

# Electron Microscopic Investigation of Liquid and Solid for Fenton Oxidation of Leachate

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# Outline

- Problem Statement
- Liquid Hydrogen Peroxide Fenton
- Solid Calcium Peroxide Fenton
- Experiments
- Electron Microscopic Investigations
- Acknowledgments

# Collecting Leachate



# Preparing Leachate



# Microscopic Aspects of Fenton Processes: Liquid vs. Solid Peroxides

- Raw leachate
- Leachate treatment options: liquid vs. solid peroxides
- Hydrogen peroxide system
- Calcium peroxide system
- Technical challenges
- Design criteria using solid vs. liquid peroxides

# Statement of Problem

- No electron microscopic characterization of both leachate and  $\text{CaO}_2$ ;
- Microscopic characterization of both leachate and  $\text{CaO}_2$  provide insight into the oxidation mechanisms;
- Oxidation mechanisms may be unveiled through the change of composition of both leachate and sediments containing Ca after  $\text{H}_2\text{O}_2$  is released.

# Objectives

- To provide direct image of both leachate and  $\text{CaO}_2$ ;
- To provide direct evidence of composition of leachate;
- To quantify the chemical composition of both leachate and  $\text{CaO}_2$ .

# Characterization of Leachate



# Conventional Pollutants in Typical Leachate

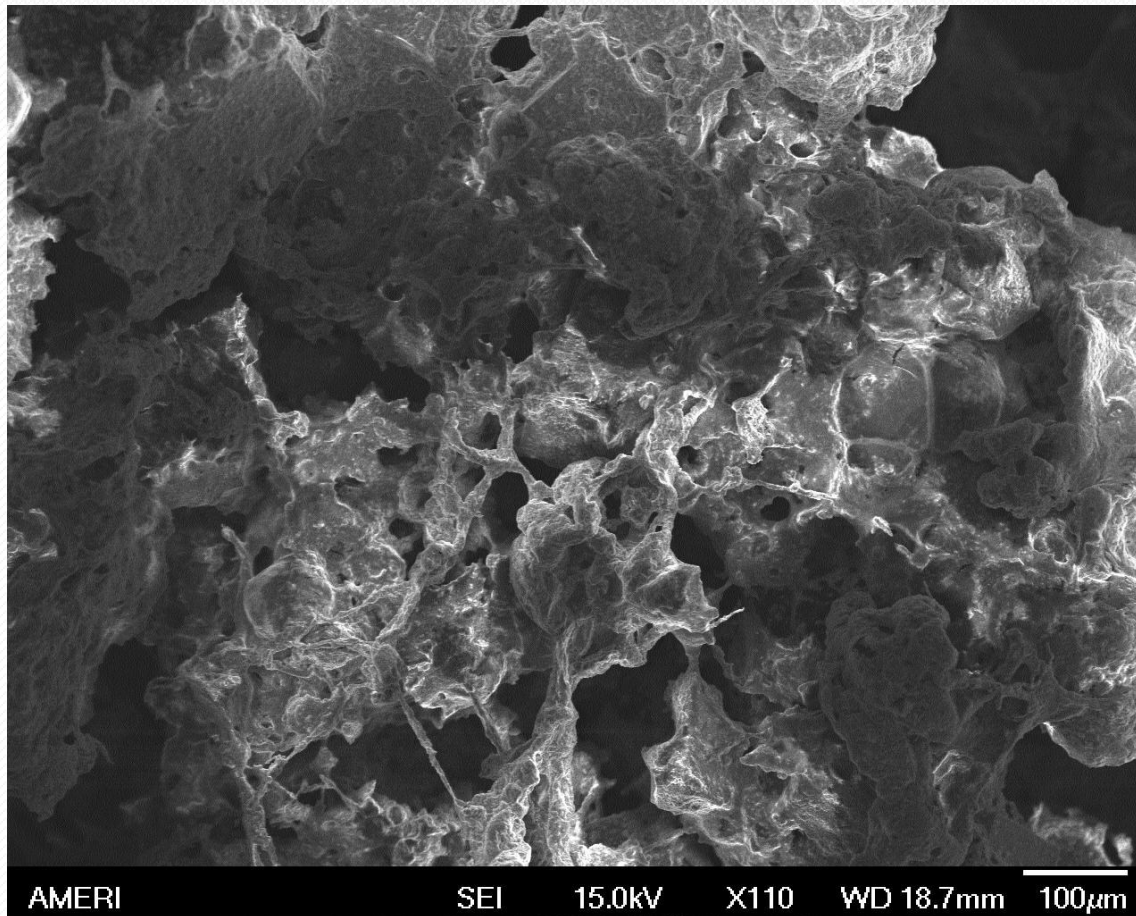
mg/L (except pH)

Constituent	<u>New Landfill (&lt; 2yrs)</u>		Mature Landfill ( > 10 yrs)
	Range	Typical	
BOD <sub>5</sub>	2,000-30,000	10,000	100-200
TOC	1,500-20,000	6,000	80-160
COD	3,000-60,000	18,000	100-500
Total suspended solids	200-2,000	500	100-400
Organic nitrogen	10-800	200	80-120
Ammonia nitrogen	10-800	200	20-40
Nitrate	5-40	25	5-10
Total phosphorus	5-100	30	5-10
Ortho phosphorus	4-80	20	4-8
Alkalinity as CaCO <sub>3</sub>	1,000-10,000	3,000	200-1,000
pH	4.5-7.5	6	6.6-7.5
Total hardness as CaCO <sub>3</sub>	300-10,000	3,500	200-500
Calcium	200-3,000	1,000	100-400
Magnesium	50-1,500	250	50-200
Potassium	200-1,000	300	50-400
Sodium	200-2,500	500	100-200
Chloride	200-3,000	500	100-400
Sulfate	50-1,000	300	20-50
Total iron	50-1,200	60	20-200

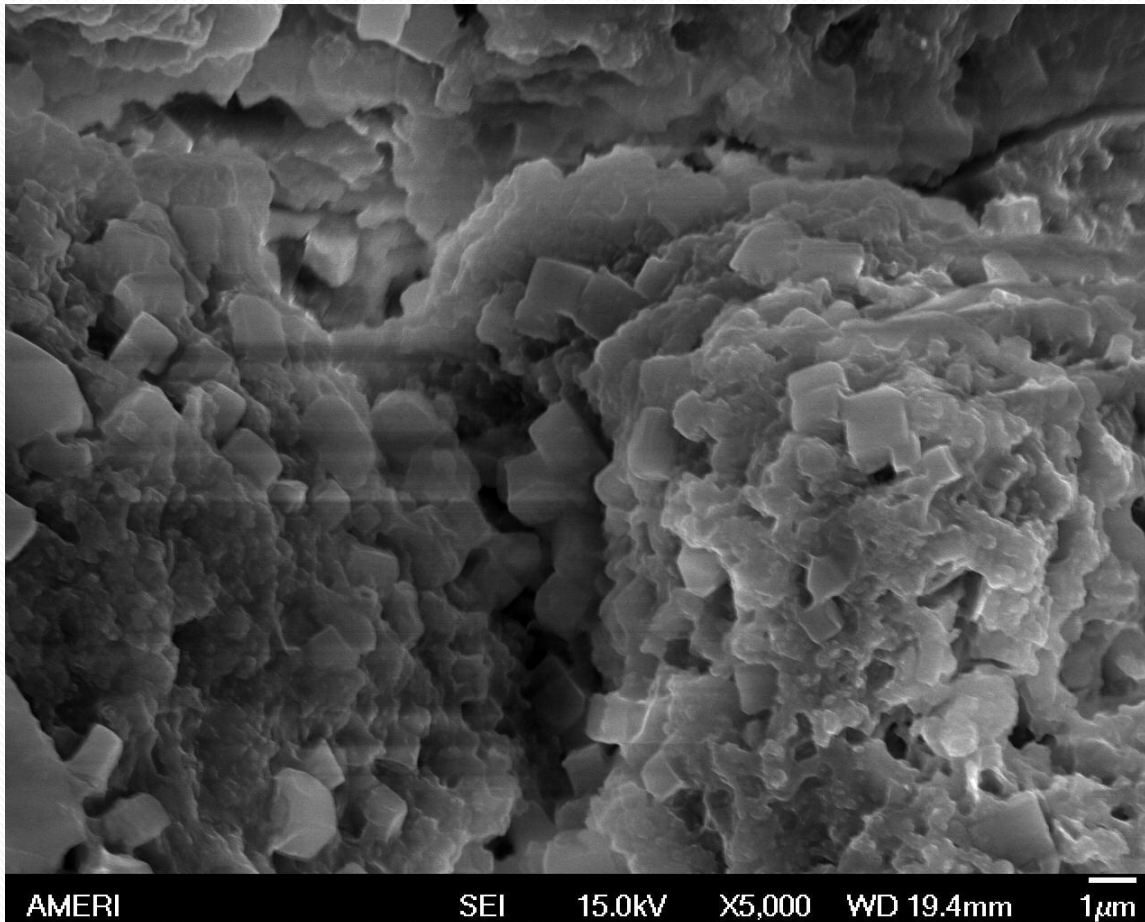
# Relative Biodegradability of Leachate

Bio-degradability	BOD/COD	COD/TOC
Low	$< 0.5$	$< 2$
Medium	$0.5 - 0.75$	$2 - 3$
High	$> 0.75$	$> 3$

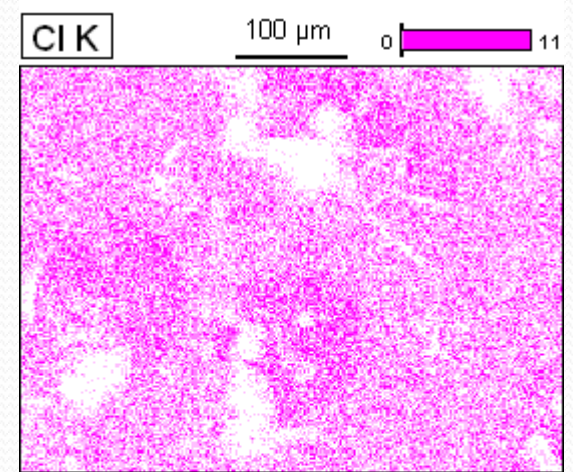
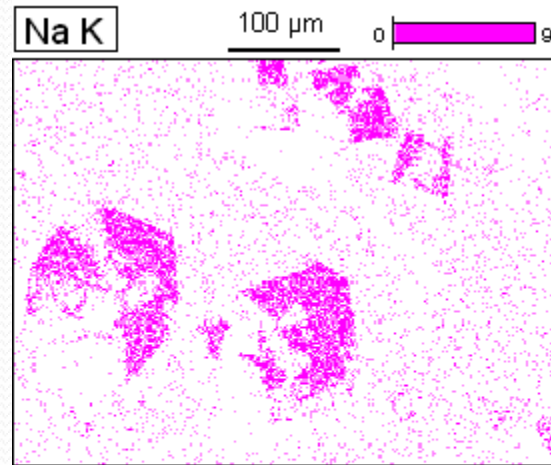
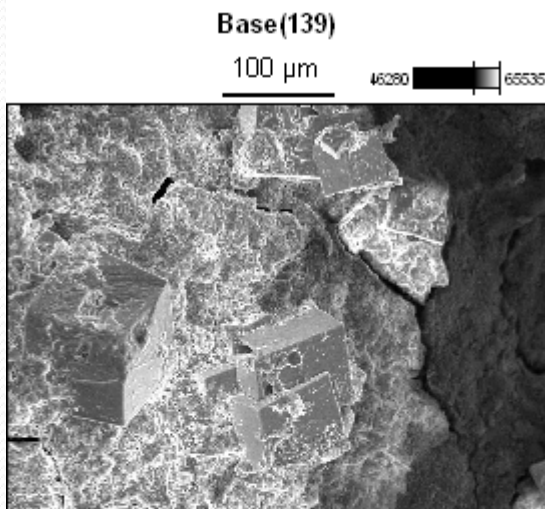
# Raw Leachate without Filtration x110



