Development of CO_2 Sequestration Module by Integrating Mineral Activation and Aqueous Carbonation

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Outline

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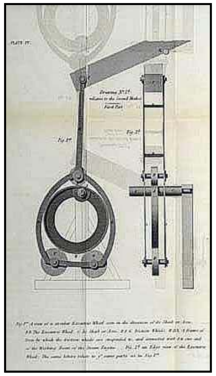
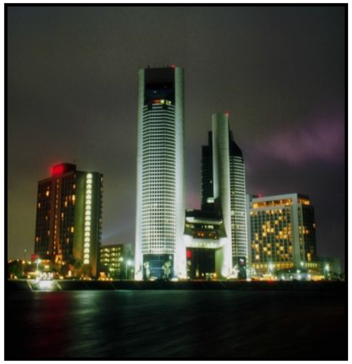
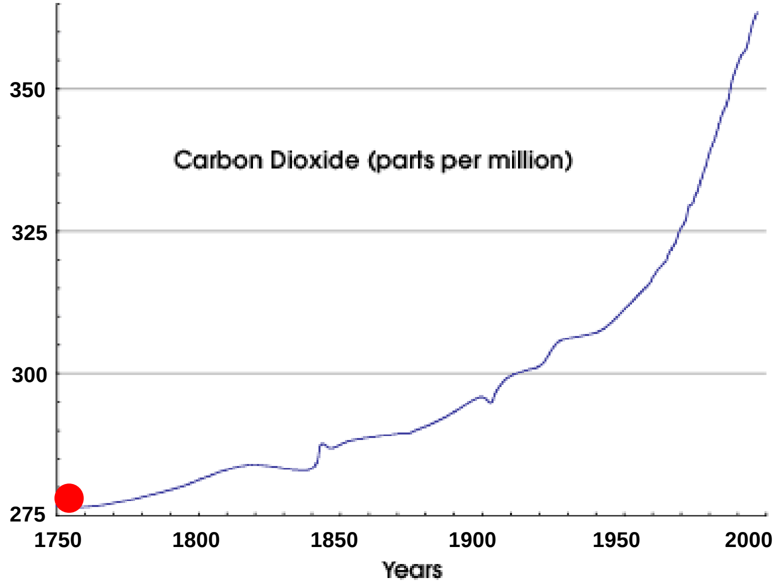
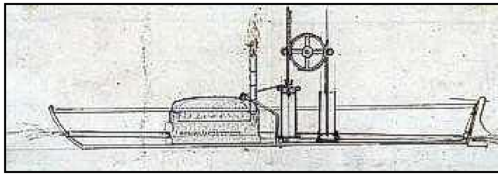
3. Sequestration Options
4. Mineral Carbonation
5. Previous PSU Research
6. Current Research
7. Results
8. Summary and Upcoming Research



