O

molecules around the hydrated Mn^{2+} can be partly or totally replaced by Cl^- as the concentration of Cl^- in the medium increases. Salts of complex ions such as trans-$[MnCl_4(H_2O)_2]^{2-}$ and trans-$[Mn_2Cl_6(H_2O)_4]^{2-}$ are also known (Cotton and Wilkinson, 1988).

Formation of organic Mn complexes

Divalent Mn also forms complexes in soil solution with organic ligands produced by various organisms. These biochemical ligands include organic acids, amino acids, hydroxamate siderophores, phenols and humic acids (Stevenson, 1982). The proportion of soluble Mn(II) present as Mn (II) complexes with organic ligands in soils is uncertain. Geering *et al.* (1969) reported high levels of complexation, ranging from 84 to 99 % of soluble Mn, in solutions collected using an anion exchange technique from the A horizons of 13 soils which had a wide range of pH and texture. In contrast, Sanders (1983) found only 10 to 65 % of Mn was complexed in five samples of a sandy loam limed to provide a pH range from 5.5 to > 7. Only in the sample limed to pH > 7 was complexing greater than 30 %. Olomu *et al.* (1973) reported that about 25 to 40 % of soluble Mn in 6 flooded soil solutions was retained by an anion exchange resin, whereas all was adsorbed by a cation exchange resin, suggesting that some forms of organically bound (but apparently labile) Mn was present. Camerlynck and Kiekcens (1982), however, reported no Mn was retained by an anion resin from water extracts of a sandy soil at pH 5, indicating that few, if any, negatively charged complexes of Mn were present.

According to the literature, the stability of organic Mn complexes is low. Irving and Williams (1948) measured stability constants of 1:1 complexes of transition metals and

solubility products of sulfides and a number of other organic compounds, including oxalate, glycinate, and ethylenediamine, at pH 8. The following sequence of complex stability, now called the Irving-Williams order, was established:

$$Mn^{2+} \prec Fe^{2+} \prec Co^{2+} \prec Ni^{2+} \prec Cu^{2+} \prec Zn^{2+}$$
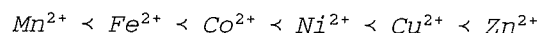
The series indicates that Mn^{2+} is the least capable of forming metal-organo-complexes.

The stability constant for a given complex increases with increasing pH and with decreasing ionic strength (Schmitt and Sticher, 1991). This may partly account for the increased availability and/or toxicity of Mn with decreasing soil pH. Formation of Mn complexes with organic matter reduces or slows down the oxidation of Mn^{2+} which also tends to increase bioavailability of Mn. Again, the importance of these ligands as complexes and chelates of Mn(II) complexes is limited by their relatively low concentrations and by their low specificity for Mn^{2+}. Generally, the stability of Mn(II) complexes are too low for Mn^{2+} to compete successfully for ligands with other polyvalent metals, including Fe^{3+}, Al^{3+}, and the relatively abundant macronutrients Ca^{2+} and Mg^{2+}.

1.2.5 Oxidation-reduction reactions

Chemical oxidation-reduction of Mn

Though the oxidation of Mn^{2+} by atmospheric O_2 to Mn(III) or Mn(IV) oxides is favored thermodynamically throughout the pH range of soils and natural waters (McKenzie, 1989), the oxidation of Mn^{2+} in simple inorganic solutions is negligible until the pH rises to 8 or more (Diem and Stumm, 1984; Morgan, 1967), and even then the reaction proceeds very slowly. However, Mn^{2+} is oxidized even in acidic soils.

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Therefore the oxidation of Mn^{2+} in soils must involve factors other than pH. Under neutral and acidic conditions, the presence of soil active surfaces such as Fe and Mn oxides and hydroxides is believed to be responsible for the chemical oxidation of Mn^{2+} (Coughlin and Matsui, 1976; Wilson, 1980). Microbial oxidation of Mn^{2+} also occurs in soils (Kamura et al., 1977; Wada et al., 1978). The oxidation of Mn on active surfaces of oxides is thought to be an autocatalytic reaction, involving specific adsorption of Mn^{2+} on the surface (Hem, 1963; Morgan and Stumm, 1964; Sung and Morgan, 1981). Stumm (1992) further explained that the OH^- ligands on the oxide donate electron density to the metal ion through both σ and π systems, which results in metal basicity and increase reducing power. Therefore, Mn(II) adsorbed on the oxide and/or present in the complex form are usually stronger reductants than free Mn^{2+}. Layer silicates and other surfaces may also contribute to oxidation of Mn^{2+} (Coughlin and Matsui, 1976; Wilson, 1980). In contrast, Meek et al. (1973) reported that surfaces of clay or sand did not catalyze the oxidation of Mn^{2+}. In the absence of other suitable surfaces, the reaction appears to be initiated on surfaces of $Mn(OH)_2$ or $MnCO_3$ formed at high pH. The initial crystalline products of oxidation of Mn^{2+} are predominantly Mn(III) oxides, which have been identified as Mn_3O_4 (hausmanite), β-MnOOH (feitknechtite) and γ-MnOOH (manganite) (Coughlin and Matsui, 1976; Hem, 1981; Murray and Dillard, 1979). The Mn(III) oxides are metastable and tend to disproportionate to Mn(II) and Mn(IV) oxides. However, not all the Mn^{2+} in the oxides is oxidized to Mn(IV). As a result, the products are generally described as hydrous MnO_x where x varies from about 1.1 to 2 (Morgan and Stumm, 1964; Norvell, 1988).

The chemical reduction of Mn(IV) requires the presence of the H^+ ion and a source of readily oxidizable material, usually organic matter (Zende, 1954):

$$MnO_2 + 4 H^+ + 2 e^- = Mn^{2+} + 2 H_2O$$
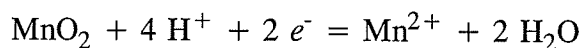
This reduction is favored by low pH, a high level of oxidisable organic matter, increased temperature and presence of moisture. Apart from oxidisable organic matter, introduction of reducing agents such as I^-, NO_2^- and Fe^{2+} with fertilizer carriers also causes reduction of Mn oxides.

Biochemical oxidation-reduction of Mn

A number of workers (Leeper, 1947; Bromfield, 1958; Meek *et al.*, 1973) suggested that soil microorganisms were responsible, enzymatically or non-enzymatically, for the oxidation of Mn^{2+}. Evidence for microbial oxidation of manganese in soil has been published. Beijerink (1913) found that bacteria and fungi from soil oxidized $MnCO_3$ in agar media. Gerretsen (1937) presented evidence that bacterial oxidation of Mn can lead to Mn deficiency in oats (*Avena sativa L.*). Tyler and Marshall (1967) concluded that the oxidation of Mn in soil was microbial since oxidation did not occur in autoclaved or azide-treated systems. Similarly, Kamura *et al.* (1977) believed that the oxidation was almost entirely accomplished by microbial activities, since Mn oxidation was depressed by addition of biological inhibitors to the soil and by lowering the incubation temperature. The immediate product of microbial oxidation is an amorphous form of manganese oxide (MnO_2) (Bromfield, 1958; Kossaya, 1967). Specific crystalline structures probably arise secondarily during abiotic aging of the amorphous manganese oxides. The work of Dubinina and Deryugina (1971), which described an amorphous

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deposit of metallic oxides (Fe and Mn oxides) on *Metallogenium*, supports this conclusion. The bacteria found to be able to oxidize Mn^{2+} include gram-positive and gram-negative forms. They are eubacteria and aerobic, represented by sporeforming and non-sporeforming rods, cocci, vibris, spirilla, and sheathed and appendaged bacteria (Ehrlich, 1990). Some mycellium-forming fungi have also been found to promote manganese oxidation, at least under laboratory conditions.

Oxidation of Mn^{2+} is mainly a microbial process. In aerobic soils reduction of Mn(III) and Mn(IV) is mostly chemical, but under poorly aerated conditions reduction can be both microbiological and chemical (Leeper, 1947). Microbial reduction of Mn oxides may be enzymatic or non-enzymatic, as in the case of microbial oxidation of manganese. Bacteria that reduce Mn oxides include gram-positive and gram-negative forms, rods, cocci, and vibrios. Some are aerobic or facultative organisms, others are anaerobes. The majority of organisms that can respire using Mn oxides as a terminal electron acceptor seem to require reduced carbon as electron donor (reductant), but a few exceptional types are able to use hydrogen (Ehrlich, 1990).

1.2.6 Mn diffusion

Diffusion of Mn can take place both in soil solution and inside solid phases of soil minerals. Diffusion is the most important mechanism by which Mn^{2+} is transported from soil to plant roots. This process is believed to be enhanced by the formation of organic manganese complexes which greatly increase both Mn^{2+} in solution and in turn the strength of the requisite concentration gradient (Tisdale *et al.*, 1985).

Manganese and other cations bound to the surface of minerals can diffuse into the

interior of the solid phase (Schmitt and Sticher, 1991). The relative diffusion rates depend on the ionic diameters and the pH as has been shown by Bruemmer et $al.$(1988) in a series of experiments with goethite. Affinity of the oxide surface for a cation increases with increasing pH up to the point where the formation of hydroxo-complexes inhibits the access of the cation to the surface. Diffusion rate decreases with increasing ionic diameter, e.g. Cd^{2+} (0.97 nm) $<Mn^{2+}$ (0.80 nm) $<$ Zn^{2+}(0.74nm) $<Ni^{2+}$(0.69nm). In the interior, the ions can neutralize negative charges and remain fixed in the appropriate positions. This phenomenon has also been observed in other minerals including manganese oxides (McKenzie, 1980), illites and smectites (Gerth, 1985). Such processes are often described as irreversible adsorption and cause ions to become immobilized and unavailable with time.

1.3 ROLE OF Mn AND Cl IN PLANTS

1.3.1 Biological importance of Mn and Cl

Manganese is an important and essential trace element in biological systems, ranging from 20 to 200 mg kg^{-1} dry tissue weight and acting as an activator of a number of enzymes, or Mn-proteins. The most striking biological role of manganese, along with Cl, is its involvement in photosynthesis, where it is the electron donor for photosystem II, and accelerates the electron transfer from water to O_2 in the light. The resulting Mn^{3+} oxidizes water and releases O_2 in the dark (Walker and Ludwig, 1970). The Mn^{2+} is firstly oxidized to Mn^{3+} in the process and then reduced to Mn^{2+} again as electron transport occurs. This reaction has been recently described by Adriano (1992) as follows:

A chemical scheme for O_2 production at a four-manganese cluster. The S-states are the five observable spectroscopic conditions. Note the involvement of Ca^{2+} and Cl^-.
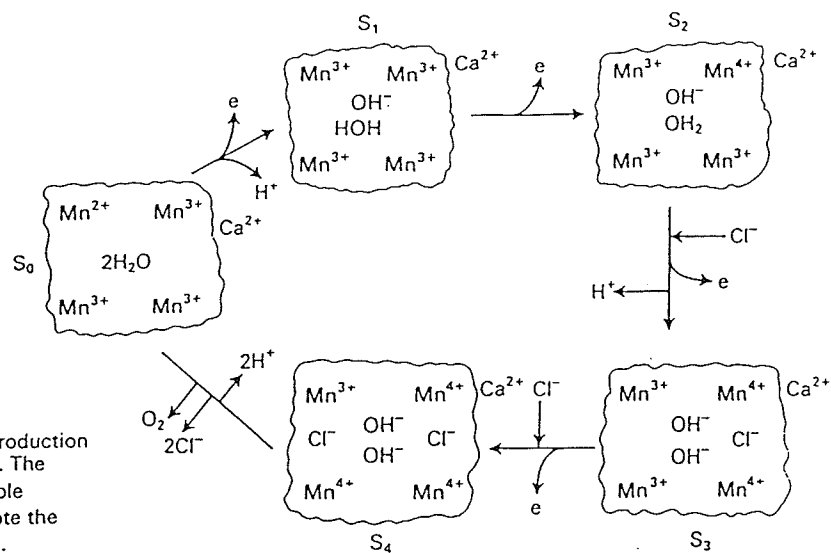
In this process, the involvement of Ca^{2+} and Cl^- is indispensable. It is thought that a chloride ion bridges two Mn^{2+} together (Salisbury and Ross, 1985). The linking between Ca^{2+}, Cl^-, and Mn^{2+}, all of which are exported from the cytoplasm, is considered as a very intriguing aspect of homeostasis.

Manganese also participates in dioxygen metabolism. For example, Mn is found in certain peroxidases, catalases, and superoxide dismutases (Adriano, 1992). Manganese activates a large number of enzymes catalyzing oxidation-reduction processes, decarboxylation, hydrolysis, and group transfer reactions in glycolysis and the Krebs cycle (Shkolnik, 1984). Tsai et al. (1971) found that Mn exerts a strong activating effect on malate dehydrogenase which catalyzes the decarboxylation of oxaloacetate, without which the malic acid enzyme that oxidizes malic acid to pyruvic acid does not function. Furthermore, Ilyinskaya and Shkolnik (1970) found the evidence of accumulation of malic acid in Mn deficient plant leaves. Besides, this element also plays a prominent role in respiration and metabolism of nitrogen, auxin, and nucleic acids (Shkolnik, 1984).

Though the physiological functions of Cl^- in plants are not fully understood, the pertinent information available is on account of its specific role in photosynthetic

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reactions and, apparently, in nitrogen and energy metabolism (Shkolnik, 1984)

1.3.2 The Role of Mn in Resistance to Plant diseases

The role of Mn in resistance to plant diseases has been widely recognized by plant pathologists and nutritionists in relatively recent years. Numerous reports on the relationship between Mn and plant diseases have been reported in literature. It was found that plants sufficient in Mn, as compared to those deficient in Mn, tended to be more resistant to infection by plant pathogens, including take-all of wheat (Graham, 1983; Huber, 1985,1987), blast of paddy-grown rice (Choong-Hoe, 1986; Choong-Hoe et al., 1988; Pearson and Jacobs, 1986), common scab of potato (Davis et al., 1976; Lapwood, 1973; Wenzel et al., 1971), root rot of sweet potato (Jones et al., 1977), powdery mildew of wheat (Huber and Keeler, 1975), barley (Vlamis and Yarwood, 1962) and pumpkin (Abia et al., 1977), and brown spot of rice (Kaur and Padmanabhan, 1979; Kaur et al., 1979). The severity of these diseases can therefore be reduced either by direct application of Mn fertilizers or by modification of the environmental conditions through cultural practices that are conducive to an increase in Mn availability to plants. For example, application of high rates of chloride fertilizers (KCl, NaCl, NH_4Cl, $CaCl_2$) also decreases take-all and inhibits nitrification (Christensen et al., 1987; Huber and Arny, 1985; Powelson and Jackson, 1978). The effect of Cl on disease depression was attributed to increased Mn availability and uptake. Other factors that enhance Mn availability also depress severity of these diseases. For example, take-all is seldom severe on acid soils (Rovira, 1981) unless soils are naturally deficient in total Mn (Graham, 1983). Take-all is decreased by NH_4-N and conditions inhibiting nitrification, and

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increased by NO_3-N (Christensen *et al.*, 1987, Huber, 1980, 1981a, 1981b, 1985). The benefit of NH_4-N is suggested to provide a reducing environment in the rhizosphere, suppressing Mn oxidizers in the rhizosphere thereby increasing the solubility of Mn^{2+} and decreasing the incidence of diseases. The uptake of NH_4-N also creates a carbon sink and stimulates metabolic activity in root tissues (Huber and Keeler, 1977). NO_3-N provides a readily available source of oxygen for microbial oxidations, increases the population of Mn oxidizers and increases take-all (Humber and Wilhelm, 1988).

Several mechanisms of disease control with Mn have been proposed, including a direct effect of Mn on pathogens through toxicity or modification of virulence, an effect on the host plant by modifying resistance or susceptibility or a combination of the two (Graham, 1983; Huber, 1980, 1981a, 1981b). Mn fertilization can enhance the activity of fungicides, possibly as a result of its toxicity to fungi (Gaur and Agnihotri, 1982). The effectiveness of the metal fungicides in reducing plant diseases was correlated with their effectiveness as a peptidase inhibitor, with Mn being the most inhibitory (Huber, 1988). Modification of disease resistance may be indirectly through root exudates or the alteration of metabolism which denies the pathogen access to an essential nutritional intermediate or directly through the production of inhibitory compounds or accumulation of toxic quantities of Mn around the infection courts and its subsequent absorption by the pathogen (Huber and Wilhelm, 1988).

1.4 FACTORS AFFECTING Mn AVAILABILITY

1.4.1 Effect of pH and carbonates

It is well known that pH has a great influence on Mn availability and uptake by plants.

However, its real effect on Mn in soil can be difficult to establish because of the many concomitant effects of pH on Mn availability, e.g. decreasing pH lowers adsorption onto the oxides (Ritchie, 1989). Based on the chemical reaction

$$MnO_2 + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O$$
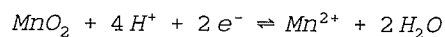
Lindsay (1972) suggested that soil soluble Mn decreases by 100 fold for each unit of pH increase. This correlation has not been established yet in practice. Quantitative comparisons of thermodynamic solubility relationships for Mn(IV) oxides with measured values of pe, pH and Mn^{2+} in soils are generally poor (Norvell, 1988). Goldberg *et al.* (1983) found that $(NH_4)_2SO_4$ increased Mn availability by decreasing pH as attributed to the acidifying effect of ammonium sulfate *per se* and NH_4^+ uptake leading to H^+ excretion by the plant roots. However, Uren (1981, 1982) found that the pattern of acid production by plant roots did not coincide with the extent of reduction of MnO_2 and therefore was not a major contributor to increased Mn availability.

The decreased adsorption of Mn on oxides and reduced stability of Mn complexes with decreases in pH may account for the higher availability of Mn in acidic or non-calcareous soils. In calcareous soils, there is no doubt that dissolution of $MnCO_3$ and desorption of Mn with decreasing pH may be of great importance.

1.4.2 Effect of Eh and organic matter

When a soil is submerged or waterlogged, the redox potential decreases with the consumption of O_2 and the amount of soluble Mn^{2+} increases in the soil. Theoretically, a redox potential of 200 mV or less is required for Mn(IV) reduction. In soils, however, manganese reduction has been observed at 500 mV and it is unclear whether redox

potentials are the cause or result of manganese reduction (Ritchie, 1989).

The rate of O_2 consumption under waterlogged conditions is correlated with organic matter content in the soil. Therefore soils rich in organic matter should have a higher rate of Mn release under reduced conditions. For upland soils, the presence of organic matter has also been shown to increase Mn availability (Ritchie, 1989). It is not always clear whether the effect is due to increased solubility by complexation, or due to organic matter acting as a chemical reducing agent or due to its stimulating effects resulting in microbial reduction. It has been suggested that the easily oxidizable portion of organic matter is responsible for microbial reduction of Mn.

1.4.3 Effect of other cations(adsorption competitors and reductants)

All cations act as competitors for exchange and adsorption sites. The affinity for a cation being adsorbed by Fe, Al and Mn oxides and hydroxides is determined by its size, charge, electronegativity, and its first hydrolysis constant. It is commonly accepted that there are two kinds of adsorption, specific and non-specific adsorption. The specific adsorption occurs strongly in all of the cryptocrystalline oxides, regardless of mineral types (McKenzie, 1989). The heavy metal ions adsorbed on MnO_2 are in the order Pb > Cu > Mn > Co > Zn > Ni (McKenzie, 1980). It is found that the addition of or presence of Cu always results in a large release of Mn from MnO_2 than that observed in the absence of Cu (Traina and Doner, 1985). Cupric salts therefore have been used to extract specifically adsorbed Mn by Warden and Reisennauer (1991)

Several cations have been found to be capable of reducing MnO_2 to the Mn^{2+} ion. For example, increases in water-soluble and exchangeable Mn have been observed after

application of Cr-bearing sewage sludge to soils (Bartlett and James, 1979; Grove and Ellis, 1980). Co^{2+}- and Fe^{2+}-induced release of Mn have been shown to occur both in soils and in pure manganese dioxides systems (McKenzie, 1967, 1970, 1980; Murray, 1975; Traina and Doner, 1985).

1.4.4 Effect of Anions

Anions affect the availability of Mn in soil in three ways: a) acting as ligands, b) acting as reducing agents and c) causing pH change in the medium.

Manganese(II) may react with several inorganic and organic ligands to form soluble Mn-complexes (Ritchie, 1989). In comparison to other heavy metals, Mn forms much weaker complexes. Nevertheless, chloride has a great effect on Mn availability and formation of $MnCl^+$ complexes has been suggested to be responsible for enhanced Mn uptake by crops after application of Cl fertilizers (Krishnamurti and Huang, 1992).

