



Studying About the Manganese Phase Diagram When Manganese Is Reacting with Calcium Hypochlorite

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Abstract. Oxidation Reduction behaviour is highly contributes to the condition of the water. Oxidation reduction potential [ORP] gives an idea about the Redox behaviour of water while the pH value give an indication about the behaviour of the Hydrogen ion concentration. When Manganese is in water, it can exist either as particulate matter or as dissolved matter and this can be showed in Manganese phase diagrams. Due to the inconvenient consequences, Manganese should be removed from the water if only it has a higher concentration. For this, oxidation can be done by using Calcium hypochlorite and the obtained precipitate can be filtered. The behaviour of different Manganese species fluctuates with different pH values and Eh values. The objective of this study was to determine the effect of pH and Eh while changing the different concentration of Calcium hypochlorite to the blended Manganese solution which is prepared by using $MnSO_4$. Final concentration of Manganese was reduced with lower concentration of Calcium hypochlorite and ORP values were reduced with the increasing pH. To conclude the result, Mn_3O_4 , Hausmannite was obtain as the Manganese species according to the Manganese phase diagram.

Keywords: Oxidation reduction potential · Redox behavior · Eh · Manganese phase diagram · Calcium hypochlorite · Hausmannite

1 Introduction

1.1 Effect of Manganese to the Water

Manganese naturally exists in earth's crust and it aggregates to water due to the dissolution of Manganese bearing minerals and rocks such as Manganosite, Manganite, Bixbyte when there is weathering. Until Manganese is in groundwater, Manganese exists as a stable form, but as soon as it is exposed to the outside air it oxidizes and precipitates out naturally (Salem *et al.* 2012).

Manganese generally does not affected human health but it may cause undesirable taste, appearance and straining (Rozainy *et al.* 2015). Presence of Manganese bearing

bacteria in water distribution systems causes bacterial growth in pipes. From the consumer's view, washing machines and boilers can be damaged due to oxidation and precipitation under conditions of excess Manganese (Barlokova and Ilavský 2009).

1.2 Manganese Phase Diagram

The Manganese phase diagram, (Fig. 1) shows the relationship of the redox potential and hydrogen-ion concentration that are relevant with specific dissolved ions and solids at chemical equilibrium in the presence of water. Phase boundary lines are called Stability field boundaries and in their activities, each adjacent species is nearly equal.

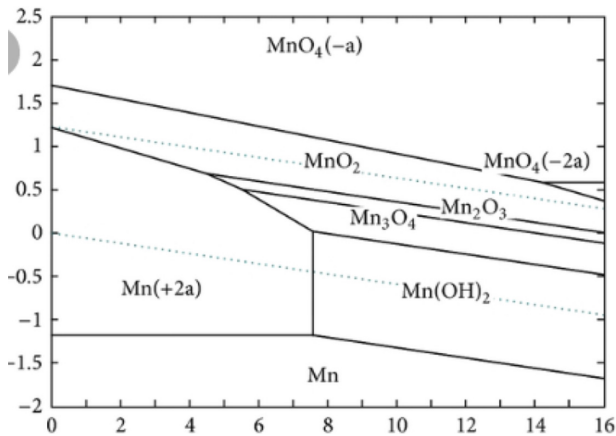


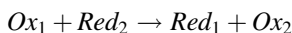
Fig. 1. Manganese phase diagram

pe is accessible as tendency of solution to donate or accept protons while Eh is known as the potential of the solution relative to the Standard Hydrogen Electrode [SHE]. In here SHE is the reference point and when all conditions are constant no reactions occur and the Eh value can be obtained from connecting the electrode containing another solution.

When Eh is higher, the solution is desirable to accept electrons from another species and when Eh is lower, the solution is desirable to donate electrons to the species. Therefore solution is reducing and oxidizing respectively.