# Raw Leachate without Filtration x5,000

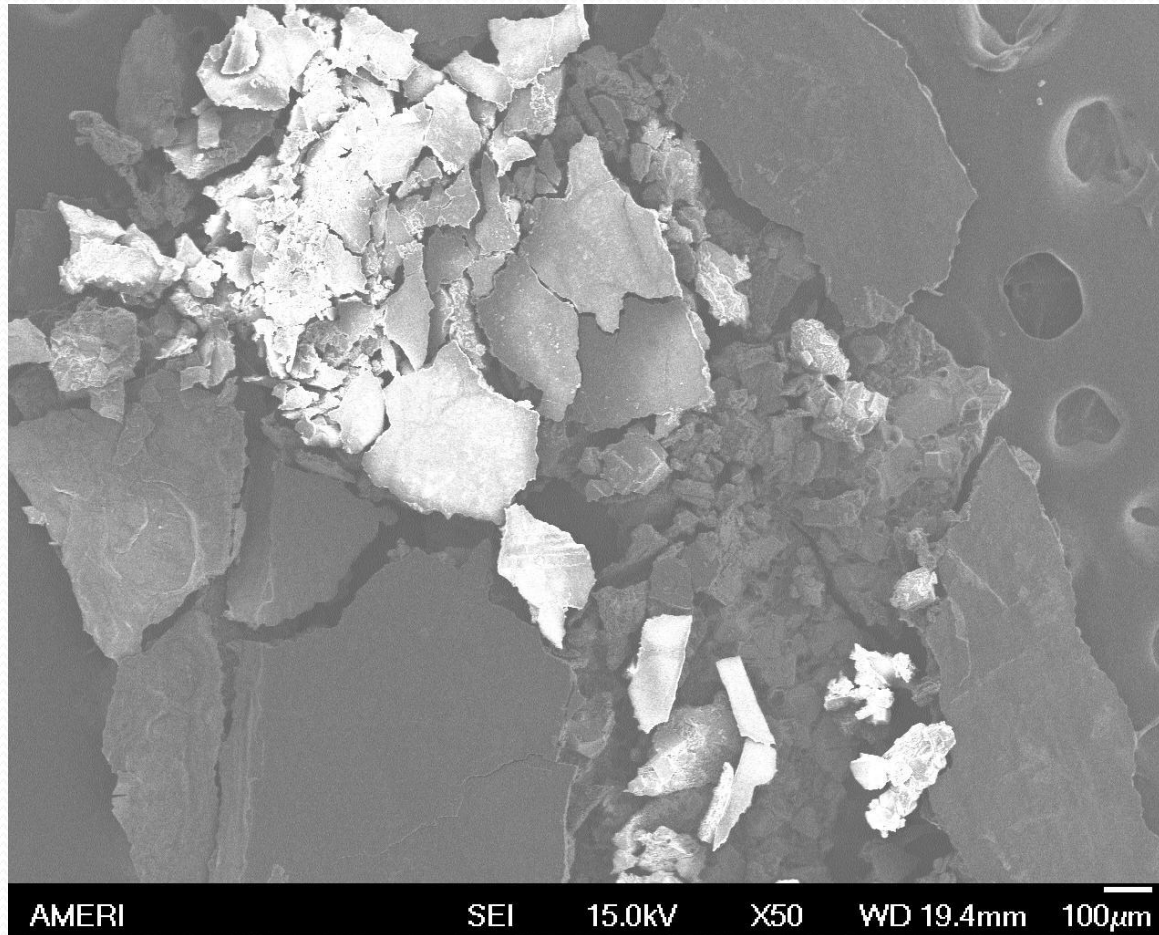


# Mapping of Elements



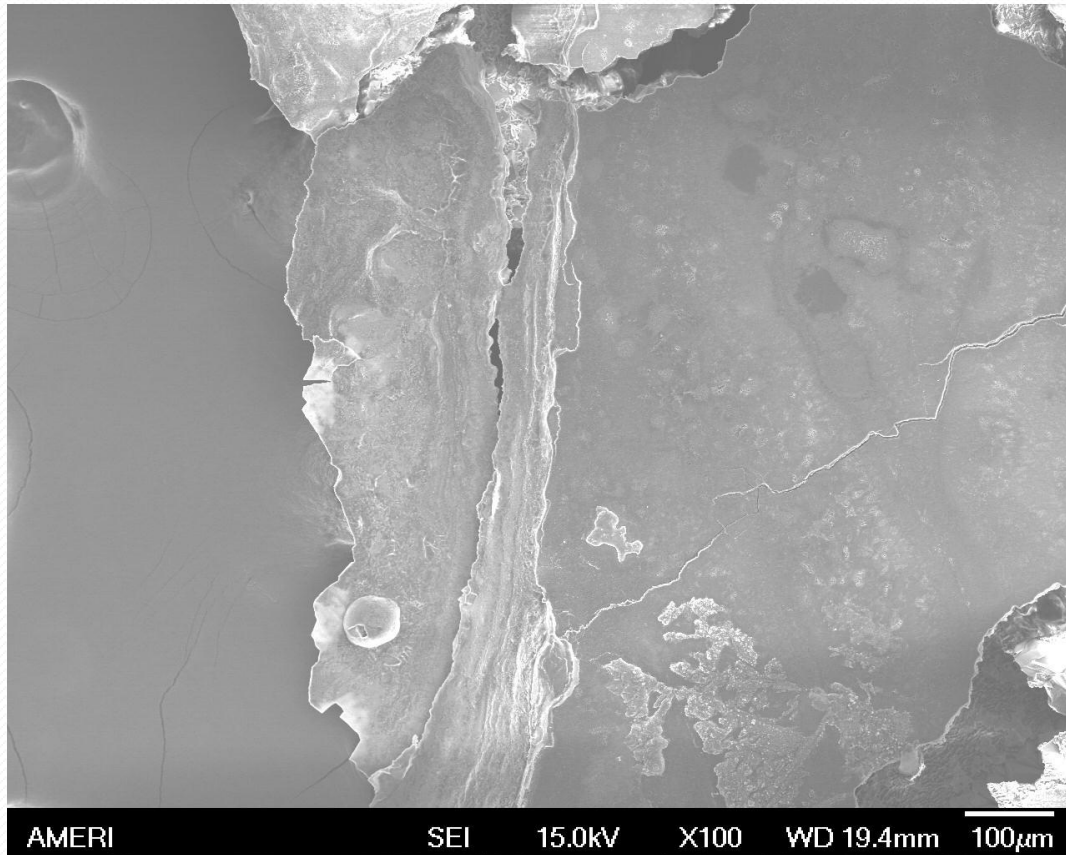
# Raw Leachate after Filtration

## x50



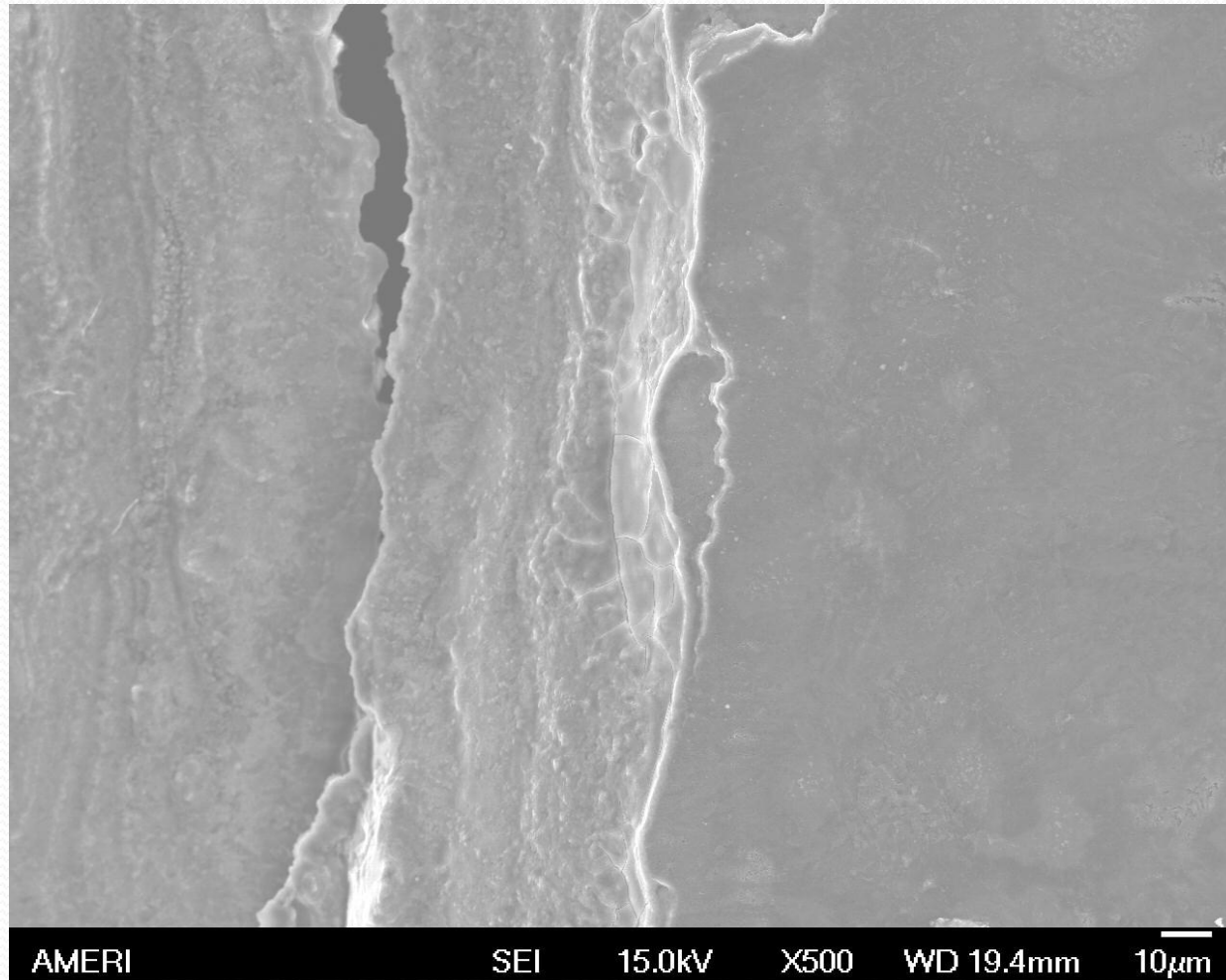
# Raw Leachate after Filtration

## x100



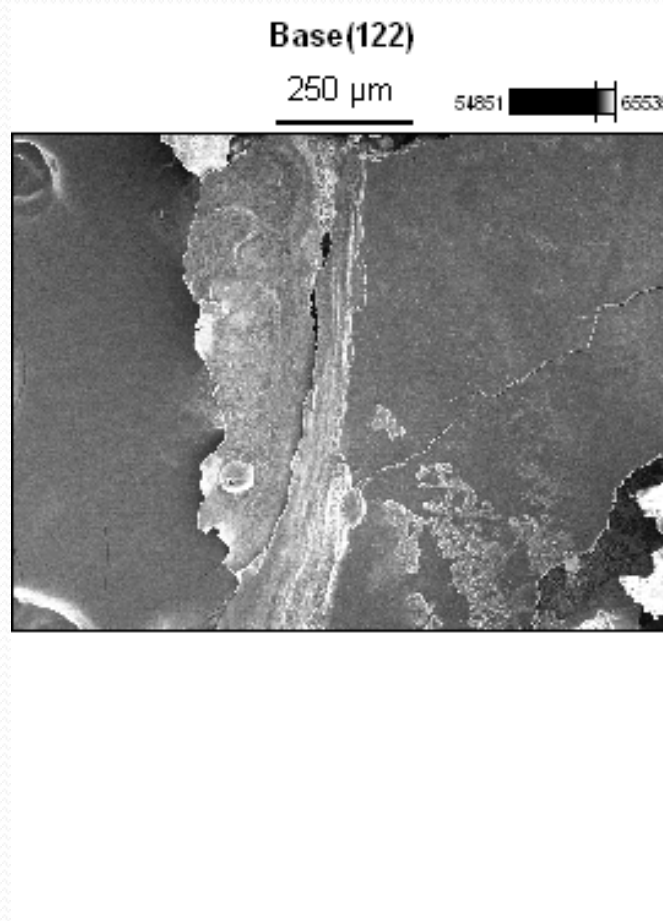
# Raw Leachate after Filtration

## x500

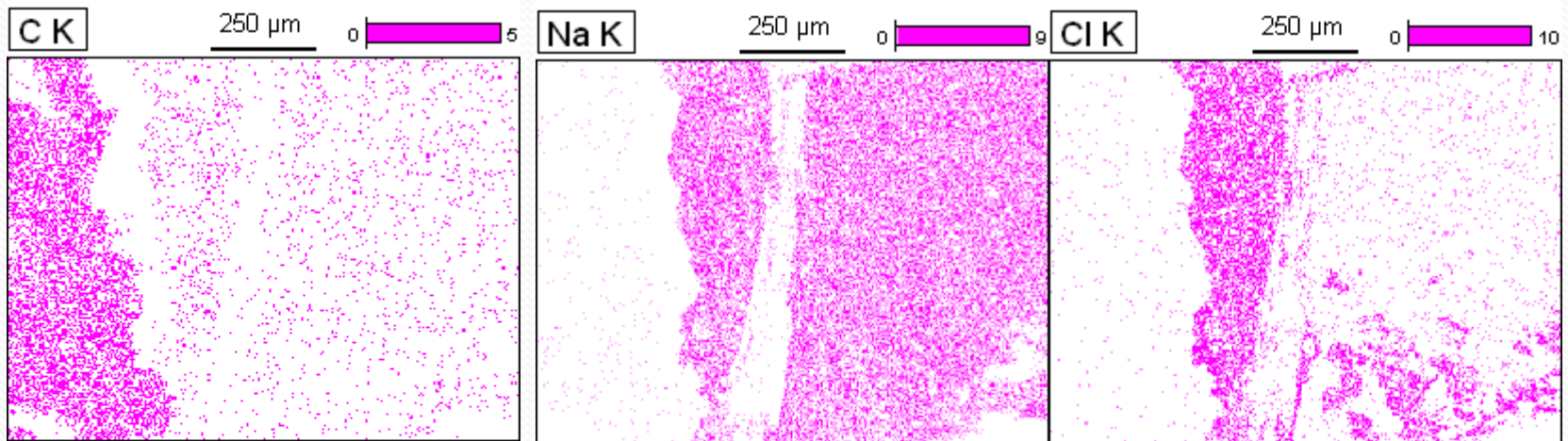




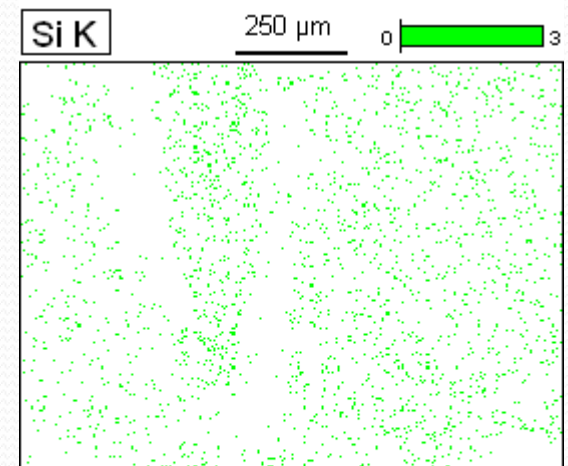
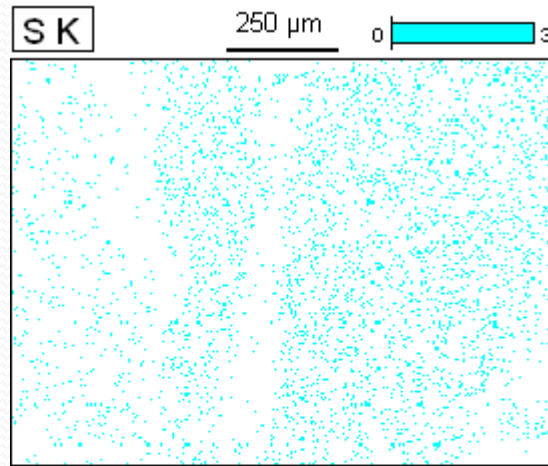
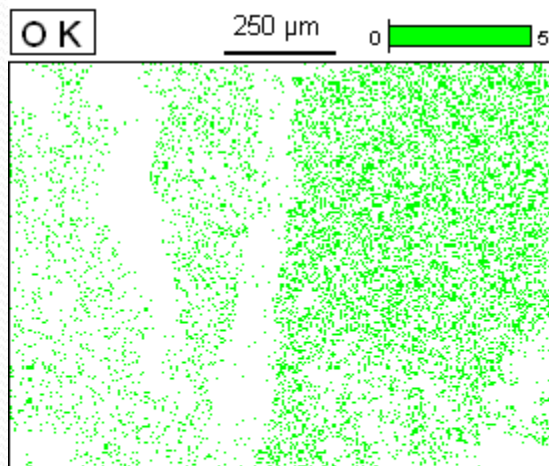
