

Documenting Reducing Conditions in Soils

- Martin C. Rabenhorst
- Environmental Science and Technology
- University of Maryland



Significance of documenting reducing conditions in soils?

- To demonstrate that a soil meets the Technical Standard for Hydric Soils
 - In order to evaluate or test new Field Indicators (FI) for Hydric soils
 - In order to confirm that a soil is hydric in the absence of a Field Indicator (disturbed site)
- To demonstrate that the soil of a recently created or restored wetland is functioning like a hydric soil

Alternate Technologies

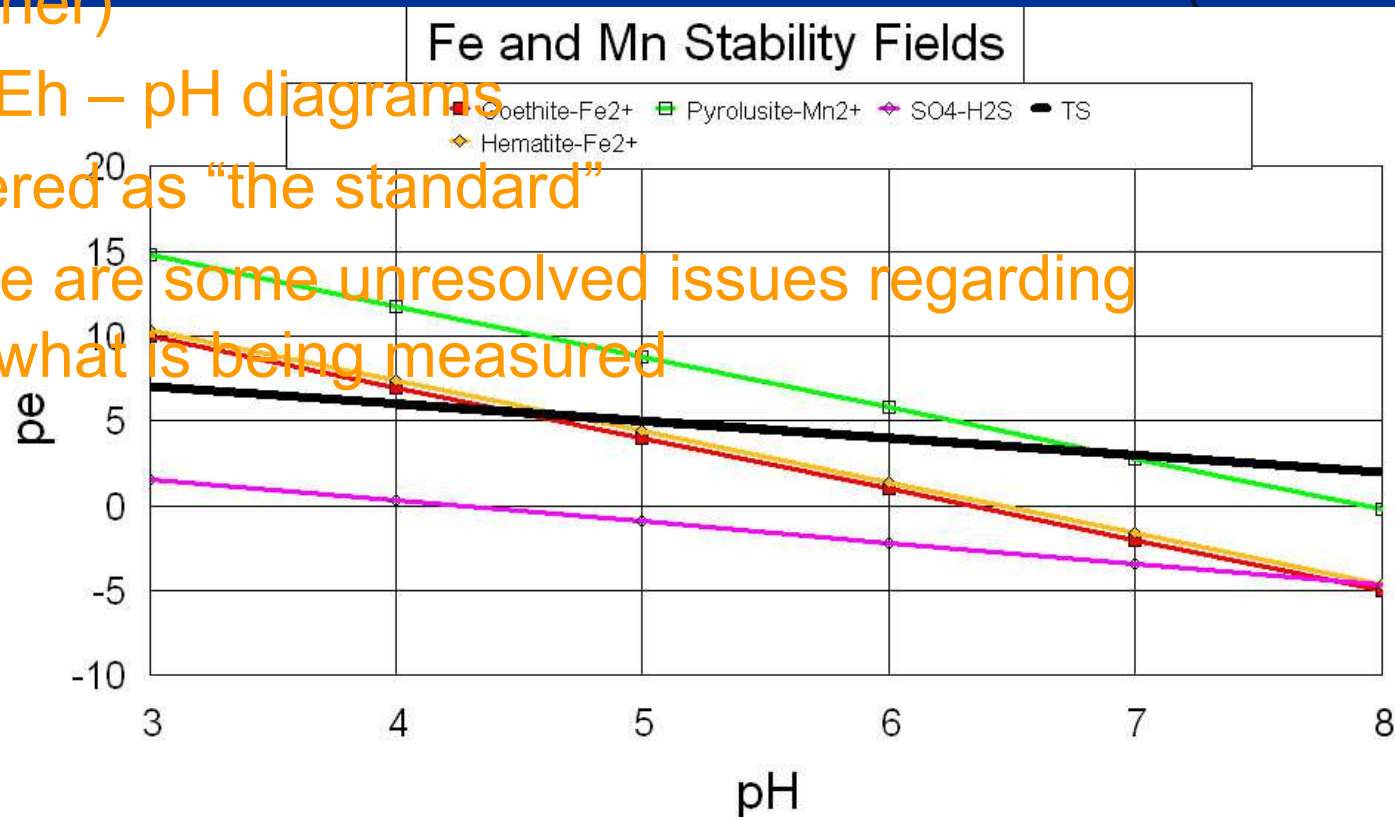
■ Eh measurements with Platinum electrodes (and pH)

■ Time consuming and a bit difficult (especially for the practitioner)

■ Plot on Eh – pH diagrams

■ Considered as “the standard”

■ But there are some unresolved issues regarding exactly what is being measured



■ Redox potential measurement using Pt electrode

Multiple electrodes used to improve the statistical reliability.



Alternate Technologies

Use of alpha-alpha-dipyridyl
Reacts with ferrous Fe^{+2} forming pink color
Difficult to obtain (hazardous)
Now available as test papers
www.gallard.com

Dipyridyl paper, Item# 90725
Pack Size: box of 200 strips; Hazard Class /UN Number: Not Restricted
Storage Temp: Room Temperature
Impregnated with α,α' -dipyridyl (= 2,2'-bipyridine),
Limit of sensitivity: 2 mg/l Fe^{2+}

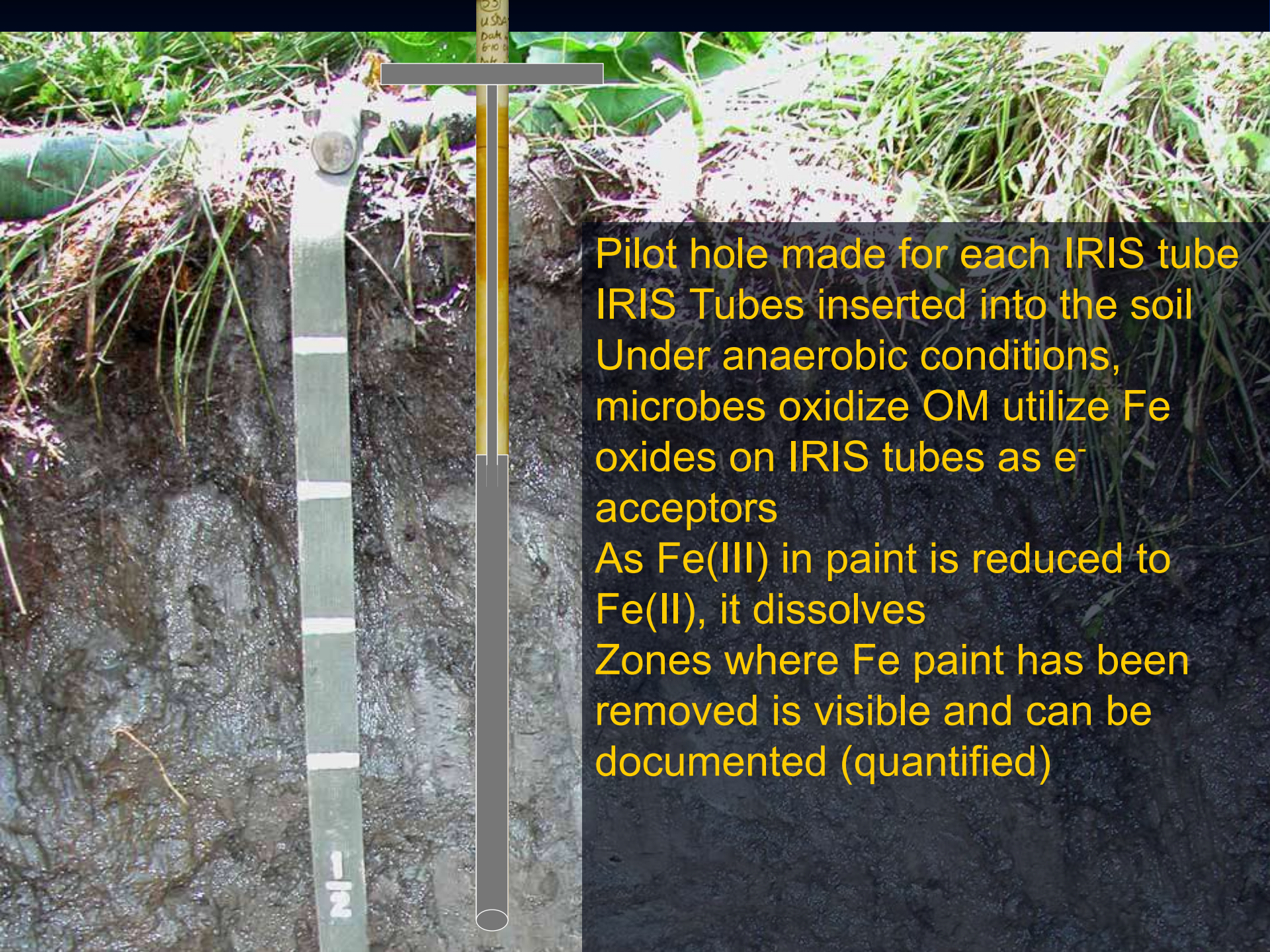


IRIS (Indicator of Reduction in Soils) Tubes

- Fe Oxide paint is applied to ½ inch schedule 40 PVC tubing while the tube is on a lathe device to ensure an even distribution of the paint.