1.3 Redox Reactions

Redox reactions are typically happens in a solution by oxidizing or reducing an electron. Hence, these reactions of oxidation or reduction do not exist in nature individually because free electrons never exist in a solution. Releasing of any electron from one species and its gain by another species happens simultaneously (Appelo and Pstma 2005).



Due to this, pe of the solution cannot be measured practically. Eh can be discovered not only by measuring but also by calculations of the Nernst equation. Therefore, Eh is the integration of both the calculated Eh and the measured Eh (Christensen *et al.* 2000).

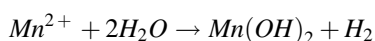
$$Eh = E_{\text{measured}} + E_{\text{reference}} \quad (1)$$

Both pe and Eh measure essentially the same and therefore the relationship between them can be written as follows;

$$Eh = \frac{2.303 RT}{F} pe \quad (2)$$

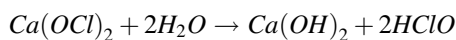
1.4 Behavior of Manganese in Water

Manganese is the 25th element of the periodic table and the most stable oxidation state is +2. When Manganese reacts with water, $Mn(OH)_2$ is obtained but it can change with the condition of the water.



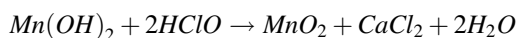
1.5 Behavior of the Calcium Hypochlorite in Water

Calcium hypochlorite, which has the commercial name of bleaching powder, is an inorganic compound. It is mostly used in water treatments because of the high efficiency and low cost. It exists as a powder form and it should be dissolved with water to acquire Calcium hypochlorite solution.



1.6 Reaction of Manganese and Calcium Hypochlorite

While $Ca(OH)_2$ is a precipitate $Mn(OH)_2$ is react with $HClO$.



1.7 Objective of the Study

To investigate the behavior of pH and Eh of the solution while changing the different concentration of Calcium hypochlorite, in certain concentrations of the Manganese rich solution by studying the Manganese phase diagram.

To discover the particulate form of the Manganese species which can be removed by filtration.

2 Materials and Methodology

2.1 Analytical Techniques

2.1.1 Determination of pH Value

pH values of the water samples were directly measured by the pH meter. Before that, the pH electrode was removed from the storage solution, rinse with distilled water and dried with tissue paper. Then, the water sample was taken to the beaker and the pH electrode was placed in it and the value on the digital screen was recorded. This pH value is at fixed temperature.

2.1.2 Determination of Concentration of Manganese

UV spectrophotometer was used to measure the dissolved Manganese concentration of the sample. A program was selected to measure the concentration of Manganese and the wavelength was kept as 525 nm. Water sample was filled to the two 10 ml cells and one is kept as reference. A Manganese citrate buffer powder pillow was added to the other cell and shaken until it dissolved well. Then, Sodium periodate reagent was added and kept for two minutes to complete the reaction. After two minutes, the reference sample was placed inside the hole of the UV spectrophotometer and calibrated to zero. After it became zero, the working cell was placed and the reading on the digital screen of UV spectrophotometer was recorded.

2.1.3 Determination of Oxidation Reduction Potential (ORP) Value

Same pH meter was used to measure the ORP value and it demonstrated the reference Eh value. To get the ORP value, the program was changed by pressing the 'Option' button. ORP value is record as millivolt.

2.1.4 Determination of Residual Chlorine (RCI) Value

Residual chlorine value gives the remaining free chlorine amount of the sample. It can be measured directly by using RCI meter. For that, the sample is filled into two cells and one was kept as reference. DPD free chlorine reagent was added to the other sample and shaken well until it fully dissolved. If Chlorine is present in the sample, light pink color appears. The reference sample was placed in the hole inside the RCI meter and calibrated to Zero and then the working sample was placed and the value given in the digital screen was recorded.

2.2 Preparation of Manganese Solution

5 L of 0.9 ppm Mn^{2+} solution was freshly prepared by dissolving 0.0124 g of MnSO_4 in to raw water sample collected from Maduru Oya. A raw water sample was used instead of tap water or distilled water, in order to obtain the natural environmental condition.