# Electron Mapping of Filtered Leachate



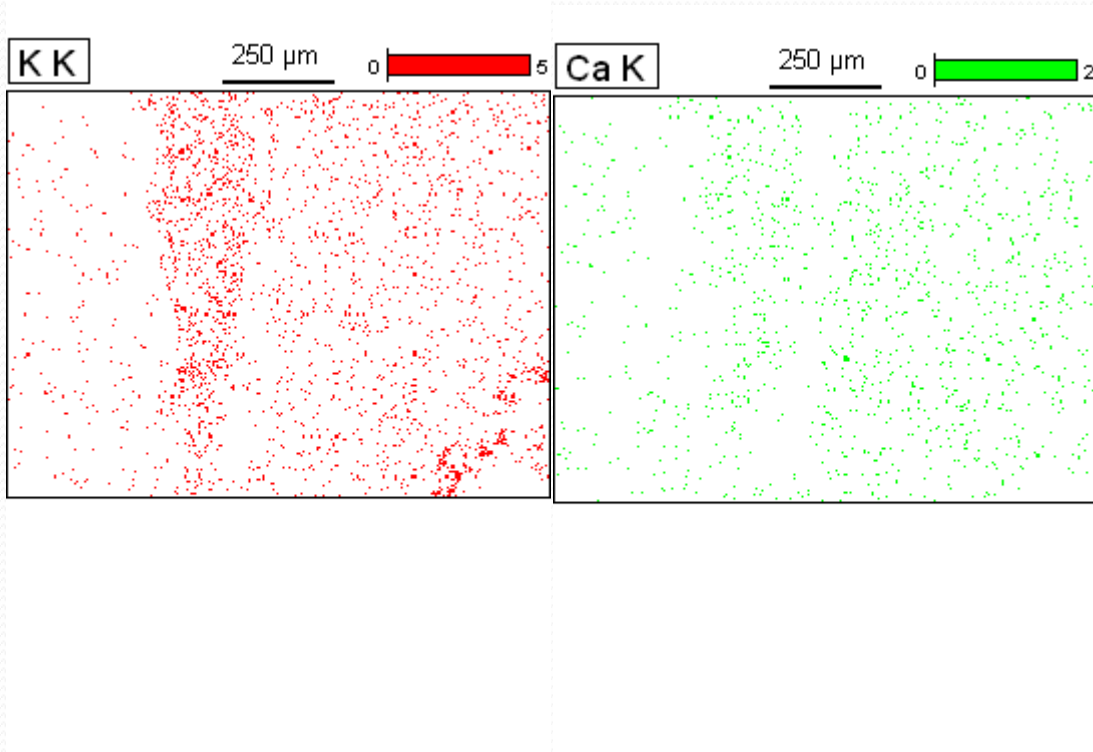
# Electron Mapping of Filtered Leachate



# Electron Mapping of Filtered Leachate

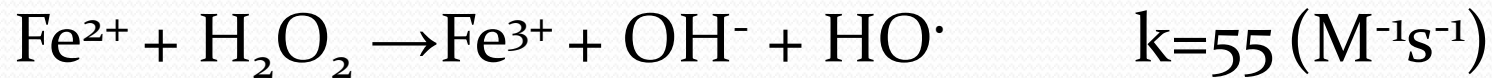


# Electron Mapping of Filtered Leachate



# Classic Fenton Processes

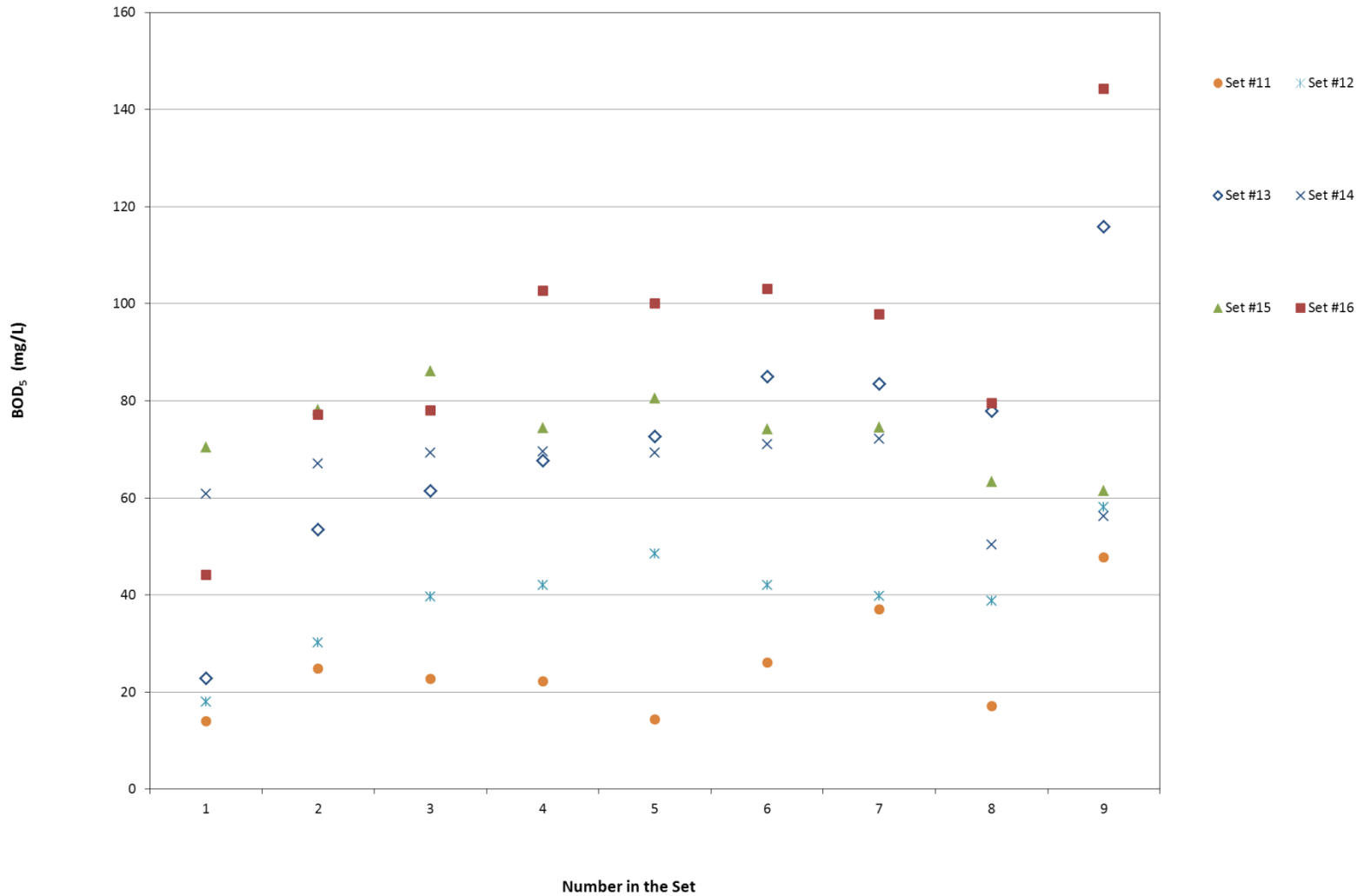
# Fenton Reaction Mechanism



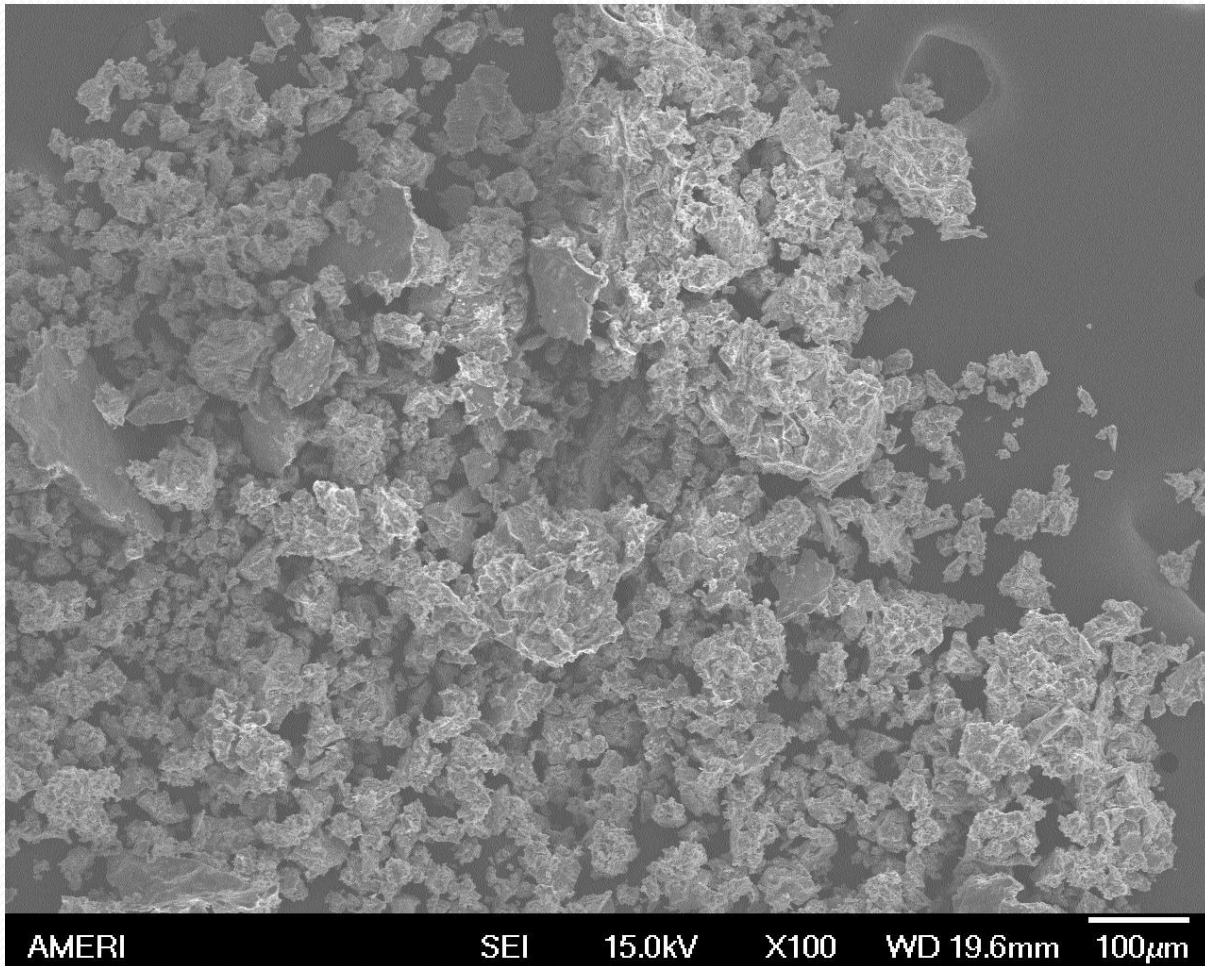
$$\text{H}_2\text{O}_2/\text{Fe}^{2+}_{\text{Opt.}} = k_{\text{OH}, \text{Fe}^{2+}}/k_{\text{OH}, \text{H}_2\text{O}_2} = 3 \times 10^8 / 2.7 \times 10^7 = 11$$

