Manganese Oxides as an Indicator of Reduction In Soils (IRIS)

DEPARTMENT OF ENVIRONMENTAL SCIENCE & TECHNOLOGY

Martin Rabenhorst

Department of Environmental Science and Technology, University of Maryland

www.enst.umd.edu

Contact: mrabenho@umd.edu

ABSTRACT

Over the last decade, IRIS (Indicator of Reduction in Soils) technology has been introduced and developed whereby Fe oxide paint is applied to PVC devices (usually tubing) and inserted into the soil. Under strongly reducing conditions during the oxidation of soil organic matter by heterotrophic microbes, Fe oxides on the tubes are utilized as an electron acceptor, and the oxidized Fe is reduced, solubilized and stripped from the device leaving white or lighter colored areas. The IRIS devices are easy to use and interpret and are less prone to difficulties associated with other methods of assessing reducing soil conditions, and have been endorsed by the National Technical Committee on Hydric Soils. For many years there has been interest in the development of Mn oxide coated tubes (Stiles et al., 2010) but until recently there have been insurmountable problems associated with poor adhesion/durability of the Mn oxide coating on the PVC tubing. Some workers have recently suggested that following the procedure of Handel et al. (2013), birnessite easily synthesized at room temperature, could be used to make Mn coated PVC IRIS devices, but it appears that there are significant difficulties associated with using birnessite synthesized according to these specifications. Although durable Mn-coated tubes can apparently be manufactured using specialized and time consuming procedures, when the Mn oxide suspension is painted onto the PVC devices in the manner normally used in making Fe coated tubes the Mn oxide coating does not adhere but rather rubs off easily. Through recent advances, the author has been able to surmount these difficulties. This paper will report on the development of an easily synthesized Mn oxide paint that can be used to quickly make IRIS tubes with a strongly adhering and durable Mn oxide coating.

INTRODUCTION

- Environmental scientists have been interested in using Mn oxide coated PVC tubes in wetland assessment, much like Fe coated IRIS tubes, but the difficulty has been in developing a way to created a durable coating.
- Previous efforts by Stiles et al. (2010) and Coffin (2012) did not result in Mn coated tubes with a durable coating.
- In recent work, Dorau, K. & Mansfeldt (2015) have shown that Mn oxides can be applied to PVC rods (or tubing), to manufacture a device with a durable coating, but their approach involves a laborious and time consuming process that limits their general usefulness.

Timeline for Research on Mn Coated Tubes

Researchers	Focus	'05	'06	'07	'08	'09	'10	'11	'12	'13	'14	'15	'16
Rabenhorst	Preliminary Mn oxide exploration	-------											
Stiles et al. (2010)	Mn vs Fe tubes MIRIS					-------	-------						
Coffin (2012)	Mn vs Fe tubes (MS Thesis)							-------	-------				
Dorau et al. (2015)	Mn coated bars (3 papers)									-------	-------	-------	
Rabenhorst	Easily applied Mn Coating										-----	-------	-------

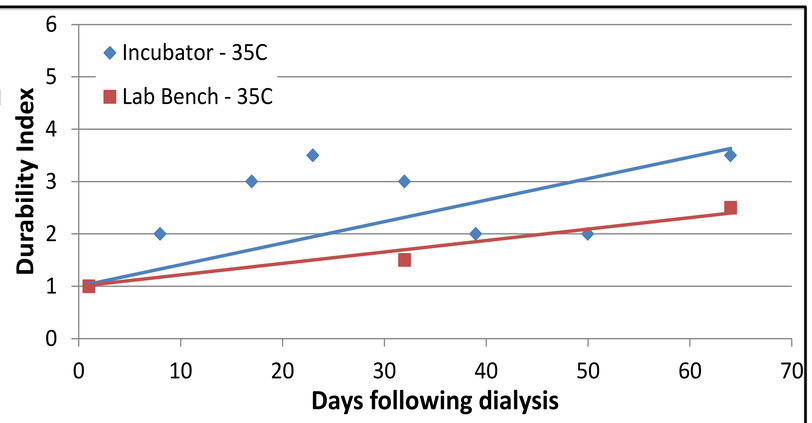
The Problem: Synthesized Mn oxides painted on PVC tubing will not adhere well

- Initially observed by Rabenhorst in 2005 – no solution
- Stiles (and Coffin) birnessite synthesis similar to McKenzie Difficult synthesis conditions (strong acids and boiling); still problematic
- Dorau and Mansfeldt – birnessite synthesis of Handel et al. (2013); cannot be painted on PVC (rubs off); requires slow polishing and burnishing; Multiple coats