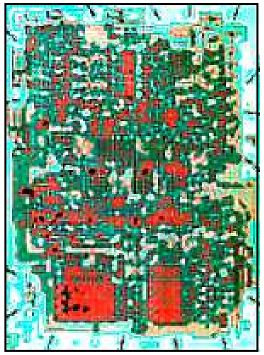
1769 - Watt steam engine



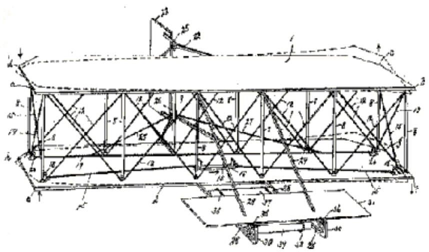




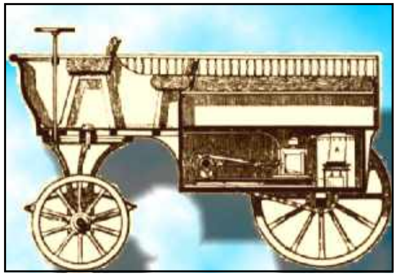
1787 – Fitch steamboat



1971 – Faggin et al. Microprocessor



1900 – Wright brother's airplane

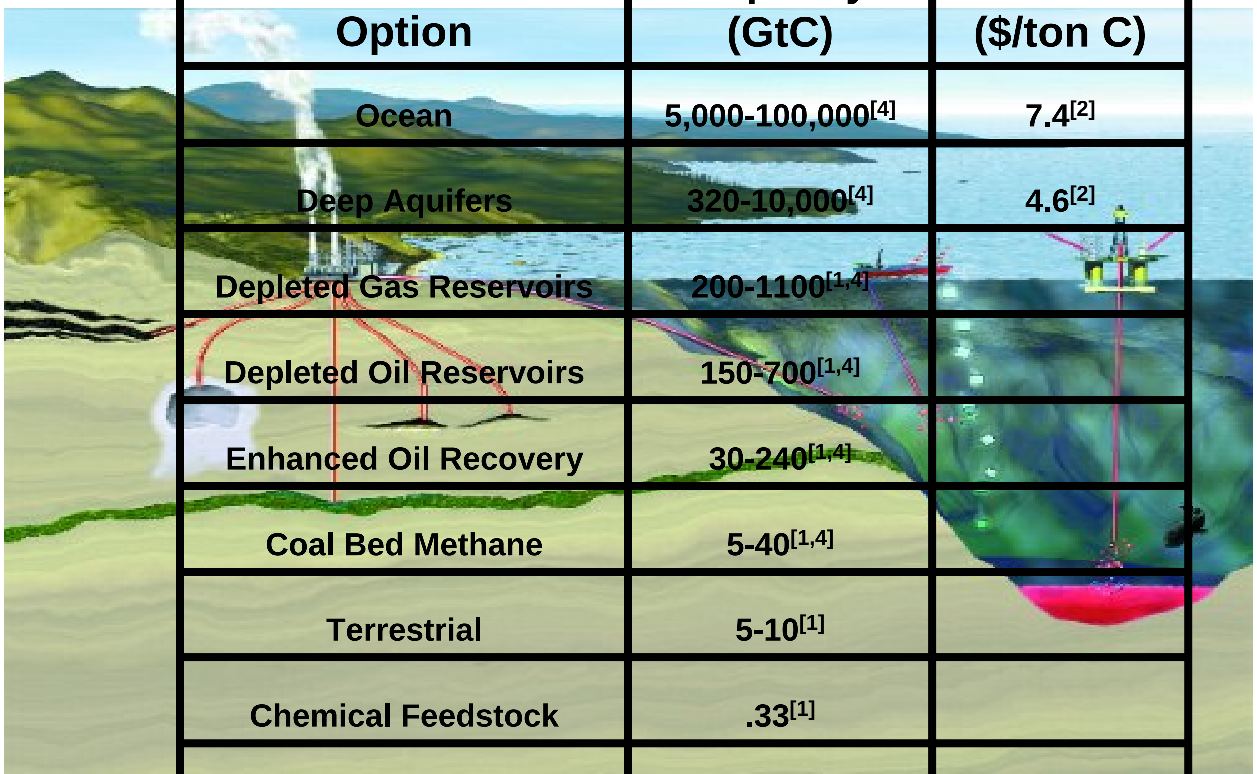


1860 – Lenoir automobile

CO_2 Options

- Alternative fuels
- Efficiency
  - Production
  - Consumption
- Utilization
  - Chemicals
  - Conversion to fuel
- Sequestration

CO_2 Storage Options



Option	Capacity (GtC)	Cost ($/ton C)
Ocean	5,000-100,000[4]	7.4[2]
Deep Aquifers	320-10,000[4]	4.6[2]
Depleted Gas Reservoirs	200-1100[1,4]	
Depleted Oil Reservoirs	150-700[1,4]	
Enhanced Oil Recovery	30-240[1,4]	
Coal Bed Methane	5-40[1,4]	
Terrestrial	5-10[1]	
Chemical Feedstock	.33[1]	
Mineral Carbonation	High[1]	14.7[3]

Note: Annual release of anthropogenic C is 1.9Gt with 1.47Gt from fossil fuels

Source: David Fierstein, Tyndall Centre for Climate Change Research

Mineral Carbonation

Mineral Carbonation – the chemical fixation of CO_2 in minerals to form geologically stable mineral carbonates

- Stability → Limited to magnesium and calcium
- Content → Mg vs. Ca
- Quantity → Mg silicates, olivine & serpentine

$$(Mg, Ca)_x Si_y O_{x+2y} + xCO_2 \rightarrow x(Mg, Ca)CO_3 + ySiO_2$$

Mineral Carbonation

(1) Olivine

(2) Serpentine

$$\Delta G$$

$$(1)\ Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3 + SiO_2 \qquad -209\ \text{kJ/mol}$$

$$(2)\ Mg_3Si_2O_5(OH)_4 + 3CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O \qquad -67\ \text{kJ/mol}$$

Characteristics

- Thermodynamically favored
- Mimic natural weathering
- Slow reaction kinetics

Physical/Chemical Treatment

- Particle size reduction
- Thermal treatment
- Molten salt
- Acids and bases

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Carbonation Reaction

Gas-Solid Reaction

$$Mg_3Si_2O_5(OH)_4 + 3CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O$$

Aqueous Mineral Carbonation

$$CO_2 + H_2O \rightarrow H^+ + HCO_3^-$$

$$Mg_3Si_2O_5(OH)_4 + 6H^+ \rightarrow 3Mg^{2+} + 2SiO_2 + 5H_2O$$

$$Mg^{2+} + HCO_3^- \rightarrow MgCO_3 + H^+$$

Physical/chemical treatments still required:

- High pressures (126 atm)
- Extensive particle comminution (-38µm)
- High temperature (185 ^oC)
- Heat pretreatment (600 ^oC)
- Long reaction times (>6 hrs)