(Tang 2004)

# Biodegradability Enhancement

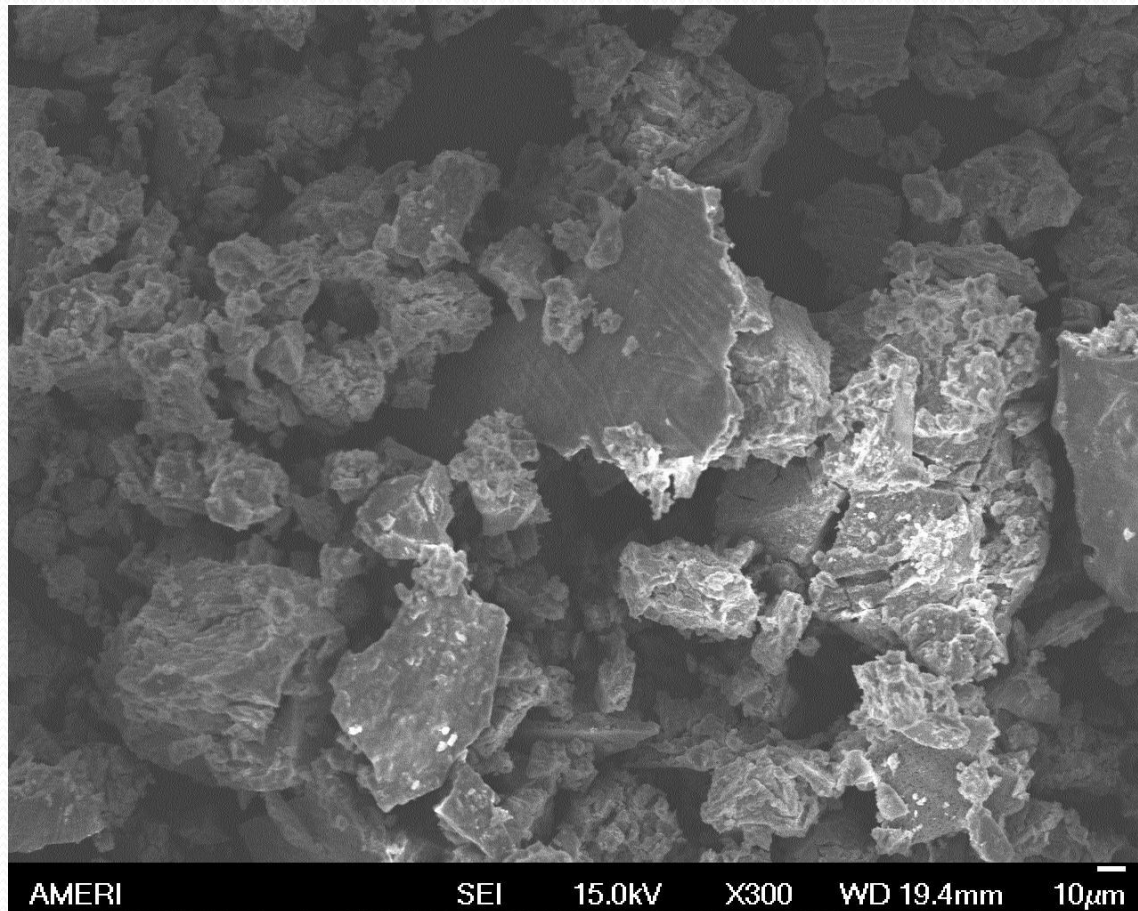


# SEM Image of $\text{Fe}(\text{OH})_3$ at x100

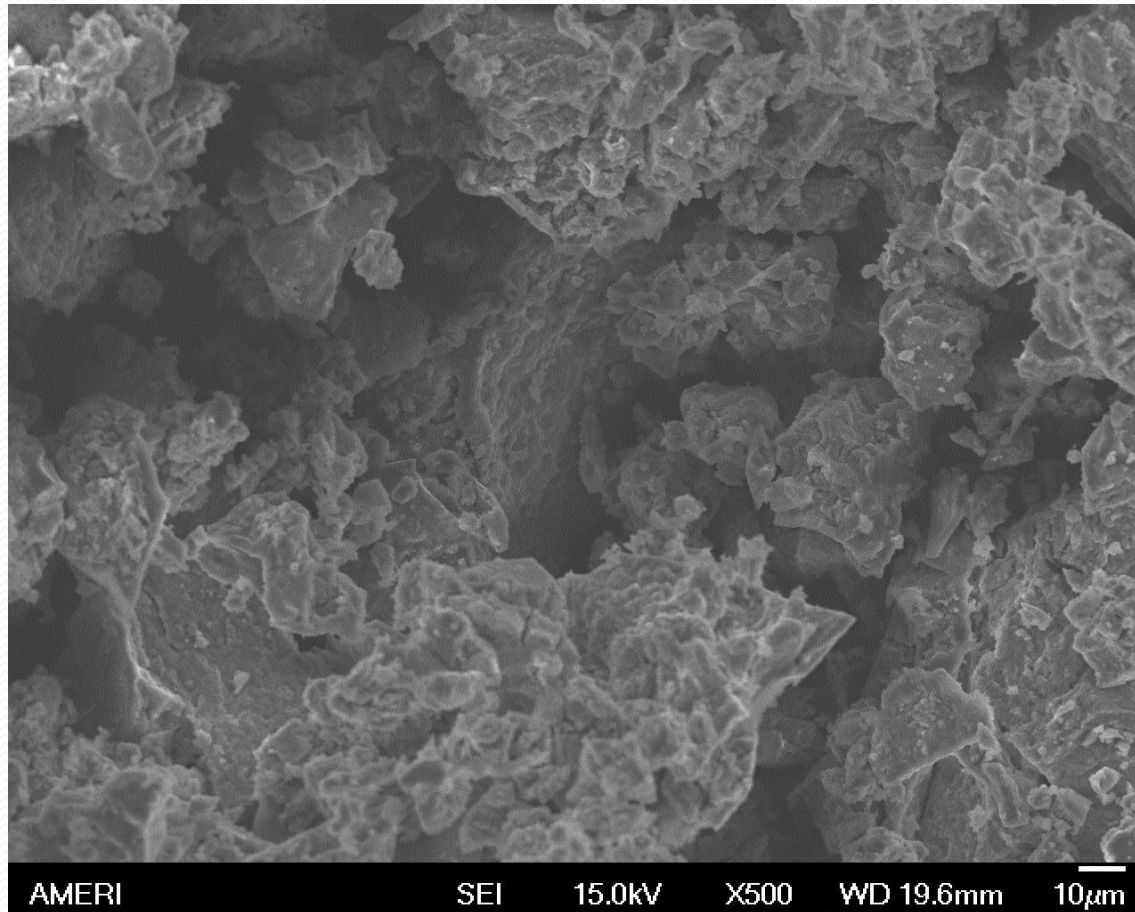




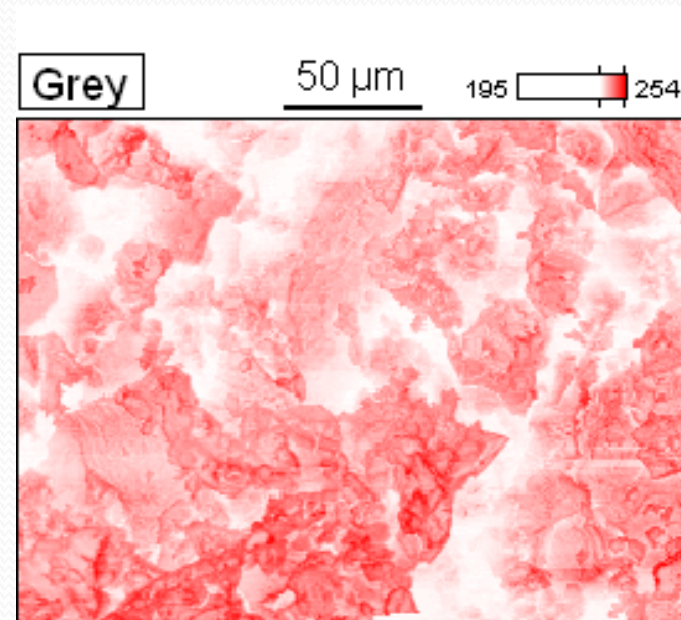
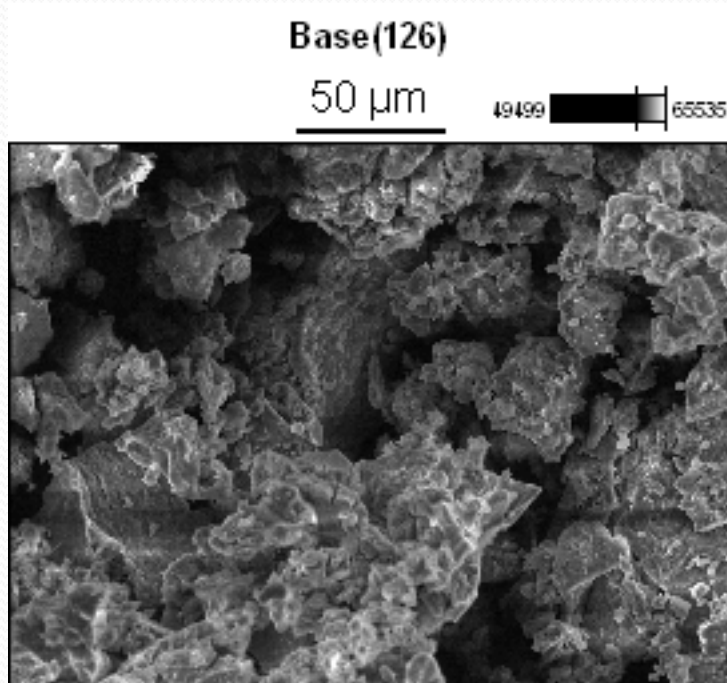
# SEM Image of $\text{Fe}(\text{OH})_3$ at x300



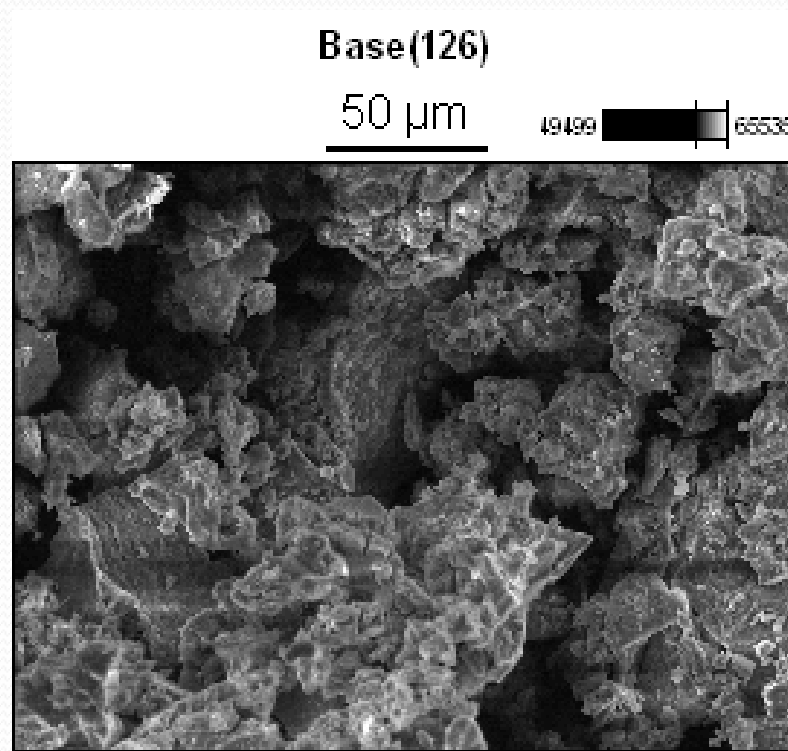
# SEM Image of $\text{Fe}(\text{OH})_3$ at x500