■ Jenkinson, B. 2002. *Indicators of Reduction in Soils (IRIS): A visual method for the identification of hydric soils*. Ph.D. Diss. Purdue Univ., West Lafayette, IN

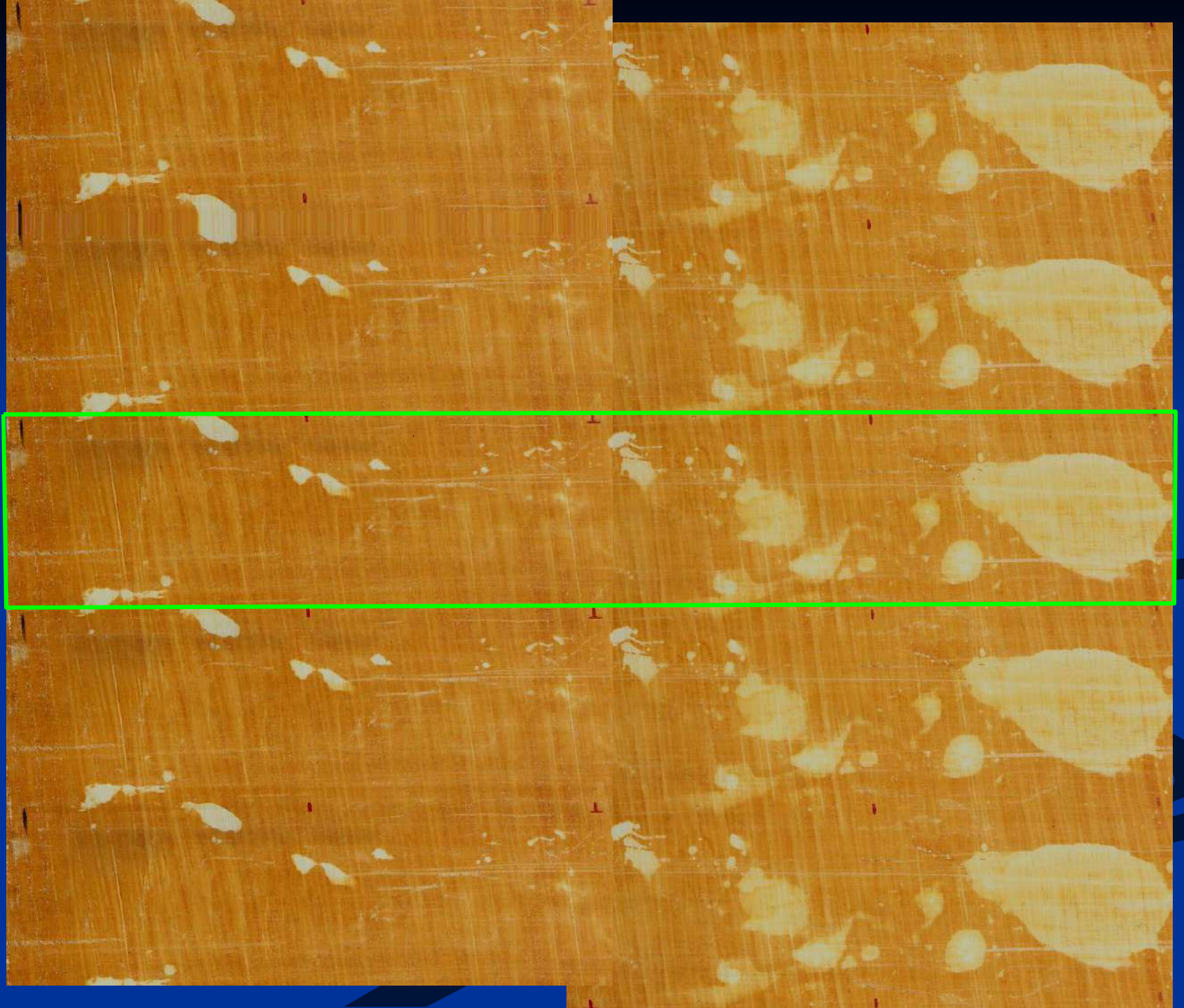


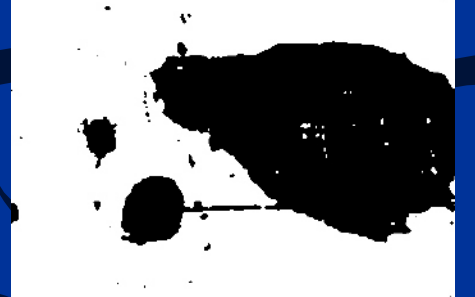
Pilot hole made for each IRIS tube
IRIS Tubes inserted into the soil
Under anaerobic conditions,
microbes oxidize OM utilize Fe
oxides on IRIS tubes as e^-
acceptors
As Fe(III) in paint is reduced to
Fe(II), it dissolves
Zones where Fe paint has been
removed is visible and can be
documented (quantified)