Previous PSU Research

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Physical Treatment

Steam/Air Activation

Remove chemically bound water

→ Increase reactivity

Chemical Treatment

Acid/Base treatment

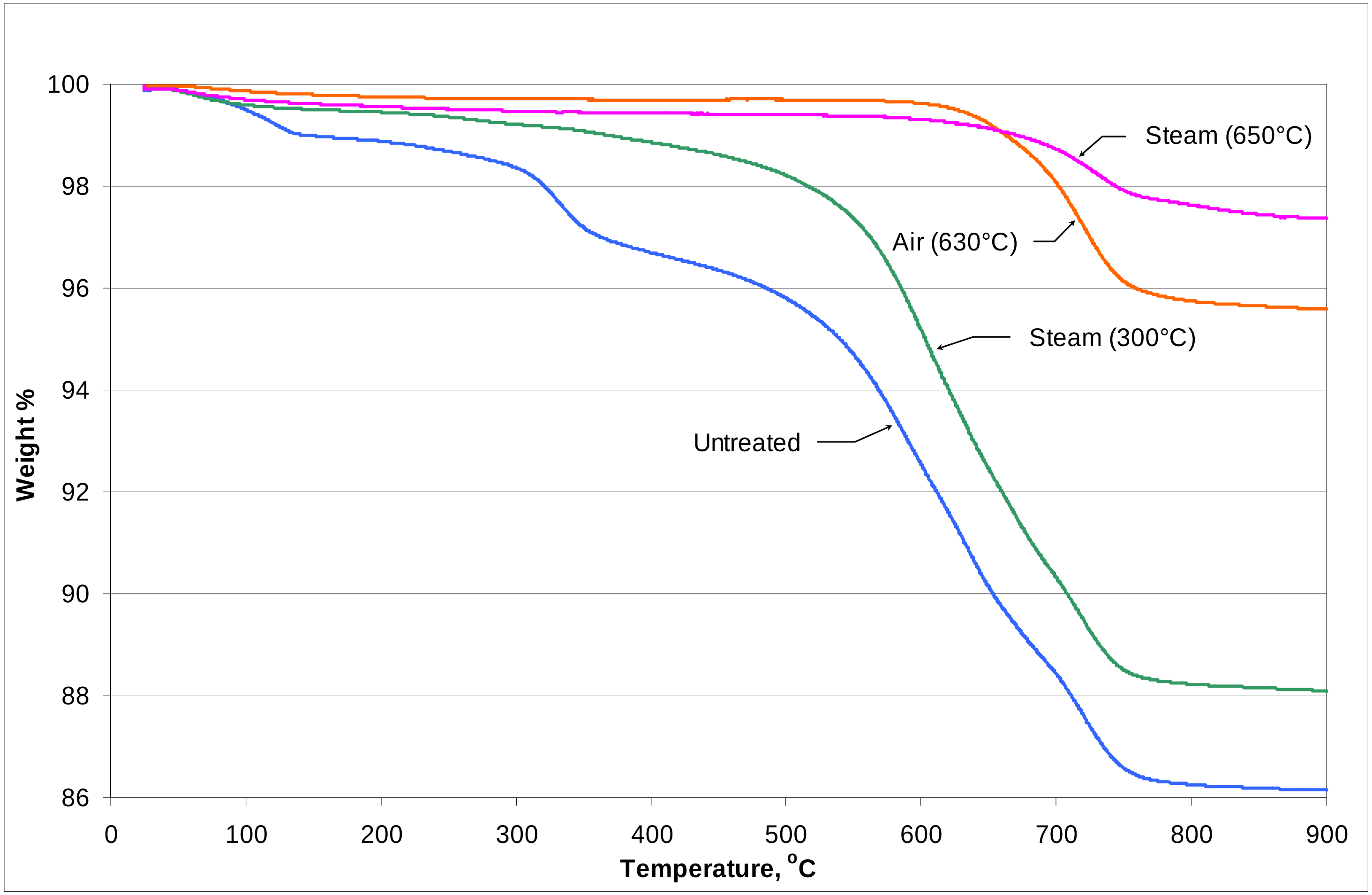
Increase surface area

→ Increase reactivity

Acid Treatment

Produce Mg-rich solution for carbonation

Thermogravitmetric Analysis



Source: Kuchta, 2004

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Previous Results

	Carbonation Conditions			
	Temperature, °C	Pressure, atm	Time, hr	Conversion %
Untreated	155	126	1	7.2
Physical Treatment				
Steam 3 hrs, 300°C				
Steam 3 hrs, 650°C	155	126	1	59.4
Air 3 hrs, 630°C				
Chemical Treatment				
HCl 24 hrs, 25°C	155	126	1	
H_2SO_4 24 hrs, 25°C	155	126	1	
H_3PO_4 24 hrs, 25°C	155	126	1	
NaOH 4 hrs, 90°C	155	126	1	
H_2SO_4 ($MgSO_4$) 8 hrs, 50°C	20	36	6	
CH_3COOH ($Mg(OAc)_2$) 8 hrs, 50°C	20	45	4	
H_2SO_4 ($Mg(OH)_2$) 8 hrs, 50°C	20	45	3.5	52.5

Source: Kuchta, 2004

Current Research

Proposal

Mineral Activation

Mineral Carbonation

Process Integration

Economic Analysis

Objectives

Accelerate reaction rates

Maximize carbonation efficiency

Mild operating conditions

Sulfuric Acid Treatment

$$Mg_3Si_2O_5(OH)_4 + 3H_2SO_4 \rightarrow 3Mg^{2+} + SO_4^{2-} + 2SiO_2 + 5H_2O$$