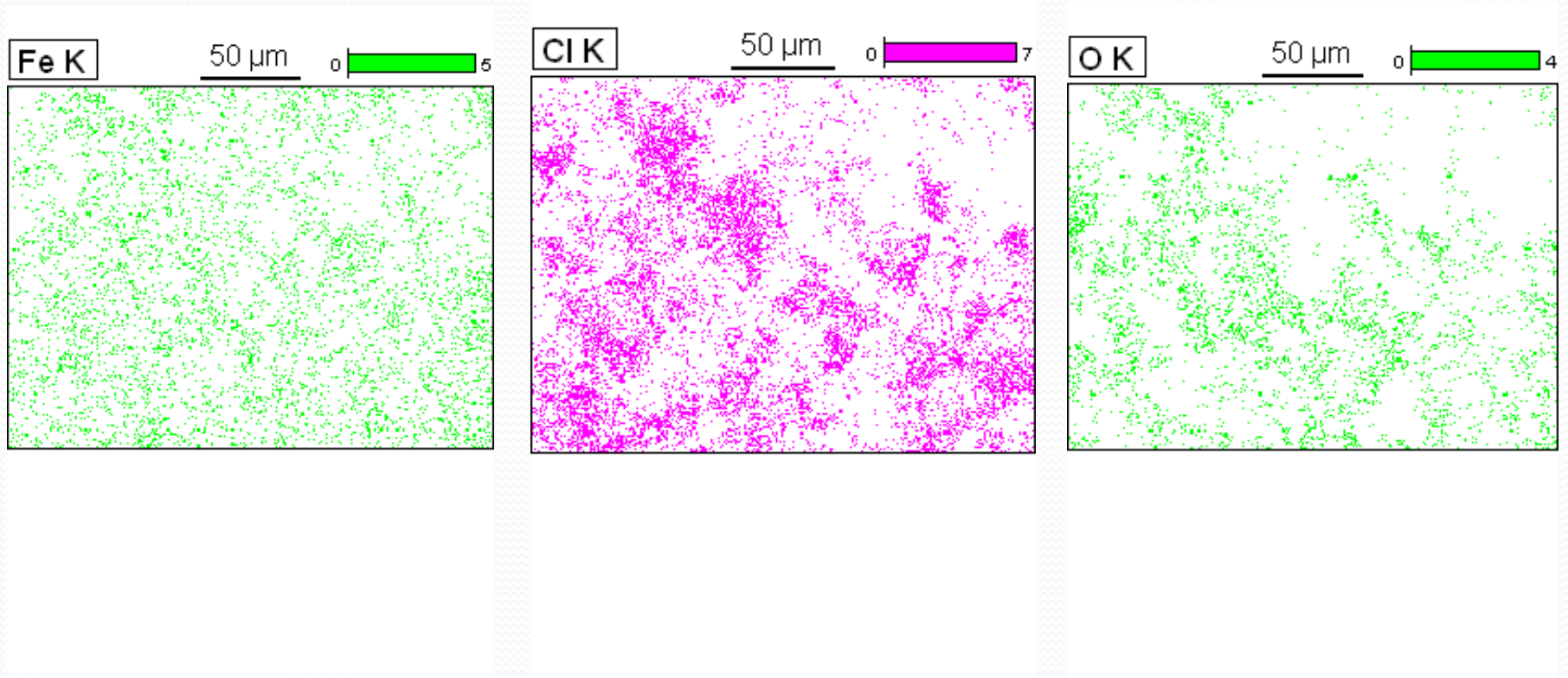
# Electron Mapping of Elements in $\text{Fe}(\text{OH})_3$ Sediment



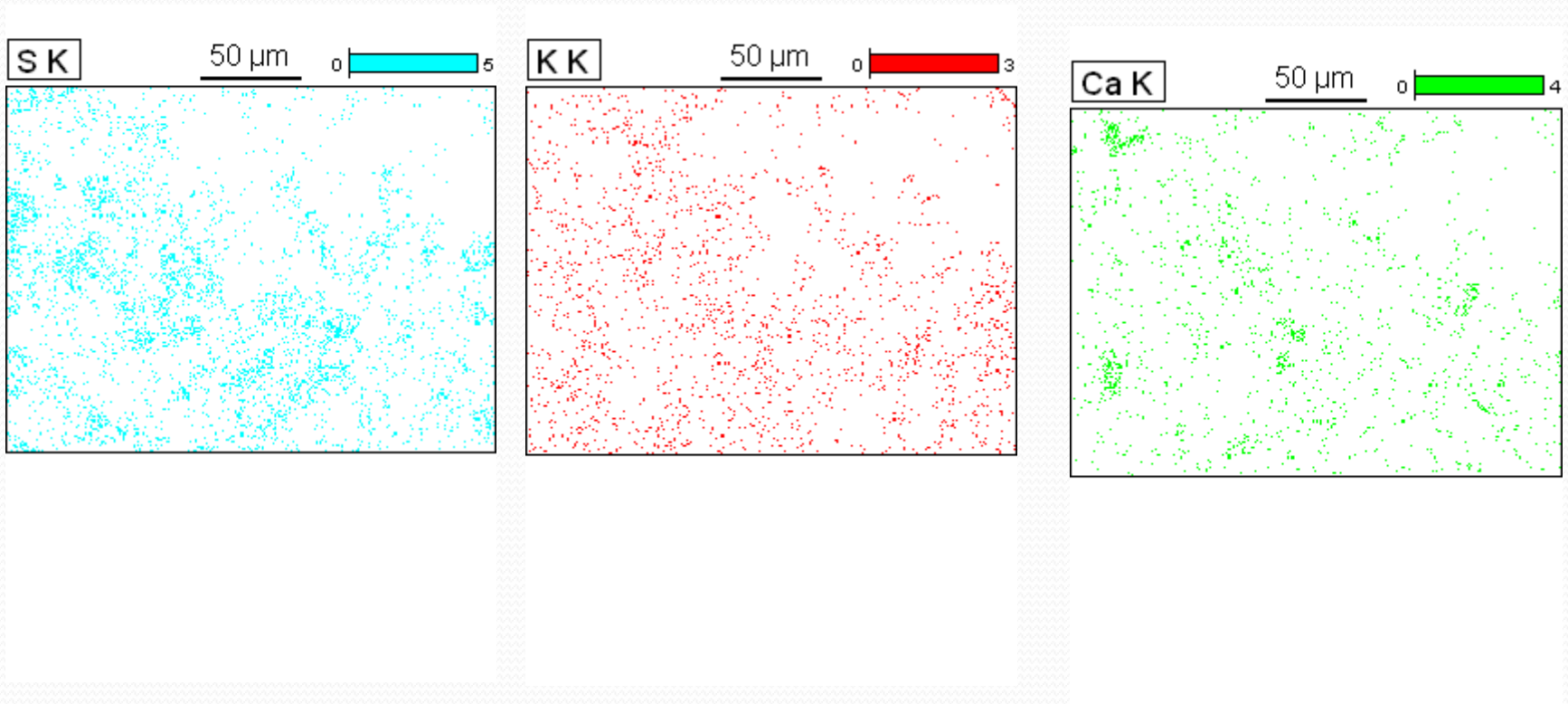
# Electron Mapping of Sediments



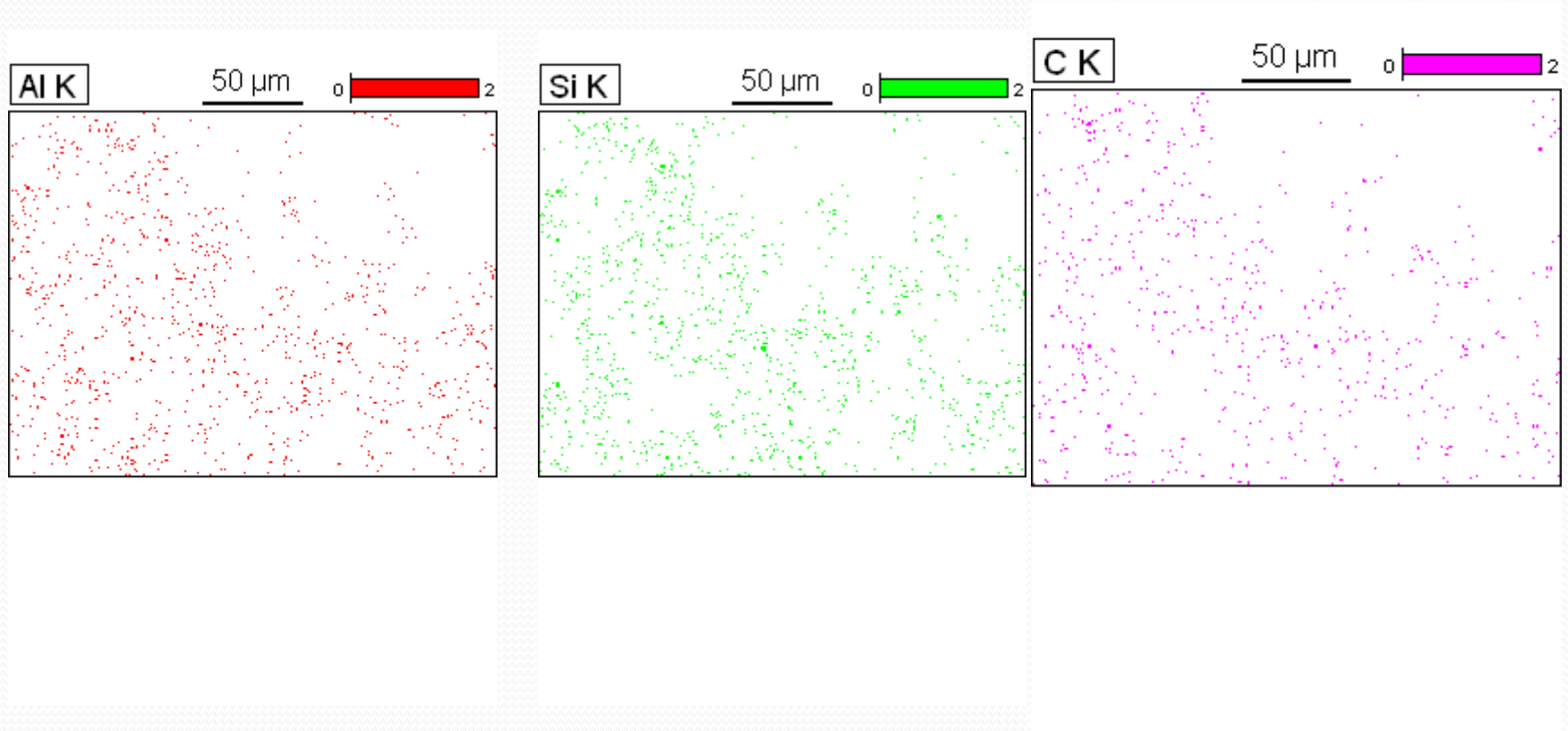
# Dominant Elements are Fe, O, and Cl by Electron Mapping



# Secondary Elements are S, K, and Ca by Electron Mapping



# Minor Elements are Al, Si, and C by Electron Mapping



# Solid Peroxide Systems

Raw Leachate

$\text{CaO}_2 + \text{Fe}^{2+} + \text{leachate}$

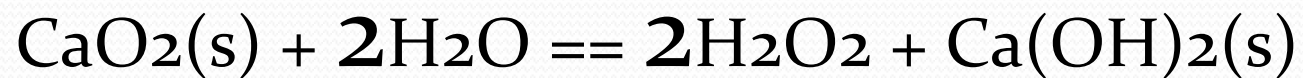
$\text{CaO}_2 + \text{Fe}^0 + \text{leachate}$

