

REMOVAL OF MANGANESE FROM ACID MINE DRAINAGE

Raymond J. Lovett

Department of Chemistry
West Virginia University
Morgantown, WV 26506

I. INTRODUCTION

Manganese is a common component of both neutral and acid mine drainage. Certain southern West Virginia drainages which are not acidic contain more than the maximum allowable concentration of manganese (2 mg/L) and require treatment. Many northern West Virginia drainages contain huge amounts of iron in addition to small, but out of compliance, levels of manganese. Such chemical diversity is common and complicates manganese removal.

Normally manganese is removed by adding some inexpensive basic chemical to the drainage. Common additives are caustic soda (sodium hydroxide), lime (CaO or Ca(OH)_2), soda ash (sodium carbonate) or ammonia (where allowed). Conventional wisdom has shown that manganese removal requires high pH, often leading to the creation of a treated water that exceeds discharge pH limits, although meeting Mn and Fe discharge limits. These high pH values lead to the resolubilization of aluminum, an element under increasingly close scrutiny.

This work is concerned with elucidating some of the fundamentals of manganese removal from aqueous solution. Various treatment chemicals are evaluated along with different solution concentrations and the presence or absence of iron. The forms of manganese in the resulting precipitates has also been investigated using titrations and X-ray diffraction analysis.

SOLUTION CHEMISTRY OF MANGANESE

Manganese exists in solution, under normal environmental conditions, as the divalent ion, Mn(II) . Calculation of the solubilities and stabilities of the ion to oxidation can be used to create an Eh-pH diagram for the $\text{Mn-O}_2\text{-H}_2\text{O}$ system (see Bricker, 1965) which reveals that manganese is stable under reducing conditions (typical mine drainage conditions) up to pH 10 or so, consistent with conventional wisdom. Raising the pH under reducing conditions produces large the hydroxide.

Another aspect of an Eh-pH diagram is the lowered solubility of Mn in water which is well oxygenated. As the system becomes more oxidizing, the aqueous Mn(II) is converted directly to various solid manganese forms, Mn_3O_4 (Hausmannite), Mn_2O_3 (manganite or Feitknechtite) and MnO_2 [many forms exist, but most probably Mn_7O_{13} Birnessite, is more appropriate (Burns and Burns, 1979)]. Birnessite and feitknechtite are the most commonly found solid forms

(Hem and Lind, 1983; Murray et al., 1985).

An Eh-pH diagram is a thermodynamic model and represents the forms that would be found at chemical equilibrium. Attainment of chemical equilibrium in a mine water manganese removal process requires that various reactions proceed at an observable rate; unfortunately, manganese oxidation is a slow process. The direct conversion of Mn(II) to solid oxide forms in water apparently does not occur without the involvement of hydroxide (Hem, 1981; Coughlin and Matsui 1976). In fact the rate of oxidation depends on the oxygen concentration and the square of the hydroxide concentration, implying that although the oxides are stable versus dissolution at moderate pH, the creation of the oxides proceeds through a manganese hydroxide intermediate form. Manganese removal is catalyzed by solids, including Mn oxides (autocatalysis) (Coughlin and Matsui, 1976; Kessick and Morgan, 1975); the presence of small amounts of solid through sludge recycling or due to turbidity may enhance the rate of Mn oxidation. Manganese removal from acidic, low oxygen mine waters presents the greatest challenge since the kinetics, pH and oxygen concentration work against Mn removal.

Neutral mine waters can also contain manganese, largely due to the extremely slow rate of Mn oxidation. Such waters can also contain substantial carbonate alkalinity. Manganese carbonate is fairly insoluble at moderate pH; a 2 mg/L can be established through manganese carbonate control at pH 8.5. Hem and Lind (1983) note that MnCO_3 (rhodochrosite) precipitates should only be present in systems where carbonate is high and oxygen depleted. They do not discuss the fact that normally, the manganese carbonate is quickly oxidized to the appropriate oxide with the release of carbon dioxide if oxygen is present initially.

SOLID MANGANESE FORMS

A variety of solid manganese forms are known to exist (Burns and Burns, 1979; Waychunas, 1991). Solid forms often contain Mn(II), Mn(III), which is unstable in aqueous solution, or Mn(IV), the thermodynamically most stable form. Certain minerals contain mixtures of oxidation states.