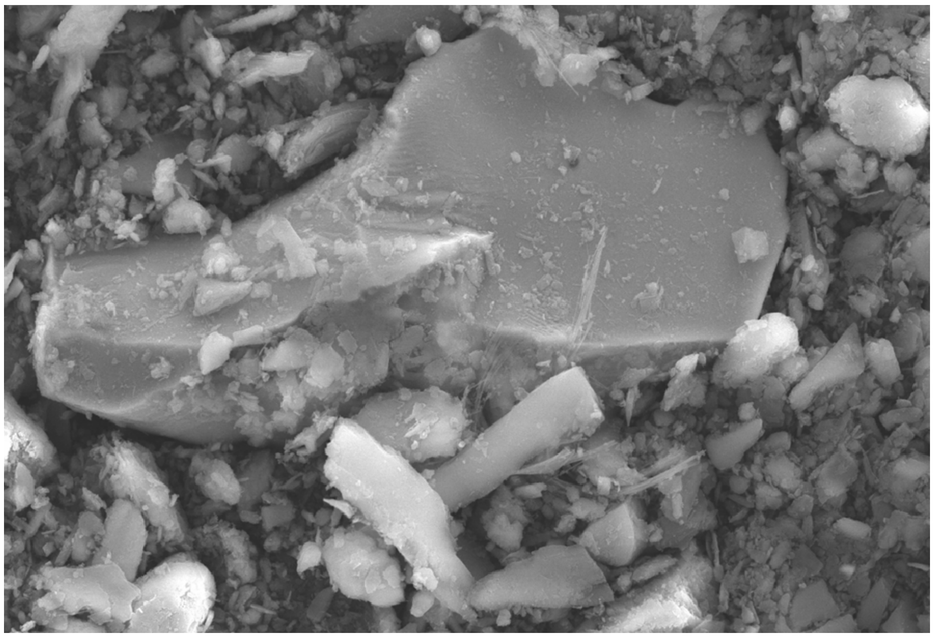
Titration

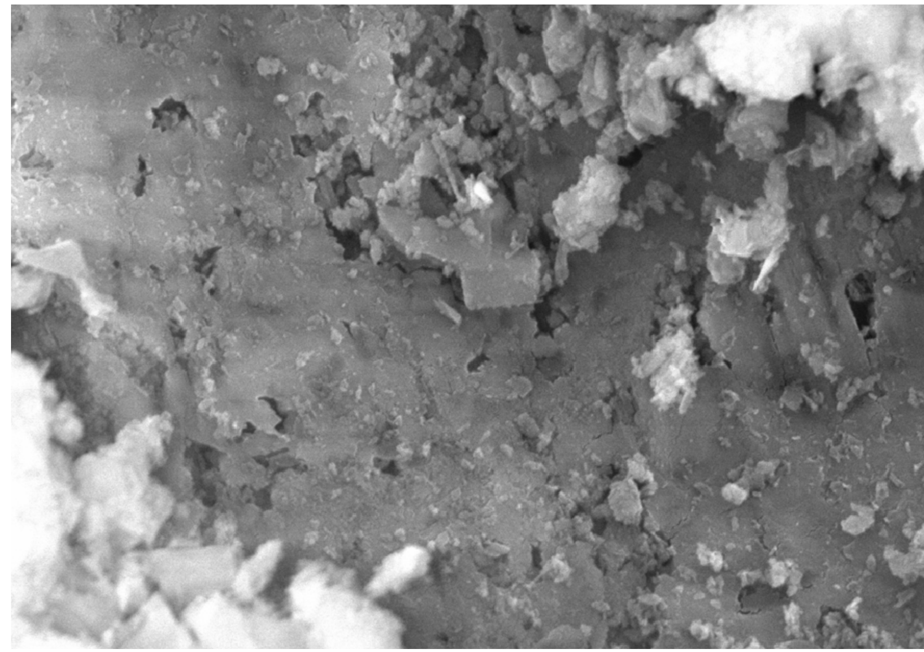
$$Mg^{2+} + SO_4^{2-} + 2NaOH \rightarrow Mg(OH)_2 + Na_2SO_4$$

Carbonation Reaction

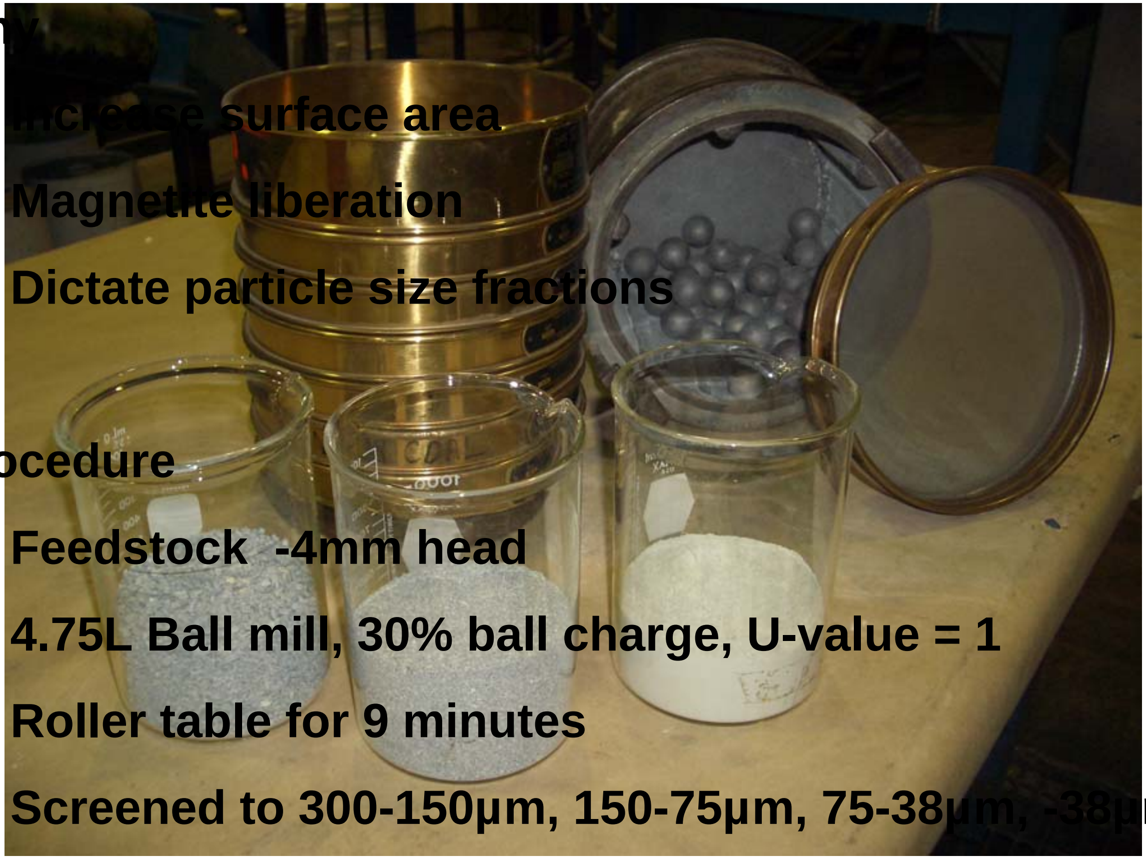
$$Mg(OH)_2 + CO_2 \rightarrow MgCO_3 + H_2O$$