2.3 Preparation of Calcium Hypochlorite Solution Series

1L of 10 ppm Calcium hypochlorite solution was made by dissolving 0.01 g of Bleaching powder in to distilled water. Bleaching solution series was selected with respect to the Residual Chlorine value given from the stock sample.

2.4 Method

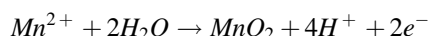
Initial concentration of the Mn^{2+} measured by using UV spectrophotometer and Bleaching solution series was added to the 4 beakers which were filled with 500 ml of Mn^{2+} sample. Each sample was mixed continuously using a shaker for almost 30 min. Finally pH, RCl, ORP and final concentration of Manganese was measured.

3 Result and Discussion

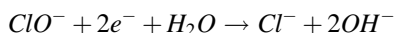
3.1 Calculating the Standard Potential

When considering the redox reactions of Mn^{2+} and ClO^-

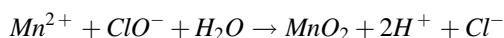
Oxidation reaction of Mn^{2+}



Reduction reaction of ClO^-



Final reaction of Mn^{2+} and ClO^-



According to Nernst equation

$$E = E^0 + \frac{RT}{2F} \ln\left(\frac{(H^+)^2(Cl^-)}{(Mn^{2+})(ClO^-)}\right)$$

The standard potential at 1 atm and 25 °C for oxidation reaction is +1.23 V, while for reduction reaction is +0.9 V.

To obtain E^0 for the final reaction, Standard potential of the reduction reaction should be subtracted from standard potential of the oxidation reaction. It is expressed as potential per electron.

Therefore standard potential of the final reaction is $1.23 \text{ V} - 0.9 \text{ V} = 0.33 \text{ V}$.

3.2 Removal Efficiency

Table 1 represents the removal efficiency of Manganese after adding the bleaching powder solution. Initial concentration of Manganese is 0.9 ppm

After 30 min, in each trial, Residual Chlorine value was zero. It indicated that at that moment, all of the bleaching powder was almost finished.

Table 1. Final concentration of Mn with respect to different dosages of ClO^- after 30 min of reaction

Trial	Concentration of ClO^- /ppm	Concentration of Final Mn^{2+} /ppm	Removal efficiency/%	Residual chlorine value/ppm
1	0.7	0.6	33.33	0
2	2	0.7	22.22	0
3	4	0.8	11.11	0
4	6	0.9	0	0

The variations of removal efficiency and the concentration of ClO^- are shown in Fig. 2. It indicated that increasing concentration of ClO^- reduces the Manganese removal efficiency.

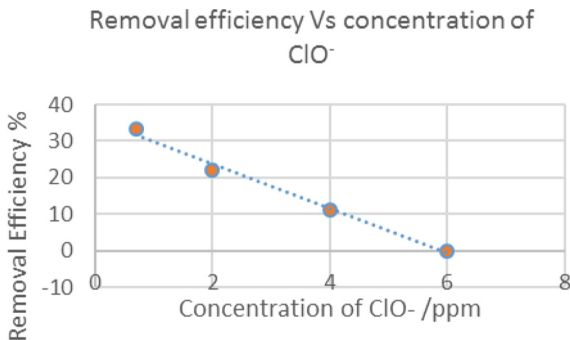


Fig. 2. Graph of removal efficiency vs concentration of ClO^-

Since this is the result of synthetic Manganese contained in raw water, it did not give the natural condition of raw water and it also influences this circumstance because in nature, Manganese mostly coexists with Ferrous (Kasim *et al.* 2017).

3.3 Relationship Between pH and ORP

Figure 3 presented the relation between pH and ORP showed in Table 2. Since the concentration of ClO^- is zero, only an oxidation reaction is occurring. According to that, the reaction produces H^+ and due to that, pH reduces. Therefore, a higher concentration of final Manganese has a lower pH.