A number of investigators (Schnitzer and Skinner, 1967; Khan, 1969; Schnitzer and Hansen, 1970) have reported that Mn only forms weak complexes with purified fulvic acids (isolated from the acid soluble components of soil organic matter) in comparison with other metals. The stability of these complexes is found to increase with pH and decrease with ionic strength. For example, Schnitzer and Hansen (1970) reported that as pH increased from 3.5 to 5 at an ionic strength of 0.1, the stability constant of the Mn complex increased 32 times. They also found that the stability constant increased 16 fold as the ionic strength decreased from 0.15 to near 0 at pH 3. The effect of pH is probably due to competition of H^+ with Mn^{2+} (Page, 1962; Stevenson, 1982) and a concomitant change in the stability constant for the reaction. It would appear that there is now more

evidence that Mn in acid soil conditions is mainly in an uncomplexed form.

Some inorganic anions such as I$^-$, and NO$_2^-$, as impurities in fertilizers, can cause reduction of Mn oxides and enhance Mn availability. Tisdale $et\ al.$(1985) compared the effect of different potassium salts on increasing extractable Mn and found the order to be KI > KBr > KCl > KNO$_3$ > K$_2$SO$_4$ >> K$_2$CO$_3$. It is obvious that I$^-$ and Br$^-$ are reducing agents; Cl$^-$ and SO$_4^{2-}$ are inorganic ligands (in acid soils the complexing ability is SO$_4^{2-}$ > Cl$^-$); while K$_2$CO$_3$ is a fairly strong base.

Application of KCl fertilizers has long been recognized in enhancing Mn uptake by crops since the 1950's (York $et\ al.$, 1954; Foy, 1964; Westermann $et\ al.$, 1971; Cheng, 1982). An increase in available Mn and Mn content of alfalfa $(Medicago\ sativa\ L.)$ and corn $(Zea\ mays\ L.)$ was observed when NaCl, KCl, or CaCl$_2$ was applied to the soil (York $et\ al.$, 1954). Jackson $et\ al.$ (1966) found that banded applications of KCl increased the Mn content of sweet corn more than K$_2$SO$_4$ in an acid soil. Using the same soil, Westermann $et\ al.$ (1971) observed that the Mn^{2+} released by KBr and KCl was greater than by equivalent additions of KNO$_3$ and K$_2$SO$_4$. In an incubation study, Khattak and Jarrell (1988) found that amounts of Mn released from the soils saturated with different concentrations of NaCl-CaCl$_2$ solution were increased with both incubation time and salt concentration. During the incubation process, there was a pH drop of about one unit observed on two soils. They attributed the pH drop associated with increased Mn in the extract to reduction of soil Mn oxides by Cl$^-$. In another experiment (1989) they observed that saline irrigation waters significantly increased (27 to 97 %) the Mn concentration and total Mn accumulation (48 to 130 %) in sugar beet tops in all soils

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tested. A number of other workers (Schild and 1Zajonc, 1983; Pasricha and Ponnamperuma, 1976; Verma and Neue, 1984) also reported that the concentration of Mn in soil solution and plant tissues increased with salinity of irrigation waters.

2. SOLUBILITY OF Mn IN SOILS TREATED WITH KCl AND SOME OTHER SALTS

2.1 INTRODUCTION

Transformation of soil Mn to available forms is primarily a function of pH, Eh and microbial activity. Apart from these factors, a number of investigators (York *et al.*, 1954; Foy, 1964; Jackson *et al.*, 1966; Cheng, 1982) have reported that chloride salts, such as KCl, NaCl, and $CaCl_2$, could increase plant available and exchangeable Mn levels in soils. Fertilizers containing Ca^{2+}, K^+, Na^+, CO_3^{2-} or OH^- can reduce Mn toxicity, while fertilizers containing Cl^-, SO_4^{2-}, H^+ or Br^- can increase Mn toxicity (Cheng, 1982). Khattak and Jarrell (1989) reported that saline irrigation waters significantly increased the Mn concentration and total Mn accumulation in sugar beet tops in all soils tested. Application of KCl was reported to have resulted in an increase in Mn content of sweet corn plants, whereas the application of K_2SO_4 or K_2CO_3 had no effect on the Mn content (Jackson *et al.*, 1966).

The increase in the Mn content of the crops associated with KCl or NaCl was attributed to the salt effect on pH in the fertilizer band (York *et al.*, 1954); these effects were more evident on the unlimed than on the limed treatments. Westermann *et al.* (1971) conducted incubation experiments with an acid, poorly drained soil treated with several potassium salts. They found that the relative order of salt effect on extractable Mn was KBr > KCl > KNO_3 > K_2SO_4. They suggested that the effects of KCl and KBr were due to reduction of Mn oxides by Cl^- and Br^-, whereas changes in soil pH were the

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dominant factors in influencing Mn extractability in KNO_3 and K_2SO_4 treatments. After working on both Mn-bearing minerals and soils treated with KCl, Krishnamurti and Huang (1988) reported that it was not possible for Cl^- to reduce Mn oxides under their experimental conditions and hence suggested that the release of Mn was due to increased ionic strength and formation of $MnCl^+$ complexes.

Because of the discrepancy in the mechanisms suggested by various researchers for the release of Mn from soils treated with KCl, studies were designed to examine the effect of pH, ionic strength, different cations and anions on release of Mn from different soils.

2.2 MATERIALS AND METHODS

Soil Characteristics

Four soils, varying in pH, inorganic carbon content and texture were collected from the surface horizons of agricultural fields in Manitoba (Table 2.1). The soils were air-dried and crushed to pass a 2-mm sieve prior to use. pH of the soils was measured on a 1:1 soil/H_2O mixture. Organic and inorganic carbon was determined as described by Yeomans and Bremner (1988) and Bundy and Bremner (1972), respectively. Soil Mn was fractionated as outlined by Warden and Reisenauer (1991) and particle size analysis of the soils was carried out as outlined by Jackson (1979).

1. *Effect of ionic strength on Mn release from soils*

Fifty mL of water or 50 mL of KCl, KBr, KI, KNO_3, K_2SO_4, K_2CO_3, K_2HPO_4 or KH_2PO_4 at ionic strengths of 0.1, 0.5 or 1.0 mol L^{-1} were shaken with 5 g of soil in a 125-mL centrifuge bottle for 24 h. A portion of the slurry was filtered through

Whatman #42 filter paper and the remaining portion was used for the pH and Eh measurement. The concentration of Mn in the filtrate was determined using atomic absorption spectrophotometry. The pH and Eh were measured using a Fisher Accumet 950 pH/ion Meter (Pittsburgh, PA) equipped with a Fisher combination pH electrode with Ag/AgCl reference and a Fisher platinum Ag/AgCl combination electrode. Prior to measurements, the pH combination electrode was calibrated using standard buffer solutions of pH 7 and 10. The platinum combination electrode was calibrated using an Eh buffer solution consisting of 0.0033 mol L^{-1} $K_3Fe(CN)_6$, 0.0033 mol L^{-1} $K_4Fe(CN)_6$ and 0.1 mol L^{-1} KCl, which gives an Eh value of 430 mV at 25^0C (ZoBell, 1946). The electrodes were allowed to equilibrate with the solution for 2 min per sample before the pH and Eh values were recorded. The electrodes were rinsed with distilled deionized water between measurements.

2. *Effect of pH and different potassium salts on release of Mn*

Five g of soil were mixed with 50 mL of water or 50 mL of solution of KCl, KBr, KI, KNO_3, K_2SO_4, K_2CO_3, K_2HPO_4 or KH_2PO_4 at an ionic strength of 1.0 mol L^{-1} in a 100-mL beaker. The sample, after addition of 0, 1, or 2 mL 0.5 mol L^{-1} HNO_3 for the noncalcareous soils and 0, 2, or 4 mL 0.5 mol L^{-1} HNO_3 for the calcareous soils, was sonicated using a Braun-Sonic 2000 sonifier (Freeport, IL) with a 9.5-mm-diameter probe at an energy level of 127 kJ L^{-1} for 2 min. One portion of the slurry was filtered through Whatman #42 filter paper and the remaining portion was used to measure the pH and Eh values as outlined above. The concentration of Mn in the filtrate was determined using atomic absorption spectrophotometry.

3. *Successive extraction of Mn from soils*

Solutions of $Ca(NO_3)_2$, $Cu(NO_3)_2$ and Ca-DTPA were prepared as outlined by Warden and Reisenauer (1991) (refer to Table 2.1) except for the concentration of $Ca(NO_3)_2$ which was modified to 1.0 mol L^{-1} in ionic strength. Twenty mL of $Ca(NO_3)_2$, $Cu(NO_3)_2$, Ca-DTPA or 1.0 mol L^{-1} KCl were shaken with 1.0 g of soil in a 25-mL centrifuge tube for 30 min. The suspension was centrifuged at 15,500 x g for 10 min. The supernatant was collected for Mn analysis. Extraction using the same soil sample was repeated 5 times using the above procedure.

4. *Effects of KCl concentration and extraction time on the release of Mn from soil*

Fifty mL of H_2O or 0.001, 0.01, 0.1, 1.0 or 3.0 mol L^{-1} KCl solution was shaken with 5 g soil in a 125-mL centrifuge tube for 0.5, 1, 2, 6, 24, and 48 h. The suspensions were filtered through Whatman #42 filter paper and analyzed for Mn content by atomic absorption spectrophotometry. The pH and Eh values were measured as described above.

5. *Reaction of synthetic birnessite with HCl, HNO_3 and H_2SO_4*

Birnessite was prepared according to the method developed by McKenzie (1971). One mole of concentrated HCl was added dropwise to a boiling solution of 0.5 mole of $KMnO_4$ in 1.25 L H_2O, with vigorous stirring. After boiling for a further 10 min, the precipitate was filtered and washed with water under suction until the filtrate was free of purple coloration. The product was air-dried at room temperature and finely ground prior to use. The X-ray powder diffraction pattern, obtained using Cu-Kα radiation, confirmed birnessite was successfully prepared. The solubility of birnessite in HCl, HNO_3, and H_2SO_4 was investigated. Fifty mL of 0.001, 0.01, 0.1, 0.5 and 1.0 mol L^{-1}

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H^+ as HCl, HNO_3 or H_2SO_4 were shaken with 50 mg of birnessite for 30 min and then filtered. The pH, Eh and Mn content of the filtrated were determined as previously outlined.

6. *Formation of complexes of Mn and Cl in aqueous solutions*

A Rexyn 101(H) cation exchange resin with a reported particle size of 0.3-0.9 mm in diameter (wet U.S. standard sieve) and a CEC of 190 cmol(+) L^{-1} (wet volume) or 461 cmol(+) L^{-1} (dry volume), and a Rexyn AG 5(OH) anion exchange resin with a particle size of 0.3-0.9 mm in diameter (wet U.S. standard sieve) and AEC of 160 cmol(+) L^{-1} (wet volume) or 650 cmol(+) L^{-1} (dry volume) were utilized in this experiment. A 7.8 g sample of wet cation exchange resin or a 9.8 g sample of wet anion exchange resin, which was equivalent to 20 cmol(+) of CEC or AEC, was packed into a buret. The packing was prepared in water to exclude air bubbles from the columns. The pore volume of the resin was determined by subtracting the initial weight of resin used from weight of resin when saturated with water.

Solutions of 0.01, 0.1, and 1.0 mol L^{-1} KCl were prepared, with or without 20 mg L^{-1} of Mn as $MnCl_2$. The cation exchange resin was leached several times with the KCl solution before addition of 10 mL of the KCl solution containing Mn. Five one-pore volume samples of KCl leachate were collected in 15-mL centrifuge tubes, following the initial purge with 10 mL of leachate. After the fifth collection, the cation exchange resin was recharged by elutriation with 20 mL of 0.1 mol L^{-1} HCl, 30 mL of H_2O, and 20 mL of KCl solution of desired concentration, and then the second solution (KCl + $MnCl_2$) was leached through the column and the elutriate collected as described above. The same

column was used for all samples until all solutions were tested. The column was recharged after each test. Studies with the anion exchange resin were conducted as outlined for the cation exchange resin except that the anion exchange resin was recharged between treatments by elutriation with 20 mL 1.0 mol L^{-1} KCl, 20 mL H_2O and 20 mL KCl solution of desired concentration. The concentration of Mn in the leachate was determined using atomic absorption spectrophotometry.

7. *Statistical analysis*

Unless otherwise noted, all experiments were conducted in duplicate. Statistical analyses were performed using SAS statistical software (SAS Institute, 1989, Cary, NC., USA). Analysis of variance (ANOVA) or general linear model (GLM) procedure was used to analyze effects of treatments, soils and interactions between treatments and soils on amounts of Mn released. Mean separation was accomplished using least significant differences (LSD) at the 0.05 level of significance (α).

2.3 RESULTS AND DISCUSSION

Effect of Ionic Strengths on Release of Mn from Soils

The amount of Mn released from the soils varied with extractant, ionic strength, soil carbonate content and texture (Table 2.2). KH_2PO_4 and KI usually extracted considerably more Mn than the other salts. KH_2PO_4 extracted more Mn than KI from all soils. Very little or no significant difference in amounts of Mn extracted from soils was noted for salts other than KI and KH_2PO_4. Amounts of Mn extracted usually increased with increases in ionic strength except for K_2SO_4 and K_2CO_3. Salts usually extracted more Mn than water and the non-calcareous soils released more Mn than the calcareous soils.

Table 2.1 Selected characteristics of the soils

Soil Characteristics	Soil Series			
	Myrtle	Wellwood	Marquette	Elm River
Great Group	Haploboroll	Haploboroll	Calciboroll	Haplaquent
Parent Materials	Lacustrine	Lacustrine and alluvial	Lacustrine	Alluvial
Texture				
Clay (%)	43.46	11.74	55.02	20.73
Silt (%)	32.96	57.91	34.51	68.39
Sand (%)	20.73	30.29	10.40	10.78
pH	6.63	6.69	8.06	8.10
$CaCO_3$ equivalent (g kg^{-1})	1.7	1.7	57.7	158.3
Organic matter (g kg^{-1})	55.0	51.3	59.6	23.2
Mn fractionation (mg kg^{-1}):				
Readily soluble Mn (0.05 M Ca(NO$_3$)$_2$)	13.0	17.4	4.4	3.8
Weakly adsorbed Mn (0.025 M CaDTPA in 0.025 M Na$_2$B$_4$O$_7$, pH 8.5)	16.5	16.4	9.8	6.5
Carbonate-bound Mn (1.6 M HNO$_3$)			135.0	161.2
Specifically-adsorbed Mn (0.05 M Cu(NO$_3$)$_2$ in 0.05 M Ca(NO$_3$)$_2$)	38.0	68.0		
Oxide Mn (0.1M NH$_2$OH.HCl in 0.01 M HNO$_3$)	250.0	479.0	204.1	370.5

Table 2.2 pH, Eh and amount of Mn extracted from soils by different K salts varying in ionic strength

Salt	Ionic strength	Myrtle				Wellwood				Marquette				Elm River			
		pH	Eh	pH+pe	Mn	pH	Eh	pH+pe	Mn	pH	Eh	pH+pe	Mn	pH	Eh	pH+pe	Mn
	mol L^{-1}		mV		mg kg^{-1}		mV		mg kg^{-1}		mV		mg kg^{-1}		mV		mg kg^{-1}
KCl	0.1	6.38	449	14.0	7.6	6.14	485	14.3	7.1	7.63	457	15.3	0.4	7.79	445	15.3	0.0
KCl	0.5	6.69	461	14.5	8.1	6.00	465	13.9	7.4	7.40	459	15.2	0.8	7.67	454	15.4	0.3
KCl	1.0	6.11	470	14.1	9.4	6.65	480	14.8	8.2	7.65	454	15.3	1.1	7.64	466	15.5	0.6
KNO$_3$	0.1	6.87	470	14.8	5.1	6.12	506	14.7	4.8	7.61	470	15.6	0.0	7.79	453	15.5	0.1
KNO$_3$	0.5	6.78	484	15.0	6.2	6.79	503	15.3	5.1	7.62	473	15.6	1.0	7.55	462	15.4	0.7
KNO$_3$	1.0	6.70	479	14.8	6.6	6.69	496	15.1	5.9	7.63	465	15.5	1.6	7.81	453	15.5	1.2
K$_2$SO$_4$	0.1	6.37	470	14.4	5.9	6.20	479	14.3	4.5	7.77	465	15.6	3.1	8.00	451	15.6	3.1
K$_2$SO$_4$	0.5	6.62	481	14.8	7.9	6.34	493	14.7	6.5	7.76	442	15.2	1.4	7.92	434	15.3	1.0
K$_2$SO$_4$	1.0	6.71	464	14.6	10.8	6.67	499	15.1	8.8	7.80	428	15.1	0.9	8.26	436	15.6	0.4
KBr	0.1	6.32	438	13.7	4.5	6.12	446	13.7	4.5	7.60	419	14.7	0.0	7.77	411	14.7	0.0
KBr	0.5	6.26	516	15.0	7.4	6.09	527	15.0	7.1	7.32	515	16.0	0.4	7.48	509	16.1	0.1
KBr	1.0	6.17	516	14.9	10.0	6.02	526	14.9	12.0	7.38	519	16.2	0.7	7.54	510	16.1	0.8
KI	0.1	6.42	349	12.3	15.0	6.25	390	12.8	25.0	7.68	363	13.8	1.0	7.79	411	14.7	0.4
KI	0.5	6.25	391	12.8	18.0	6.22	411	13.2	45.0	7.40	374	13.7	1.8	7.56	375	13.9	2.6
KI	1.0	6.25	384	12.7	21.0	6.23	337	11.9	55.0	7.42	365	13.8	3.6	7.57	374	13.9	5.6
K$_2$CO$_3$	0.1	10.8	278	15.6	1.5	10.9	274	15.3	2.1	10.9	266	15.4	0.0	11.3	269	15.8	0.0
K$_2$CO$_3$	0.5	11.4	252	15.7	0.8	11.4	255	15.7	1.7	11.4	257	15.8	0.0	11.6	256	15.9	0.0
K$_2$CO$_3$	1.0	11.6	230	15.5	0.4	11.6	232	15.5	1.2	11.6	235	15.6	0.0	11.8	245	15.9	0.0
K$_2$HPO$_4$	0.1	7.75	375	14.1	1.1	7.90	397	14.3	0.9	7.96	409	14.9	0.3	8.25	401	15.0	0.4
K$_2$HPO$_4$	0.5	8.52	389	15.1	2.0	8.56	386	15.0	3.3	8.50	395	15.2	1.9	8.82	384	15.3	2.3
K$_2$HPO$_4$	1.0	8.85	359	15.0	3.2	8.88	379	15.3	7.6	8.82	382	15.3	1.7	9.22	361	15.3	2.4
KH$_2$PO$_4$	0.1	4.96	512	13.6	13.5	5.02	569	14.6	15.5	5.83	547	15.1	10.4	5.79	549	15.1	17.6
KH$_2$PO$_4$	0.5	4.67	580	14.5	52.4	4.62	627	15.2	62.0	5.44	591	15.4	30.0	5.70	568	15.3	35.6
KH$_2$PO$_4$	1.0	4.41	607	14.7	76.5	4.37	635	15.2	121.5	5.06	604	15.3	53.5	5.34	588	15.3	96.0
H$_2$O		7.03	422	14.1	0.2	6.89	444	14.4	0.4	7.88	403	14.7	0.0	8.01	384	14.5	0.0

Significant differences at LSD (P < 0.05) for salt effects on amounts of Mn extracted[1]

Salt	Soil				Ionic strength		
	Myrtle	Wellwood	Marquette	Elm River	1.0	0.5	0.1
KH$_2$PO$_4$	47.5 a	66.0 a	31.3 a	49.7 a	14.0 a	45.0 a	86.9 a
KI	18.0 b	41.7 b	2.1 b	2.9 b	10.4 b	16.9 b	21.3 b
KCl	8.4 bc	7.6 c	0.8 b	0.3 b	3.8 b	4.2 c	4.8 c
K$_2$SO$_4$	8.2 bc	6.6 c	1.8 b	1.5 b	4.2 b	4.2 c	5.2 c
KBr	7.3 bc	7.9 c	0.4 b	0.3 b	2.3 b	3.8 c	5.9 c
KNO$_3$	6.0 bc	5.3 c	0.9 b	0.7 b	2.5 b	3.3 c	3.8 c
K$_2$HPO$_4$	2.1 c	3.9 c	1.3 b	1.7 b	0.7 b	2.4 c	3.7 c
K$_2$CO$_3$	0.9 c	1.6 c	0.0 b	0.0 b	0.8 b	0.6 c	0.4 cd

[1]Means with the same letter in each column are not significantly different.

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The two loam soils released greater amounts of Mn than their two counterpart clay soils, which corresponded to the higher Mn content of the two loam soils.

Amounts of Mn extracted by K_2SO_4 from the calcareous soils decreased with increases in ionic strength whereas amounts of Mn extracted from the non-calcareous soils increased with increases in ionic strengths. Amounts of Mn extracted by K_2CO_3 from the non-calcareous soils decreased with an increase in ionic strength. Amounts of Mn extracted by K_2CO_3 from the calcareous soils were less than that which could be detected by the procedures used. The decrease in amounts of Mn extracted by K_2CO_3 was obviously due to an increase in pH with increased ionic strength of K_2CO_3. The decrease in amounts of Mn extracted at high ionic strength of K_2SO_4 may be due to an increase in pH at high ionic strength. The increases in pH at higher ionic strengths of K_2SO_4 was probably a result of OH^- being replaced by sulfate on soil adsorption surfaces (Parfitt and Smart, 1978). Since extraction of Mn by KCl and KBr did not differ significantly from that extracted by KNO_3 and K_2SO_4, it can be concluded that Cl^- and Br^- did not cause reduction of Mn under the conditions encountered. The Eh values when these salts were used were similar to that obtained in water for the various soils.