SEM Pictures





Mineral Processing



Why

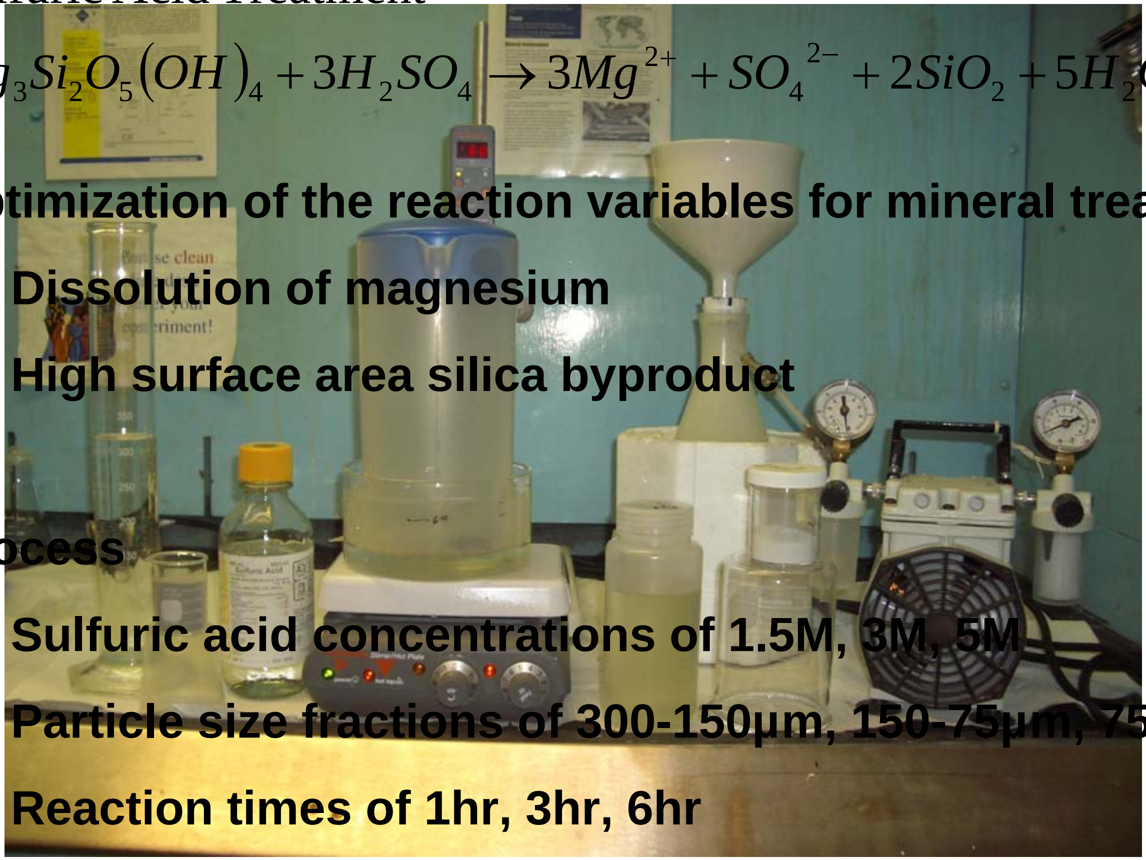
- **Increase surface area**
- **Magnetite liberation**
- **Dictate particle size fractions**

Procedure

1. **Feedstock -4mm head**
2. **4.75L Ball mill, 30% ball charge, U-value = 1**
3. **Roller table for 9 minutes**
4. **Screened to 300-150µm, 150-75µm, 75-38µm, -38µm**
5. **Magnetite removal**

Task 1: Mineral Treatment

Sulfuric Acid Treatment



$$Mg_3Si_2O_5(OH)_4 + 3H_2SO_4 \rightarrow 3Mg^{2+} + SO_4^{2-} + 2SiO_2 + 5H_2O$$

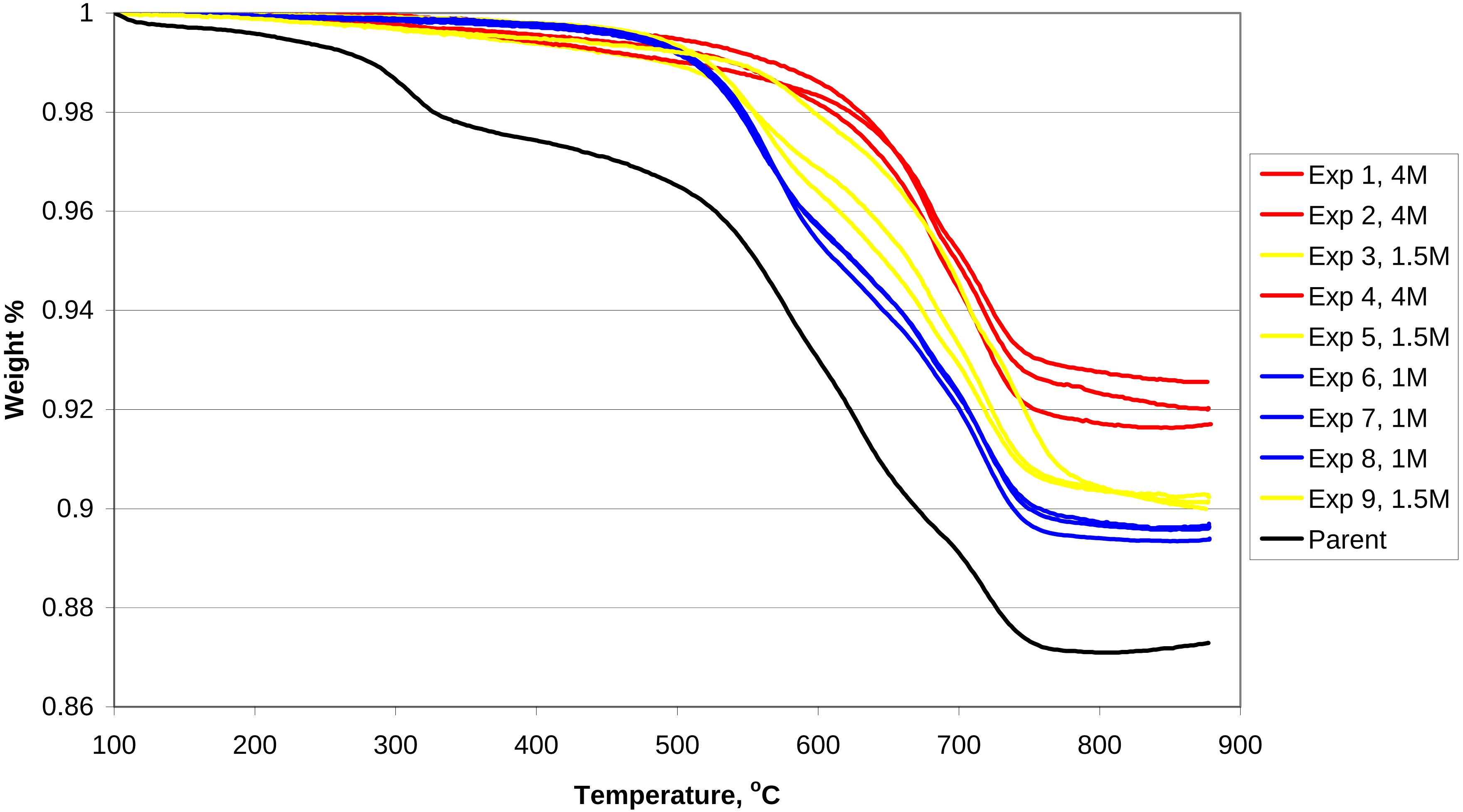
Optimization of the reaction variables for mineral treatment