Figure 3 indicates that the ORP value is decreasing with increasing pH. For the most part, ORP increased with increasing oxidant dosage (James *et al.* 2004). In this experiment, ClO^- is oxidant and from trial 1 to trial 4, concentration of the concentration of ClO^- is increased. Therefore, ORP value is increasing from trial 1 to trial 4.

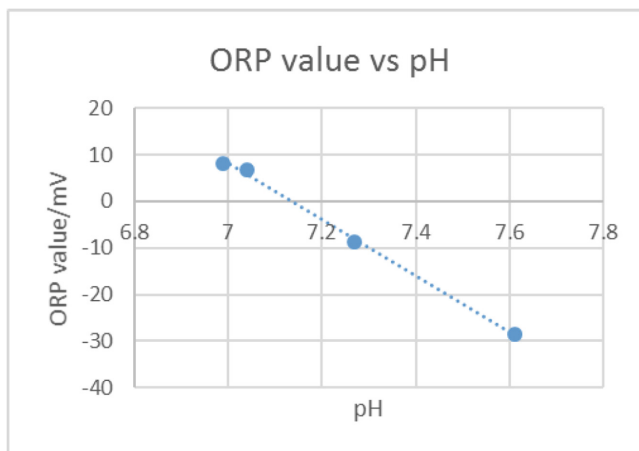


Fig. 3. Graph of ORP value and pH

Table 2. pH and ORP value of the each sample

Trial	Temperature/ $^{\circ}$ c	pH	ORP [E_{measured}]/mV
1	25.3	7.61	-28.5
2	25.2	7.27	-8.6
3	25.2	7.04	6.7
4	25.3	6.99	8.2

3.4 Calculating $Eh_{\text{reference}}$

$Eh_{\text{reference}}$ value depends on the concentrations of Mn^{2+} , ClO^{-} , H^{+} , and Cl^{-} . Final concentration of Cl^{-} is zero, and under that condition $Eh_{\text{reference}}$ value of the each trial is equal to the standard potential of the reaction as shown in Table 3.

Table 3. $Eh_{\text{reference}}$ values calculated from Nernst equation for each trial

Trial	Concentration of Mn^{2+} /ppm	Concentration of ClO^{-} /ppm	Concentration of H^{+} /ppm	Concentration of Cl^{-} /ppm	Temperature/K	$Eh_{\text{reference}}$ /V
1	0.6	0.7	10.22×10^{-8}	0	298.45	0.33
2	0.7	2.0	9.12×10^{-8}	0	298.35	0.33
3	0.8	4.0	5.37×10^{-8}	0	298.35	0.33
4	0.9	6.0	2.45×10^{-8}	0	298.45	0.33

Since the Eh value is the integration of both ORP value and the calculated Eh value from Nernst equation, Table 4 illustrates the final Eh value and pe value, which is acquired from the relationship of Eh and pe (Appelo and Pstma 2005).

Since the higher pe value has higher tendency to accept protons, according to the obtained pe, propensity to accepting protons is developed from trial 1 to trial 4

respectively as shown in Table 5. Therefore, the solution of trial 1 is more oxidized than the trial 2 solution.

Figure 4 shows that Eh is reduce with increasing pH of the solution.

Table 4. Indicate that $E_{reference}$ values influence to the Eh more than $E_{measured}$ values.

Trial	$E_{measured}/V$	$E_{reference}/V$	Eh/V	pe/V
4	-0.0285	0.33	0.3015	5.0906
3	-0.0086	0.33	0.3214	5.4285
2	0.0067	0.33	0.3367	5.6869
1	0.0082	0.33	0.3382	5.7103

In this experiment, pH of the samples exist between 6.8 and 7.8. According to the Manganese phase diagram shown in Fig. 4, at that level, Manganese can exist as a dissolved species (Mn^{2+}) or as a precipitate such as Mn_3O_4 , MnO_2 , Mn_2O_3 , and MnO_4 (Bruins *et al.* 2014).