Utilization of scanner to collect undistorted images



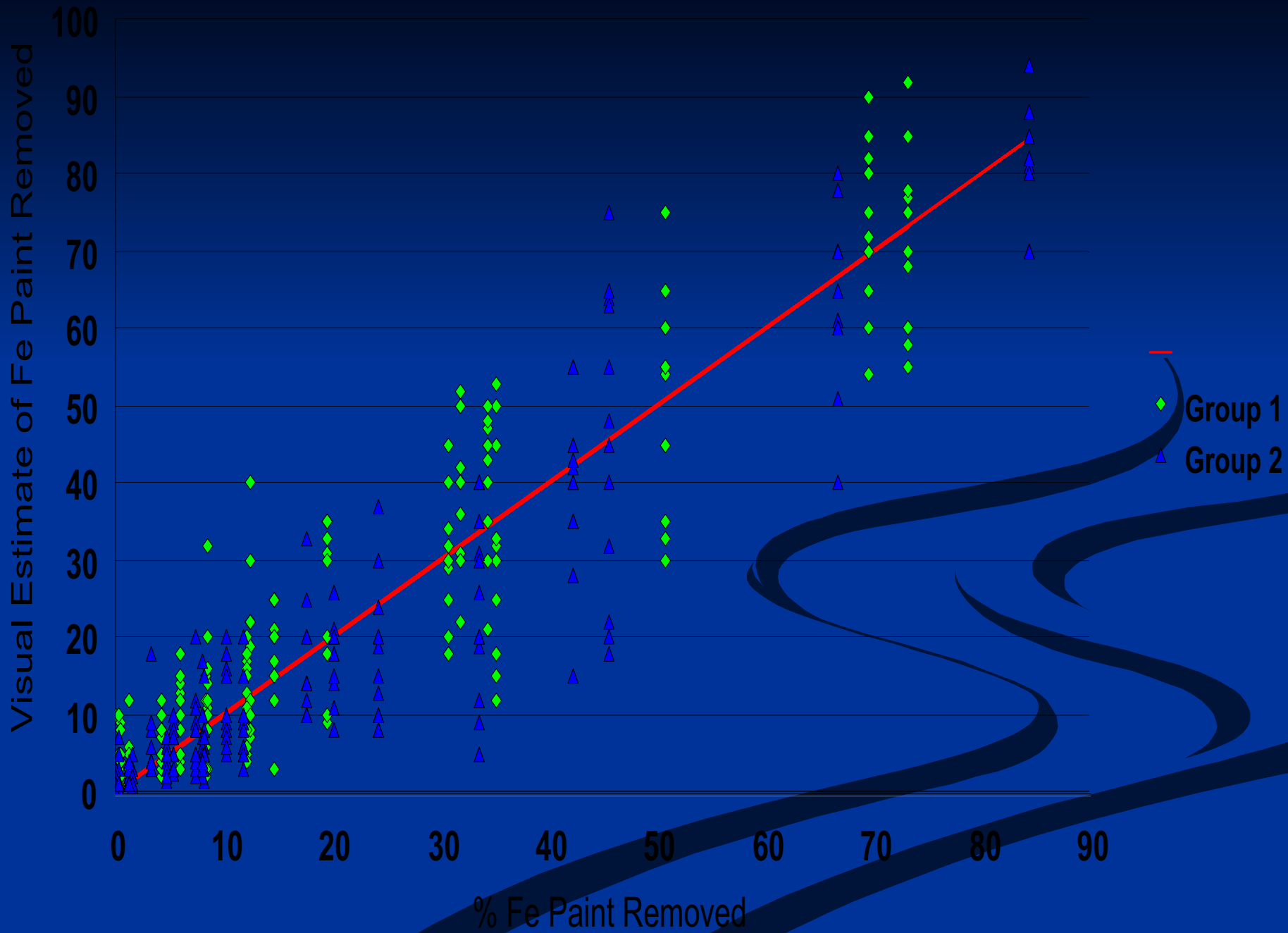
Images must be composited



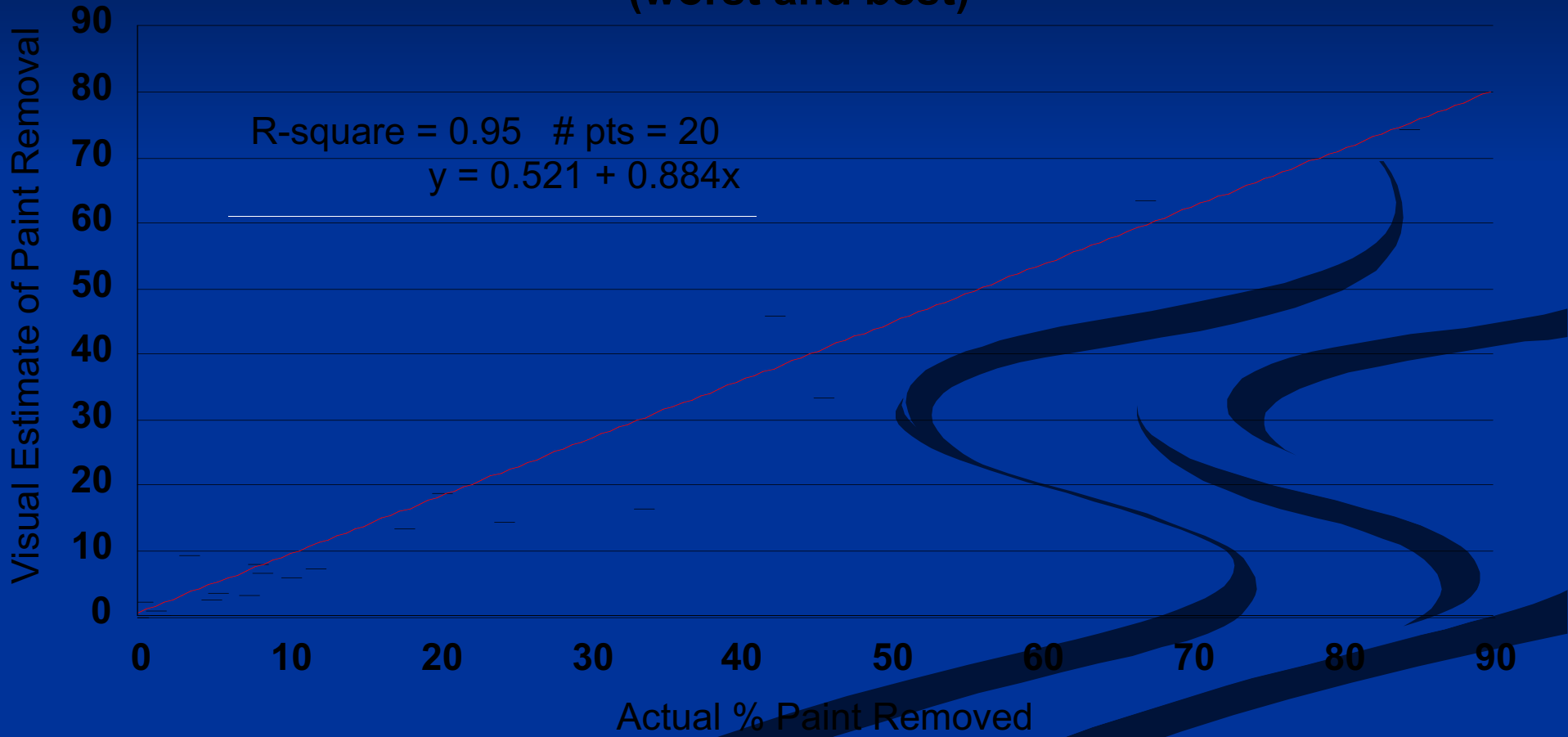


How effective are visual estimates of IRIS paint removal?

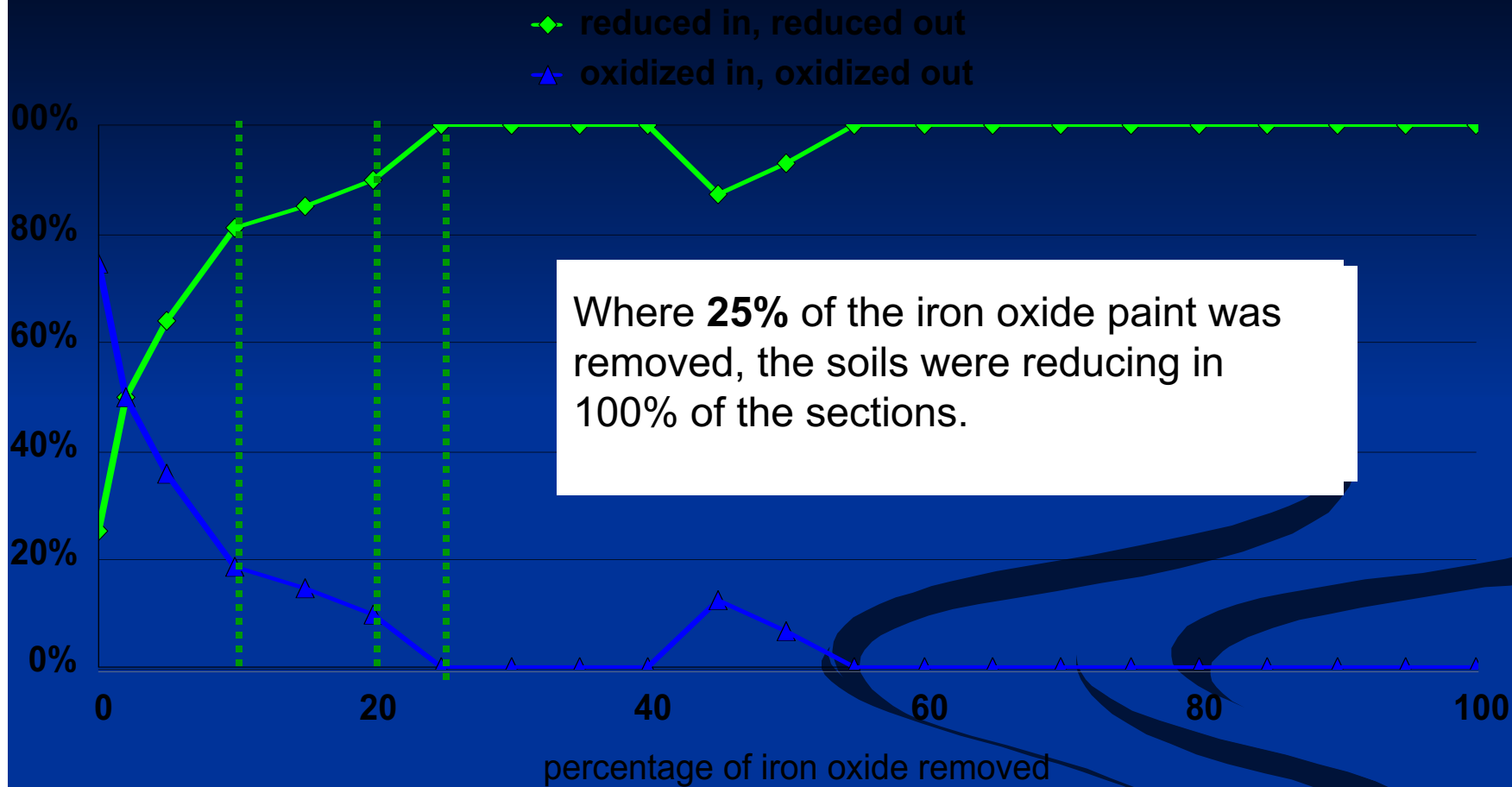




Average of Two Individual Estimates (worst and best)



Percentage of Observations Oxidized or Reduced by the TS



Castenson, K. L. and M. C. Rabenhorst. 2006. Indicator of reduction in soil (IRIS): Evaluation of a new approach for assessing reduced conditions in soil. *Soil Sci. Soc. Am. J* 70: 1222-1226.