- **Dissolution of magnesium**
- **High surface area silica byproduct**

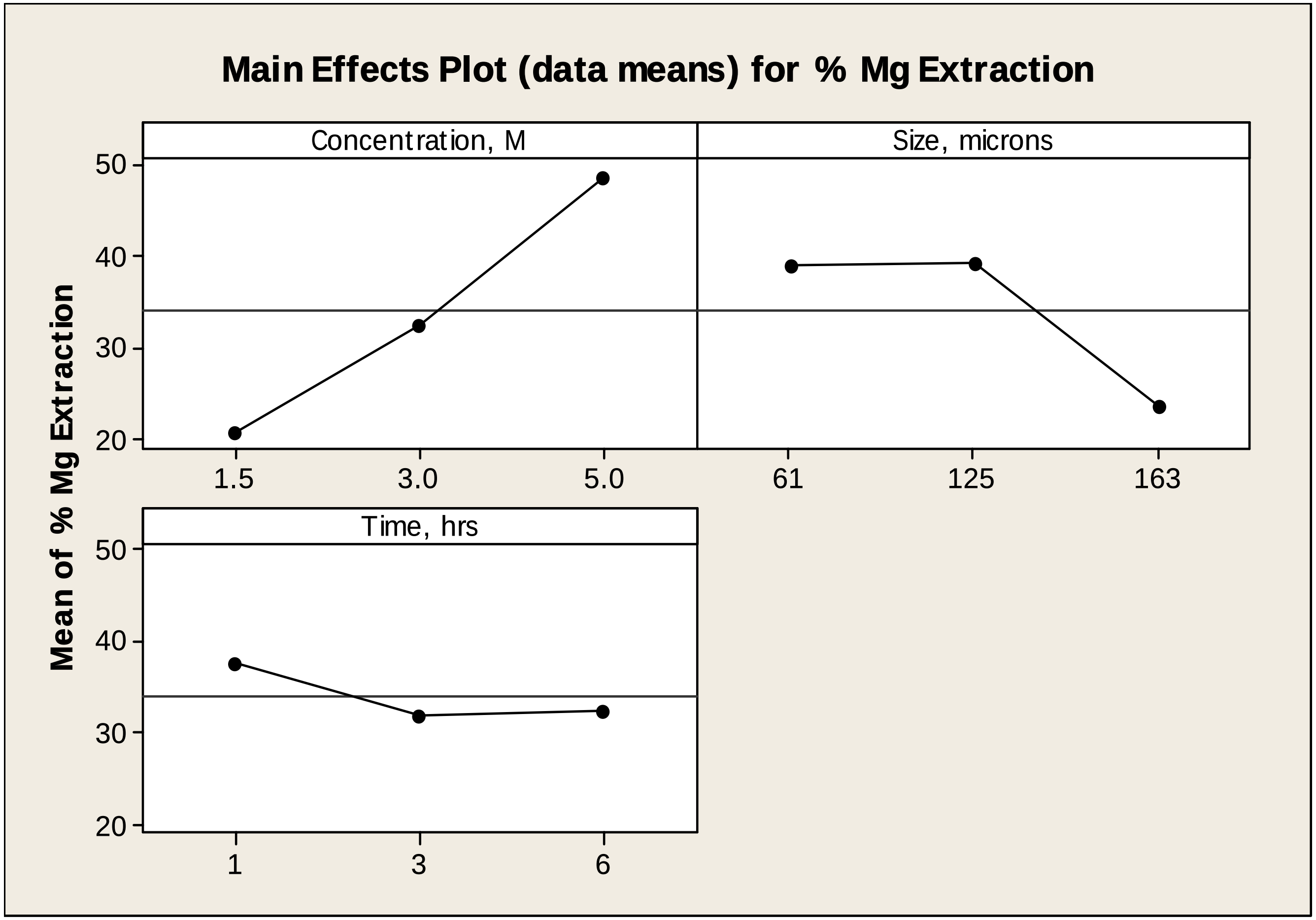
Process

1. **Sulfuric acid concentrations of 1.5M, 3M, 5M**
2. **Particle size fractions of 300-150µm, 150-75µm, 75-38µm**
3. **Reaction times of 1hr, 3hr, 6hr**