Table 5. pH values and Eh values of each trial

Trial	pH	Eh/V
1	7.61	0.3015
2	7.27	0.3214
3	7.04	0.3367
4	6.99	0.3382

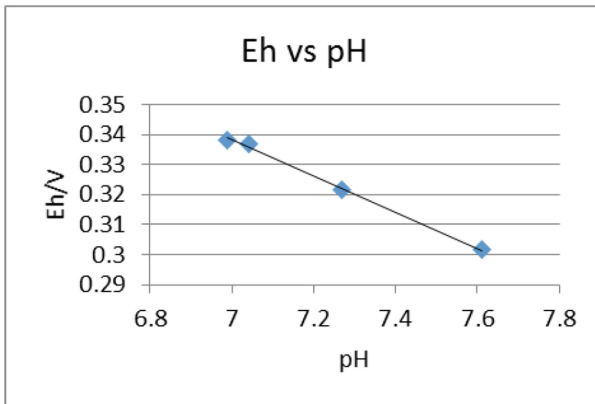


Fig. 4. Graph of Eh vs pH

Here, Eh value exists between 0.3 and 0.4. Type of the Manganese species to be obtained varies with the pH and the Eh as shown in Fig. 5. From the above result of Mn_3O_4 , Hausmannite was obtained after adding bleaching powder solution between 0.7 ppm and 6 ppm to 0.9 ppm Mn^{2+} solution.

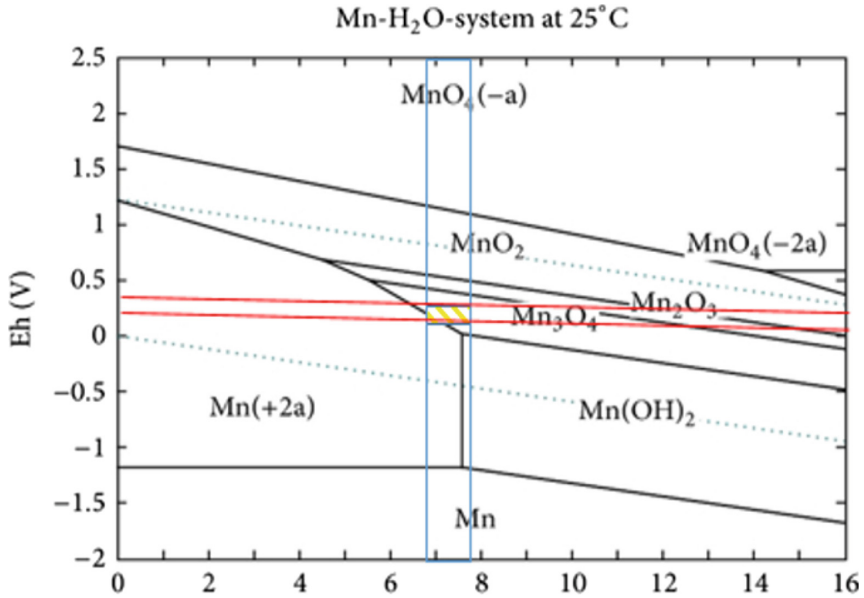


Fig. 5. Phase diagram with analyzed data

After obtaining the particles, they may be removed by using a filtration process (Isaeva and Castro 2011).

If water contains higher concentrations of Manganese as a dissolved form, before removal it should be converted to its particular form by changing the pH or Eh values. pH can be changed by adding diluted acid or base and Eh can be amended by changing the concentration of the initial concentration of the Manganese solution and the bleaching solution. Particulate form can be selected according to the Manganese phase diagram considering the adequate pH and Eh values.

4 Conclusion

Mn₃O₄, Hausmannite occurs as a final product when 0.9 ppm synthetically prepared Manganese solution reacts with different concentration of Calcium hypochlorite solutions. Final product can be observed after some time as a brown colour precipitate. This precipitate can be removed by using an adequate filtration method.

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