The difference in amounts of Mn extracted by K_2CO_3 and KH_2PO_4 were most likely due to differences in pH; K_2CO_3 increased soil pH whereas KH_2PO_4 decreased soil pH. In most cases, the pH difference in the soil solutions between treatments of K_2CO_3 and KH_2PO_4 was about 6 units, with pH values of 11 to 12 for K_2CO_3 and 4 to 6 for KH_2PO_4. Thus, the Mn extracted from the soils increased with decreasing pH. It should

be noted that there was a decrease in Eh with K_2CO_3 and an increase in Eh with KH_2PO_4. The changes in Eh were due to changes in pH. The pH+pe values were slightly greater for the K_2CO_3 than for the KH_2PO_4 treatments. The results imply that pH and ionic strength affected amounts of Mn extracted by K_2CO_3 and KH_2PO_4 with pH playing the major role. For the other salts (KCl, KBr, KNO_3), since the solution pH values were relatively constant with increased ionic strength, ionic strength effects governed the amount of Mn released.

KI extracted more Mn than any other salts except KH_2PO_4. The pH values with KI were similar to that with KCl, KBr, KNO_3, or K_2SO_4, but usually much higher than with KH_2PO_4. However, the pH+pe values with KI were lower than for the other treatments. Thus, amounts of Mn extracted by KI was due to reduction of Mn oxides as well as ionic strength effects.

Effect of pH and Different Potassium Salts on Mn Release

As expected, pH decreased with the addition of 0.5 mol L^{-1} HNO_3 to the soil; the magnitude of the pH decrease corresponded to the amount of acid added, nature of the soil and extractant (Table 2.3). pH changes in the solutions of K_2CO_3, KH_2PO_4 and K_2HPO_4 with addition of acids were not as large as in the solutions of the other salts due to the buffering of the carbonate and phosphate salts. The calcareous soils had a higher acid buffering capacity than the non-calcareous soils. The amount of Mn released by each salt increased significantly with an increase in acidity of the solution, but the amount of Mn extracted varied from soil to soil. In general, a much higher amount of Mn was extracted from the non-calcareous soils than from the calcareous soils. After acidifying

Table 2.3 pH, Eh and amount of Mn extracted from soils by different K salts at different solution pHs after 2 min of sonication

Salt	Myrtle				Wellwood				Marquette				Elm River			
	pH	Eh	pH+pe	Mn	pH	Eh	pH+pe	Mn	pH	Eh	pH+pe	Mn	pH	Eh	pH+pe	Mn
		mV		mg kg^{-1}		mV		mg kg^{-1}		mV		mg kg^{-1}		mV		mg kg^{-1}
KCl-1[1]	6.07	443	13.6	4.8	5.91	484	15.1	6.0	7.46	466	15.3	0.7	7.81	451	15.5	0.5
KCl-2	4.05	489	12.3	16.9	3.74	521	12.5	19.1	6.48	472	14.5	4.1	6.65	467	14.6	3.4
KCl-3	3.40	551	12.7	32.3	2.61	582	12.5	38.5	5.82	472	13.8	11.3	6.27	459	14.0	8.1
KNO$_3$-1	5.60	534	14.6	2.7	5.54	563	15.0	3.2	7.45	462	15.3	0.6	7.94	456	15.6	0.1
KNO$_3$-2	4.24	572	13.9	9.7	3.75	616	14.2	13.2	6.47	468	14.3	3.4	6.63	482	14.8	2.0
KNO$_3$-3	3.60	618	14.0	20.6	2.63	652	13.7	35.4	5.66	496	14.0	8.2	6.25	489	14.4	5.7
K$_2$SO$_4$-1	6.61	542	15.8	8.8	5.72	536	14.8	4.8	7.46	493	15.9	0.0	8.03	464	15.8	0.3
K$_2$SO$_4$-2	4.43	602	14.6	10.7	4.14	671	15.5	14.8	6.84	521	15.6	1.8	7.30	494	15.7	4.2
K$_2$SO$_4$-3	3.48	659	14.6	16.9	3.33	693	15.0	30.2	6.27	500	14.7	8.1	6.72	490	15.0	8.6
KBr-1	6.06	536	16.1	4.1	5.66	668	17.0	4.4	7.13	633	17.8	0.0	7.49	570	17.1	0.0
KBr-2	3.85	663	15.0	19.3	3.42	684	15.0	26.4	6.10	620	16.6	5.1	6.29	578	16.1	6.1
KBr-3	2.83	723	15.0	30.5	2.53	717	14.7	37.1	5.45	626	16.0	12.9	5.97	572	15.7	11.8
KI-1	6.37	393	13.0	8.9	6.08	415	13.1	11.9	7.24	378	13.6	5.0	7.54	390	14.1	18.9
KI-2	4.50	428	11.7	74.9	4.06	458	11.8	144.7	6.16	448	13.7	24.9	6.30	451	14.0	42.5
KI-3	2.83	444	10.3	126.9	3.47	465	11.3	272.4	5.60	451	13.3	60.4	5.94	520	14.7	112.2
K$_2$CO$_3$-1	11.7	272	16.3	0.3	11.7	228	14.6	0.8	11.7	246	15.8	0.0	11.9	227	15.7	0.0
K$_2$CO$_3$-2	11.6	218	15.3	0.3	11.6	204	15.0	0.3	11.5	232	15.4	0.0	11.6	235	15.6	0.0
K$_2$CO$_3$-3	11.5	204	15.0	0.3	11.5	214	15.1	0.4	11.4	240	15.4	0.0	11.8	245	15.9	0.0
K$_2$HPO$_4$-1	8.94	336	14.6	1.0	8.90	364	15.1	2.0	8.96	351	14.9	0.0	9.07	334	14.6	0.4
K$_2$HPO$_4$-2	8.52	354	14.5	1.2	8.69	377	15.1	2.2	8.52	371	14.8	0.6	8.61	367	14.8	1.5
K$_2$HPO$_4$-3	8.55	360	14.6	1.6	8.52	370	14.8	2.8	8.34	360	14.4	0.7	8.35	365	14.5	2.8
KH$_2$PO$_4$-1	4.20	564	13.7	32.5	4.20	605	14.4	34.5	4.71	561	15.2	35.5	5.79	549	15.1	30.0
KH$_2$PO$_4$-2	3.99	612	14.3	36.7	3.99	635	14.8	35.7	4.57	591	14.6	35.4	4.88	485	13.1	29.1
KH$_2$PO$_4$-3	3.75	604	14.1	38.5	3.75	646	14.7	40.6	4.19	545	13.4	41.0	4.72	478	12.9	27.0
H$_2$O-1	7.05	472	15.0	0.4	6.86	465	14.7	1.3	7.76	455	15.6	0.3	7.89	440	15.3	0.3
H$_2$O-2	4.24	530	13.2	5.5	3.86	610	14.2	7.3	6.33	564	15.9	1.6	6.42	537	15.5	1.4
H$_2$O-3	3.16	620	13.6	16.6	2.84	682	14.3	21.8	5.66	560	15.2	5.8	6.08	550	15.4	5.3

Significant differences at LSD (P < 0.05) for salt effects on amounts of Mn extracted[2]

Salt	Soil				Acidification		
	Myrtle	Wellwood	Marquette	Elm River	1	2	3
KI	70.2 a	143.0 a	30.1 a	57.9 a	11.2 b	71.8 a	143.0 a
KH$_2$PO$_4$	35.9 b	36.9 b	37.3 a	28.7 b	33.1 a	34.2 b	36.8 b
KCl	18.0 bc	21.2 c	5.4 b	4.0 b	3.0 b	10.9 c	22.6 c
K$_2$SO$_4$	12.1 bc	16.6 c	3.3 b	4.4 b	3.4 b	7.9 c	16.0 c
KBr	18.0 b	22.6 c	6.0 b	6.0 b	2.1 b	14.2 c	23.1 c
KNO$_3$	11.0 b	17.3 c	4.1 b	2.6 b	1.7 b	7.1 c	17.9 c
K$_2$HPO$_4$	1.3 c	2.3 c	0.4 b	1.6 b	0.2 b	1.1 cd	17.9 c
K$_2$CO$_3$	0.3 c	0.5 c	0.0 b	0.0 b	0.3 b	0.2 cd	0.2 d

[1]1 - no acid added; 2 - 1 ml 0.5 mol L^{-1} HNO$_3$ added to the non-calcareous soils and 2 mL to the calcareous; 3 -2 mL 0.5 mol L^{-1} HNO$_3$ added to the non-calcareous and 4 mL to the calcareous.
[2]Means with the same letter in each column are not significantly different.

the extractant with dilute HNO_3, KI was the most capable of releasing Mn from the soils, whereas K_2CO_3 and K_2HPO_4 were the least capable. Amounts of Mn extracted by salts other than KI and KH_2PO_4 did not differ significantly. The KI treatments lowered Eh and the pH+pe of the solution more than any other treatments. This indicates that the larger quantity of Mn released by KI treatments can be attributed to reduction of Mn oxides in the soils due to the lowered redox potentials, whereas the Mn released by the other salts was mainly due to ion exchange and pH effects. In the non-calcareous soils, a larger amount of Mn was released from the loam soil than from the clay, corresponding to its higher Mn content, whereas in the calcareous soils this held true only for the KI treatment. At this point it is reasonable to conclude that the acidity, whether it was contributed from the soil *per se* or from the extractant, had a substantial effect on the amount of Mn extracted from the soil.

Westermann *et al.* (1971) studied extraction of soil Mn from acid soils by potassium salts and suggested that the greater release of Mn by KCl and KBr from the soils may be due to reduction of Mn oxides to the Mn^{2+} ion by Cl^- and Br^-. However, according to the Eh values needed to reduce Mn oxides (Krishnamurti and Huang, 1988) and the relationships between pH, Eh and Mn concentration in solution, our calculations indicated that it is not possible for Cl^- to reduce Mn oxides to Mn^{2+} to a detectable level even in 1 mol L^{-1} KCl solution at pH 1. Both calculations and experimental results (Appendix I) also showed that Br^- can reduce Mn oxides to a detectable extent only when the pH is below 3 at a concentration of 1.0 mol L^{-1} Br^-. In contrast, KI is highly capable of reducing Mn(IV) to Mn(II) at normal soil pH values. The Mn released by KCl, as

suggested by Krishnamurti and Huang (1992), can therefore be attributed to the increased ionic strength and formation of $MnCl^+$ complexes in the solution, rather than an oxidation-reduction reaction.

Divalent Mn is adsorbed not only by soil clay minerals but also by organics (Page, 1962; Ellis and Knezek, 1972; McBride, 1982). Main and Schmidt (1935) suggested that Mn can form complexes with α-OH and bicarboxyl acids. McBride (1982) provided evidence, using ESR techniques, that Mn can form complexes with a number of natural and synthetic organics. The nature of the complexation (inner-sphere or outer-sphere) depends on the number of carboxylic groups and their steric arrangement on the compound. The stability of the complexes decrease with increases in acidity. Polycarboxylic acids (peat, humic acid) and synthetic polymers (polymethacrylate, polygalacturonic acid) bond Mn^{2+} electrostatically (outer-sphere complexation) at low pH, with inner-sphere complexation increasing with increases in pH (McBride, 1982). Fulvic acid formed strong complexes with Mn^{2+} only at pH values > 6.0. Therefore, the decreased stability of these Mn complexes at low pH was partly responsible for the increase in amounts of Mn extracted by a salt as soil pH decreased.

Successive Extraction of Mn from Soils

Manganese extracted by KCl from soil probably came from exchangeable sources. However, it was not clear whether the Mn extracted by KCl came from a particular fraction such as readily soluble Mn, weakly adsorbed Mn, or specifically adsorbed Mn. Therefore, the successive extraction study was conducted to study the relationships between KCl-extractable Mn and the amount of soil Mn in these fractions.

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Amounts of Mn extracted decreased with times of extraction, but remained relatively constant after the first or second extraction (Table 2.4). The first extraction removed about 33 to 78 % of the total Mn extracted. Effects of the extractants on amounts of Mn extracted decreased in the order of $Cu(NO_3)_2 > Ca-DTPA > Ca(NO_3)_2 > KCl$.

Table 2.4 Successive extractions of Mn from soils with KCl, $Ca(NO_3)_2$, $Cu(NO_3)_2$ and Ca-DTPA

		Extraction No.					
Soil	Extractant	1st	2nd	3rd	4th	5th	Total
		------------------ Mn extracted mg kg^{-1} -------					
Myrtle	KCl	6.4	1.7	1.0	0.7	0.7	10.5
	$Ca(NO_3)_2$	9.1	5.3	2.8	2.0	1.7	20.9
	Ca-DTPA	35.0	3.4	2.6	2.2	2.0	45.2
	$Cu(NO_3)_2$	62.8	17.4	14.2	12.0	10.2	116.6
Wellwood	KCl	9.1	3.0	1.8	1.4	1.3	16.6
	$Ca(NO_3)_2$	18.8	7.1	3.8	2.7	2.3	34.7
	Ca-DTPA	49.0	5.4	4.0	4.0	3.8	66.2
	$Cu(NO_3)_2$	67.6	14.2	9.8	8.8	7.6	108.0
Marquette	KCl	1.8	0.9	0.8	0.8	0.9	5.2
	$Ca(NO_3)_2$	2.0	1.1	0.9	0.9	0.9	5.8
	Ca-DTPA	23.2	5.6	4.2	4.2	3.8	41.0
	$Cu(NO_3)_2$	54.0	16.2	12.8	11.4	10.2	104.6
Elm River	KCl	1.2	1.0	1.0	1.0	0.7	4.9
	$Ca(NO_3)_2$	1.0	0.5	0.4	0.4	0.4	2.7
	Ca-DTPA	12.0	6.0	6.0	5.8	5.8	35.6
	$Cu(NO_3)_2$	36.2	27.2	20.0	14.6	10.4	108.4

Significant effects[1]
Soil   Myrtle(49.5) ab   Wellwood(56.4) a Marquette(39.2) b   Elm River(37.9)b
Extractant $Cu(NO_3)_2$(107.4)a CaDTPA(47.0) b $Ca(NO_3)_2$(17.3) c   KCl(9.3) c

[1]Means (in brackets) in each row with the same letter are not significantly different at LSD ($P < 0.05$).

Amounts of Mn extracted by KCl was correlated to the fractions extracted by $Ca(NO_3)_2$ ($r^2=0.9424$) and CaDTPA ($r^2=0.9258$), but not to fractions extracted by $Cu(NO_3)_2$ ($r^2=0.0229$). Amounts of Mn extracted by $Cu(NO_3)_2$ was not significantly different between soils, whereas the other three salts always extracted more Mn from the non-calcareous soils than from the calcareous soils. The amount of Mn extracted by KCl from the non-calcareous soils was less than that extracted by $Ca(NO_3)_2$. In contrast, KCl extracted equal or more Mn than $Ca(NO_3)_2$ from the calcareous soils. However, the difference between amounts of Mn extracted by these two extractants was not significant. The results suggest that the Mn extracted by KCl was from the same source as that extracted by $Ca(NO_3)_2$, i.e., readily soluble Mn. The ability of the Cu^{2+} ion in extraction of Mn has been attributed to its similar size to Mn and its high hydrolysis constant (McKenzie, 1980). Furthermore, the 0.05 mol L^{-1} $Cu(NO_3)^2$ has a pH value of 4.4 and this would be well-buffered due to the high tendency of hydrolysis of Cu^{2+} (i.e., $Cu^{2+} + H_2O = CuOH^+ + H^+$) (Warden and Reisenauer, 1991). The low pH would cause dissolution of carbonate bonded Mn in the calcareous soils and also reduce the stability of organically complexed Mn, resulting in increased release of Mn. Anions such as DTPA which can complex or scavenge Mn from the soil solution can also increase amounts of Mn extracted from soils. Though Cl⁻ has been considered to be able to form complexes with Mn, its impact on Mn release in this short term extraction study was not as obvious as reported by Westermann et al.(1971) and also in Chapter 3 of this thesis in the incubation and/or plant studies. The dramatic reduction in amounts of Mn extracted by $Ca(NO_3)_2$ as compared to KCl from Elm River soil may be due to a

common ion effect. A build-up of the Ca^{2+} ion in the solution would inhibit solubility of $CaCO_3$ and hence restrain Mn release from the $(Mn,Ca)CO_3$ co-precipitates. In the Marquette soil, KCl and $Ca(NO_3)_2$ extracted similar amounts of Mn. The Marquette soil contained less $CaCO_3$ than the Elm River soil, and as a result, the common ion effect would not be as pronounced as in the Elm River soil. This may also explain why the report by Cheng (1982) showed an inhibitory effect of fertilizer carriers containing Ca on Mn uptake by crops.

Reactions of Synthetic Birnessite with HCl, HNO₃ and H₂SO₄

Amounts of Mn released from birnessite increased with concentration or acidity (Table 2.5). Similar amounts of Mn were released among acids when concentration of H^+ was

Table 2.5 Amounts of Mn released from synthetic birnessite after treatment with HCl, HNO_3 and H_2SO_4.

Acid	Conc.	pH	Eh	Mn released
	mol L^{-1}		mV	g Mn kg^{-1} MnO$_2$
HCl				
	0.001	3.11	567	0.0 c[1]
	0.01	2.00	609	0.02 c
	0.1	1.02	614	0.06 c
	0.5	< 1	616	0.57 b
	1.0	< 1	621	2.64 a
HNO₃				
	0.001	3.21	598	0.0 c
	0.01	2.02	626	0.01 c
	0.1	0.98	643	0.07 c
	0.5	< 1	732	0.45 b
	1.0	< 1	716	1.24 b
H₂SO₄				
	0.0005	2.80	600	0.0 c
	0.005	2.05	641	0.03 c
	0.05	1.04	666	0.06 c
	0.25	< 1	733	0.52 b
	0.5	< 1	696	0.89 b

[1] Means with the same letter are not significantly different at LSD (P < 0.05).

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at and/or below 0.5 mol L^{-1}. Solubility of birnessite at H^+ concentrations of 0.1 mol L^{-1} or lower were very low.

The amount of Mn released with HCl was about 2 times of that with HNO_3 and 3 times of that with H_2SO_4 at a H^+ concentration of 1.0 mol L^{-1}. The large release of Mn with HCl, at the highest concentration, was probably due to reduction of birnessite by Cl^-. Our calculations indicated that Cl^- was capable of reducing MnO_2 at pH values below 1.0. The release of Mn from birnessite, at H^+ concentrations of 1.0 mol L^{-1} or lower, was probably due to reduction of MnO_2 by H_2O, as suggested by Murray (1974). The results also showed that KCl was not able to reduce MnO_2 at normal soil pHs.