Most studies of the precipitation of manganese have been concerned with its removal under natural conditions and its diagenesis into manganese nodules (cf. Hem and Lind 1983). Studies such as these utilize pH-stats and attempt to cause removal under constant pH conditions. Studies of the actual precipitation upon fast addition of base are not available.

Hem and Lind (1983) and Murray et al. (1985) both studied the forms of manganese found upon precipitation. Hem and Lind precipitated the Mn(II) (10⁻² M, 550 mg/L) at 25 °C with NaOH near pH 9 and found that Hausmannite (Mn_2O_3) initially formed. Aging of the solids eventually led to manganite. Precipitation at 0 °C initially formed feitknechtite, which aged to an indeterminate form of composition $\text{MnO}_{1.67}$ (note that Hausmannite is $\text{MnO}_{1.33}$ and feitknechtite is $\text{MnO}_{1.5}$). Hereafter all species will be referred to the MnO_x form and x shall refer to the oxygen subscript (which is also the oxygen to manganese ratio). Murray et al. used an ammonia/ammonium buffer at pH 9 and scrupulously avoided introducing carbonate. They also found x approximately equaled 1.33 initially at 25 °C, but upon aging (1 year) reached 1.5 (Hausmannite to manganite). Their solid phases (as with Hem and Lind) were also identified by X-ray powder diffraction.

II. EXPERIMENTAL

Precipitates of manganese oxides were generally prepared by the addition of a measured amount of treatment chemical to 100 mL of a 100 mg/L Mn solution at a pH below 3. The added base was swirled for 15 to 30 seconds and the system allowed to stand. Sample pH and metal concentrations were determined at various times after treatment. All metal samples were taken by withdrawing about 3 mL with a syringe, then filtering the sample through a 0.2 mm filter. The aqueous sample was analyzed with a Varian SpectrAA Model 20 atomic absorption spectrometer and the filter containing solid material was placed back in the original beaker.

The degree of oxidation of the solids was determined in one of two ways (Murray et al 1984; Hem, 1981). In all cases, the sample was acidified with one mL of acid to a pH below 1. This acidification stopped further oxidation and disproportionated all oxidized manganese into Mn(II) and birnessite [Mn(IV)]. In certain samples, where iron was absent, an excess of iodide was added (the Mn (IV) reacts to form iodine) and the liberated iodine was titrated with standardized sodium thiosulfate (Murray et al., 1984). When iron was present, excess oxalic acid was added to the beaker and reacted. The unreacted oxalate was determined by permanganate titration (Hem, 1981). Such titrations with reagent grade MnO₂ consistently gave values of $x = 2.00 \pm 0.05$. The oxalate method worked in the presence of iron, whereas the iodide method did not.

Precipitation titrations of metal solutions were performed by adding measured amounts of base to the solution, then reacting (with magnetic stirring) for 30 minutes followed by sampling (with filtering). Subsequent additions were performed and the metal solution concentrations are plotted versus added base.

III. RESULTS AND DISCUSSION

PRECIPITATION OF MANGANESE

Precipitation of manganese from synthetic solutions (100 mg/L and pH 2.5) with sodium hydroxide consistently yielded solutions free of manganese and a solid which conformed approximately to Hausmannite (MnO_{1.35}), as found by Murray et al(1985) and Hem and Lind(1981). X-ray diffraction confirmed the presence of Hausmannite. Removal of manganese was relatively fast (order of an hour), but the final pH was not well controlled ranging from 6 to 9 (Table 1).

The precipitation of a lower concentration of manganese (10 mg/L) yielded a solid with a much higher oxygen to manganese ratio. This result is consistent with the observations of Bricker (1965) that the manganese will use the available oxygen, thus low concentrations of Mn are more highly oxidized (Fig. 1). Another study, which was coincidentally concerned with Fe-Mn coprecipitation, yielded increasing amounts of Mn precipitation with dose. The doses where little Mn was precipitated gave highly oxidized Mn ($x = 1.7$) (used available oxygen) while the Mn precipitated with larger doses were less highly oxidized.