Thermogravitmetric Analysis

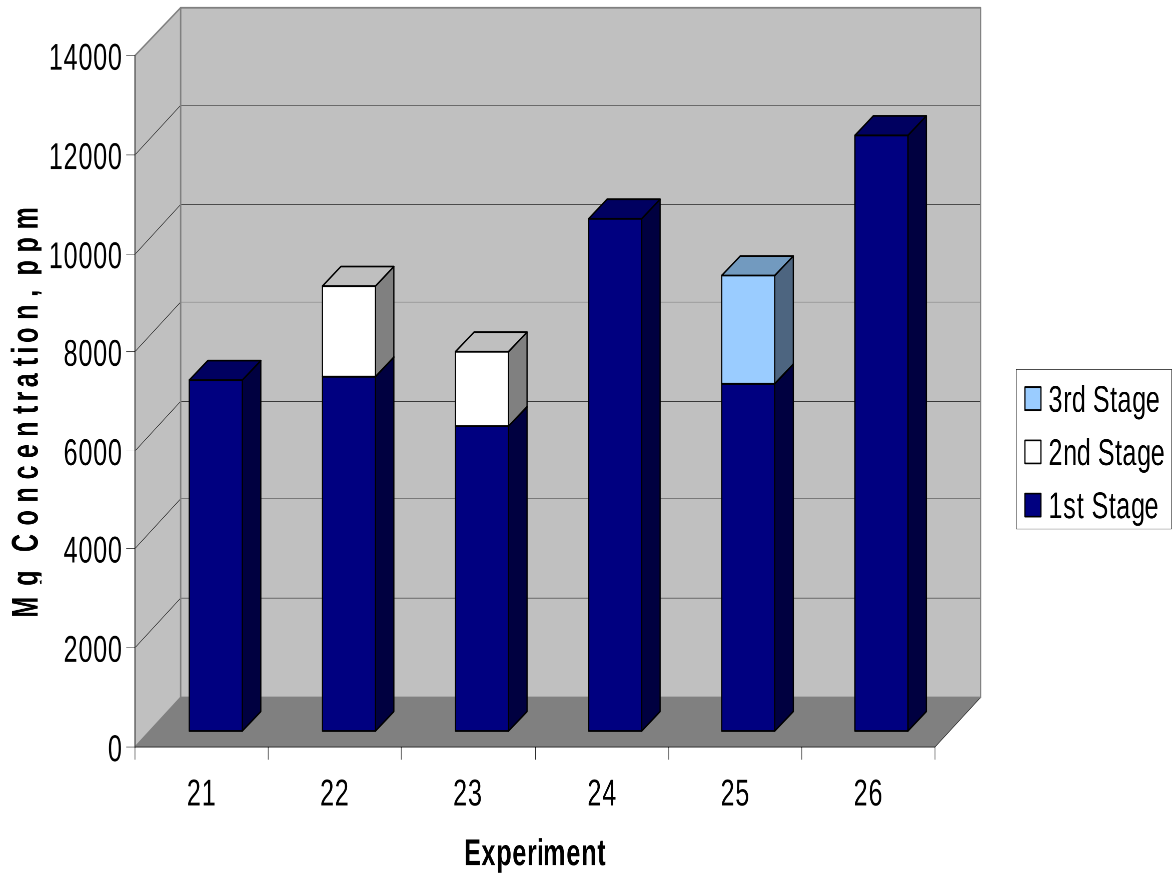


Results – Mg Extraction, Solids

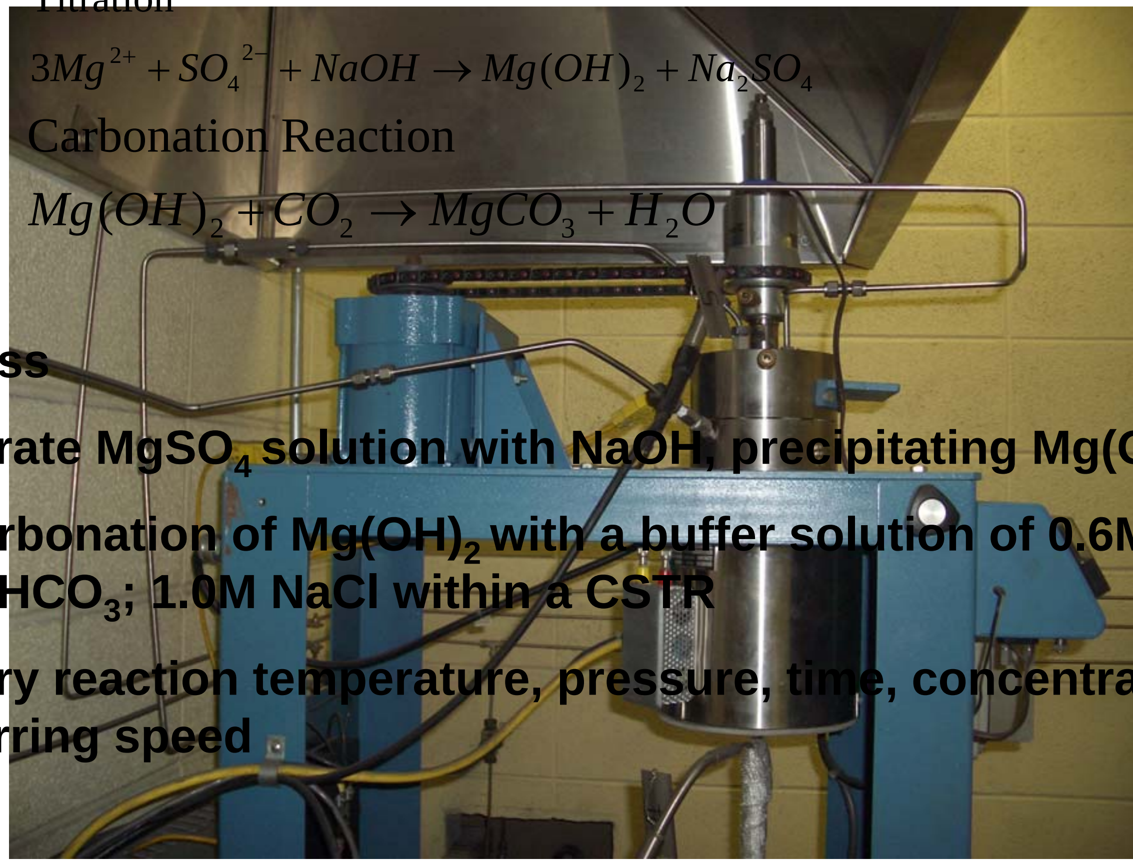


Additional Experimentation

Experiment	Reason	Concentration
21	Baseline	2M H_2SO_4
22-1	2-stage	2M H_2SO_4
22-2		2M H_2SO_4
23-1	2-stage	1M H_2SO_4
23-2		1M H_2SO_4
24	24 hours	2M H_2SO_4
25-1	3-stage	2M H_2SO_4
25-2		1M NaOH
25-3		2M H_2SO_4
26	50 C	2M H_2SO_4



Task 2: Mineral Carbonation



Titration

$$3Mg^{2+} + SO_4^{2-} + NaOH \rightarrow Mg(OH)_2 + Na_2SO_4$$

Carbonation Reaction

$$Mg(OH)_2 + CO_2 \rightarrow MgCO_3 + H_2O$$

Process

1. **Titrate $MgSO_4$ solution with NaOH, precipitating $Mg(OH)_2$**