Effect of Extraction Time and KCl Concentration on Release of Mn from Soils

Since very little Mn was extracted by 0.001 and 0.01 mol L^{-1} KCl, the data for these treatments were not included in Figure 2.1. Amounts of Mn released increased with increase in extraction time and KCl concentration (Figure 2.1). The highest release, therefore, occurred at the highest concentration (3.0 mol L^{-1}) and at the longest extraction time (48 h). Again, the amount of Mn extracted by KCl from the non-calcareous soils was much greater than that extracted from the calcareous soils. For example, after 48 h of shaking at a KCl concentration of 3.0 mol L^{-1}, the non-calcareous Myrtle clay released 10 times more Mn than from the calcareous Marquette clay. These results indicate that non-calcareous or acid soils usually contain higher amounts of KCl extractable Mn than calcareous soils as previously discussed. The increases in amounts of Mn extracted with increases in time of extraction may be due to continued release of Mn from the readily soluble and weakly adsorbed phases.
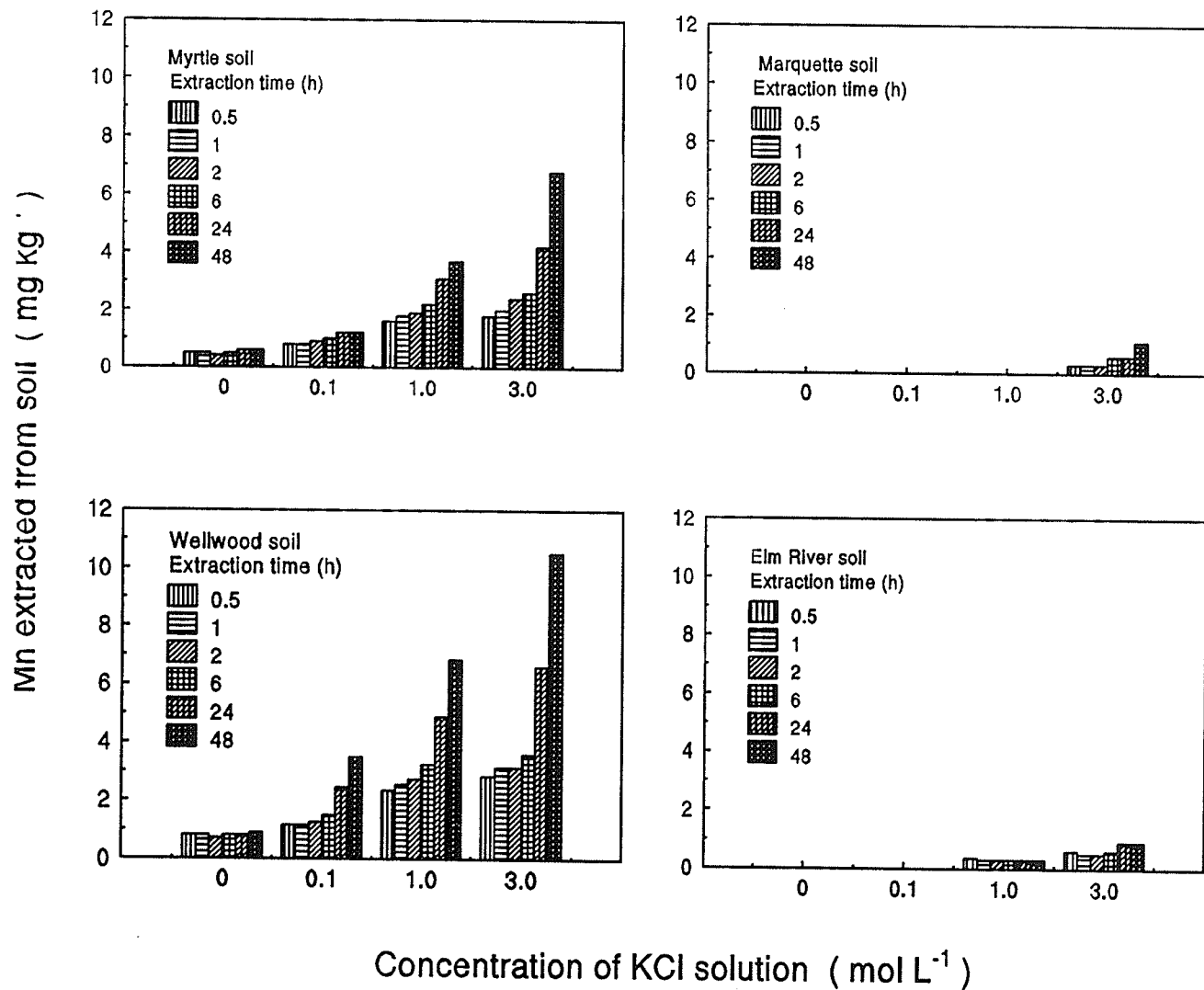
Figure 2.1 Amounts of Mn extracted from soils as affected by different concentrations of KCl and extraction time

Mn-Cl complex formation

It has been proposed that Mn^{2+} forms complexes of $MnCl^+$ and $MnCl_2^0$ with Cl^- in soil solution (Lindsay, 1979), and that the formation of these complexes may be responsible, at least partly, for the increased solubility and bioavailability of Mn in KCl treated soils (Krishnamurti and Huang, 1992). Cotton and Wilkinson (1988) reported existence of salts of complex ions of Mn and Cl such as *trans*-$[MnCl_4(H_2O)_2]^{2-}$ and *trans*-$[Mn_2Cl_6(H_2O)_4]^{2-}$. Thus studies were conducted to investigate the nature of ionic complexes of Mn and Cl in solutions of KCl. Two resins, a cation and an anion exchange resin, were used for the study. This study was based on the theory that: (1) if Mn^{2+} and Cl^- form positive and neutral species, they will not be adsorbed by an anion exchange resin, and (2) if Mn^{2+} and Cl^- form negative and neutral species they will not be adsorbed by a cation exchange resin.

Mn^{2+} added to the cation exchange resin was completely adsorbed when leached with 0.01 or 0.1 mol L^{-1} KCl containing 20 mg L^{-1} of Mn, but only partly retained when leached with 1.0 mol L^{-1} KCl (Table 2.6). These results indicate that negatively charged complexes of Mn and Cl formed at the high concentrations of KCl and thus moved downward in the column along with the leachate and/or the positively charged species was replaced by the high concentration of K^+. Studies with the anion exchange resin showed that large amounts of Mn were retained when the resin was leached with 0.1 or 1.0 mol L^{-1} KCl containing Mn. Thus negatively charged Mn-Cl complexes were formed in the solution. The amount of Mn adsorbed on the anion exchange resin was the highest for the 0.1 mol L^{-1} KCl solution. A slight decrease in amounts of Mn adsorbed with 1.0

mol L^{-1} KCl solution may be due to the high concentration of Cl^- in the solution replacing some of the adsorbed anionic Mn-Cl complexes on the resin.

Table 2.6 Concentration of Mn in the leachate from cation and anion exchange resins after treatment with $MnCl_2$ and washed with KCl solutions

KCl conc. (M)	10 ml leachate	1 pv	2 pv	3 pv	4 pv	5 pv
	------------------------------mg L^{-1} ----------------------------------					
Cation resin:						
0.01	0	0	0	0	0	0
0.1	0	0	0	0	0	0
1.0	4.36	5.45	5.28	4.91	4.54	4.15
Anion resin:						
0.01	2.74	4.02	3.42	2.55	1.84	1.46
0.1	0.29	0.19	0.19	0.14	0.13	0.09
1.0	0.35	0.36	0.33	0.28	0.26	0.23

pv - pore volume

2.4 CONCLUSIONS

Amounts of Mn extracted from soils by KCl increased with increases in concentration of KCl and extraction time. Amounts of Mn extracted by KCl from the non-calcareous soils were always more than from the calcareous soils.

Amounts of Mn extracted by a K salt depended not only on its ionic strength, but also on its ability to lower pH of the solution and its reducing power. The large quantity of Mn released by KI was directly a reflection of its reducing power and ionic strength, whereas amounts of Mn extracted by salts such as KH_2PO_4, K_2CO_3, K_2HPO_4 were due to pH and ionic strength effects. Since KCl was unable to reduce Mn(IV) oxides to Mn(II) under ordinary soil conditions, mechanisms responsible for release of Mn from

soils by KCl were exchange reactions, salt effects on solubility of soil Mn and anionic

Mn-Cl complex formation.

3 EFFECT OF KCl ON CHEMISTRY AND

BIOAVAILABILITY OF Mn

3.1 INTRODUCTION

Soluble Mn fertilizers are rapidly converted to nonexchangeable forms shortly after application (Sanchez and Kamprath, 1959; Murphy and Walsh, 1972; Zhang and Zhang, 1984). The decrease in solubility of applied Mn is generally more pronounced in calcareous soils than in noncalcareous soils or after liming an acid soil (Sanchez and Kamprath, 1959).

Several investigators (York *et al.*, 1954; Foy, 1964; Jackson *et al.*, 1966; Westermann *et al.*, 1971; Cheng, 1982), have reported that application of KCl fertilizer enhanced Mn uptake by crops. An increase in available Mn and Mn content of alfalfa (*Medicago sativa L.*) and corn (*Zea mays L.*) was observed when NaCl, KCl, or $CaCl_2$ was applied to the soil and this effect was attributed to a lowering of soil pH in the fertilizer band (York *et al.* 1954). A study by Hamilton and Lathwell (1965) showed that Cl salts were more effective than other salts in increasing the diffusion of soluble Mn^{2+} from fertilizer bands of either $Ca(HPO_4)_2$ or $(NH_4)_2HPO_4$. The pH adjacent to the $Ca(H_2PO_4)_2$ band was reduced by the salts; however, no relationship was found between the salt-associated pH changes and the amount of soluble Mn. Westermann *et al.* (1971), incubated KCl, KNO_3, KBr, or K_2SO_4 with an acid, poorly drained soil and found that the level of extractable Mn was increased by these salts in the order $KBr > KCl > KNO_3 > K_2SO_4$. They suggested that soil pH changes accounted for the majority of KNO_3 and K_2SO_4 treatment effects, but not for KBr and KCl. The effects of KBr and KCl in

increasing extractable Mn from the soil were attributed to reduction of Mn oxides by Br^- and Cl^-. However, Krishnamurti and Huang (1988) reported that it was not possible for Cl^- to reduce Mn oxides under their experimental conditions or in the pH range found in most agricultural soils (also refer to Chapter 2 of this thesis). The increases in amount of extractable Mn in soils treated with KCl was suggested to be due to increased ionic strength and formation of the $MnCl^+$ complex (Krishnamurti and Huang, 1992) or formation of anionic complexes of Mn and Cl (Chapter 2).

The initial objective of this study was to determine if KCl application alone or in combination with Mn fertilizer would increase the bioavailability of indigenous and applied Mn. The studies conducted showed that bioavailability was increased and thus further experiments were conducted to study some of the possible mechanisms by which KCl enhanced Mn uptake. The effect of KCl on the solubility of Mn from $MnSO_4$ fertilizer bands as well as the effect of K_2SO_4 and KCl on the solubility of native and applied Mn were investigated.

3.2 MATERIALS AND METHODS

Mn Uptake by Wheat as Affected by $MnSO_4$ and KCl Fertilization

A calcareous Elm River soil with a pH value of 8.1 and a noncalcareous Wellwood soil with a pH value of 6.7, were selected for study (Table 2.1). The soils, obtained from the surface 10 cm layer, were air-dried, crushed, and passed through a 2-mm sieve. Four kg of soil were treated with 100 μg N g^{-1} soil as NH_4NO_3 and 25 μg P g^{-1} soil as $NH_4H_2PO_4$, thoroughly mixed, and then placed in five-litre plastic pots (20 cm in diameter). In experiment one, treatments consisted of two KCl carriers (fertilizer grade

and reagent grade KCl), applied at rates of 0, 50, 100, and 300 μg K g^{-1} soil. One additional treatment, 50 μg K g^{-1} soil as reagent grade KCl plus a trace amount of KI (accounting for 5 % of the KCl by weight), was added. A treatment with KI and reagent grade KCl was included to test whether or not trace amounts of KI normally present in fertilizer grade KCl may reduce and solubilize soil Mn. The fertilizers were placed 10 cm below the soil surface in small piles to simulate granules of the fertilizer grade KCl. The fertilizers were placed in about 10 piles in each pot. Treatments, arranged in a completely randomized design, were replicated three times.

In experiment two, the treatments consisted of KCl(200), K_2SO_4, K_2CO_3, NaCl, $MnSO_4$, KCl(50)+KI, KCl(200)+$MnSO_4$, and KCl(50)+$MnSO_4$+KI. KCl was applied at 50 and 200 μg K g^{-1} soil, designated as KCl(50) and KCl(200), respectively, whereas the other salts were added at rates of 200 μg K g^{-1} soil as K_2SO_4 and K_2CO_3, 200 μg Cl g^{-1} soil as NaCl, 7.5 μg Mn g^{-1} soil as $MnSO_4$, and KI at 5 % of weight of KCl added.

Prior to seeding, the soil was watered to field capacity and allowed to stand at room temperature for 2 d. Katepwa wheat seeds were germinated at room temperature by placing seeds between wet paper towels for 2 d. Five uniformly germinated seeds were planted in each pot at a depth of 0.5 cm, and allowed to grow for 56 d with a 16 h-photoperiod at 25 ^{0}C day temperature and 17 ^{0}C night temperature with a relative humidity of 70 % during the day and 95 % at night. The light intensity close to the plant canopy was 500 to 550 μ moles s^{-1} m^{-2}. The soil moisture in the pots was maintained between 100 to 70 % of field capacity throughout the growing period.

The plants were harvested at the flowering stage by cutting the plant shoots at the soil surface. The plant tissues were air-dried in nylon net bags in a forced draft room at room temperature for 3 d, and then dried in an oven at 65 ^{0}C. The samples were weighed, ground, mixed and a 1.0-g subsample digested using a HNO_3-$HClO_4$ mixture. The Mn concentration in the digests was determined by atomic absorption spectrophotometry.

Effect of KCl and K_2SO_4 on Water Extractable Mn from Native Soil Mn and $MnSO_4$ Fertilizer Sources with Time

An experiment was conducted to study the fate of added Mn and the effect of KCl on the solubility (bioavailability) of the added Mn as a function of time. The effect of KCl and K_2SO_4 on the solubility of native Mn was also examined. Fifteen g of Elm River or Wellwood soil was placed into a 125-mL plastic bottle. After the soil was wetted to field capacity, KCl, K_2SO_4, or $MnSO_4$+KCl was spread uniformly onto the soil surface. The rates of application based on soil weight were: 200 μg g^{-1} of K as KCl or K_2SO_4, 7.5 μg g^{-1} of Mn as $MnSO_4$.H_2O. A control treatment, with no salt, was also prepared. Each treatment was replicated twice. The samples were incubated for 0, 1, 3, 7, 14, 28, 42, and 56 d at 21 ^{0}C. After incubation, 50 mL of distilled-deionized water was added to each bottle, the suspension shaken for 30 min, and then filtered through #42 filter paper. The Mn concentration in the filtrate was determined using an atomic absorption spectrophotometer.

3.3 RESULTS AND DISCUSSION

Effect of KCl Application on Mn Content of Wheat

Yield of shoots did not vary significantly among most treatments (Table 3.1). Yield

Table 3.1 Yield, Mn concentration and Mn uptake of wheat shoots as affected by fertilizer grade (F-K) and reagent grade KCl (R-K)

	Rate of K fertilizer application (μg K g^{-1})							
	0	50		100		300		50 + KI
		F-K	R-K	F-K	R-K	F-K		R-K
Wellwood soil:								
Yield (g pot^{-1})	20.9 ab	20.9 ab	20.8 ab	20.7 ab	20.2 ab	19.4 b	19.3 b	21.7 a
Mn Conc.(μg g^{-1})	50.8 d	52.5 d	54.8 d	66.7 c	73.5 bc	138 a	137 a	80.3 b
Mn uptake (mg pot^{-1})	1.06 e	1.10 e	1.14 de	1.39 cd	1.49 bc	2.68 a	2.63 a	1.75 b

Means with the same letters are not significantly different at P=0.05. $LSD_{0.05}$: yield = 1.7, Mn conc. = 10.0, and Mn uptake = 0.28

Elm River Soil:								
Yield (g pot^{-1})	29.3 a	29.1 ab	29.2 ab	28.0 ab	27.9 ab	27.1 b	27.8 ab	27.4 ab
Mn conc.(μg g^{-1})	32.2 b	31.5 b	34.3 b	35.8 b	35.2 b	54.3 a	56.8 a	34.7 b
Mn uptake (mg pot^{-1})	0.95 b	0.92 b	1.00 b	1.00 b	0.98 b	1.47 a	1.58 a	0.96 b

Means with the same letters are not significantly different at P=0.05. $LSD_{0.05}$: yield = 2.2, Mn conc. = 5.5, and Mn uptake = 0.22

on the Wellwood soil treated with 300 μg K g^{-1} was significantly less than with 50 μg K g^{-1} plus KI. Also, yield on the Elm River soil treated with 300 μg K g^{-1} (fertilizer grade) was significantly less than the control. Shoot yield on the Elm River soil was greater than on the Wellwood soil. These results indicate that shoot yield tended to decrease with increases in amount of KCl added, despite no significant yield differences among most of these treatments. Though the reason(s) for these yield decreases are not evident from the data obtained, it is possible that the very high amounts of KCl reduced growth by an osmotic effect at the high salt concentrations. Other analyses did not show any apparent effect of rates of KCl on amounts of Fe, Zn and Cu uptake by the plant (Appendix II).

The Mn concentration and uptake by wheat generally increased with increased rates of KCl, particularly on the noncalcareous soil. The lowest application rate that caused a significant increase in Mn content in wheat was 100 μg K g^{-1} soil on the noncalcareous soil and 300 μg K g^{-1} soil on the calcareous soil, indicating that the effect of KCl on Mn bioavailability is greater on noncalcareous soils than on calcareous soils. There was no significant difference between the two sources of KCl in affecting Mn content of the plant. Adding KI to the KCl significantly enhanced Mn content in the plant on the noncalcareous soil but not on the calcareous soil. The results indicate that enhancement of Mn uptake by KI is a function of pH and occurs only at lower pHs. These results are in agreement with those observed by Sherman *et al.* (1943) who found that reduction of Mn oxides by I$^-$ was favored below pH 6 to 7 and increased with decreases in pH.

Effect of KCl, MnSO$_4$ and Some Other Salts on Mn Content of Wheat

The Mn content in plants treated with KCl alone or with MnSO$_4$ was always greater than without KCl, whereas Mn content of the control plants was greater than with K$_2$SO$_4$ or K$_2$CO$_3$ (Table 3.2). MnSO$_4$ with KCl at the rate of 200 μg K g^{-1} soil was the most effective of all treatments in promoting Mn uptake by wheat. KCl(200) or NaCl alone was the second most effective treatment in enhancing Mn uptake by the plant. The relative order of single salt treatments in increasing Mn uptake by wheat was NaCl $\approx$ KCl > MnSO$_4$ > K$_2$SO$_4$ > K$_2$CO$_3$. The above results suggest that KCl, if applied in sufficient quantity, would enable certain soils to supply large amounts of Mn to crops, whereas K$_2$SO$_4$ and especially K$_2$CO$_3$ could depress Mn uptake by plants.

Yield, on the noncalcareous soil, was not related to Mn concentration in shoots. Yield, however, increased above that of the control whenever a sulfate containing fertilizer was applied (Table 3.2), suggesting the noncalcareous soil under test was somewhat S deficient. As a result, the effect of Mn concentration on shoot yield may be confounded by S deficiency on the noncalcareous soil.

All treatments containing MnSO$_4$+KCl significantly increased Mn content in wheat shoots grown on the calcareous soil (Table 3.3). It was interesting that, even on a calcareous soil, NaCl or KCl at the rate equivalent to 200 μg K g^{-1} soil was as effective as MnSO$_4$ in increasing Mn uptake by wheat at the application rate of Mn selected. K$_2$SO$_4$, K$_2$CO$_3$, and the low rate of KCl and KCl+KI did not significantly affect Mn utilization by wheat. Again, K$_2$CO$_3$ was the least effective in enhancing Mn uptake. The results of this experiment were in good agreement with results of the extraction study

Table 3.2 Yield, Mn concentration and Mn uptake of wheat shoots as affected by KCl, MnSO$_4$, and some other salts - Wellwood soil

	Mn conc.	Mn uptake	Yield
------ g^{-1} soil---------	μg g^{-1}	mg pot^{-1}	g pot^{-1}
KCl+MnSO$_4$ (200 μg K+7.5 μg Mn)	197 a	2.3 a	11.7 a
NaCl (200 μg Cl)	185 b	1.8 b	9.5 d
KCl (200 μg K)	183 b	1.8 b	9.6 d
KCl+MnSO$_4$+KI*(50 μg K+7.5 μg Mn)	154 c	1.8 b	11.4 a
KCl+KI (50 μg K)	136 d	1.3 d	9.7 cd
KCl+MnSO$_4$ (50 μg K+7.5 μg Mn)	134 d	1.6 c	11.7 a
MnSO$_4$ (7.5 μg)	115 e	1.3 d	11.3 a
KCl (50 μg K)	111 ef	1.1 ef	10.3 b
Check	108 efg	1.1 ef	10.1 bc
K$_2$SO$_4$ (200 μg K)	102 fg	1.2 e	11.7 a
K$_2$CO$_3$ (200 μg K)	98 g	1.0 f	9.8 cd

Means with the same letters are not significantly different at P=0.05. LSD$_{0.05}$: Mn conc =10.2, Mn uptake =0.15, yield =0.57.

* - KI was added at 5 % of KCl by weight, the same as in Table 3.1

Table 3.3 Yield, Mn concentration and Mn uptake of wheat shoots as affected by KCl, MnSO$_4$, and some other salts - Elm River soil

	Mn conc.	Mn uptake	Yield
------ g^{-1} soil----------	μg g^{-1}	mg pot^{-1}	g pot^{-1}
KCl+MnSO$_4$ (200 μg K+7.5 μg Mn)	89 a	0.8 a	8.7 bc
KCl+MnSO$_4$+KI (50 μg K+7.5 μg Mn)	76 b	0.7 b	8.9 ab
KCl+MnSO$_4$ (50 μg K+7.5 μg Mn)	71 b	0.7 b	9.2 a
MnSO$_4$ (7.5 μg)	56 c	0.5 c	8.7 bc
NaCl (200 μg Na)	56 c	0.5 c	8.5 bcd
KCl (200 μg K)	51 c	0.5 c	8.5 bcd
K$_2$SO$_4$ (200 μg K)	43 d	0.4 d	7.9 e
KCl+KI (50 μg K)	42 d	0.3 d	8.5 bcd
Check	41 d	0.3 d	8.2 cde
KCl (50 μg K)	40 d	0.3 d	8.1 de
K$_2$CO$_3$ (200 μg K)	39 d	0.3 d	8.3 cde

Means with the same letters are not significantly different at P=0.05. LSD$_{0.05}$: Mn conc = 5.1, Mn uptake = 0.05, yield = 0.52.

presented in Chapter 2. The results of the previous study showed that of the salts tested, K_2CO_3 was the least capable of extracting Mn from soils, especially in the calcareous soil where amounts of Mn extracted by K_2CO_3 was virtually nil even when 0.01 mol L^{-1} K_2CO_3 solution was used. Jackson *et al.* (1966) also reported that increasing levels of added Cl increased the level of Mn in bush beans and sweet corn in both field and greenhouse studies, whereas the application of K_2SO_4 or K_2CO_3 had no effect on Mn content. The specific effect of K_2CO_3 on reducing solubility of soil Mn was probably due to its fairly strong alkalinity which led to a rise in pH and subsequent precipitation of soluble Mn in the solution.