At 25°C, about 8 mg/L of O₂ (0.5 mM) can be found in well oxygenated water. The reaction

ratio of manganese to oxygen is 2 for MnO_2 , 4 for feitknechtite and 6 for Hausmannite, indicating that the composition should be about MnO_2 for up to 50 mg/L of manganese, Feitknechtite for 50 to 100 mg Mn/L and Hausmannite for manganese levels from 100 to 200 mg/L. Notably, NaOH produces Feitknechtite at low temperature, where the oxygen solubility is much larger (Hem and Lind, 1981) indicating that for NaOH, the initial oxygen concentration determines the degree of oxidation of the product.

The precipitation of manganese with lime typically gave precipitates with Mn/O near 1.45-1.5 (Feitknechtite) and pHs near 8. The enhanced oxidation of manganese with lime versus NaOH under the same conditions is not easily explained. In all cases where differentiation can be made, lime precipitates manganese more slowly than NaOH, thus the initial precipitate may be less voluminous and able to oxidize to a greater extent with lime. If the initial form of the precipitate dictates the overall stoichiometry, since the oxidation is autocatalytic (Coughlin and Matsui, 1976), then the more highly oxidized starting material may lead to a more oxidized product. The ultimate product is the result of catalytic oxidation on solid surfaces by diffusing oxygen. Fast precipitation, such as with NaOH, may use the oxygen originally in the water immediately and generate the less oxidized Hausmannite. In all cases, however, production of any manganese solid depends on the presence of either carbonate at moderate pH or sites of localized high pH to initiate precipitation. The precipitate, once formed, is quickly oxidized (noting that Mn(II) is used in the Winkler oxygen titration to immobilize the oxygen). The resultant oxidized Mn species are stable at pH 6.5 to 9 and able to catalytically, although often slowly, remove the remaining soluble manganese.

The concept of localized high pH can be realized with addition of concentrated NaOH or the slow dissolution of highly alkaline $\text{Ca}(\text{OH})_2$ particles. Evidence of the requirement for high alkalinity and the noninvolvement of carbonate rest largely on indirect evidence. Attempts to remove Mn (100 mg/L) from a solution using NaOH, lime and calcium carbonate (limestone) all raised the pH to about 6.5, but the limestone did not remove manganese even after 9 days. The very slow, homogeneous dissolving of the limestone did not provide the localized high concentration needed to initiate the manganese removal. Dissolved limestone also did not provide enough carbonate to initiate precipitation of Mn.

The means of removal indicate that, although pH 10 in the resultant solution is not required for Mn removal, localized regions of pH 9 or 10 and allowance for a reasonable reaction time can remove Mn with receiving water pHs near 8.

MANGANESE REMOVAL IN THE PRESENCE OF IRON

Iron is present in most mine drainages. Iron removal requires the two ingredients needed for Mn removal, hydroxide and oxygen. Oxygen is not strictly necessary for iron removal, but reduced iron will react efficiently with oxygen and deprive the manganese of oxygen. If iron uses all of the available oxygen, then manganese oxidation will not occur and a pH of 10 is needed to remove the Mn as the hydroxide. Coughlin and Matsui (1976) note that hydrous iron oxides can provide catalytic sites for Mn oxidation. In addition, iron hydroxides are known to co-precipitate other metals.

Large amounts of iron appear to efficiently co-precipitate manganese if the iron to manganese ratio is two or larger and the base is added quickly. Lime tends to oxidize the

manganese more efficiently, which may be due to the slower reaction rate with lime due to slow lime dissolution. The degree of oxidation can be determined using the oxalate titration method and is found to be as low as 1.03 with 20 mg/L Mn and 100 mg/L Fe. Upon acidification, over 80% of the manganese resolubilizes, indicating that the solid is not particularly stable. These precipitations occur at pHs near 8, so $\text{Mn}(\text{OH})_2$ is not the product; manganese is being dragged into the precipitate due to the fast formation of hydrous iron oxides.

A test of the hypothesis that occlusion, or inclusion, is the means by which the manganese is incorporated into the precipitate can be made by doing a slow addition titration on a manganese-iron solution. With an Fe concentration of 250 mg/L and a manganese concentration of 10 mg/L, almost all of the iron is removed prior to manganese removal (Fig. 2). The slow precipitation reaction demonstrates that Mn removal in the presence of high Fe is not accomplished by chemical reaction, but is due to the physical removal of Mn during the extensive iron hydroxide formation.