Jenkinson called for synthesis of
ferrihydrite $\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$

(FeCl_3 titrated to pH 7.5 with KOH)

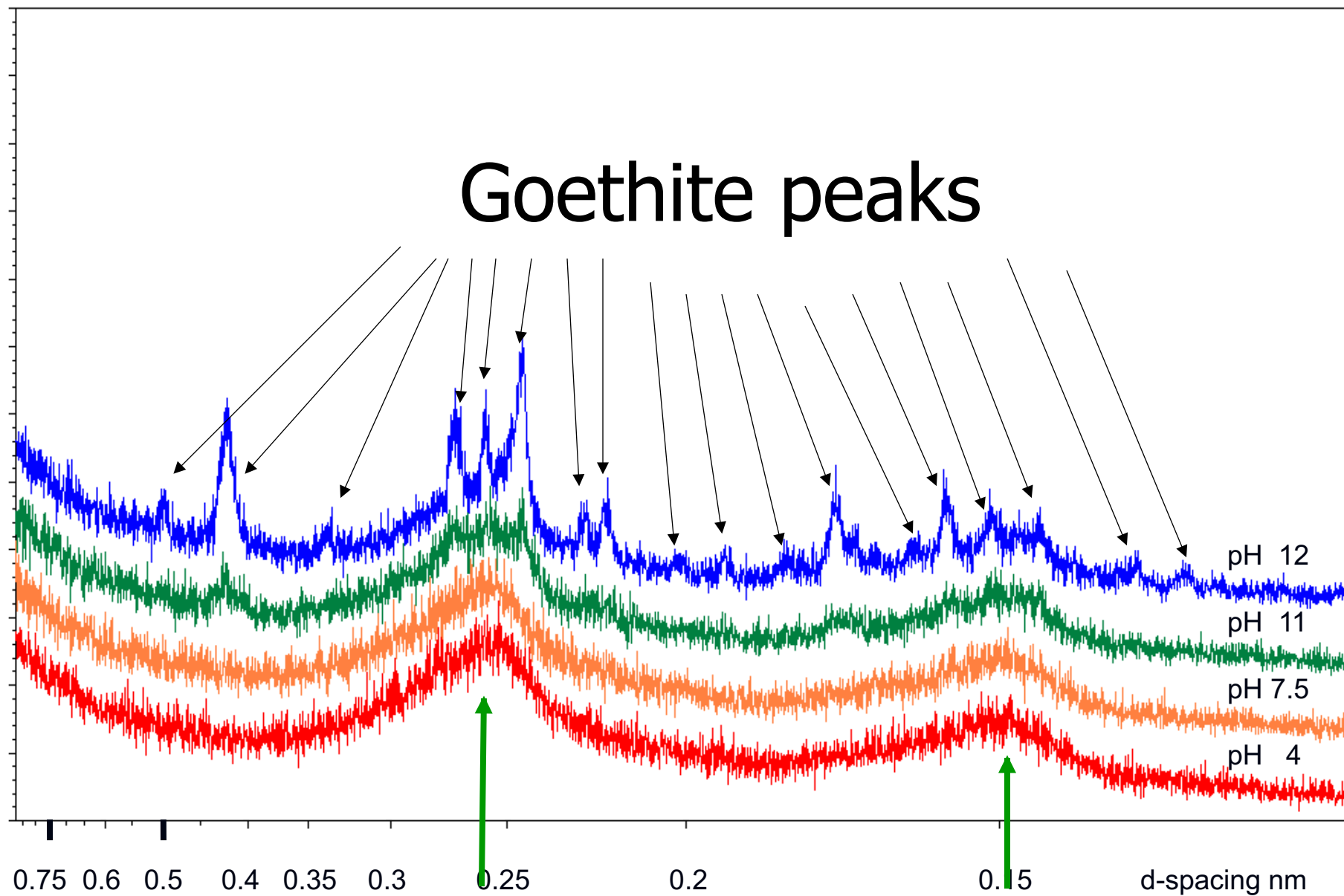


Problem with Newly Synthesized Paint

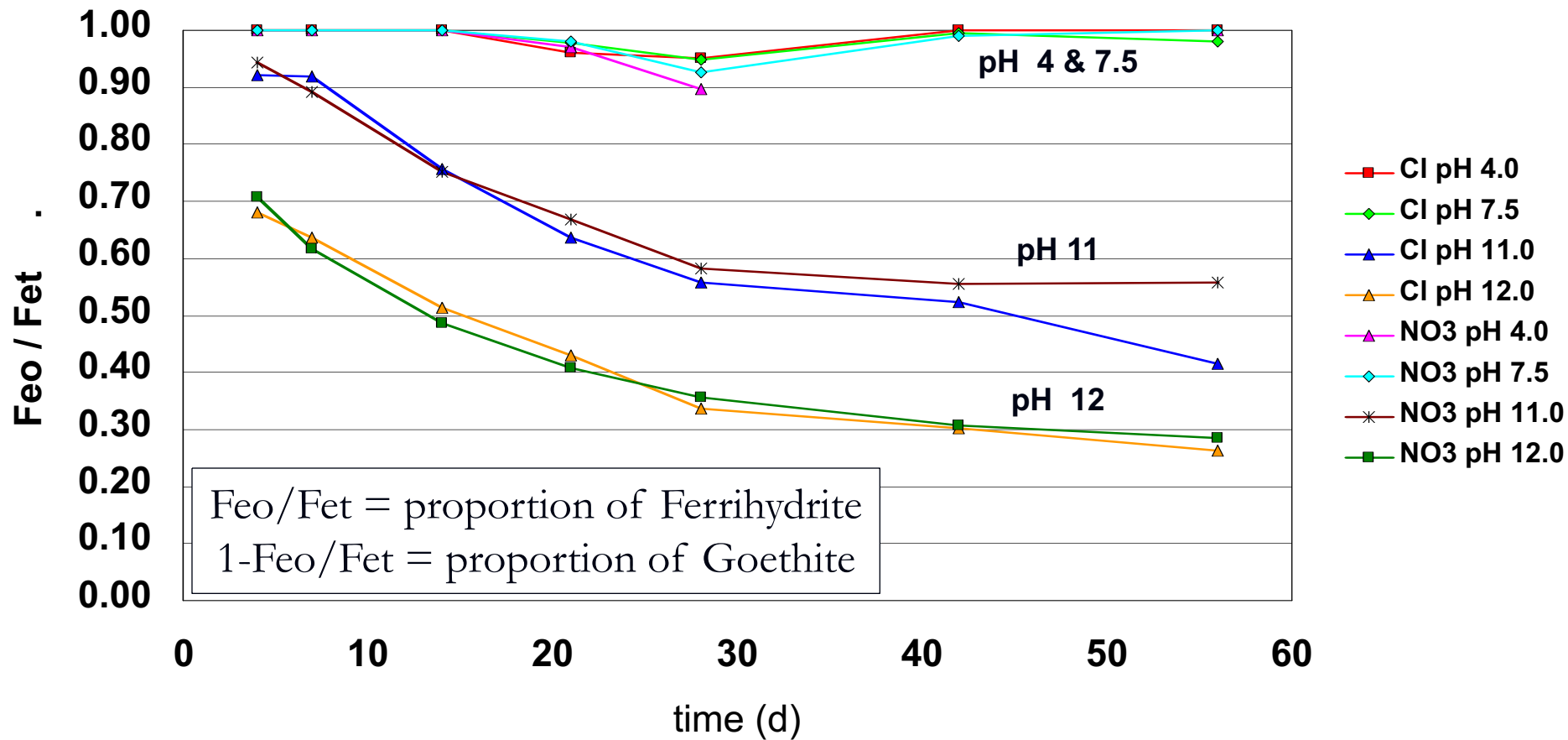
- We noticed that newly synthesized paint would not adhere well to the PVC.
- A number of observations led us to postulate that variation in mineralogical composition might affect behavior of the paint.



Newly formed Fe oxides (4 days old)