$\text{CaO}_2 + \text{Fe}^{2+}$

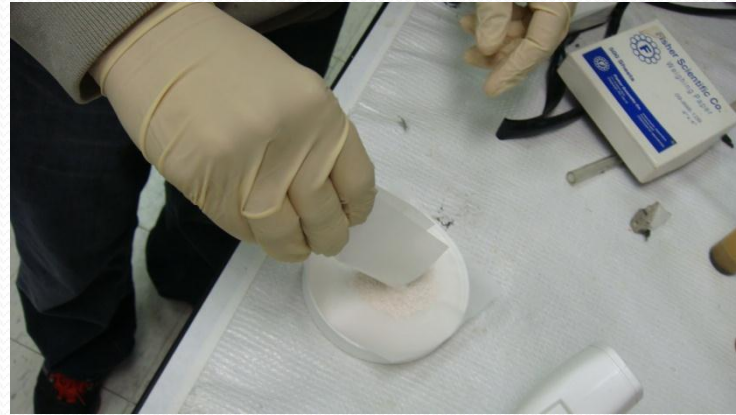
$\text{CaO}_2 + \text{Fe}^0$



# Solid Peroxides



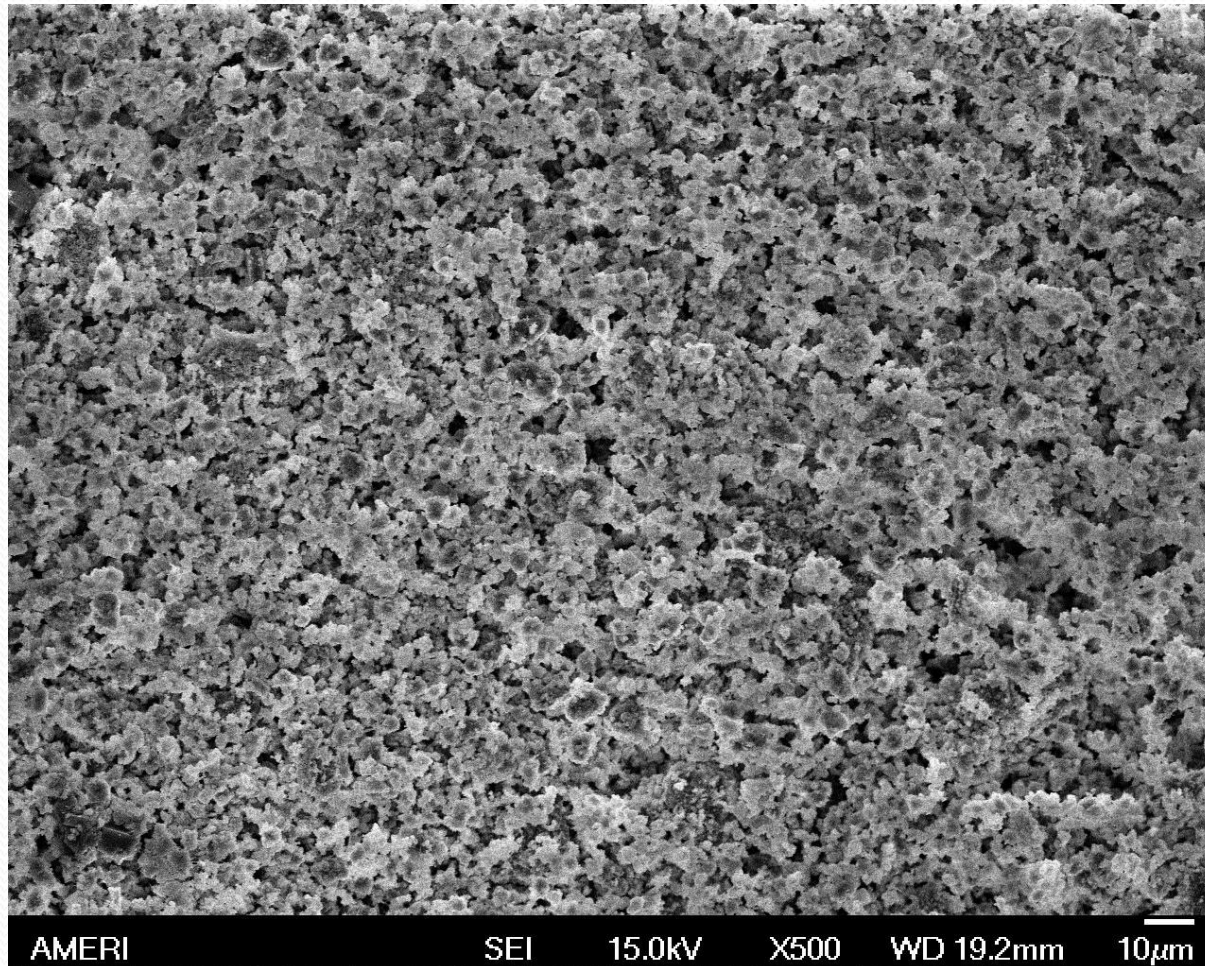
# CaO<sub>2</sub>



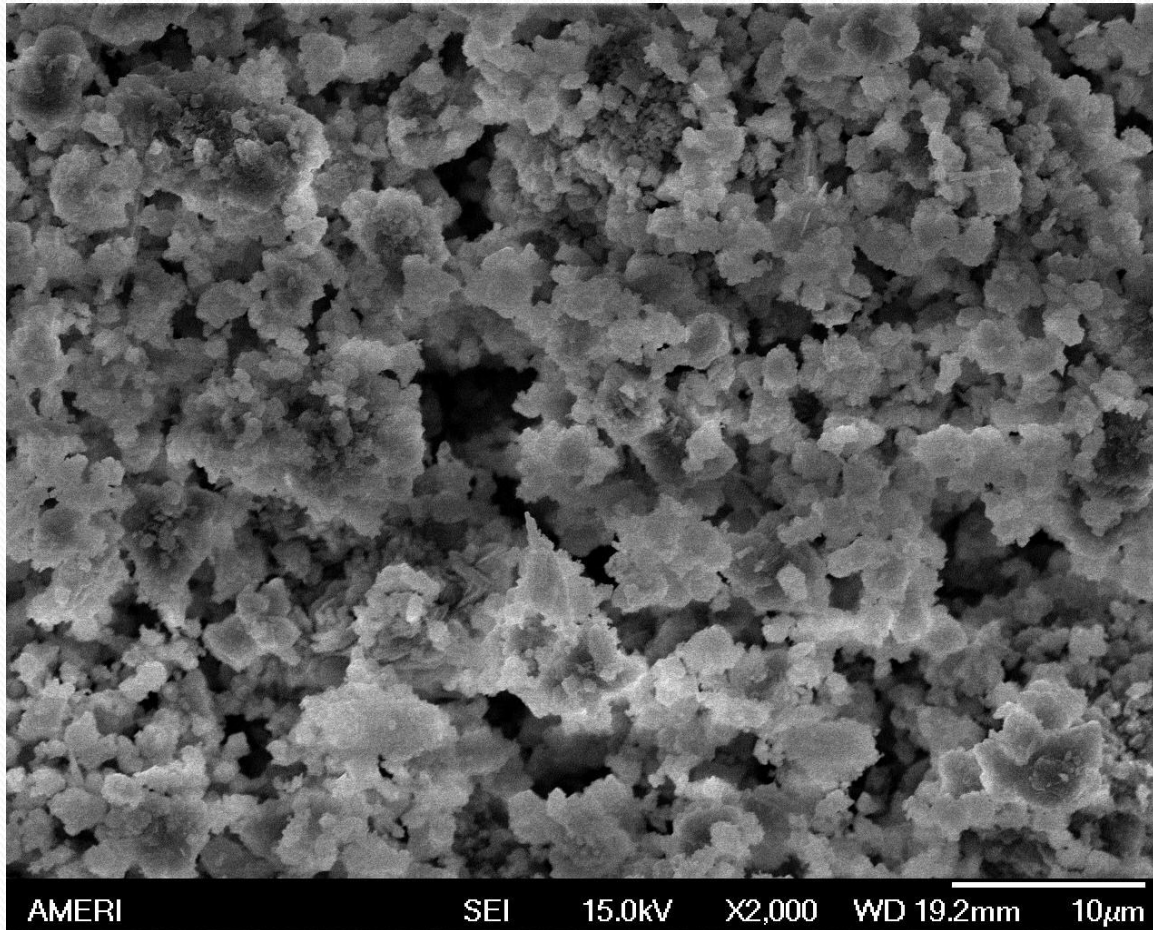
# Elemental Iron Powder



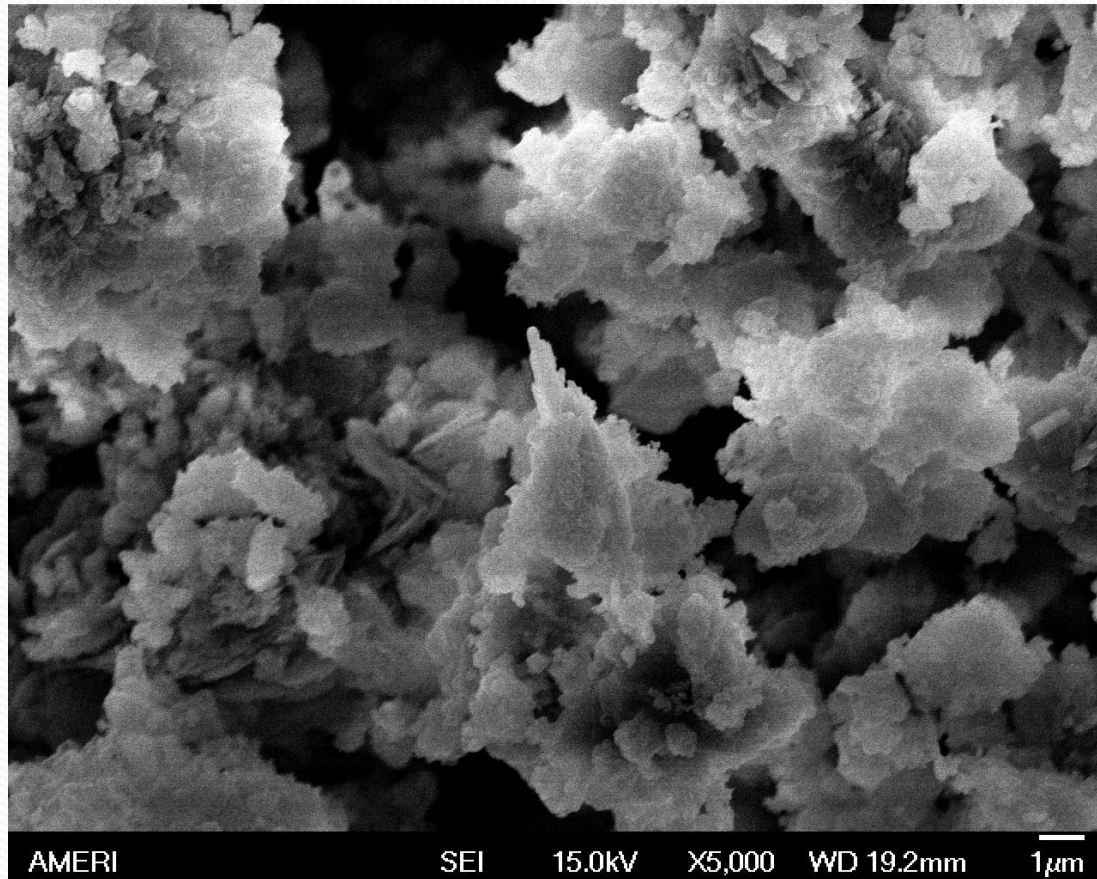
# SEM Image of $\text{CaO}_2$ at x500



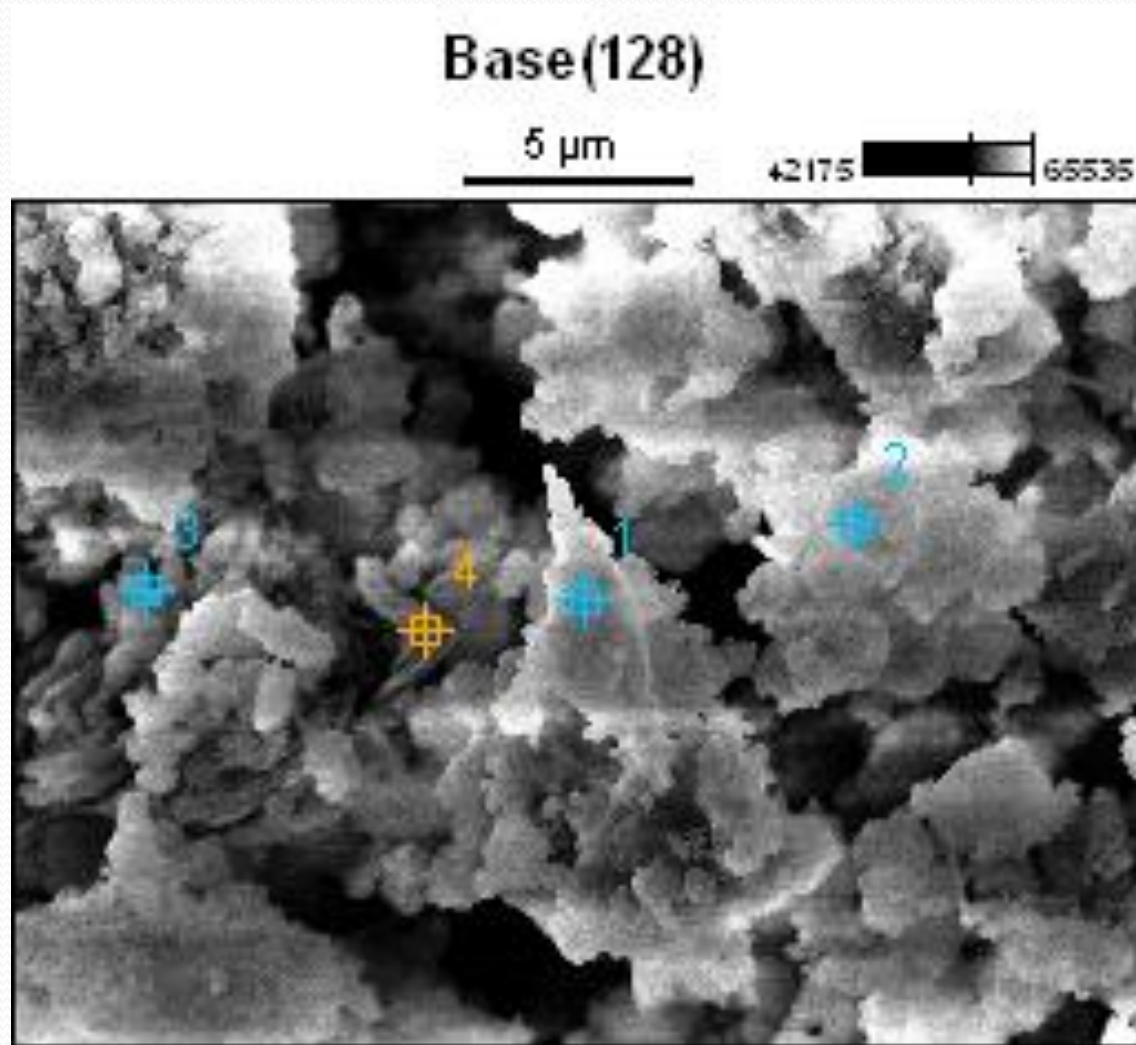
# ESM Image of $\text{CaO}_2$ at x2000



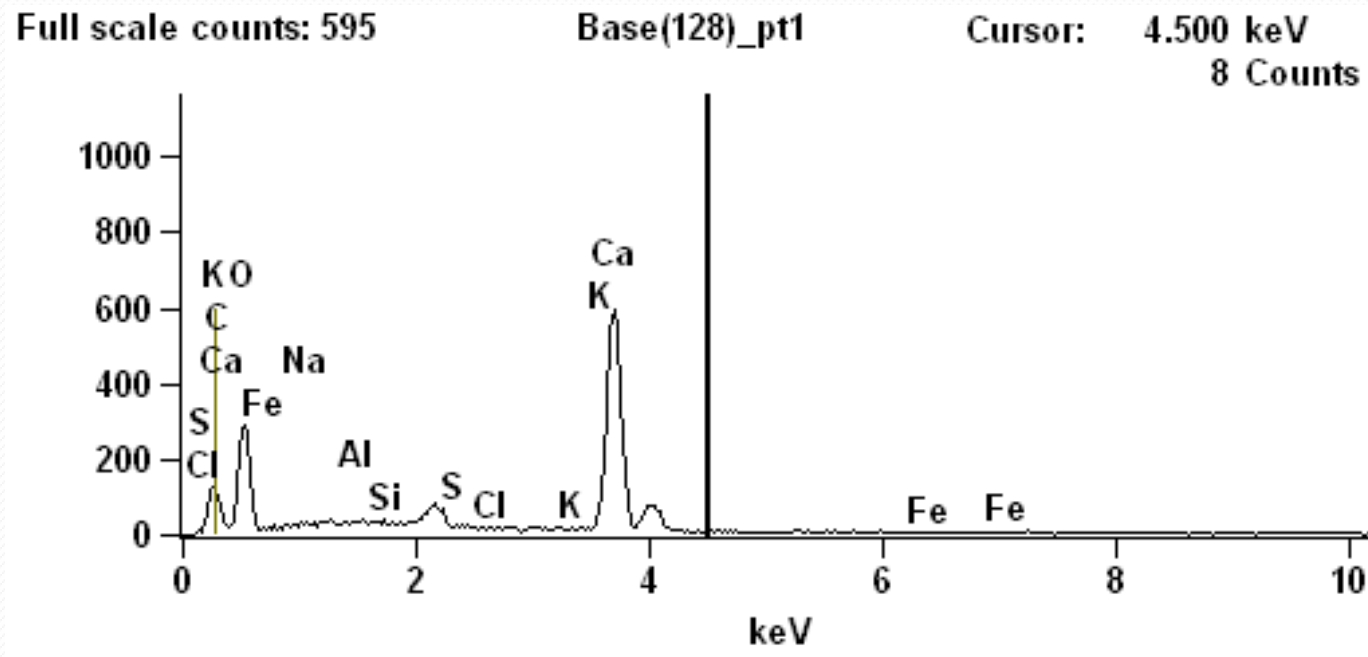
# SEM Image of $\text{CaO}_2$ at x5000



# Specific Points of the $\text{CaO}_2$ Sample



# Electron Density of Ca and O





# Chemical Composition

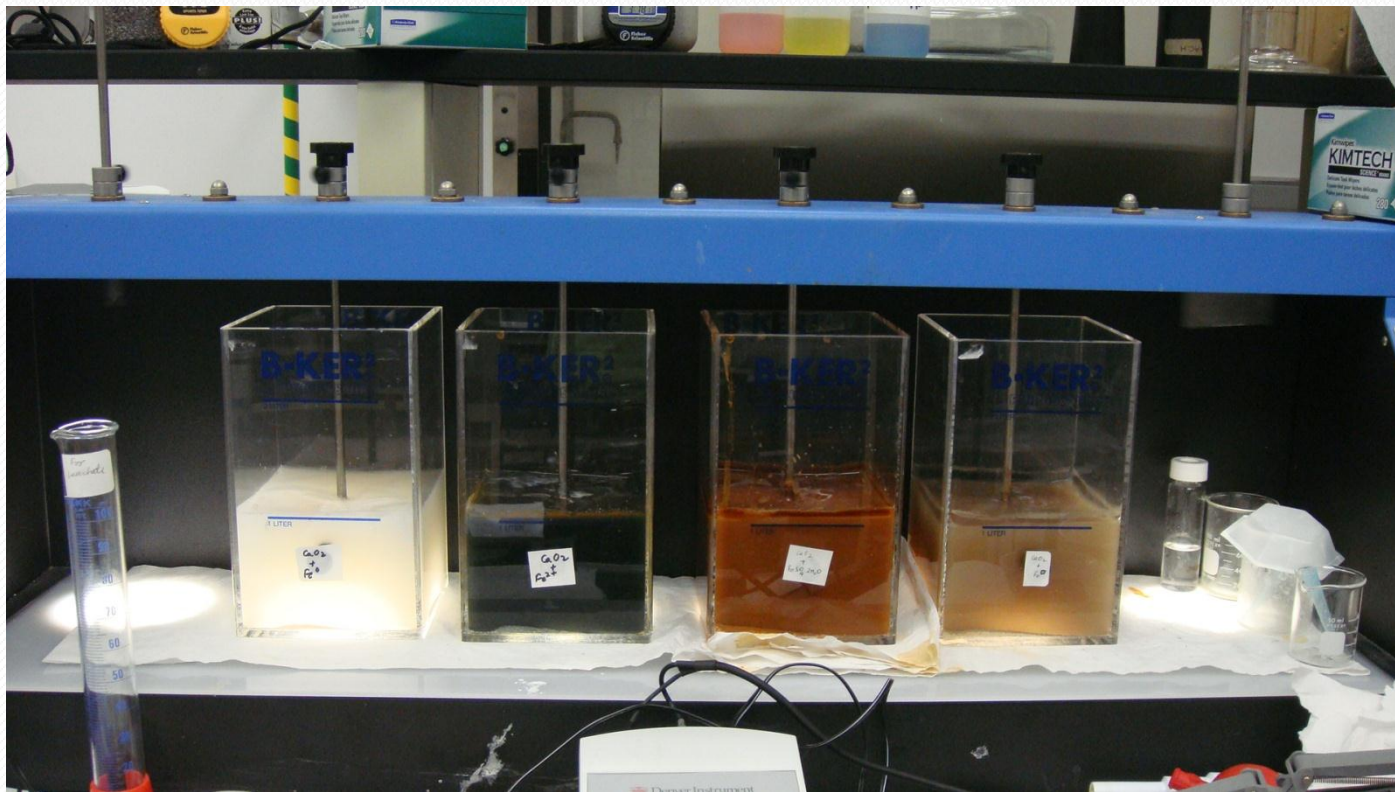
Table 1: Chemical composition by weight % at 4 different points of CaO<sub>2</sub>