IV. CONCLUSIONS

Manganese removal by the addition of base can be accomplished in a system with an overall pH near 8 as long as the addition of base allows the formation of pockets of high pH where solid oxidized material can form. The solid oxidized material catalytically aids in the removal of Mn. Slow addition of treatment chemical will remove iron first, then manganese, but the fast addition of base to an iron rich drainage appears to drag Mn down with the iron sludge.

Manganese solids are least highly oxidized when coprecipitated with iron. Caustic or ammonia removal of high concentrations of Mn leads to Hausmannite, but lime typically produces Feitknechtite, both of which disproportionate in acid solution.

Manganese removal is typically a slow process (some removals require a day of reaction) and long retention time ponds are recommended.

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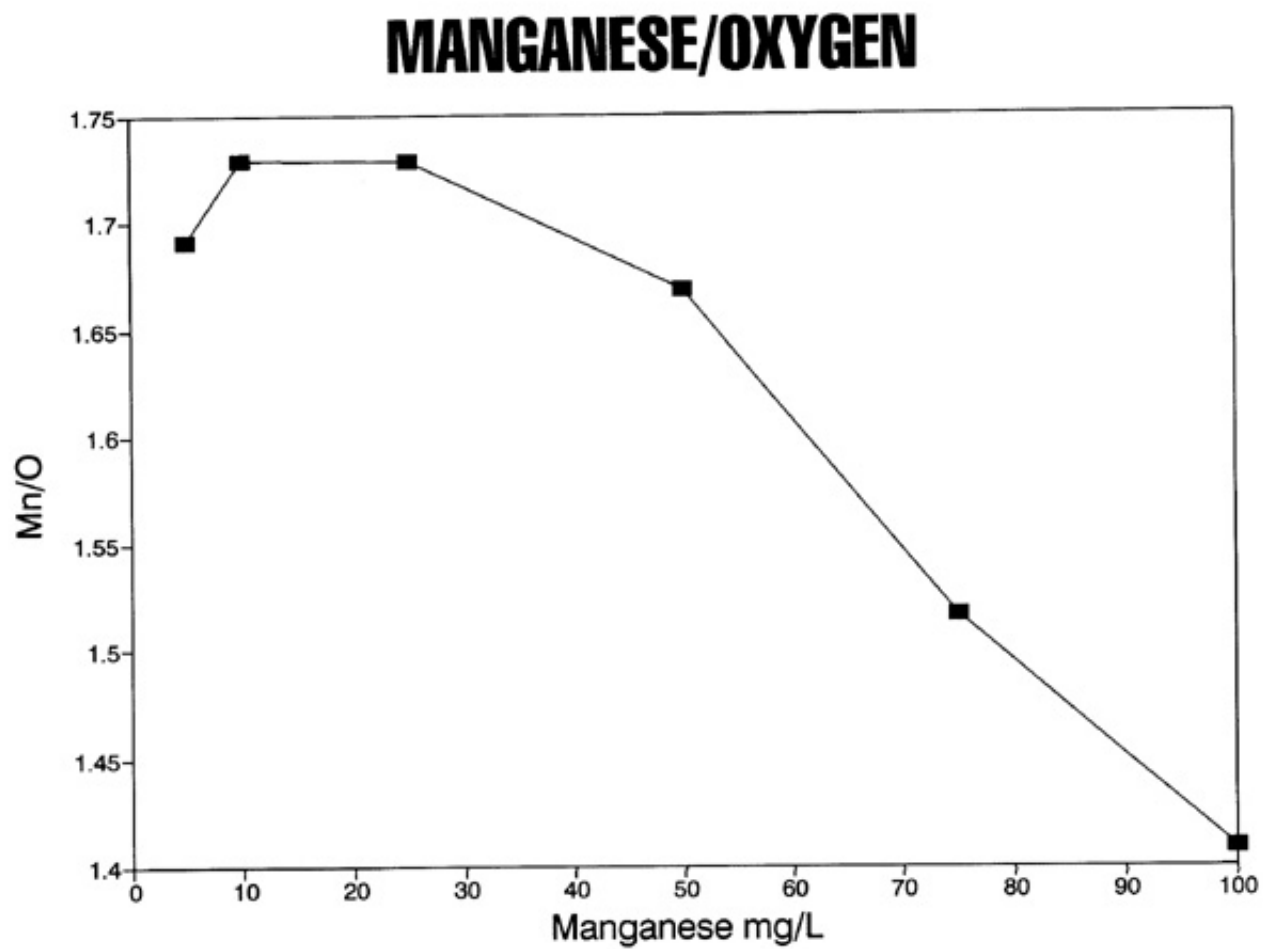


Fig. 1

500 mL. of 250/10 ppm Fe 2+/Mn 2+ t
 1.00 M NaOH (ambient).