2 broad peaks for ferrihydrite



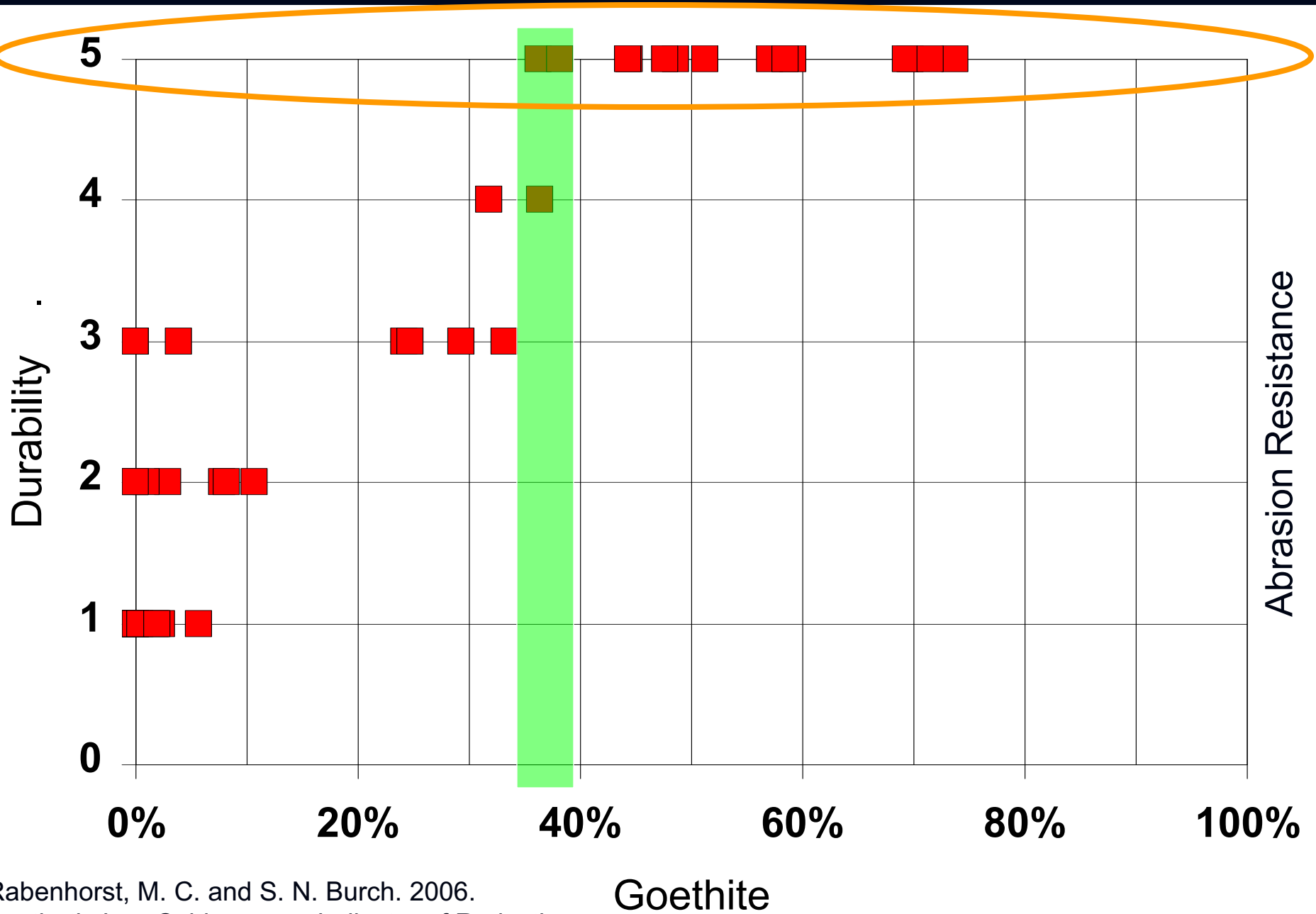
- Fe oxides formed by titration to pH 4 or 7.5 remain as essentially entirely oxalate extractable phases over time (confirming dominance of ferrihydrite)

- When Fe oxides were formed by titration to pH 11 or 12, a substantial portion of the Fe oxides initially were not oxalate extractable (8% and 30% respectively), and they continued to show alteration to more crystalline phases over time

Abrasion Resistance and Durability

- 1 - paint wipes off when applying very slight pressure
- 2 - paint wipes off when applying slight pressure
- 3 - paint wipes off when applying moderate pressure
- 4 - paint wipes off only when applying firm pressure
- 5 - paint does not wipe off when applying firm pressure.





Abrasion Resistance

Goethite

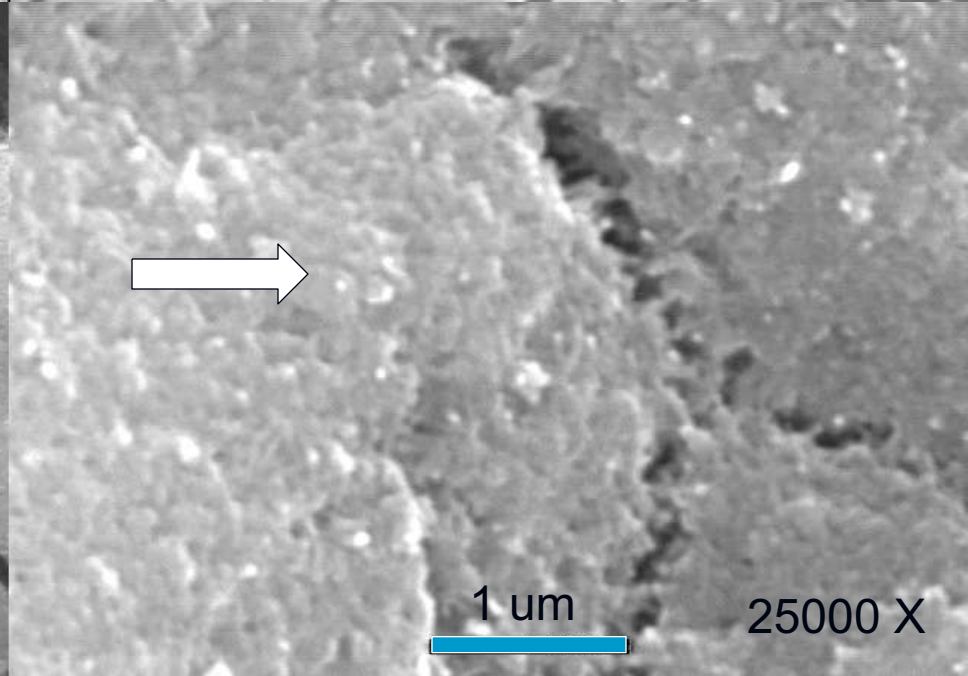
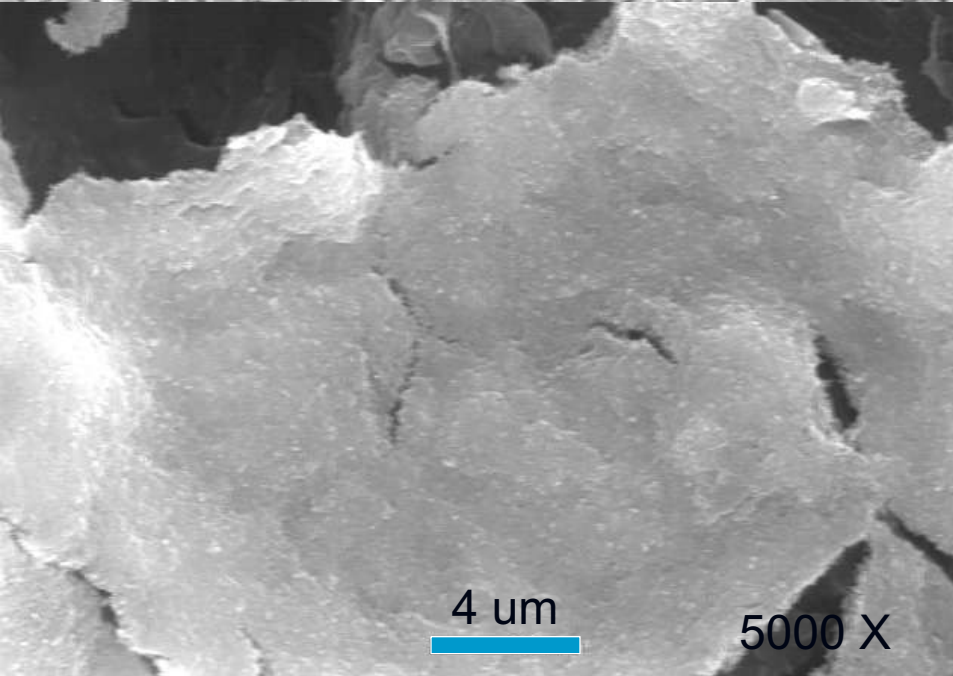
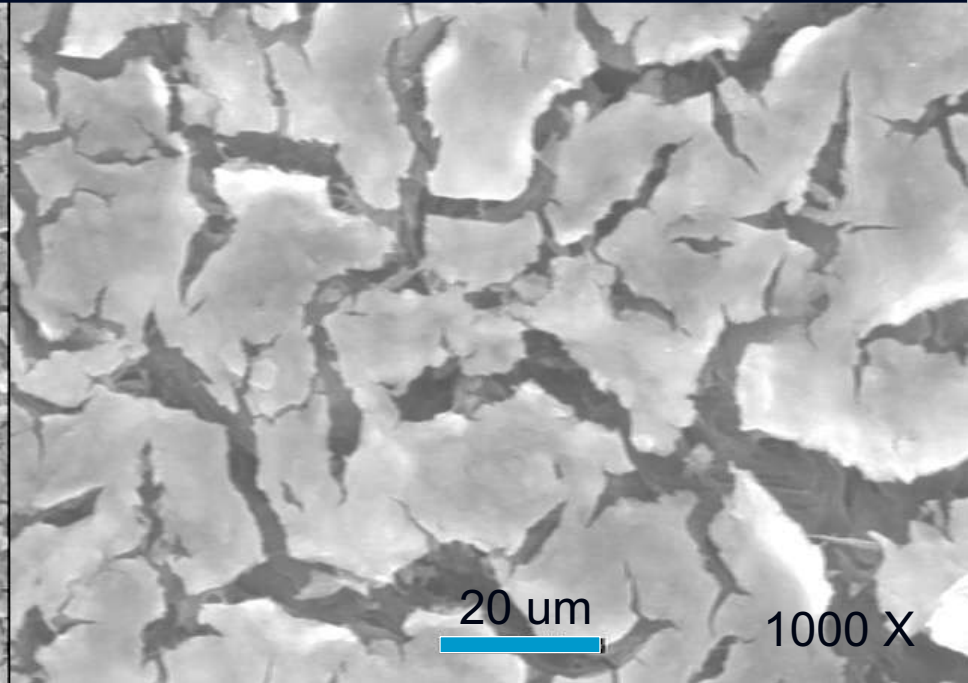
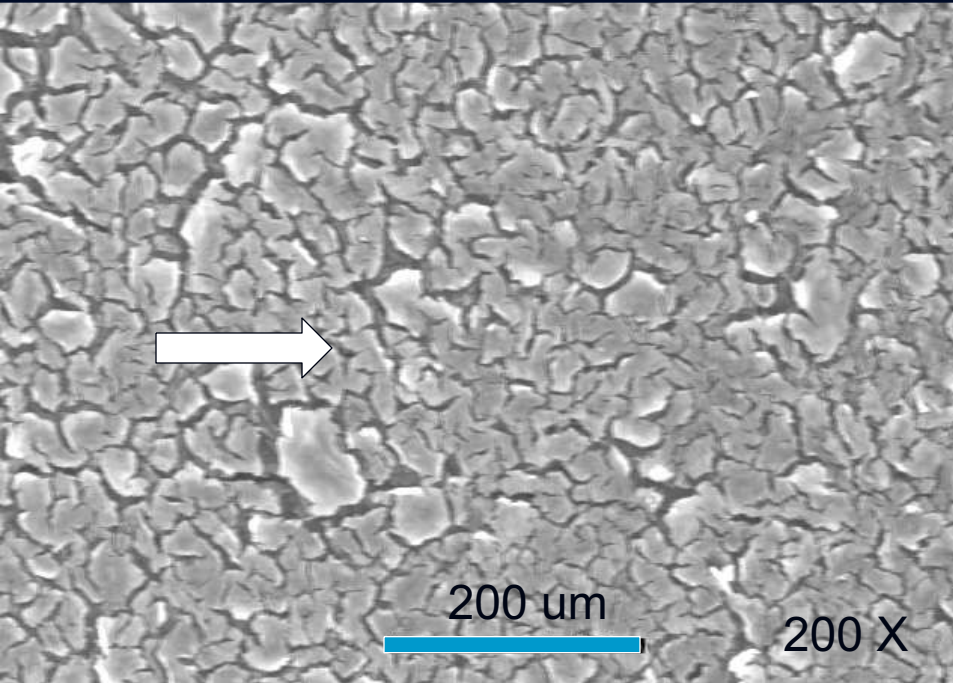
Rabenhorst, M. C. and S. N. Burch. 2006.
 Synthetic Iron Oxides as an Indicator of Reduction
 in Soils (IRIS). Soil Sci. Soc. Am. J. 70: 1227-1236.