OBJECTIVE: To develop a Mn oxide phase that can be easily and quickly applied to PVC tubing to produce a durable coating

Experiment 1 – Ageing and Incubation

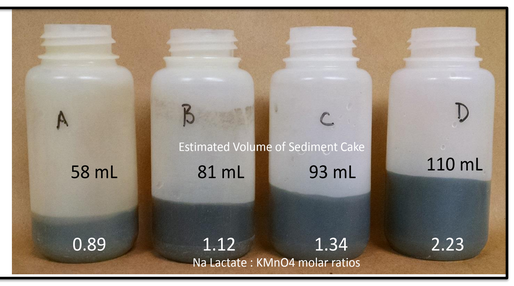
- Birnessite was synthesized following procedure of Handel et al. (2013) modified to add 3 days of dialysis following centrifuge washing to remove excess reactants
- Na Lactate:$KMnO_4$ ratios were 1.2
- Birnessite suspensions were stored on lab bench (21C) for 64 days
- Samples were also incubated at 35C for 64 days
- Periodically evaluated durability when painted on PVC

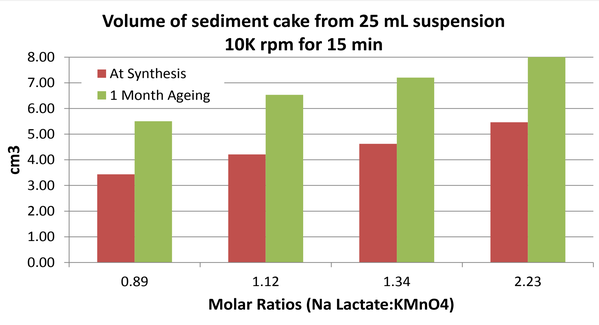


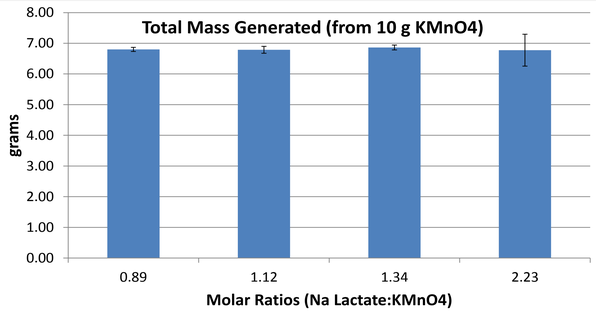
RESULTS: Birnessite suspensions aged for up to 64 days at room temperature did not demonstrate durability greater than 2.5. Incubation of the birnessite suspensions at 35C did not result in substantially better durability of the Mn oxide coatings.

Experiment 2 – Synthesis of birnessite with minor modification in reductant

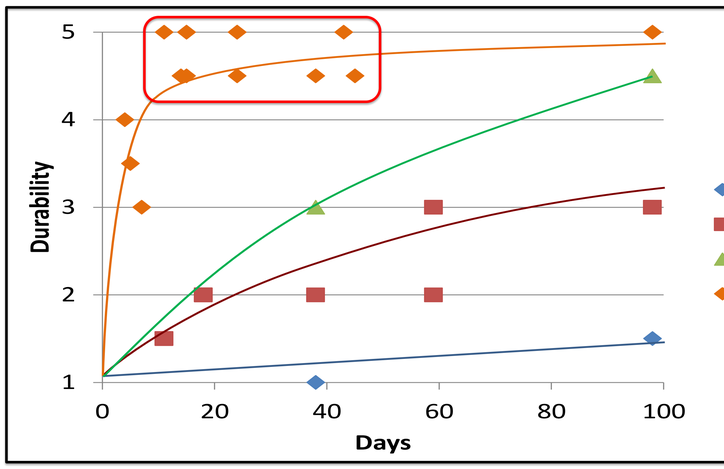
- Started with synthesis of birnessite following Handel et al. (2013)
- 10 g $KMnO_4$
- Modified quantity of reductant (Na Lactate) relative to $KMnO_4$
- Na Lactate – $KMnO_4$ molar ratios used
  - 0.89 (Handel et al., 2013)
  - Also 1.12, 1.34, 2.23







RESULTS: All treatments produced the same mass of birnessite (6.84 grams) expected from 10.00 grams of KMnO4. The change in the molar ratios of Na Lactate to KMnO4 did however change the volume of the Mn oxide produced indicating that physical properties of the mineral may be different.