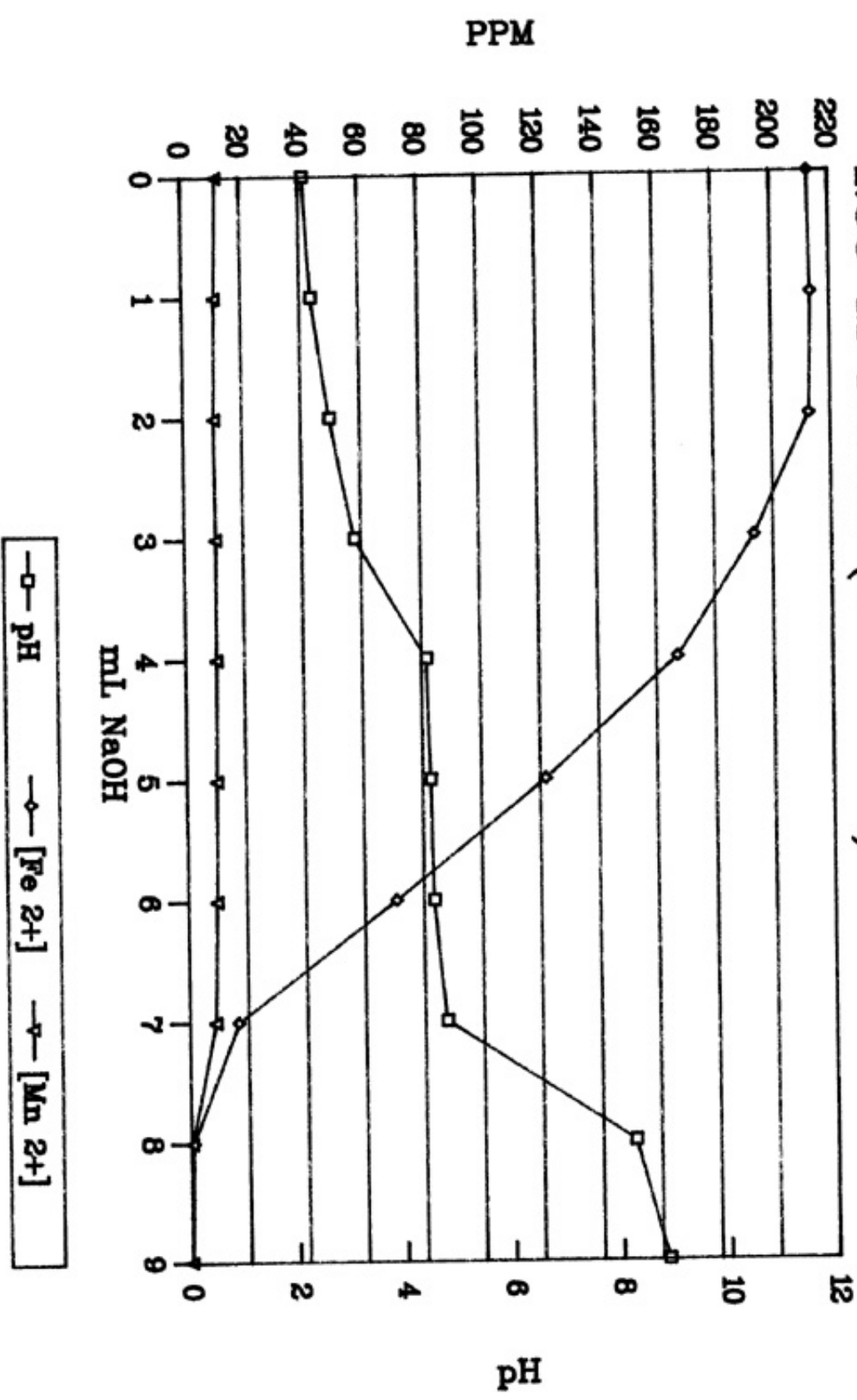


Fig. 2