What does the goethite do?



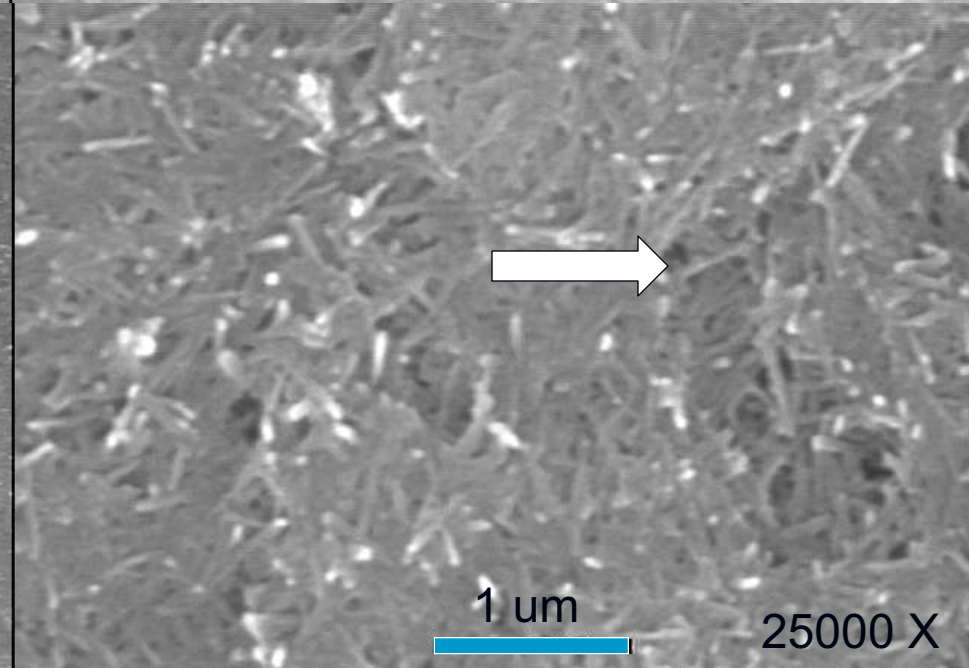
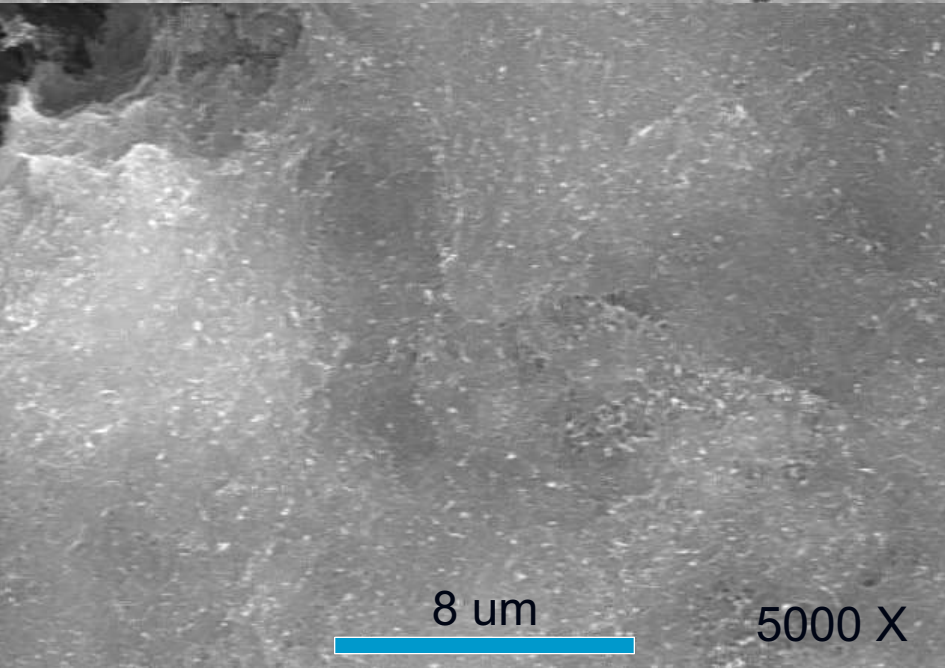
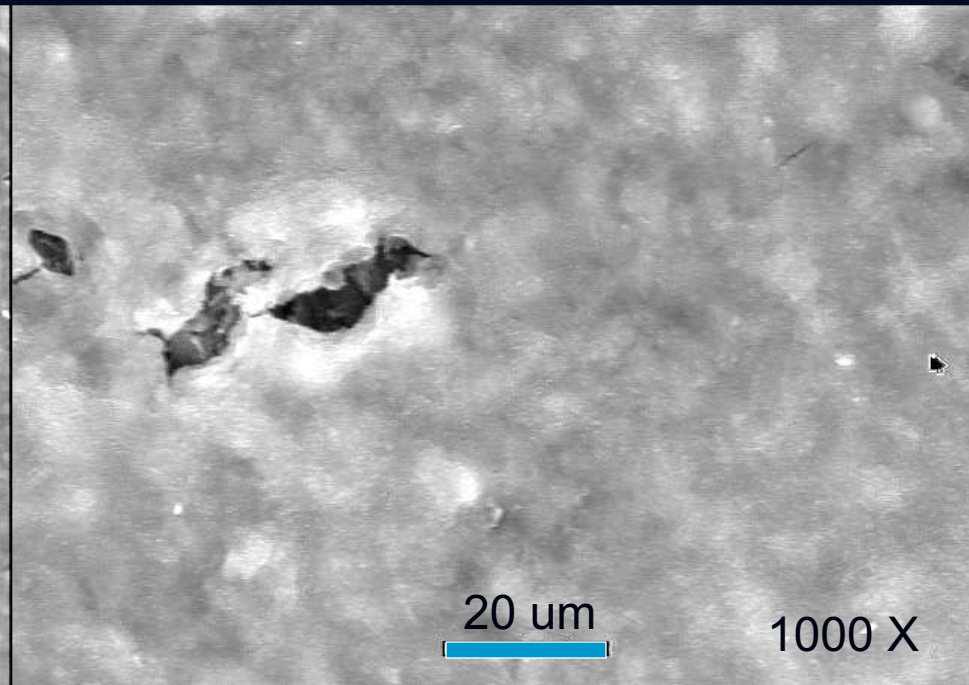
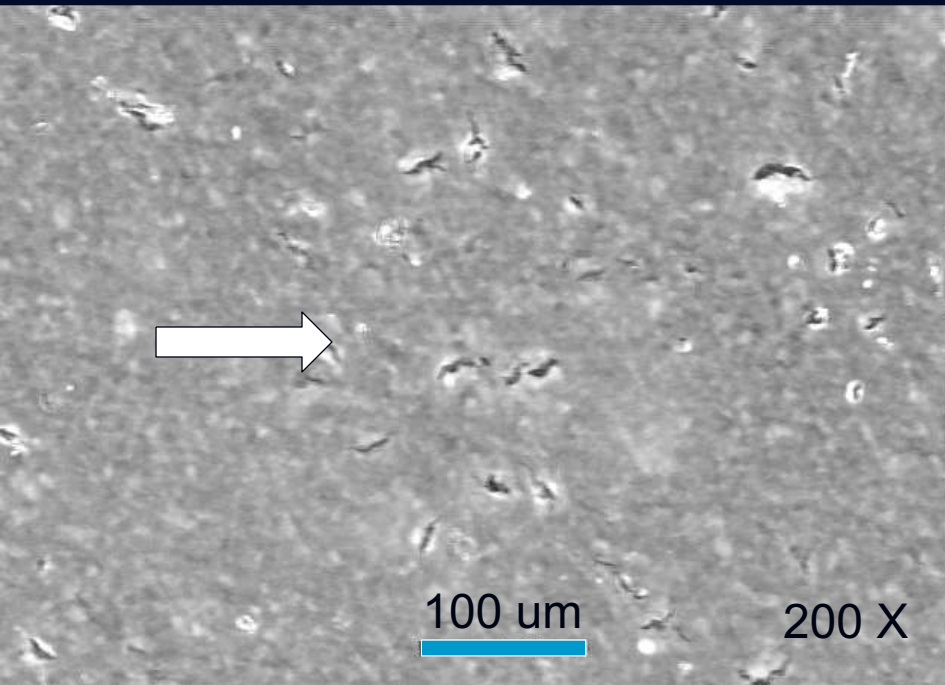
15% Goethite; 85% Ferrihydrite 1:5.7