	C-K	O-K	Na-K	Al-K	Si-K	S-K	Cl-K	K-K	Ca-K
Base(128) _pt1	24.83	46.46	0.12	0.08	0.03	0.00	0.00	0.00	28.48
Base(128) _pt2	22.54	42.33	0.10	0.15	0.44	0.00	0.00	0.00	34.45
Base(128) _pt3	10.07	27.69	0.02	0.05	0.19	0.00	0.00	0.00	61.98
Base(128) _pt4	18.50	38.56	0.02	0.22	0.51	0.00	0.00	0.07	42.13

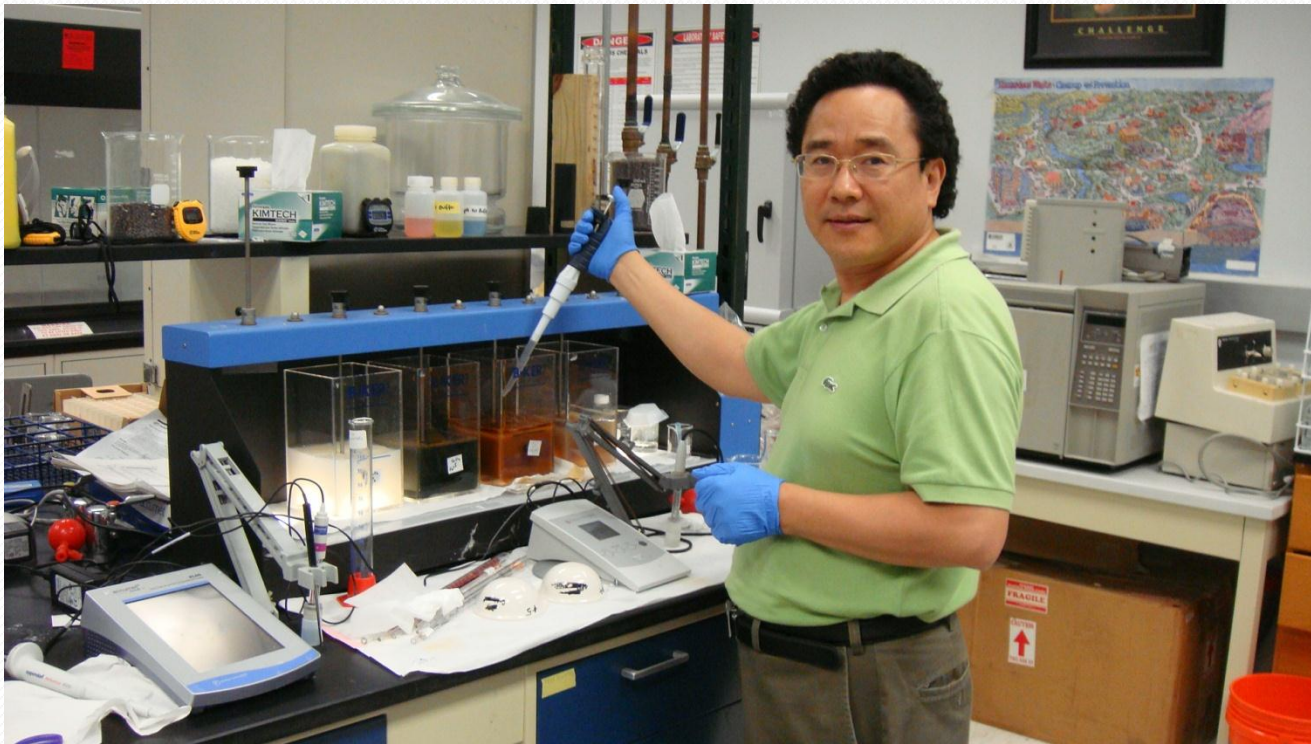
Table 2: Chemical composition by Atom % at 4 different points of CaO<sub>2</sub>

	C-K	O-K	Na-K	Al-K	Si-K	S-K	Cl-K	K-K	Ca-K
Base(128) _pt1	36.33	51.02	0.09	0.05	0.02	0.00	0.00	0.00	12.49
Base(128) _pt2	34.70	48.93	0.08	0.10	0.29	0.00	0.00	0.00	15.89
Base(128) _pt3	20.33	41.95	0.02	0.04	0.17	0.00	0.00	0.00	37.49
Base(128) _pt4	30.62	47.91	0.01	0.16	0.36	0.00	0.00	0.04	20.90