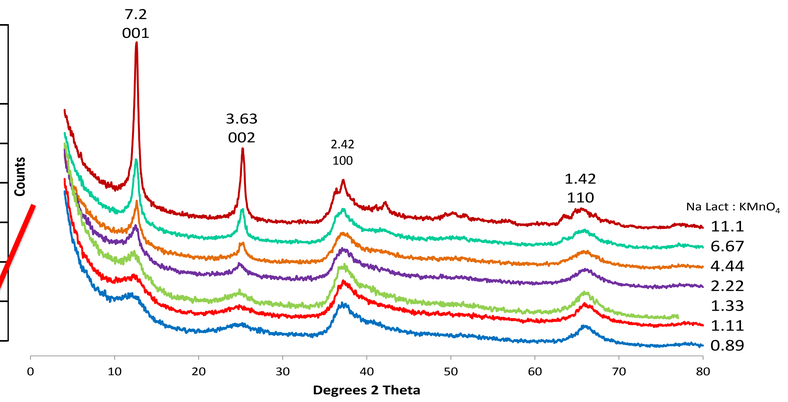
RESULTS

- Increasing the ratio of Na Lactate to $KMnO_4$ did appear to improved the durability of the Mn oxide coating on the PVC tubing.
- However, repeated testing of synthesized birnessite using the highest molar ratio of 2.2 did not produce a coating that would consistently have the desired durability of 5, even when the suspensions were permitted to age for up to 50 days.
- These data did suggest, however, that using higher Na Lactate to $KMnO_4$ ratios might improve durability.

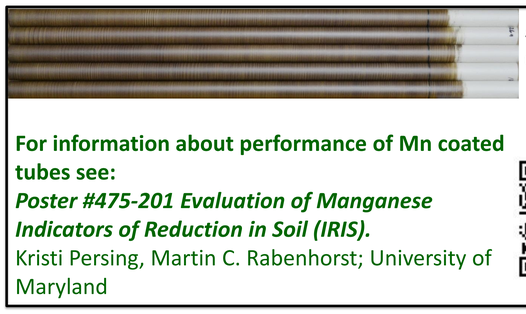
Experiment 3 – Larger Ratios of Na Lactate – $KMnO_4$

- Used birnessite synthesized following the dialysis modification to the Handel et al. (2013) method
- Higher Na Lactate to $KMnO_4$ ratios were used: 2.2, 3.3, 4.4, 6.7, 8.9, 11.1
- Durability tested 4 days after emerging from dialysis (8 days after initial syntheis)

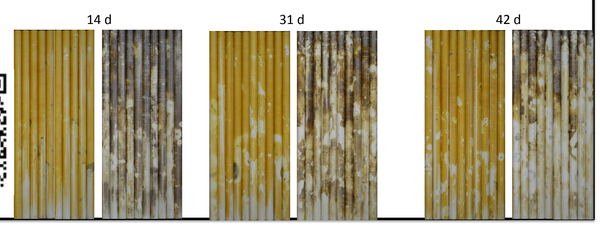
Na Lactate: KMnO4 Molar Ratio	Durability
2.2	4 to 5
3.3	4 to 5
4.4	4 to 5
6.7	5
8.9	5
11.1	5



RESULTS: Increasing the Na Lactate:$KMnO_4$ molar above 4.4 resulted in birnessite coatings on PVC tubes that consistently had a durability of 5. X-ray diffraction analysis of the synthesized Mn oxide showed that birnessite was formed, and that when higher Na Lactate:$KMnO_4$ ratios were used, the birnessite had a higher degree of crystallinity as demonstrated by the sharper and more intense peaks, especially of the 001 and 002 reflections (with d spacings of 7.2 and 3.6 angstroms, respectively.) At left is shown the testing of the durability of Mn oxide coatings synthesized under various conditions.



At left are IRIS tubes successfully painted with well-adhering and durable paint. Average time to paint each tube was 1 to 2 minutes.



For information about performance of Mn coated tubes see:

Poster #475-201 Evaluation of Manganese Indicators of Reduction in Soil (IRIS).

Kristi Persing, Martin C. Rabenhorst; University of Maryland

CONCLUSIONS

- Previously published methods of Handel et al. (2013) or McKenzie (1971) for synthesizing birnessite do not result in a phase that will adhere to PVC tubing and produce a durable coating when painted in the way that Fe coated tubes have been made.
- By increasing the ratio of Na Lactate:$KMnO_4$ to 6.7 (ie > 4.4.), followed by 3 days of dialysis, a more crystalline birnessite is produced which does form a durable coating when painted on PVC tubing.
- This method for synthesizing birnessite can be used to quickly and easily manufacture Mn oxide coated tubes that can be utilized in environmental assessment – particularly in the documentation of moderately reducing conditions in soils of wetlands.
- Further testing should be done in order to be able to compare the performance of Mn coated tubes relative to the more traditional Fe coated tubes.

REFERENCES

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