Durability Index = 1 to 2



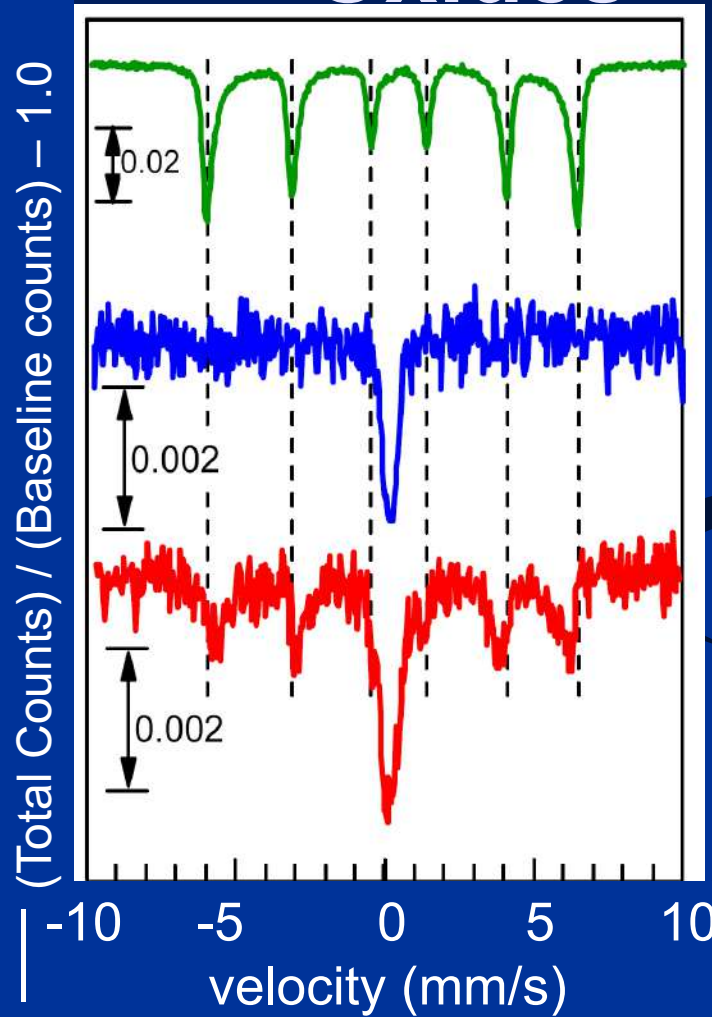
44% Goethite; 54% Ferrihydrite 1:1.3

Durability Index = 5



- The lath-shaped goethite crystals are prevalent and appear to form a reinforcing network.
 - analogous to the common (19th century) practice of masons adding some strong fibrous material to plaster such as hair or hemp
 - or the ancient practice of adding straw to clay when making bricks to increase their strength and cohesion.
- Thus, the growth of lath-shaped goethite crystals within the Fe oxide mixture appears to contribute strength and cohesion of the material.

What do the variations in color represent? Partial removal of Fe Oxides



Reference Goethite

Blank (peak from Fe in detector window)

Sample from "yellow" area on IRIS tube
RICH IN GOETHITE

Out 6/16/06
Indiantauu

Red

Yellow

Means of four replicate analyses

saturated soil

		Fe _{ox}	Fe _{6M HCl}	Fe _{Total}	Fh	Gt
		ug/cm ²			%	
	mean	55.5	56.2	111.6	49.8%	50.2%
Red	SE	3.0	4.1	7.0	0.7%	0.7%

GOETHITE

Rabenhorst, M. C., D. W. Ming, and R. V. Morris. 2006. Synthesized Iron Oxides Used as a Tool for Documenting Reducing Conditions in Soils. 18th World Congress of Soil Science, Philadelphia, PA. July 9-15, 2006.

Next Question

- Does the mineralogical composition of the paint affect how IRIS tubes will behave in the soil?
- We know we need 30-40% goethite for good durability of the paint, but does the proportion of goethite relative to ferrihydrite make any difference in how they function?



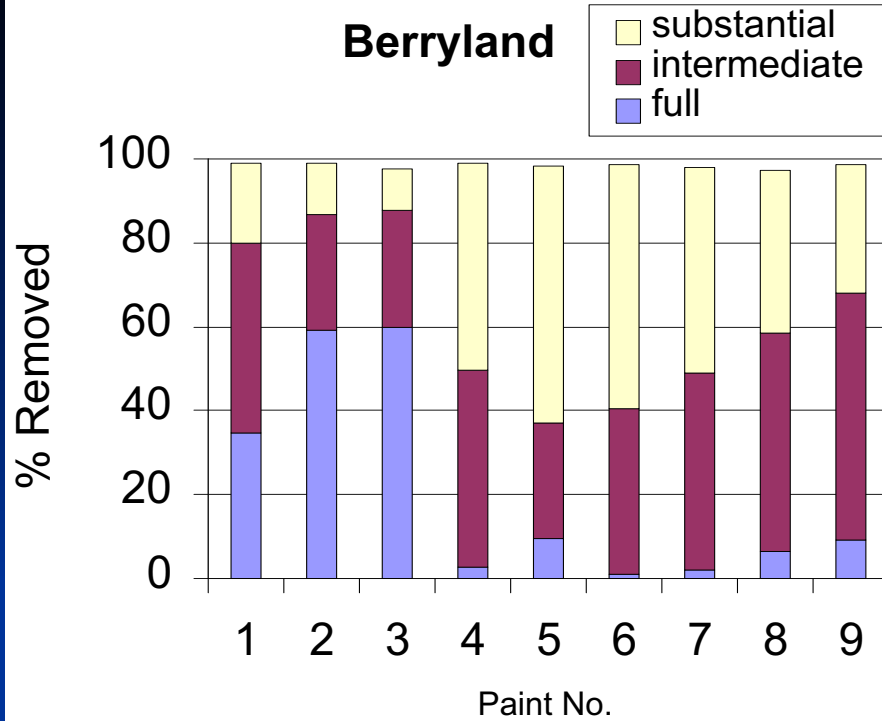
Mesocosms filled with two different soil materials (Indiantown A horizon and Berryland A horizon) and each containing 36 IRIS tubes representing 4 replicates of 9 different paints

Mineralogical composition* of the nine Fe oxide paints examined in this study.