Shoot yield with $MnSO_4$ tended to be higher than without (Table 3.3). Generally the higher yields were associated with plants of high Mn content.

Effect of KCl and K_2SO_4 on Mn Solubility

Amounts of Mn extracted from soils was increased greatly by both KCl and K_2SO_4 during initial periods of incubation as compared to the control (Table 3.4). With time of incubation, amounts of Mn extracted from the soils treated with KCl remained constant (calcareous soil) or increased (noncalcareous soil). In contrast, Mn extracted from soils treated with K_2SO_4 decreased with time of incubation, particularly after 3 d of incubation. It is known that both SO_4^{2-} and Cl$^-$ form complexes with Mn^{2+} in soil solution (Lindsay, 1991; Mattigod and Sposito, 1977). However, the stability constant of $MnSO_4^0$ (K=204) was about 40 times greater than that of $MnCl^+$ (K=5.5) (Mattigod and Sposito, 1977). Accordingly, Norvell (1988) suggested that the $MnSO_4^0$ complex should be present in significant concentrations under many soil conditions. However, the

Table 3.4 Amounts of Mn extracted from soils by water after treatment with KCl, K_2SO_4, or $MnSO_4$

| Treatment | Time | Mn released | |
		Elm River soil	Wellwood soil
	d	------------- $\mu g\ g^{-1}$ soil------------	
Check			
	0	0.08	0.37
	1	0.08	0.37
	3	0.08	0.37
	7	0.08	0.30
	14	0.07	0.28
	28	0.08	0.49
	42	0.08	0.43
	56	0.08	0.40
KCl			
	0	0.30	4.60
(200 μg K g^{-1} soil)	1	0.25	4.67
	3	0.32	5.43
	7	0.32	5.80
	14	0.46	6.83
	28	0.30	8.60
	42	0.30	8.90
	56	0.80	9.23
K_2SO_4			
	0	0.33	4.50
(200 μg K g^{-1} soil)	1	0.20	4.47
	3	0.18	4.08
	7	0.13	2.42
	14	0.08	1.57
	28	0.10	0.90
	42	0.10	0.83
	56	0.20	0.74
$MnSO_4$			
	0	-*	0.40
(7.5 μg Mn g^{-1} soil)	1	-	0.43
	3	-	0.27
	7	0.03	0.27
	14	0.03	0.40
	28	0.07	0.37
	42	0.03	0.40
	56	0.10	0.37
$MnSO_4$ + KCl			
	0	0.67	5.77
(7.5 μg Mn +	1	0.60	6.37
200 μg K g^{-1} soil)	3	0.47	7.06
	7	0.20	7.53
	14	0.23	8.07
	28	0.23	9.03
	42	0.60	9.17
	56	0.60	9.57

* - none detected

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higher stability constant of $MnSO_4^0$ cannot explain the results obtained from this study and by some other workers (Jackson *et al.*, 1966; Westermann, 1971), in which KCl was more effective than K_2SO_4 in increasing Mn solubility in soil and/or increasing Mn uptake by crops. As a result, additional factor(s) must be responsible. The previous study(Chapter 2) indicated that the specific effect of KCl on solubility of soil Mn was mainly due to formation of anionic complexes of Mn and Cl rather than $MnCl^+$ and/or $MnCl_2^0$, as formerly thought.

MnSO$_4$, applied alone, did not increase water soluble Mn in either soil as compared to the control, even when the soil was extracted immediately after mixing with $MnSO_4$. This result is in good agreement with some other investigators' work. For example, Sanchez and Kamprath (1959) reported that even large amounts of Mn fertilizer added to soils can be rapidly converted to nonexchangeable forms. Zhang and Zhang (1984) reported that added Mn was rapidly converted to nonexchangeable form with the result that addition of large amounts of Mn fertilizer reduced the exchangeable Mn content of the soil. Dual banding KCl with $MnSO_4$ increased the solubility of the $MnSO_4$ fertilizer in both soils. The results obtained indicate that the synergistic effect of KCl on Mn uptake is at least partly due to soil chemical reactions, i.e., the KCl increased the solubility of soil and applied Mn through complexation of Mn and Cl and hence the bioavailability of Mn.

3.4 CONCLUSIONS

KCl fertilizers enhanced solubility and bioavailability of indigenous soil Mn and Mn applied as $MnSO_4$. Increases in solubility and bioavailability, due to KCl, were greater

on the noncalcareous soil than on the calcareous soil. Other salts, such as K_2SO_4 and K_2CO_3, were not as effective as KCl or not effective in increasing the solubility and bioavailability of soil and/or applied Mn. The increase in solubility and bioavailability of Mn with KCl was attributed to formation of anionic complexes between Mn and Cl.

4 RETENTION OF Mn BY SOIL CLAY MINERALS AND OXIDES OF Fe, Mn AND Al, AND RELEASE OF Mn FROM BIRNESSITE

4.1 INTRODUCTION

The previous studies indicated that Mn released from soils by KCl or other neutral salts was mainly from the exchangeable phase. It is therefore of importance to find out which components of the soil are responsible for the retention and release of Mn that is readily available to plants. For this reason, studies were conducted to examine amounts of Mn^{2+} that can be retained by several soil clay minerals and Fe, Al and Mn oxides. The preliminary studies showed that the Mn oxide, birnessite (MnO_2), retained surprisingly higher amounts of Mn^{2+} than any other minerals tested. To understand the mechanism for the retention of Mn^{2+} by birnessite a study was conducted to examine whether this retained Mn^{2+} was non-specifically and/or specifically held, or oxidized on birnessite surfaces by extracting the Mn^{2+} held on birnessite with KCl, HCl and $Cu(NO_3)_2$ solutions.

4.2 MATERIALS AND METHODS

Preparation of Birnessite

Birnessite was prepared according to the method developed by McKenzie (1971). The detailed procedure for preparation of birnessite was described in chapter 2.

Retention of Mn^{2+} by Different Soil Minerals

(a) Six natural minerals, montmorillonite (Wyoming), vermiculite (Libby, South Africa), kaolinite (Mesa Alta, New Mexico), goethite (Biwabik, Minnesota), hematite

(Ironton, Minnesota), bauxite - a mixture of gibbsite, boehmite and diaspore (Little Rock, Arkansas) (obtained from Ward's Natural Science Establishment, Inc.), and one synthetic birnessite were used for study. After grinding in a Shatter Box (Model AA 151, Davies & Nelson Engineering Co. Ltd.), the powdered kaolinite and oxides were suspended in ethanol and passed through a 140-mesh sieve ($< 100~\mu$m). Fractions of $< 2~\mu$m of vermiculite and montmorillonite were collected according to Jackson's procedure (Jackson, 1979).

$MnSO_4$ stock solutions were prepared with concentrations of 100, 200, 400, 800, 1600 and 3200 μg Mn mL^{-1}. A 1.0 g sample of the oxide or kaolinite was placed into a 50-mL volumetric flask containing 25 mL of the stock $MnSO_4$ solution and 20 mL of deionized water. Samples of vermiculite and montmorillonite, instead of directly being added to the $MnSO_4$ solution, were first prepared as a stock suspension (2.5 g of sample in 200 mL deionized water), and then an aliquot of the suspension containing 0.25 g of clay was pipetted into a 50-mL volumetric flask. The pH of each suspension was adjusted with dilute NaOH or HNO_3 to 6.5 while stirring. Each flask was then brought to a volume of 48 mL with deionized water and the pH was once again adjusted. The mixtures were shaken and pH was checked frequently each day until it became constant. The suspension was brought to a volume of 50 mL with deionized water. The suspensions of vermiculite, montmorillonite and birnessite were filtered through 0.025 μm cellulose nitrate membrane and the other samples were filtered through #42 filter paper. After appropriate dilution, Mn in the filtrate was determined using atomic absorption spectrophotometry.

(b) The results of the above study indicated that Mn^{2+} in the solution was completely

sorbed by birnessite except in the suspension with the highest concentration of $MnSO_4$.

To examine the maximum adsorption capacity of MnO_2 for Mn^{2+} and the effect of pH on the adsorption, another experiment was conducted in which the concentration of Mn^{2+} was 400, 800, 1,200, 1,600, 2,000, 2,400, 2,800, 3,200, 3,600, or 4,000 μg mL^{-1} and the pH of the suspension was either adjusted to 6.5 or not adjusted (pH 2.9 to 2.5, corresponding to Mn^{2+} concentrations from 400 to 4,000 μg mL^{-1}) during the reaction. Other procedures were as outlined above.

Release of Mn^{2+} Retained by Birnessite

A study was conducted to examine amounts of Mn which could be released from birnessite previously treated with Mn^{2+} and obtain more information on the bioavailability of the Mn^{2+} retained. The birnessite was pretreated with Mn solution of two concentrations (100 and 300 μg Mn mL^{-1}) at a solid:solution ratio of 1:100 for 30 min or 6 d (without or with aging), and then extracted using different concentrations of KCl, HCl (0.001, 0.01, 0.1, 0.5, and 1.0 mol L^{-1}) or $Cu(NO_3)_2$ (0.033 and 0.33 mol L^{-1}, equivalent to ionic strength of 0.1 and 1.0, respectively). Untreated birnessite was used as a control. A 0.2 g of sample was placed in a 125-mL plastic centrifuge bottle containing 50 mL of extractant. The mixtures were shaken for 30 min, and then filtered immediately through a 0.025 μm cellulose nitrate membrane. About 10 mL of filtrate was collected for Mn analysis using atomic absorption spectrophotometry.

4.3 RESULTS AND DISCUSSION

Retention of Mn^{2+} by Different Minerals

Amounts of Mn^{2+} retained by different soil minerals at pH 6.5 varied greatly (Figure

4.1 and 4.2a). In general, the 2:1 clay minerals (montmorillonite and vermiculite) retained about 3 times more Mn^{2+} kaolinite and the Fe and Al oxides (Figure 4.1). The Mn oxide showed the highest capacity for Mn retention (Figure 4.2a), whereas goethite had the least ability to adsorb Mn^{2+}. The amount of Mn^{2+} retained by birnessite at pH 6.5 was about 10 times higher than that retained by the 2:1 clay minerals and 30 times greater than that retained by Kaolinite, bauxite and hematite. The amount of Mn^{2+} retained by goethite was negligible regardless of the concentration of Mn^{2+}.

It is easy to understand that the 2:1 clay minerals, because of their high CEC, have a greater ability to retain Mn^{2+} than kaolinite and the oxides of Fe and Al. The very high retention of Mn by birnessite cannot be readily explained by the conventional view on the chemistry of oxides, that is, the oxides of Mn, similar to oxides of Fe and Al, bear pH-dependent charge and these charges are the main sites of retention. Research on Mn oxides, especially in last decade, has revealed that Mn oxides have some striking differences from oxides of Fe and Al in their crystal structure. They are characterized by poor crystallinity, structural defects, domain intergrowths, cation vacancies and solid solution (Davis and Kent, 1990). The Mn(IV) vacancies and substitution of Mn(II) and Mn(III) for Mn(IV) in the structure develop a permanent structural charge. This charge is compensated by adsorbed cations that occupy a range of interstitial positions. These cations are exchangeable, as are some of the Mn(II) in the structure. Therefore, Mn oxides can exhibit a large variety of types of adsorption sites (Davis and Kent, 1990). Minerals in the birnessite group usually have much lower PZC (1.5 to 2.5) (McKenzie, 1981) than do the oxides and hydroxides of Fe (7.0 to 9.0) (Chwertmann and Taylor,
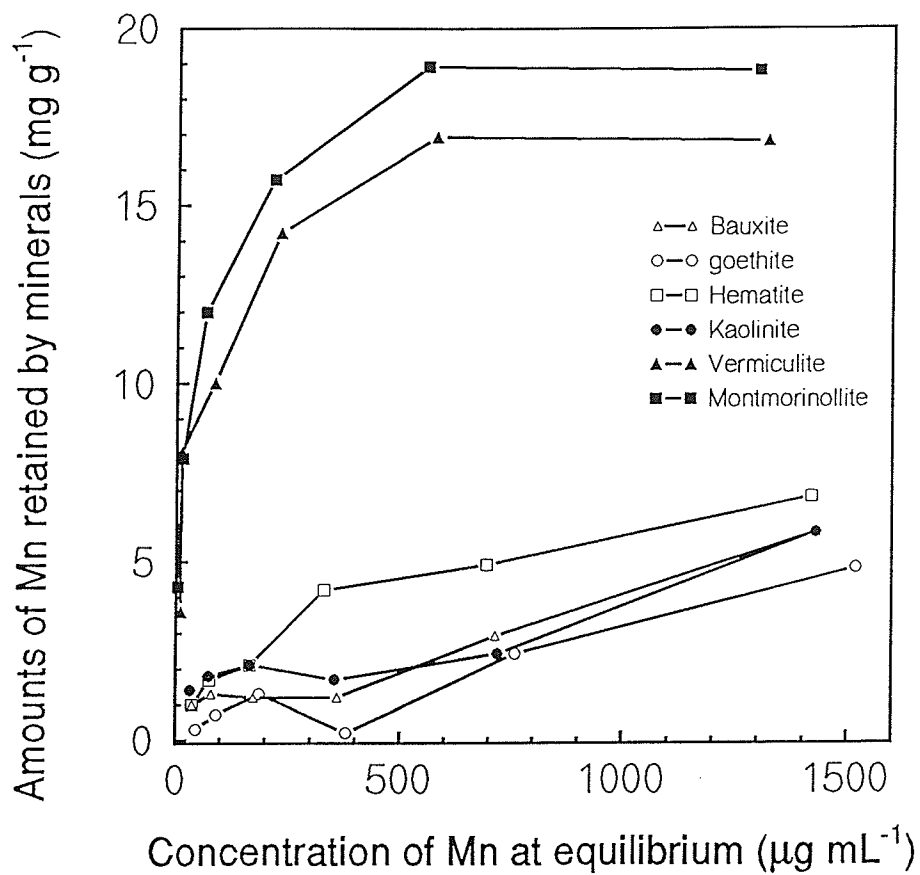
Figure 4.1 Amounts of Mn adsorbed by different minerals from a solution of $MnSO_4$ at pH 6.5
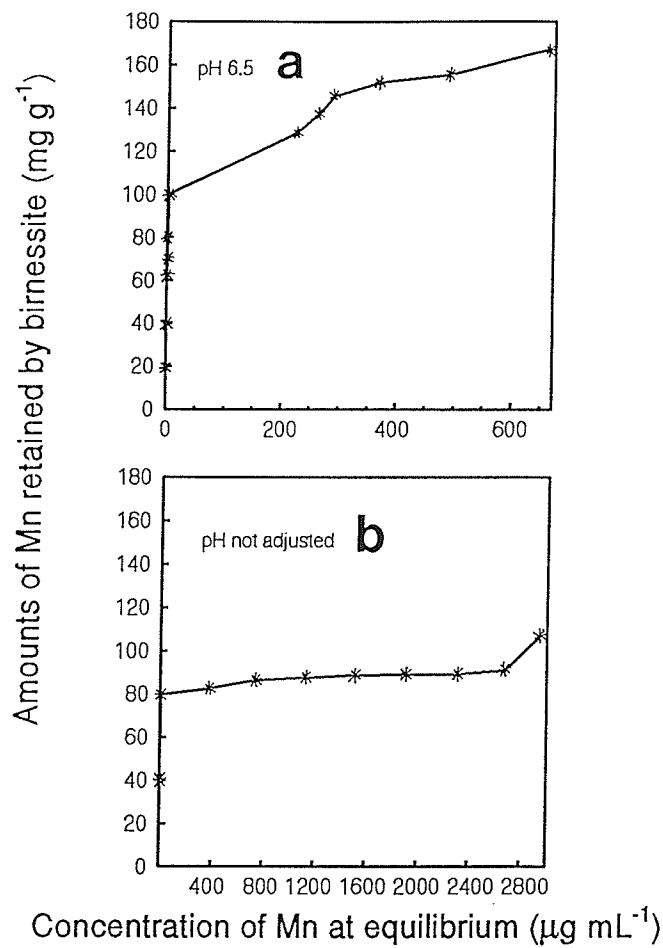
Figure 4.2 Amounts of Mn adsorbed by synthetic birnessite from a solution of $MnSO_4$ at two pHs

1989) or Al (8.0 to 9.2) (Hsu, 1989) so that they can develop high surface negative charge and large cation exchange capacities as the pH rises (Balistrier and Murray, 1982; McKenzie, 1981). Values of 63 and 167 cmol(+) kg^{-1} for the CEC of two birnessites at pH 7 were reported by McKenzie (1981) and a CEC of 240 cmol(+) kg^{-1} for a relatively well-crystallized birnessite at pH 5.5 was reported by Golden *et al.* (1986). The high charge on birnessite, along with some other characteristics as stated above, would therefore facilitate high retention of Mn or other cations.

The mechanisms responsible for retention of Mn^{2+} onto different minerals and oxides are obviously different. The adsorption curves showed a Langmuir Isotherm for the two 2:1 clay minerals, linear type for kaolinite, bauxite and hematite, and irreversible for the birnessite, at least at lower concentrations of Mn^{2+}.

During the process of Mn retention, protons were released, resulting in pH decreases, usually within a few seconds after initiation of the reaction. The magnitude of pH decreases appeared to be correlated to amounts of Mn^{2+} adsorbed by the oxide. For example, when the concentration of Mn^{2+} was increased from 400 μg mL^{-1} to 4,000 μg mL^{-1} the pH of the suspension was lowered from about 2.9 to 2.5. The correlation between Mn adsorption and release of H^{+} was probably directly due to replacement of H^{+} by Mn^{2+} from the birnessite surface. The release of H^{+} upon retention of Mn^{2+} by oxides has been observed by several workers (Loganathan *et al.*, 1977; McKenzie, 1978, 1979, 1980). The above authors attributed this release of H^{+} to (1) the specific interaction of the metal ions with surface sites and (2) exchange reactions in the double layer. In addition, H^{+} can be released due to hydrolysis of the metal ion (Parks, 1990).

In the case of Mn^{2+}, however, very little hydrolysis occurs at pH values less than about 9.0 (Linsay, 1979). Thus, the first two mechanisms are mainly responsible for the release of protons when the Mn^{2+} was retained by birnessite at low pHs. About a 1:1 ion ratio for H^+/M^{2+} exchange has been suggested by Murray (1975) and McKenzie (1978, 1979), implying that the adsorbed cations are associated with a single surface-OH (Norvell, 1988). The sorption reaction of Mn^{2+} onto birnessite is very rapid and is completed in < 1 s (Fendorf et al., 1993).

The amount of Mn^{2+} retained by birnessite was much less when the pH of the suspension was not adjusted than when the pH was adjusted to 6.5 (Fig. 4.2b). Also, the adsorption maximum without pH adjustment was attained at a lower concentration than when pH was adjusted. The effect of pH on Mn^{2+} adsorption may be attributed to pH-induced changes in the CEC of birnessite or dissociation of H^+ from the surface functional groups and strong competition between H^+ and Mn^{2+} for the adsorption sites. Though some Na^+ was introduced to the solution in association with a pH adjustment to 6.5, Na^+ was less capable of competing with Mn^{2+} for adsorption sites and thus affected amounts of Mn^{2+} adsorbed. As pH decreases the CEC of the birnessite and the competitive ability of Mn^{2+} over H^+ for the adsorption sites are decreased. Consequently, amounts of Mn retained decreased with decreases in pH.