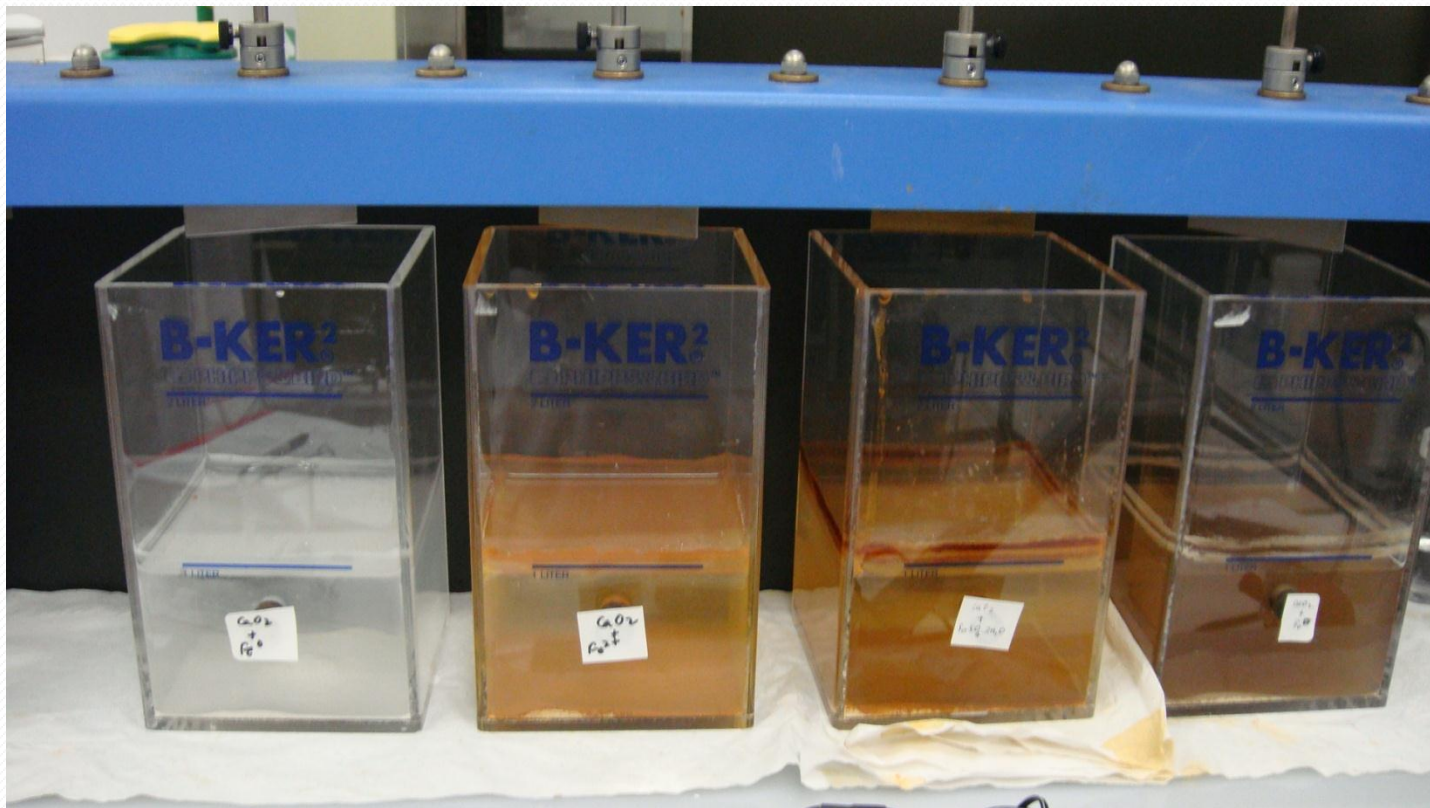
# One Hour after Reaction



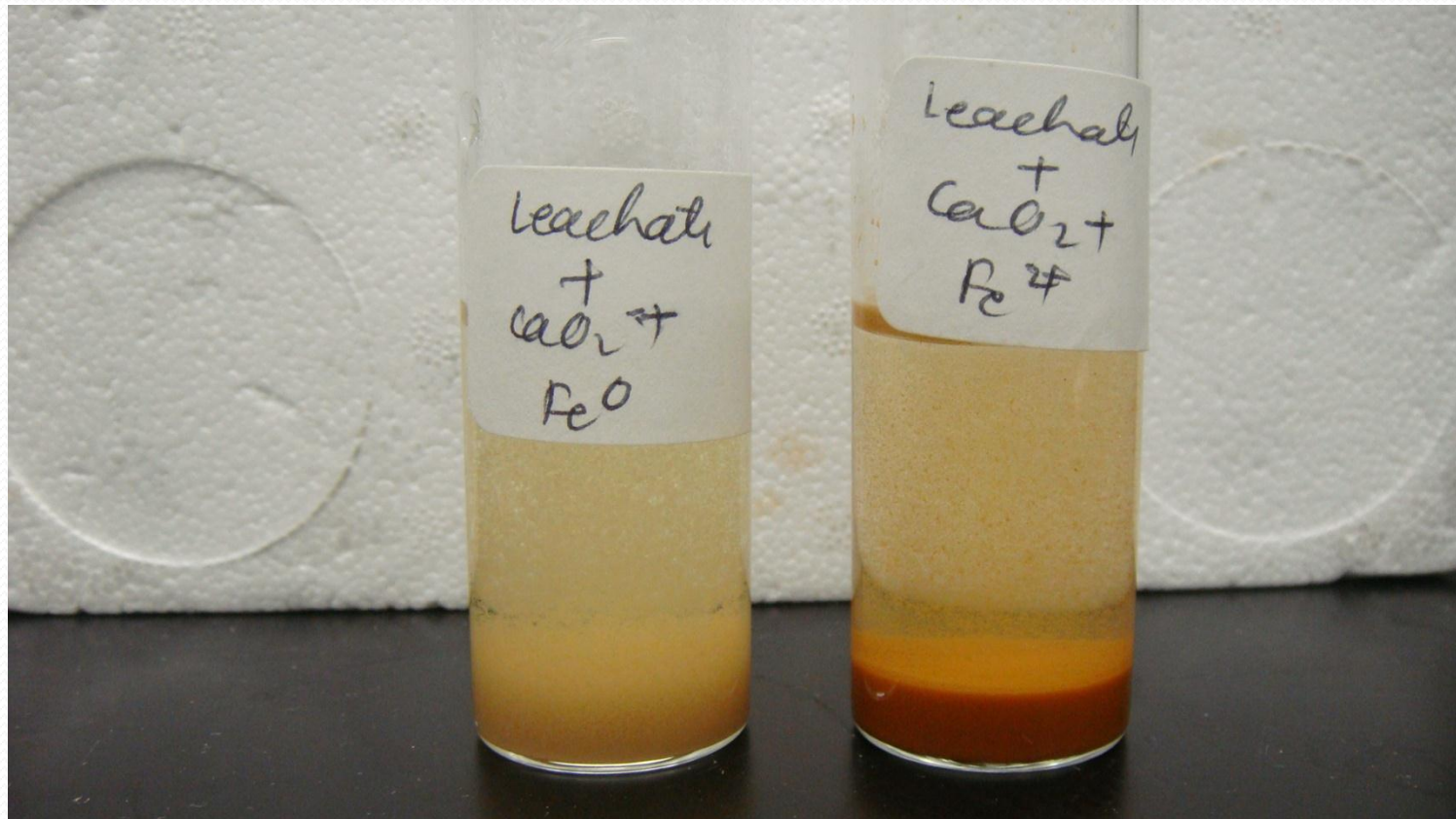
# Taking Samples after Reaction



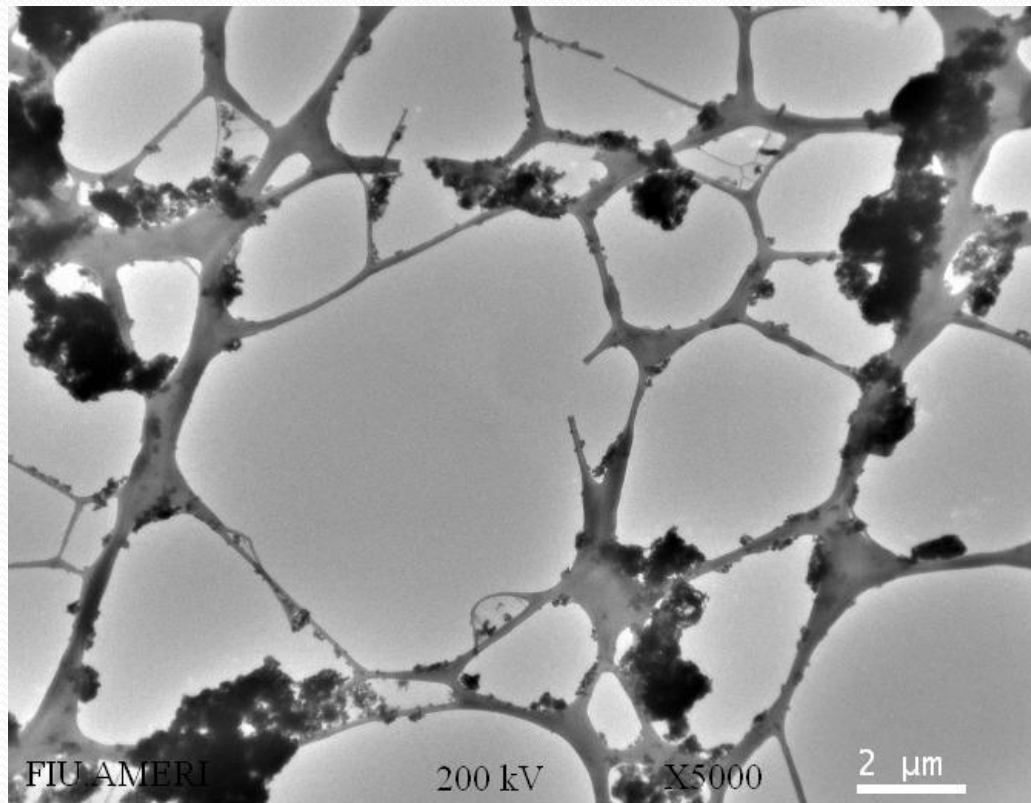
# After 24 Hours

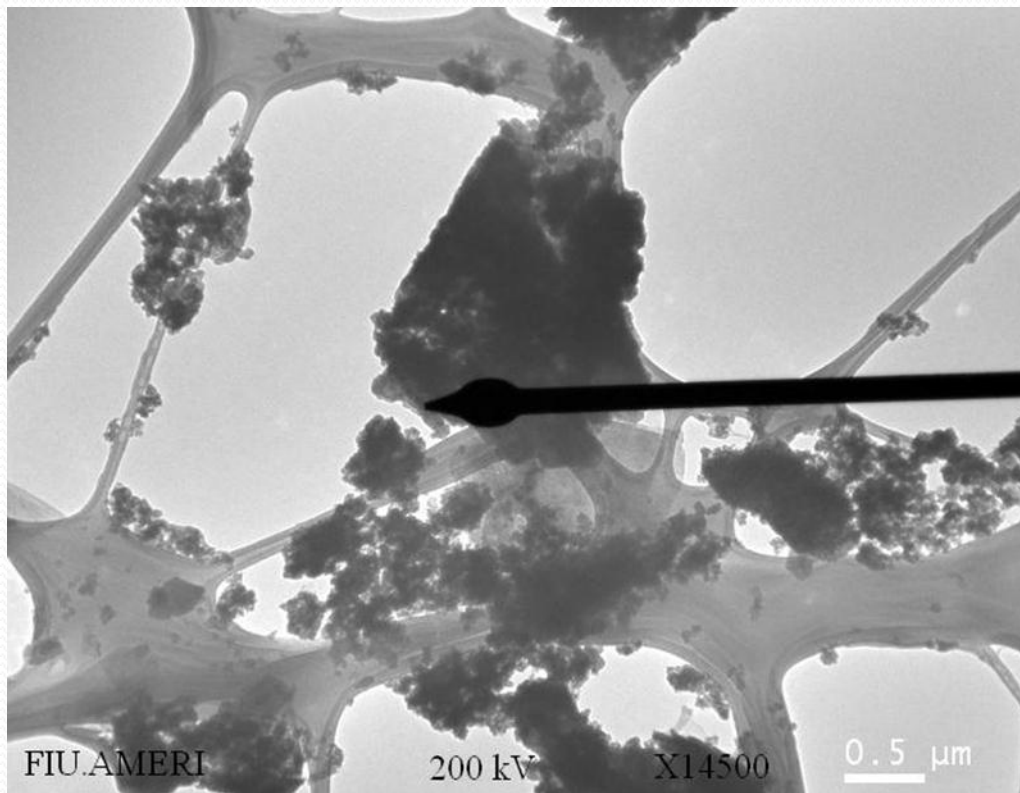


# After 24 Hours

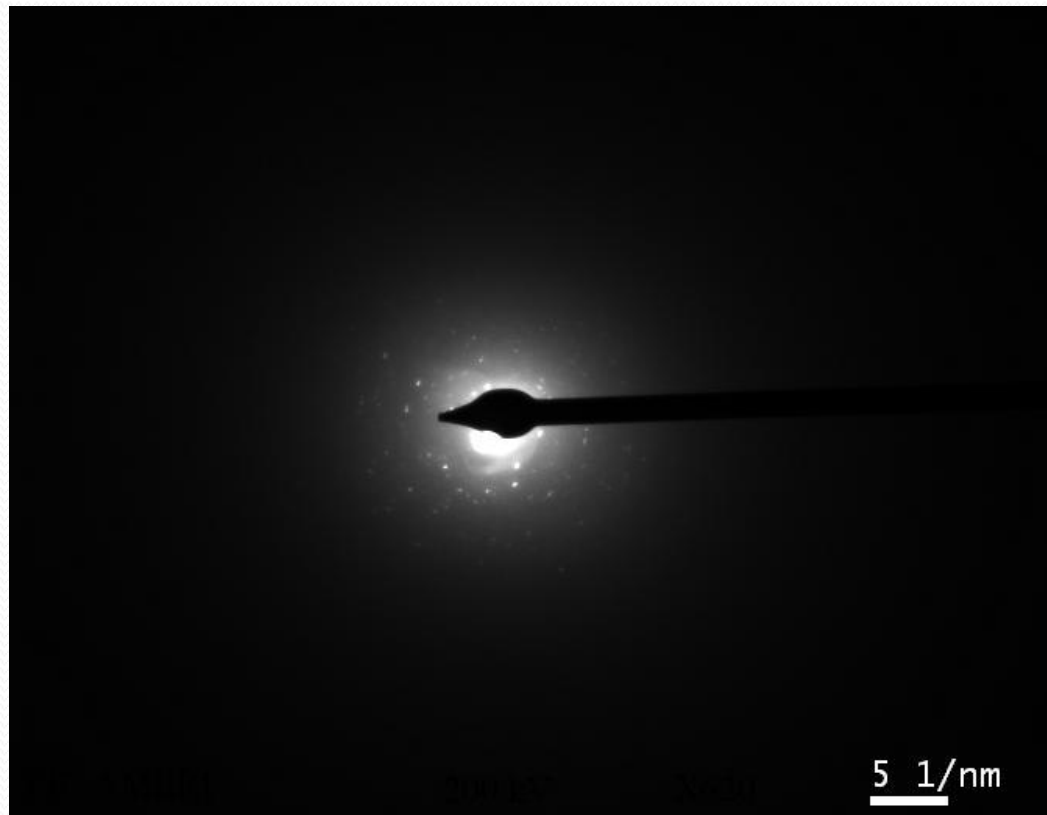


# $\text{CaO}_2 + \text{Fe}^{2+} + \text{leachate}$





# CaO<sub>2</sub> Atoms Spatial Distribution





# Acknowledgements

- We greatly appreciate financial support by the Hinkley Center for Solid and Hazardous Waste Management at the University of Florida. We thank Professor John Shert and Tim Vinson for their constructive suggestions for our project and Mrs. Rhonda Rogers for administrative support.

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- Dr. Anna Bricker
- Ms. Emma Lopez
- Mr. Richard Urban
- Ms. Allison Vo

# Thanks to Our Research Team!





***Thank You !***