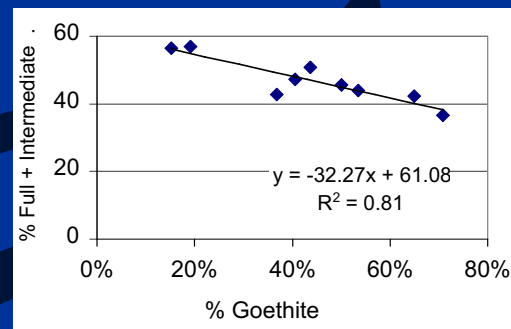
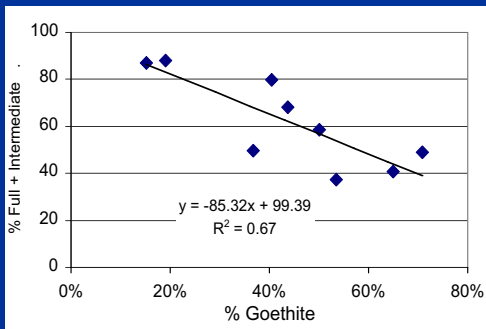
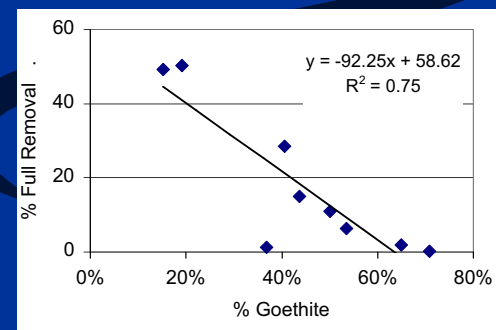
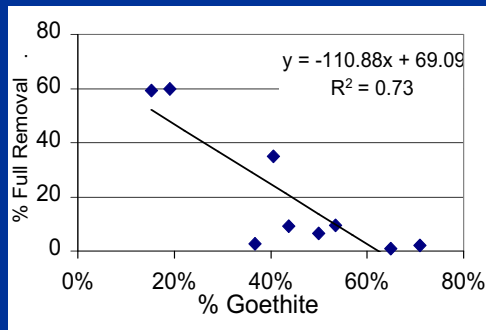
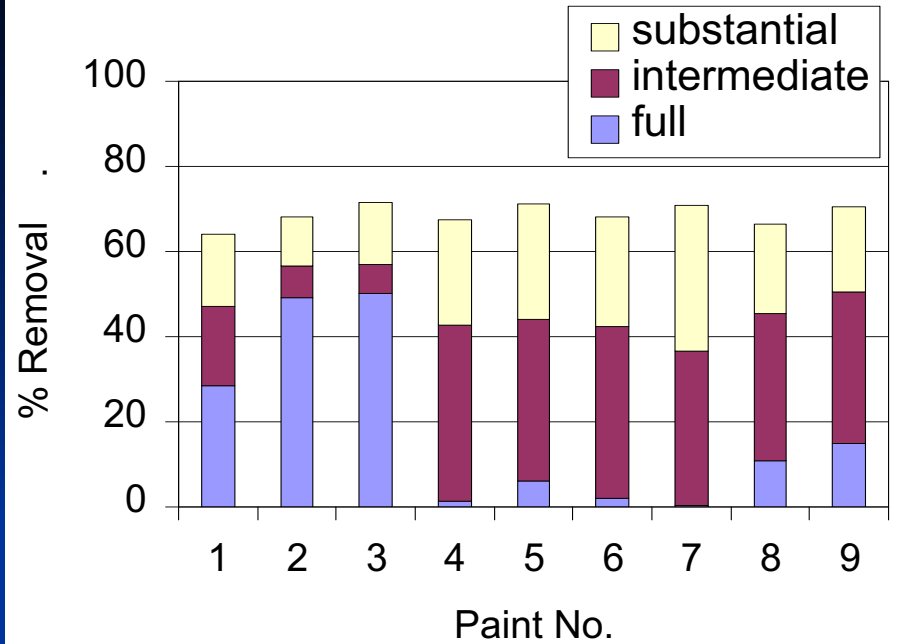
#		% Fh	% Gt	Fh:Gt
1	0520 75d	59.5	40.5	1.47
2	0521 22d	84.8	15.2	5.58
3	0521 33d	80.9	19.1	4.24
4	0523 36d	63.3	36.7	1.72
5	0601 10d	46.6	53.4	0.87
6	0601 14d	35.0	65.0	0.54
7	0602 9d	29.1	70.9	0.41
8	0603 4d	50.0	50.0	1.00
9	0604 9d	56.3	43.7	1.29

* – based upon acid ammonium oxalate and total Fe analyses. Fh – ferrihydrite; Gt – goethite.

Berryland



Indiantown

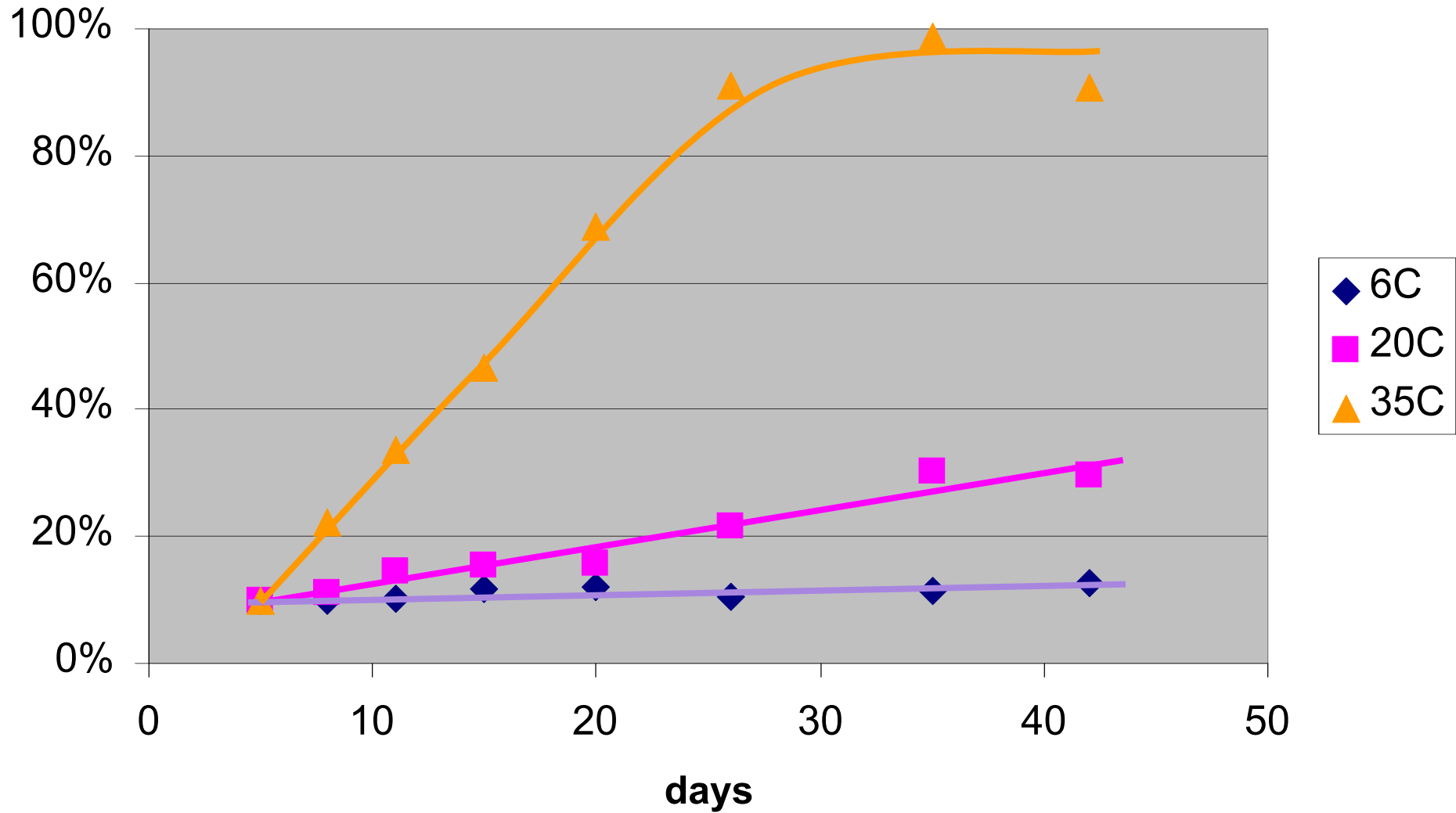


Target – 40-60% goethite; 60-40 % ferrihydrite

**How then to increase “pot life” of the
paint**

The bottom half of the slide features several thick, black, wavy lines that sweep across the frame from the bottom left towards the right, creating a sense of motion and depth against the solid blue background.

Estimates of Goethite content based upon peak heights



Conclusions

- We know how to make IRIS tubes
- We know how to synthesize the paint so that it will adhere, and we know why it adheres
- We know what the variations in color represent
- We know that mineralogical composition affects performance
- We know how to preserve “pot life” of the paint to slow mineralogical change
- We know how to interpret removal of the paint with respect to the Technical Standard of NTCHS.
- We know how to use them – Protocol to be covered in workshop

finis