Release of Mn^{2+} Retained by Birnessite

Amounts of Mn extracted from the Mn^{2+}-pretreated birnessite increased with amount of Mn retained and concentration of the extractant but decreased with time of aging (Table 4.1). Also, amounts of Mn extracted differed considerably with type of extractant

Table 4.1 Amounts of Mn released from freshly prepared and Mn^{2+} treated synthetic birnessite by KCl, HCl, and $Cu(NO_3)_2$

Extractant and conc.	control	100 μg Mn^{2+} mL^{-1}		300 μg Mn^{2+} mL^{-1}	
		Time of aging		Time of aging	
		30 min	6 d	30 min	6 d
mol L^{-1}	--------------------------------------mg g^{-1} -------------------------				
KCl					
0.001	-*	0.02	-	0.01	-
0.01	-	0.08	-	0.20	-
0.1	0.02	0.34	-	0.50	0.01
0.5	0.06	0.83	0.02	0.88	0.06
1.0	0.13	1.08	0.07	1.38	0.13
HCl					
0.001	-	0.09	0.01	0.10	-
0.01	0.02	0.41	0.02	1.25	0.11
0.1	0.06	1.28	0.19	3.88	2.06
0.5	1.49	4.88	0.98	11.50	6.25
1.0	2.62	5.96	2.25	20.50	10.43
$Cu(NO_3)_2$					
0.033	0.10	2.10	0.61	7.13	1.31
0.33	0.26	4.38	1.33	9.53	3.84
Total Mn^{2+} retained before extraction					
	0.00	10.00	10.00	30.00	30.00

* - not detected.

used. Among the three extractants, KCl showed the least and HCl the highest ability to extract Mn from birnessite. Though amounts of Mn extracted by KCl from the non-aged samples increased with concentration of the pretreated Mn^{2+} solution, the increases were

very small when compared to the other two extractants. However, amounts of Mn extracted by KCl from the birnessite which was aged after pretreatment with Mn^{2+} was similar to the amounts of Mn extracted from the untreated birnessite, indicating that the KCl-extractable Mn^{2+} initially retained by birnessite became non-extractable by KCl with time. Since KCl is not able to reduce MnO_2 to Mn^{2+} to any appreciable extent at pH above one (Appendix I) and could only extract Mn^{2+} mainly from exchangeable phases, this portion of Mn initially extractable by KCl but no longer extractable after aging was considered to become specifically adsorbed or oxidized and/or incorporated into the crystal structure. The migration of Mn^{2+} adsorbed on the surface into the interior structure is very likely because birnessite has a number of structural defects, has cation vacancies and exhibits solid solution behavior (Davis and Kent, 1990).

Amounts of Mn extracted by HCl increased substantially with an increase in the pretreated Mn^{2+} concentration regardless of aging. The amount of Mn extracted by 1.0 mol mL^{-1} HCl accounted for about 60 % of the total amount initially retained, when birnessite was pretreated with 100 μg Mn^{2+} mL^{-1}. The amount of Mn extracted by HCl was about 70 % of that retained by birnessite pretreated with 300 μg Mn^{2+} mL^{-1}. After aging, the amount of Mn extracted with HCl was slightly less than that for the control when pretreated with the lower concentration of Mn^{2+}, but about 4 times greater than that for the control when pretreated with the higher concentration of Mn^{2+}. Unlike KCl, HCl is capable of reducing MnO_2 to Mn^{2+} when its concentration is above 0.1 mol L^{-1} (Appendix I). Differences in amounts of Mn extracted by KCl and HCl were greater before than after aging. Thus, the results suggest that some of the Mn retained by

birnessite was initially retained in an exchangeable and/or in an easily reducible form, i.e., a form more soluble or easily-reducible than birnessite. After aging, the retained Mn was most likely incorporated into the structure of birnessite which then transformed the birnessite to a form of Mn oxide similar to birnessite in terms of resistance to HCl reduction and/or extraction by KCl.

$Cu(NO_3)_2$, at a concentration of 0.033 mol L^{-1} (0.1 mol L^{-1} in ionic strength), extracted more Mn than KCl or HCl at a concentration of 0.1 mol L^{-1}. However, the highest concentration of HCl extracted more Mn than 0.33 mol L^{-1} (1.0 mol L^{-1} in ionic strength) $Cu(NO_3)_2$ probably due to reduction of birnessite by the high concentration of HCl. Cu^{2+} is very capable of extracting specifically adsorbed Mn^{2+} (Warden and Reisenauer, 1991). Thus, the result indicates that much of Mn retained by birnessite was specifically adsorbed. The amount of Mn extracted by $Cu(NO_3)_2$ decreased after aging of the birnessite indicating that the type of bonding or retention mechanism changed with aging from exchangeable (both nonspecific and specific) forms to some other nonexchangeable forms.

The retention of Mn^{2+} by birnessite has drawn great interest from soil chemists in the past years. The mechanism of this retention, however, was not clear. The high affinity of birnessite for Mn^{2+} was attributed to specific adsorption or an autocatalytic oxidation mechanism (Pankow and Morgan, 1981). Ritchie (1989) suggested that the high affinity of birnessite for Mn^{2+} may be due to the oxidation of Mn^{2+} to Mn^{4+} catalyzed by the oxide surfaces at which the Mn^{2+} and OH^- are accumulated. It is also possible that Mn bound to the surface of the mineral can diffuse into the interior of the solid phase

(Schmitt and Sticher, 1991). The results of this study indicates that the mechanism of Mn^{2+} adsorption on birnessite is likely a combination of specific adsorption plus an autocatalytic oxidation reaction. Apart from this, some Mn^{2+} was non-specifically held on birnessite at the early stages of reaction. The results of latter studies (Chapter 5) revealed that the process of Mn^{2+} reaction with birnessite was not simply an *in situ* surface adsorption-oxidation process because *in situ* surface oxidation of such a large amount of Mn^{2+} on the adsorption sites would cause a significant pH decrease in the solution, as was shown by the initial adsorption of Mn^{2+} on the surface. Also, if the reaction was surface oxidation-coupled crystal growth, the interior structure of the birnessite would not be altered. However, the results showed that the pH of the suspension increased from 2.4 to 3.7 at the end of the reaction period when the initial pH was not adjusted (Appendix III). The pH would have decreased if all the adsorbed Mn^{2+} was directly oxidized on the surface. Moreover, the retention of Mn caused complete alteration of birnessite (Chapter 5). Therefore, the Mn ions initially adsorbed on the surface most likely migrated into the structure causing some H^+ released which was retained during the initial stages of adsorption to be re-adsorbed onto the surface. The Mn then probably underwent oxidation within the lattice positions. The potassium in birnessite underwent a similar reaction to that of H. McKenzie (1970) observed a rapid release of K on the first day after treatment of birnessite with $CuCl_2$. Much of the K was then slowly readsorbed during aging. During these transformations the extractability and hence bioavailability of Mn^{2+} retained by birnessite was reduced.

4.4 CONCLUSIONS

The 2:1 clay minerals retained much greater amounts of Mn^{2+} from solution than the 1:1 clay mineral and the oxides of Al and Fe. The Mn oxide (birnessite), however, retained much higher amounts of Mn than the clay minerals and Fe and Al oxides. The Mn^{2+} retained by birnessite, shortly after reaction, was probably both specifically and non-specifically adsorbed. With time, the non-specifically adsorbed Mn^{2+} became specifically adsorbed and/or incorporated into the structure and then, if not all, directly oxidized to Mn(III) and/or Mn(IV) in the lattice positions. Thus the extractability of the adsorbed Mn was reduced rapidly with time.

5 TRANSFORMATIONS OF SYNTHETIC BIRNESSITE AS AFFECTED BY pH AND Mn CONCENTRATION

5.1 INTRODUCTION

Birnessite is one of the most common Mn minerals in soils (McKenzie, 1989). It has a layer lattice structure, with high specific surface areas (50 to 300 m^2 g^{-1}) (Healy et al., 1966; McKenzie, 1980b) and the lowest point of zero charge (PZC) (pH 1.5 to 2.5) among the known Mn minerals (McKenzie, 1981). Thus birnessite develops a high surface charge and large CECs (63 to 240 cmol(+) kg^{-1}) (McKenzie, 1981; Golden et al., 1986) at pH values normally encountered in soils.

McKenzie (1980a) reported that Mn oxides have a much higher affinity for Mn^{2+} than for other divalent cations such as Ni^{2+} and Zn^{2+}. The sorption study (Chapter 4), using three clay minerals (vermiculite, montmorillonite and kaolinite) and four oxides or hydroxides of Fe (hematite, goethite), Mn (birnessite), or Al (bauxite - a mixture of gibbsite, boehmite and diaspore), showed that birnessite had the highest adsorption capacity for Mn in solution, retaining 3 to 30 times more Mn than the other adsorbents. Fendorf et al. (1993) showed that the sorption reaction of Mn^{2+} onto birnessite was very rapid and was completed in < 1 s, with > 80 % of the Mn^{2+} being adsorbed within 200 ms.

The nature and fate of the Mn^{2+} retained by birnessite are not fully understood. Pankow and Morgan (1981) proposed that specific adsorption was responsible for the high affinity of Mn oxides for Mn^{2+}, similar to adsorption of other transition metal ions

on oxide surfaces of Al and Fe. The sorbed Mn^{2+} on the surface of Mn oxides was suggested to be oxidized to Mn^{4+} and the oxidation reaction was catalyzed by the oxide surface at which the Mn^{2+} and OH^- accumulated. Murray and Dillard (1979), using x-ray photoelectron spectroscopy, were unable to detect any Mn^{2+} on the surface of birnessite after adsorption of Mn^{2+}.

Hydrous Mn oxides are characterized by their poor crystallinity, structural defects, domain intergrowths, cation vacancies, and solid solutions (Davis and Kent, 1990). The Mn^{2+} initially sorbed on the surface may later become incorporated into the Mn oxide structure at sites of structural defects and cation vacancies and/or as a result of extensive substitution of Mn^{2+} and Mn^{3+} for Mn^{4+} (Krauskopf, 1972; McKenzie, 1989). The results of Chapter 4 indicated that the Mn^{2+} was retained in easily exchangeable as well as nonexchangeable forms when Mn^{2+} was reacted with birnessite for a short period of time. The exchangeable form then changed to a non-exchangeable form with time. However, it was not clear whether the Mn^{2+} ion was oxidized *in situ* at the adsorption site or incorporated into the crystal structure of birnessite. Furthermore, there is no information available whether the adsorbed Mn would cause any structural alteration of birnessite at different solution pHs. Therefore, the objective of this study was to study the effect of concentration of Mn and solution pH on the alteration of birnessite after adsorption of Mn.

5.2 MATERIALS AND METHODS

Preparation of Birnessite

Birnessite was prepared according to the method developed by McKenzie (1971). The

detailed procedure for birnessite preparation was described in chapter 2.

Reactions of Mn^{2+} with Birnessite

Birnessite, 0.33 g in weight, was suspended in a 100 mL beaker containing 30 mL of 0.33 mL L^{-1} $MnSO_4$ solution. The initial pH of the suspension was 2.4 (pH not adjusted). Further, suspensions were adjusted to pH values of 4, 5, 6, 7, or 8 using dilute NaOH. The pH, when adjusted to a particular value, was continually adjusted to the desired pH for the first two hours of reaction. The concentrations of $MnSO_4$ used for the suspensions of pH 2.4 and 8 were 0, 0.0033, 0.033 or 0.33 mol L^{-1}. In order to compare the effect of Mn with some other cations on the structural changes of birnessite, the birnessite was also suspended in 0.33 mol L^{-1} $Ca(NO_3)_2$, or $Cu(NO_3)_2$, or 1.0 mol L^{-1} KCl solution without pH adjustment. The beakers were covered with parafilm but aeration was allowed through pin holes on the cover. The suspensions stood at room temperature (21 ^0C) and were stirred occasionally.

About 20 mg of sample was taken daily from each beaker with a transfer pipette and washed in a cellulose nitrate membrane filter (pore size 0.025 μm) with about 30 mL of deionized water for X-ray analysis. The sampling was continued until no more change was observed in X-ray diffraction patterns. The final products were filtered and washed on #42 filter paper until free of sulfate and then air-dried for X-ray diffraction analysis and for its crystal morphological examination under the transmission electron microscope (TEM). In order to elucidate the mechanism of transformation of birnessite, a subsample, taken from the treatment with 0.33 mol L^{-1} $MnSO_4$ at pH 2.4, 4 and 6 after 1, 3 and 5 d, respectively, and washed in a cellulose nitrate membrane filter (pore size 0.025 μm)

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until free of sulfate, was examined under the TEM.

The powder samples of the final products were used for X-ray diffractometry. Step scan X-ray diffraction data were collected from 5-75^0 2θ, using a step interval of 0.05^0 2θ and a counting time of 2 s/ step, using a Philips automated diffractometer system PW1710. A PW1050 Bragg-Brentano goniometer equipped with incident- and diffracted-beam Soller slits, 1.0^0 divergence and anti-scatter slits, a 0.2 mm receiving slit and a curved graphite diffracted-beam monochromator was used. The normal focus Cu X-ray tube was operated at 40 kV and 40 mA, using a take-off angle of 6^0. The step scan data were then converted to Siemens .RAW file format prior to being processed using Siemens DIFFRAC software. A peak search routine was run to generate a list of d-spacings and intensities (.DIF file) and then the pattern profiles were printed. The data files were then used with Fein-Marquart's μPDSM Search-Match software in an attempt to identify the phases present. The μPDSM software searches the most recent Powder Diffraction File database (PDF-2 on CD-ROM, Set 42) of the International Centre for Diffraction Data (ICDD).

Prior to transmission electron microscopic (TEM) examination, 1 - 5 mg of sample was dispersed in 10 mL distilled water using ultra-sonication. One drop of this suspension was placed onto electron transparent Formvar (ethylenedichloride) support films, which was previously mounted on 300 mesh copper support grids and coated with carbon. After the particles had settled for 2 - 3 min, the excess suspension was removed with a piece of specially cut filter paper. The specimen was dried in a petri dish and then kept in a desiccator prior to examination. Examination of the specimen was performed

using a Phillips TEM 420 transmission electron microscope.

5.3 RESULTS AND DISCUSSION

Effect of Salts and pH on Transformation of Birnessite

Synthesized birnessite has major x-ray diffraction (XRD) peaks near 0.727, 0.361, 0.246, 0.233, 0.204, 0.172, and 0.142 nm (McKenzie, 1989) and has a layer lattice structure. The birnessite synthesized in this work, however, had only four major XRD peaks near 0.735, 0.366, 0.244, and 0.141 nm, similar to the birnessites found in soils by other workers (Jones and Milne, 1956; Frondel *et al.*, 1960; Brown *et al.*, 1971; Koljonen *et al.*, 1976). The difference in the XRD patterns between the synthetic birnessite as shown in the Powder Diffraction File and the one in this work may be due to the difference in the methods of preparation. The former, a sodium birenssite, was prepared by oxidation of $Mn(OH)_2$ in an alkaline suspension upon dehydration, whereas the later was prepared by reducing $KMnO_4$ with concentrated HCl in a boiling solution and the final product was air-dried only. Since the lines near 0.727 and 0.360 are the basal spacings resulting from the separation of the sheets of the MnO_6 octahedra of about 0.72 nm, it is possible that the partly hydrated birnessite may result in wider spacings than 0.727 nm. Under a transmission electron microscope (Figure 5.1a), birnessite was observed as needles which were clustered into balls. No transformation of birnessite occurred in water with a pH adjusted to 1.5, or 8.0 or in the KCl, $Ca(NO_3)_2$, and $Cu(NO_3)_2$ solution, even after one month of incubation, indicating that neither addition of H^+ or OH^- nor any other cations apart from Mn were able to initiate transformation of the crystal structure of birnessite at room temperatures in a relatively short period of

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time (Figure 5.2).

Transformation of Birnessite as Affected by MnSO$_4$ at Different pHs

When suspended in MnSO$_4$ solution, birnessite readily underwent transformation to other forms of Mn(III) and/or Mn(IV) minerals at room temperature. The transformations observed were not only governed by the pH of the mother liquor, but also by the concentration of Mn^{2+}. The newly-formed Mn minerals from birnessite in a 0.33 mol L^{-1} MnSO$_4$ solution, as affected by different pH, were identified by the XRD patterns (Figure 5.3 and Table 5.1) and morphology as seen in electron micrographs (Figure 5.1b-f). The original peaks obtained from birnessite either disappeared or shifted after the birnessite was suspended in the MnSO$_4$ solution (Figure 5.3). At a pH of about 2.4, two Mn minerals were identified from the XRD patterns: nsutite, a Mn hydroxide with a chemical formula of γ-Mn(O,OH)$_2$ (JCPDS-ICDD 17-0510), and ramsdellite, a Mn oxide with a chemical formula of MnO$_2$ (JCPDS-ICDD 30-0375) (Powder Diffraction File, Set 42, 1992). Their XRD patterns are shown in Figure 5.3 and the corresponding numerical data all listed in Table 5.1. The *d* spacings for the identified nsutite are similar to those described in the JCPDS-ICDD 17-0510, except for the absence of one medium and one weak peak for the experimental sample (Table 5.1). For ramsdellite, the XRD patterns are almost identical to those described in the JCPDS-ICDD 39-0375. The crystal morphology of the newly-formed Mn minerals are shown in the electron micrograph (Figure 5.1b). There were two types of crystals observed as fibrous crystals (F) and shuttle-shaped crystals (SH) (Figure 5.1b and Figure 5.5b and c, enlarged). For comparative purpose, a nsutite, prepared in a similar experiment with MnCl$_2$ or

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$Mn(NO_3)_2$ at pH 1.85, showed shuttle-shaped crystals in an electron micrograph (Appendix IV). This suggests that the shuttle-shaped crystals were probably the nsutite, and the other was ramsdellite.

At pH 4, a major proportion of the birnessite was transformed into cryptomelane, as seen from the XRD peaks at 0.698, 0.497, 0.484, 0.3149, 0.3110, 0.2399, 0.217, 0.1843, and 0.1654 nm (Figure 5.3c and Table 5.1). There was two medium-strong and a weak peak missing as compared to those of cryptomelane-M, a potassium manganese oxide with a chemical formula $K_2Mn_8O_{16}$ (JCPDS-ICDD 4-0778). In addition, a comparison of the experimental XRD data at 0.702, 0.494, 0.314, 0.2406, 0.216 and 0.1839 nm to those of manjiroite-M, $(Na,K)Mn_8O_{16}.xH_2O$ (JCPDS-ICDD 21-1153), showed only one weak peak missing. The transmission micrograph of the experimental sample was similar to that shown by McKenzie for cryptomelane (1989). Also, the conversion of birnessite to cryptomelane was achieved by several workers (Buser *et al.*, 1954; Gattow and Glemser, 1961; Glemser *et al.*, 1961) by directly igniting synthetic birnessite at 400 ^{0}C or boiling birnessite which had been pre-washed with $MnSO_4$ solution or dilute HCl. In the latter method the upper and lower limits of K in the birnessite were 7% and 0.25%, respectively. Within this range, a successful transformation of birnessite to crymptomelane can be achieved. Thus, the lath-shaped crystals were most likely cryptomelane rather than manjiroite. The lath-shaped crystals (CR in Figure 5.1c), about 0.4 μm in length, were most likely cryptomelane. Only trace amounts of birnessite was altered to two other Mn minerals that could be easily distinguished in the electron micrograph as moss-like crystals (M) and the crystals (SS

Figure 5.1 Transmission electron micrographs showing a synthetic birnessite (a) and newly-formed Mn minerals (b-f) from the birnessite after treatment with 0.33 mol L^{-1} $MnSO_4$ solution at different pHs after 10 to 60 days. (a) synthetic birnessite, balls of needles; (b) pH 2.4 (not adjusted), fibrous crystals (F) of ramsdellite and shuttle-shaped crystals (SS) of ramsdellite; (c) pH 4, lath-shaped crystals of cryptomelane (CR), moss-like crystals (M) and pseudo-hexagonal stacks (SS); (d) pH 5, rod-shaped crystals (R) and hexagonal cones (HC); (e) pH 6, hexagonal cones(HC) and parallel intergrowths of slat-shaped crystals (bundle of needles) (S); (f) pH 8, short rod-shaped crystals of manganite (SR) and long rod-shaped crystals of an unknown (LR).
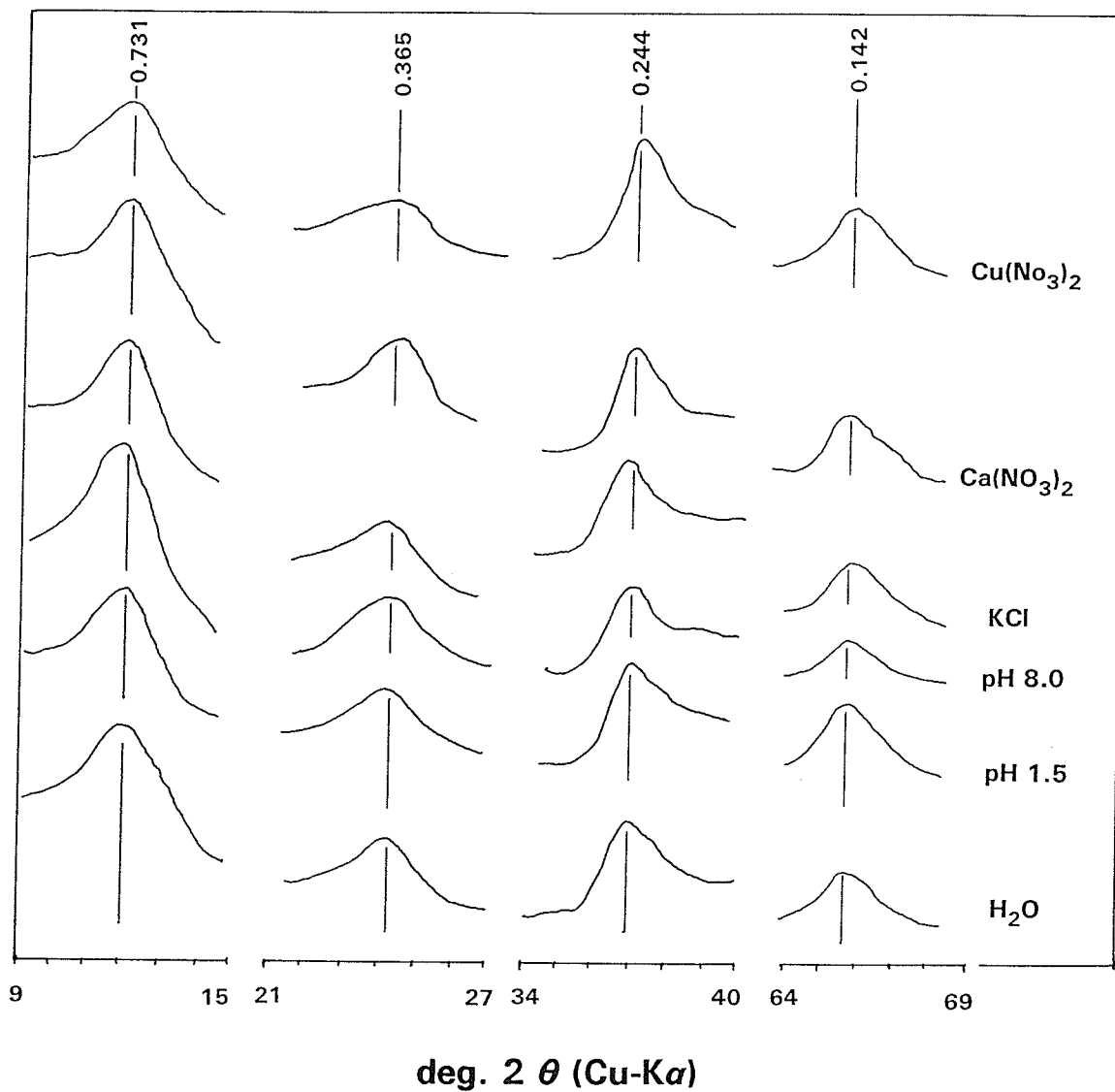
79
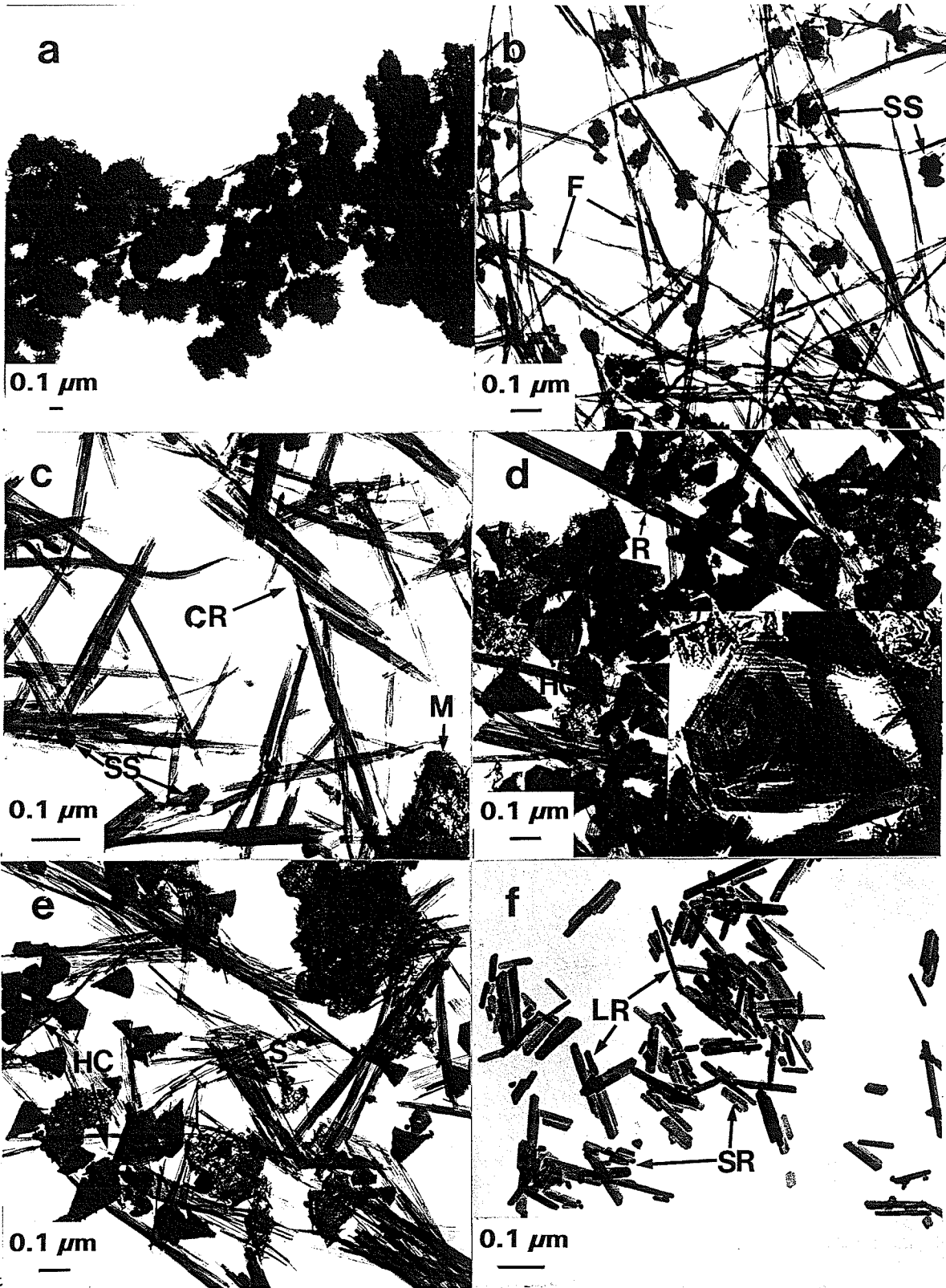
Figure 5.2 X-ray diffraction patterns of synthetic birnessite after aging in water at different pH and solution conditions.
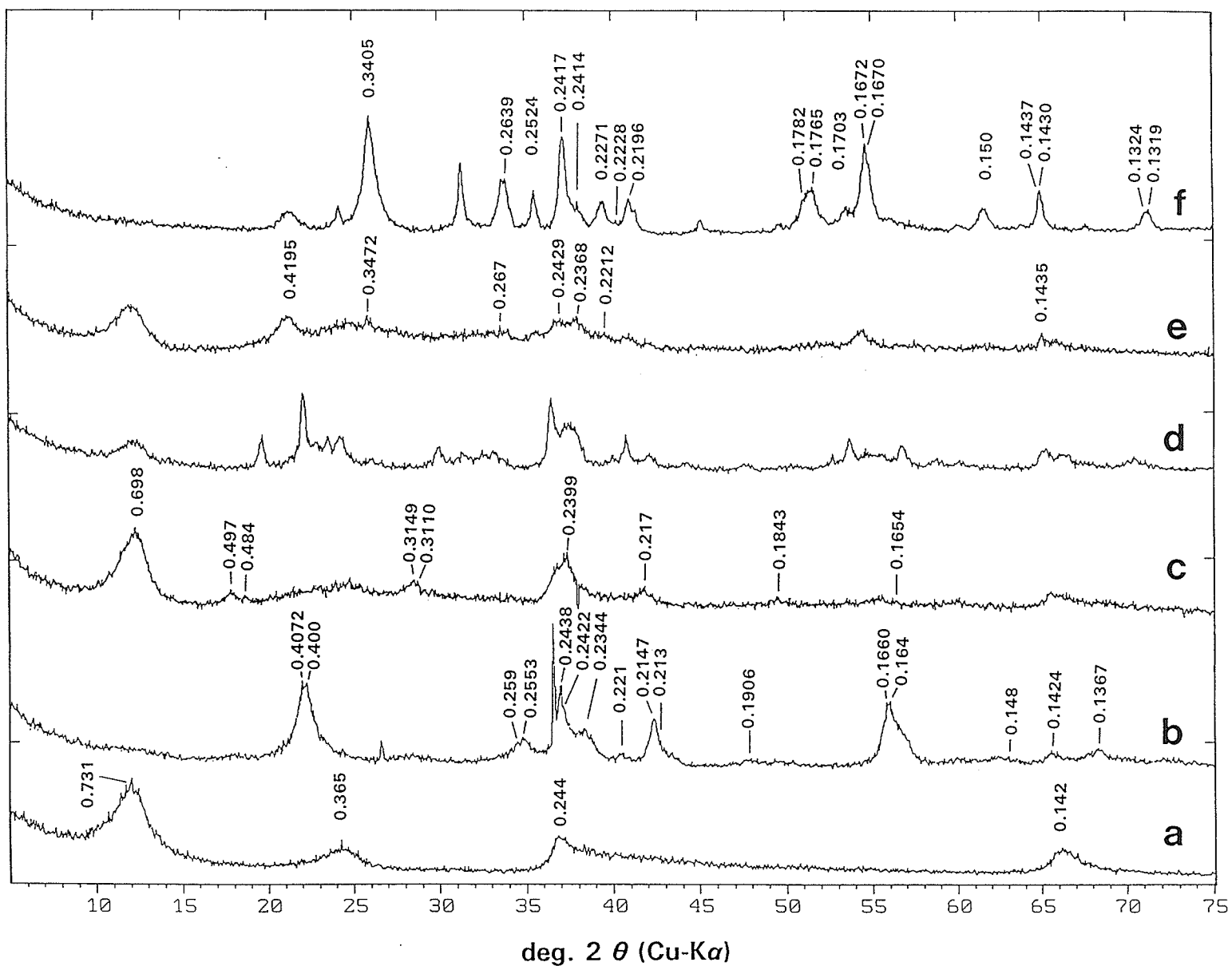
Figure 5.3 X-ray diffraction patterns of a synthetic birnessite (a) and the products transformed from the birnessite after treatment with 0.33 mol L^{-1} MnSO$_4$ solution at different pHs (b-f): (b) pH 2.4, (c) pH 4, (d) pH 5, (e) pH 6, and (f) pH 8. The labelled peaks are identified.

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Table 5.1 X-ray diffraction data and identified phases for the final products formed from birnessite after treatment with 0.33 mol L^{-1} $MnSO_4$ solution at different pH values

Treatment	d spacings (nm) and intensities (%)	JCPDS card

pH 2.4   0.4250 0.4038 0.4003 0.3349 0.2601 0.2575 0.2456 0.2428 0.2346 0.2224 0.2132

           (23)   (62)   (60)   (23)   (22)   (25)   (100)   (59)   (31)   (15)   (38)

           0.2087 0.1898 0.1650 0.1642 0.1487 0.1423 0.1372

           (15)   (11)   (36)   (48)   (13)   (17)   (19)

Identified phases: Mn oxide hydroxide/Nsutite = $Mn(O,OH)_2$ Hexagonal a:0.965 c:0.443   17-0510

           0.400   0.259   0.242   0.233   0.221   0.213   0.207   0.190   0.164   <0.160>

in Figure 5.1c) that appeared similar in shape to those observed at pH 2.4 (SS in Figure 5.1b).

The XRD patterns obtained from the products at pH 5 could not be matched with any Mn minerals filed in the most recent Powder Diffraction File database (PDF-2 on CD-ROM, Set 42) by the international Centre for Diffraction Data (ICDD). The electron micrograph showed that there were two kinds of crystals: rods (R) and hexagonal-cones (HC in Figure 5.1d). Owing to the lack of information on the XRD patterns and previous description of their morphology in the literature their identification appears difficult using only x-ray data and the TEM graphs. The electron micrograph seemingly showed the presence of a third moss-like mineral at pH 5.

By scrutinizing the micrograph, we found this material was frequently associated with the broken cones as shown in the micrograph. This led us to believe that this material was debris of the broken cones, most likely produced from mechanical damage during the process of sample preparation. At first glimpse, the cones appear to be hollow inside. However, the broken cones revealed to us that the cones are not hollow and that the cones could be layers of hexagonal crystals. Also, the cones consist of various sizes of cones in which cones of smaller diameter are stuck inside those of larger diameter (HC in Figure 5.1d). In several cases, the separation of the cone layers along the cleavage was clearly observable (Figure 5.1d, inset). The rod-shaped crystals measured about > 1.2 μm in length, 3 times longer than the cryptomelane prepared by aging birnessite in 0.33 mol L^{-1} MnSO$_4$ at pH 4 (Figure 5.1c).

The products formed at pH 6 gave XRD patterns which indicate the presence of

groutite, a α-MnOOH (JCPDS-ICDD 24-0713). The experimental sample lacked only one peak at 0.281-nm as compared to the standard groutite (Table 5.1). Two types of crystals were evidently distinguishable in the electron micrograph (Figure 5.1e): the hexagonal cones (HC) and parallel intergrowths of slat-shaped crystals (bundles of needles) (S). The needle-shaped mineral had a length similar to the fibrous crystals formed at pH 2.4, but unlike that mineral, it occurred in bundles and seemed rigid so that broken pieces were commonly observable in the micrographs. Also unlike the rod-shaped mineral formed at pH 5, the crystals of this mineral were much shorter and thinner, resulting in increased transparency. Since the hexagonal cones occurred both at pH 5 and 6, which was not identified from the XRD data, and this needle-shaped phase formed only at pH 6, it can be inferred that these needles must be groutite. The moss-like crystals, similar to those described at pH 4, were also observed in the micrograph at pH 6. The XRD data of the moss-like crystals resembled, more or less, its parent material (birnessite). Thus, this suggests that the moss-like material may be the intermediate of the transformation of birnessite to other Mn minerals at pH 4 and 6.

The XRD patterns obtained from the products at pH 8 indicate the formation of manganite (MnOOH) (JCPDS-ICDD 41-1379) with eight most intense peak lines positioned at 0.341, 0.264, 0.178, 0.2417, 0.1672, 0.2414, 0.1670, and 0.252 nm. Under the electron microscope, manganite appeared as short rod-shaped crystals < 0.08 μm in length (Figure 5.1f, SR), with the same crystal morphology as the product prepared by titrating a $MnSO_4$ solution with NaOH. This suggests that manganite formed at pH 8 as a result of oxidation of $Mn(OH)_2$ that was precipitated from $MnSO_4$ during

the process of pH adjustment with NaOH. The longer rod-shaped crystals (Figure 5.1f, LR), about 0.2 μm in length, was not identified by x-ray diffractometry.

Transformation of Birnessite as Affected by Concentration of MnSO$_4$

The rate of alteration of birnessite to a new Mn mineral increased with an increase in concentration of Mn at a given pH. It took only 9 d for complete transformation of birnessite to manganite and another unidentified mineral at a concentration of 0.33 mol L^{-1} MnSO$_4$ and a suspension pH 8, whereas no change of birnessite occurred at 0.0033 mol L^{-1} MnSO$_4$ even after one month (Figure 5.4 and Appendix III). The XRD pattern obtained at 0.033 mol L^{-1} MnSO$_4$ showed the presence of birnessite (Figure 5.4b).

The Mechanism of Birnessite Transformation

The TEM micrographs in Figure 5.5 illustrate the sequential morphological alteration of the birnessite after treatment with 0.33 mol L^{-1} MnSO$_4$ at day 1, 3, and 5 (referred to, as a, b, and c at pH 2.4, and d, e, and f at pH 6, respectively). The micrographical evidence showes that the transformation of birnessite was solid form transformation, yielding several solid phases. At pH 2.4, the separation of some aggregates from the parent material was visible after one-day reaction. However, by day 3, formation of needle-shaped and shuttle-shaped crystals were observed. The transformation was close to completion by day 5. At pH 6, the rate of reaction was much faster than that at pH 2.4. The parent material was reorientated or converted to fine fibrous crystals by day 1. After 3 days, the fine fibrous crystals changed to thicker separate needle crystals (bundles of fibres). After 5 days, both the hexagonal cones and needle-like crystals were clearly identifiable.
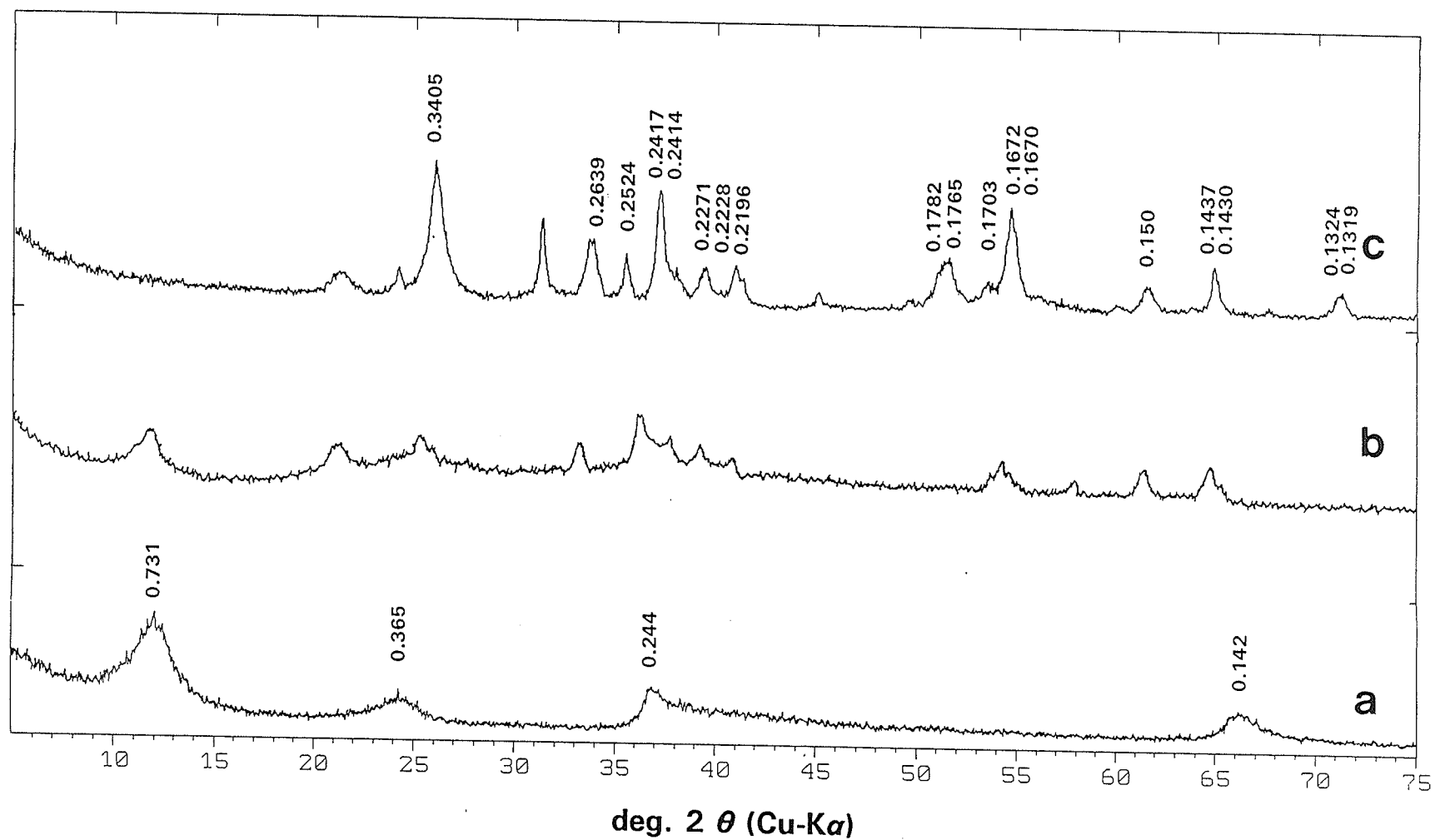
Figure 5.4 X-ray diffraction patterns of products formed after treatment of birnessite with solutions of (a) 0.0033, (b) 0.033 and (c) 0.33 mol L^{-1} $MnSO_4$ at pH 8.0. The labelled peaks are identified.
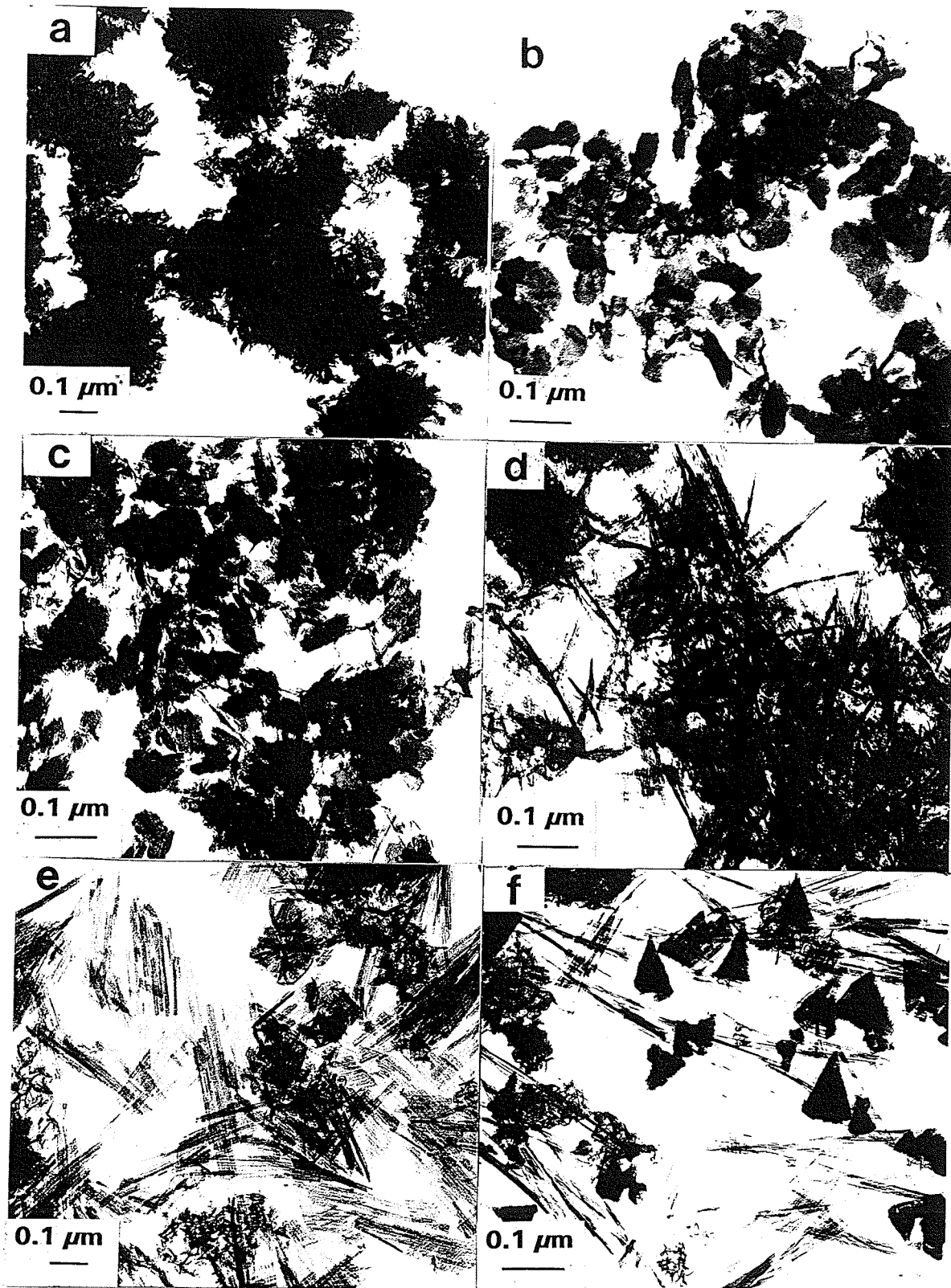
Figure 5.5 Sequential alteration of birnessite crystals accompanying new crystal formation as observed after treatment with 0.33 mol L^{-1} MnSO$_4$ at pH 2.4 and 6.

The results clearly demonstrated that the presence of Mn^{2+} in thesolution acted both as a catalyst and essential component for the transformation of birnessite, without which the reaction would not proceed. The pH of the medium, on the other hand, was in control of the direction of the reaction, i.e., determining types of final products. Finally, both the concentration of Mn^{2+} and pH were of great importance in determining the rate of the reaction.

The fate of Mn^{2+} scavenged by birnessite has puzzled researchers for years. Pankow and Morgan (1981) proposed that specific adsorption was responsible for the high affinity of Mn oxides for Mn^{2+}. After comparing Mn^{2+} to other more hydrolysable metals, however, Ritchie (1989) suggested that the retention of Mn^{2+} by Mn oxides cannot be readily explained by just specific adsorption of Mn^{2+} alone or surface induced hydrolysis. A number of workers (Hem, 1963; Morgan and Stumm, 1964; Sung and Morgan, 1981) believed that the adsorbed Mn^{2+} onto the Mn oxides was oxidized to Mn^{4+} through autocatalytic reaction by the oxide surfaces. The oxidation of adsorbed Mn^{2+} on the oxide surfaces was suggested by Murray and Dillard (1979), who, using x-ray photoelectron spectroscopy, were unable to detect any Mn^{2+} on the surface of birnessite after adsorption of Mn^{2+}. The results of this study and the desorption study discussed previously (Chapter 4) provided evidence to elucidate the fate and chemistry of the adsorbed Mn^{2+} by birnessite. It is clear that Mn^{2+} was rapidly adsorbed both non-specifically and specifically after birnessite was suspended in a $MnSO_4$ solution. Some of the Mn^{2+} adsorbed were incorporated into the structure of the birnessite and then some, if not all, were oxidized to Mn(III) and/or Mn(IV) with time. The adsorbed

Mn^{2+} and/or the oxidized Mn^{3+} or Mn^{4+} subsequently induced spontaneous rearrangement and reorientation of atoms in the birnessite lattice structure, leading to the transformation of birnessite into a series of new Mn minerals. The type of minerals formed depended on the solution pH. It did not appear that the new minerals formed ex-solution either, since the appearance of the newly formed products was at the expense (i.e. disappearance) of birnessite. We were also unable to synthesize the same products at any pH with the exception of manganite at pH $\geq$ 7 when $MnSO_4$ solutions were aged alone, i.e. in the absence of birnessite. Finally, we did not observe any dissolution of the suspended birnessite followed by recrystallization or reprecipitation of new products. Therefore, the unique effect of pH on types of Mn minerals formed may be directly attributed to ratio of O/OH that connect with Mn and to the extent that adsorbed Mn^{2+} can be oxidized to Mn^{3+} and/or Mn^{4+} at a given pH. As was seen from the XRD and electron transmission data, the reaction with Mn^{2+} transformed birnessite from a relatively unstable and poorly crystallized mineral into more stable and well crystallized products. This transformation virtually converts solution Mn^{2+} into an insoluble solid form in the lattice of the newly formed minerals where Mn may exist in oxidation states from Mn(II) to Mn(IV).

5.4 CONCLUSIONS

This study, along with the previous study (Chapter 4), helped to elucidate the nature and fate of Mn^{2+} after retention by birnessite, and the alteration of birnessite after treatment with Mn^{2+} at different pHs. Sorption of Mn^{2+} by birnessite at room temperature caused formation of new Mn phases. The final products of transformations

were determined by solution pH and the rate of the transformation was determined by Mn^{2+} concentration and pH. Among phases that were crystalline by X-ray diffractometry, nsutite and ramsdellite were identified at pH 2.4, cryptomelane at pH 4, groutite at pH 6, and manganite at pH 8. The newly-formed phases were the results of structural conversion since dissolution of birnessite and reprecipitation of new phases were not observed.

6 SUMMARY AND CONCLUSIONS

Several studies were conducted to investigate the mechanisms of KCl-enhanced Mn uptake by crops and the nature and fate of Mn^{2+} adsorbed onto birnessite. The experiments conducted included extraction studies, plant growth studies, studies on the solubility of soil indigenous and applied Mn as affected by KCl after incubation and formation of complexes of Mn and Cl in aqueous solution, studies on sorption and desorption of Mn on birnessite and transformations of birnessite as affected by Mn concentration and pH.

The results revealed that amounts of Mn extracted by KCl from soils, during a short period of time, were similar to those extracted by other neutral K-salts, such as K_2SO_4, suggesting that the Mn extracted by KCl was mainly from the exchangeable phase. However, KCl application alone or in combination with Mn fertilizer significantly increased the solubility and bioavailability of soil indigenous and applied Mn over an extended period of time whereas solubility with other salts was no greater than for untreated soils after incubation. The increase in solubility and bioavailability of Mn with KCl was always greater than with K_2SO_4 or K_2CO_3, and more pronounced on the noncalcareous soils than on the calcareous soils. The results indicated that the increase in solubility and bioavailability of Mn by KCl was mainly due to formation of anionic complexes of Mn and Cl.

The 2:1 clay minerals appeared to be mainly responsible for adsorbing and releasing Mn that is readily available to plants, whereas kaolinite and oxides of Fe and Al only

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adsorbed small amounts of Mn. Birnessite, however, was able to not only adsorb large quantity of Mn^{2+} from solution, but also convert the adsorbed Mn^{2+} to non-exchangeable form and eventually reduce its availability. During this reaction, the Mn^{2+} adsorbed on birnessite transformed birnessite from a relatively unstable and poorly crystallized mineral into an array of more stable and highly crystalline Mn minerals.

The results of these studies are obviously of great agronomic importance. These results suggest that in order to improve availability and efficiency of applied Mn fertilizers on Mn deficient soils, Mn fertilizers should be applied with KCl or other Cl fertilizers. In contrast, application of KCl on Mn abundant soils, especially when acidic, should be avoided. Under such conditions, K_2SO_4 may be the preferable K carrier.

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APPENDICES

APPENDIX I

Concentrations of Halides and pH required to reduce MnO_2 at 1 atm. and 25 ^0C

(1). General reaction:

$$MnO_2 + 4 H^+ + 2 X^- \text{ --- } Mn^{2+} + X_2 + 2 H_2O$$

where X stands for Cl, Br or I.
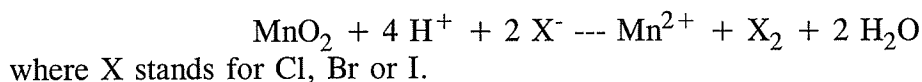
(2). Half-reactions and their reduction potentials:

$$MnO_2 + 4 H^+ + 2 e \text{ --- } Mn^{2+} + 2 H_2O \qquad \epsilon^0 = 1.21 \text{ V}$$
$$2 Cl^- \text{ ---- } Cl_2 + 2 e \qquad \epsilon^0 = -1.36 \text{ V}$$
$$2 Br^- \text{ ---- } Br_2 + 2 e \qquad \epsilon^0 = -1.09 \text{ V}$$
$$2 I^- \text{ ---- } I_2 + 2 e \qquad \epsilon^0 = -0.54 \text{ V}$$
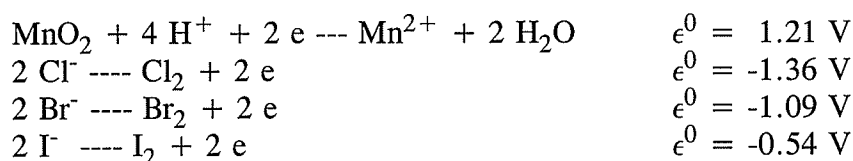
(3) calculations of $K_{eq.}$ and concentration of Mn^{2+} in MnO_2/Mn^2 system:

i. In the case of Cl:

$$MnO_2 + 4 H^+ + 2 e \text{ --- } Mn^{2+} + 2 H_2O \qquad \epsilon^0 = 1.21 \text{ V}$$
$$2 Cl^- \text{ --- } Cl_2 + 2 e \qquad \epsilon^0 = -1.36 \text{ V}$$

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$$MnO_2 + 4 H^+ + 2 Cl^- \text{ --- } Mn^{2+} + Cl_2 + 2 H_2O \qquad \epsilon^0 = -0.15 \text{ V}$$
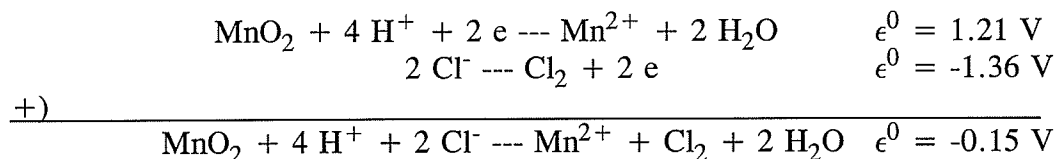
$$\Delta G^0 = - RT \ln K = -nF\epsilon^0$$
$$= -2 * 96.5 * (-0.15)$$
$$= 28.95 \text{ KJ mol}^{-1}$$

$$\ln K = -\frac{\Delta G^0}{RT} = -\frac{28.95 \times 10^3}{8.314 \times 298} = -11.685$$

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$$\frac{}{[MnO_2] [H^+]^4 [Cl^-]^2}$$

According to convention, the value of $[Cl_2]$, $[H_2O]$, or $[MnO_2]$ is assumed to be 1, thus

$$[Mn^{2+}] = 10^{-5} [Cl^-]^2 [H^+]^4$$

If we assume $[Cl^-] = 1.0$ mol L^{-1}, then $[Mn^{2+}] = 10^{-5} [H^+]^4$ mol L^{-1}. The

concentration of Mn at different pHs can be calculated and are as follows:

pH	$[H^+]^4$	$[Mn^{2+}]$
7	10^{-28}	10^{-33}
5	10^{-20}	10^{-20}
2	10^{-8}	10^{-13}
1	10^{-4}	10^{-9}
0.5	10^{-2}	10^{-7}
0	1	10^{-5}

As $[Cl^-]$ decreases for 10 times, $[Mn^{2+}]$ decreases for 100 times at a given pH.

Conclusion: Cl^- is not able to reduce MnO_2 under ordinary agricultural soil pHs.

ii. <u>In the case of Br^-:</u>

$$MnO_2 + 4\ H^+ + 2\ Br^- \text{ --- } Mn^{2+} + Br_2 + 2\ H_2O \qquad \epsilon^0 = 0.12\ V$$
$$[Mn^{2+}] = 1.15 * 10^4\ [Br^-]^2\ [H^+]^4 \approx 10^4\ [Br^-]^2 [H^+]^4$$
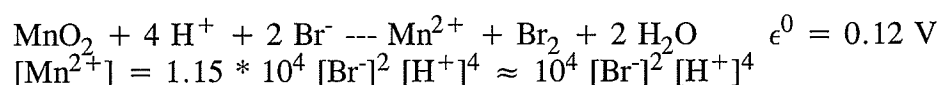
If we assume $[Br^-] = 1.0$ mol L^{-1}, then $[Mn^{2+}] = 10^{-5}\ [H^+]^4$ mol L^{-1}. The concentration of Mn at different pHs can be easily calculated:

pH	$[Mn^{2+}]$
7	10^{-24}
5	10^{-16}
3	10^{-8}
2	10^{-4}
1	1
0	10^4

iii. <u>In the case of I^-:</u>

$$MnO_2 + 4\ H^+ + 2\ I^- \text{ --- } Mn^{2+} + I_2 + 2\ H_2O \quad \epsilon^0 = 0.67\ V$$
$$[Mn^{2+}] = 4.6 * 10^{22}\ [I^-]^2\ [H^+]^4$$
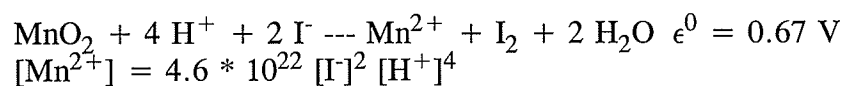
If we assume $[I^-] = 1.0$ mol L^{-1}, then $[Mn^{2+}] = 4.6 * 10^{22}\ [H^+]^4$ mol L^{-1}. The concentration of Mn at different pHs can be calculated as follows:

pH	$[Mn^{2+}]$
7	$4.6 * 10^{-6}$
6	$4.6 * 10^{-2}$

Let $[I^-] = 0.01$ mol L^{-1}, then $[Mn^{2+}] = 4.6 * 10^{18}\ [H^+]^4$ mol L^{-1}. we obtain

pH	$[Mn^{2+}]$
7	$4.6 * 10^{-10}$
6	$4.6 * 10^{-6}$

Let $[I^-] = 10^{-6}$ mol L^{-1}, then $[Mn^{2+}] = 4.6 * 10^{10}$ $[H^+]^4$ mol L^{-1}. we obtain

pH	$[Mn^{2+}]$
7	$4.6 * 10^{-18}$
5	$4.6 * 10^{-10}$
4	$4.6 * 10^{-6}$

Conclusion: I^- is very capable of reducing MnO_2 in acidic soils.

(4) Experimental data on reduction of MnO_2 by halides varying in concentration and pH

Treatment	pH 5		pH 3	
	Eh	Mn^{2+} in solution	Eh	Mn^{2+} in solution
mol L^{-1}	mV	---- μg g^{-1} ----	mV	---- μg g^{-1} ----
KCl				
0.01	927	0.0	1067	0.0
0.1	935	0.03	1066	0.04
0.5	941	0.07	1068	0.10
1.0	931	0.18	1057	0.23
KBr				
0.01	945	0.04	1002	0.04
0.1	922	0.06	990	0.07
0.5	917	0.10	965	0.55
1.0	921	0.31	952	2.73
KI				
0.001	788	0.39	934	0.85
0.01	663	65	756	255
0.1	566	375	558	all MnO_2 dissolved
0.5	503	all MnO_2 dissolved	498	"
1.0	476	"	470	"

HAcO	Eh	pH	Mn^{2+} in solution
0.5	989	2.9	0.0
1.0	1090	2.4	0.0

Conclusions: KCl was not able to reduce MnO_2 at pH 5 to 3 regardless of its concentration. KBr was capable of reducing MnO_2 at pH 3 when its concentration was above 0.1 mol L^{-1}. KI was highly capable of reducing MnO_2. An acid without a reducing agent, such as HAcO, was not able reduce MnO_2. These results are in good agreement with the theoretical calculations

APPENDIX II

Concentration and uptake of Cu, Zn and Fe in wheat shoots as affected by fertilizer grade and reagent grade KCl

KCl added	Concentration			Total Uptake		
	Cu	Zn	Fe	Cu	Zn	Fe
-μg K g^{-1} soil-	----------μg g^{-1} ----------			----------mg pot^{-1} --------		

Elm River soil:

Fertilizer grade KCl:

KCl added	Cu	Zn	Fe	Cu	Zn	Fe
0	4.7	30.8	34.0	0.14	0.90	1.00
50	4.0	37.5	34.8	0.12	1.05	1.01
100	4.0	29.3	38.0	0.11	0.82	1.06
300	4.0	23.8	38.2	0.11	0.65	1.04

Reagent grade KCl:

KCl added	Cu	Zn	Fe	Cu	Zn	Fe
0	4.7	30.8	34.0	0.14	0.90	1.00
50	5.5	23.0	35.7	0.16	0.67	1.04
100	5.5	22.5	34.5	0.15	0.63	0.96
300	4.5	20.6	40.8	0.13	0.57	1.13
50+KI	4.0	24.3	36.7	0.11	0.67	1.01

Wellwood soil:

Fertilizer grade KCl:

KCl added	Cu	Zn	Fe	Cu	Zn	Fe
0	4.8	52.3	58.2	0.10	1.09	1.22
50	5.0	61.8	57.2	0.11	1.29	1.20
100	4.5	56.3	49.2	0.09	1.17	1.02
300	5.0	72.5	54.5	0.10	1.41	1.06

Reagent grade KCl:

KCl added	Cu	Zn	Fe	Cu	Zn	Fe
0	4.8	52.3	58.2	0.10	1.09	1.22
50	4.8	65.5	50.0	0.10	1.36	1.04
100	4.3	59.5	52.0	0.09	1.21	1.05
300	4.0	63.2	54.5	0.08	1.22	1.05
50+KI	4.5	55.5	49.2	0.10	1.20	1.07

APPENDIX III

Time (d) at which alteration of birnessite was observed after 0.3 g of birnessite treated with 0.33 mol L^{-1} $MnSO_4$.
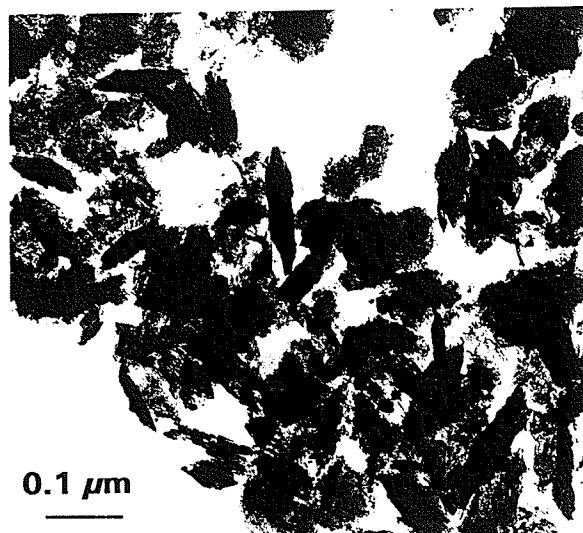
Treatment and initial pH	Final pH	Time required to observe a change		
		TEM_{start}	XRD_{start}	$XRD_{complete}$
		------------------ d ------------------		
2.4	3.7	1	4	9
4.0	4.1	3	33	50
5.0	4.2	-*	5	14
6.0	4.6	< 1	5	15
7.0	5.2	-	4	9
8.0	5.7	-	2	9

* - samples were not studied under TEM.

Electron micrographs of nsutite formed from birnessite treated with:

a) 0.33 mol L^{-1} $MnCl_2$ at pH 1.85 (pH not adjusted)

0.1 μm

b) 0.33 mol L^{-1} $Mn(NO_3)_2$ at pH 1.85 (pH not adjusted)

0.1 μm