2. **Carbonation of $Mg(OH)_2$ with a buffer solution of 0.6M $NaHCO_3$; 1.0M NaCl within a CSTR**
3. **Vary reaction temperature, pressure, time, concentration and stirring speed**

Task 3: Integration of the Treatment and Carbonation Units & Preliminary Economic Analysis

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Summary

- CO_2 Problem & Options
- Mineral Carbonation
  - Thermodynamics
  - Capacity and Integrity
  - Kinetics/Cost??
- Objectives
  - Accelerate reaction rates
  - Maximize carbonation efficiency
  - Mild operating conditions
- Current Status
- Upcoming Research

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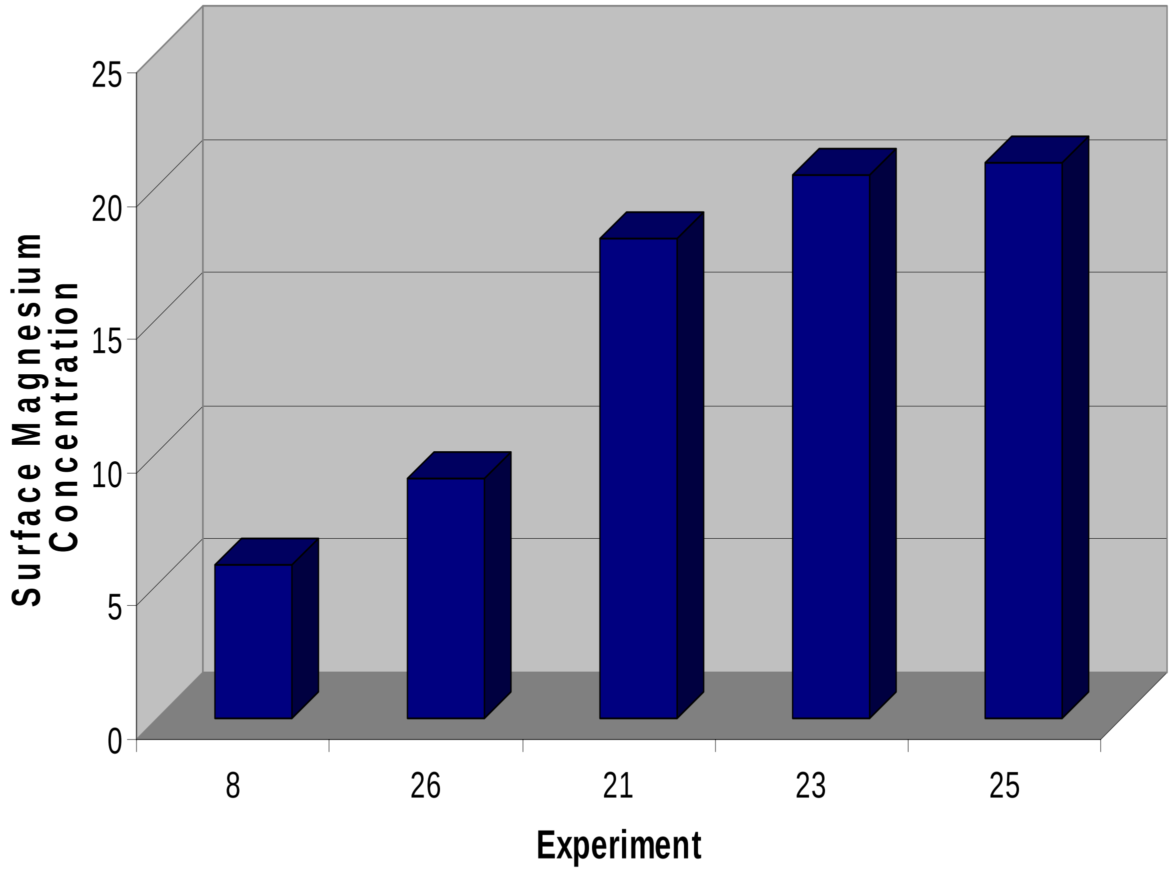
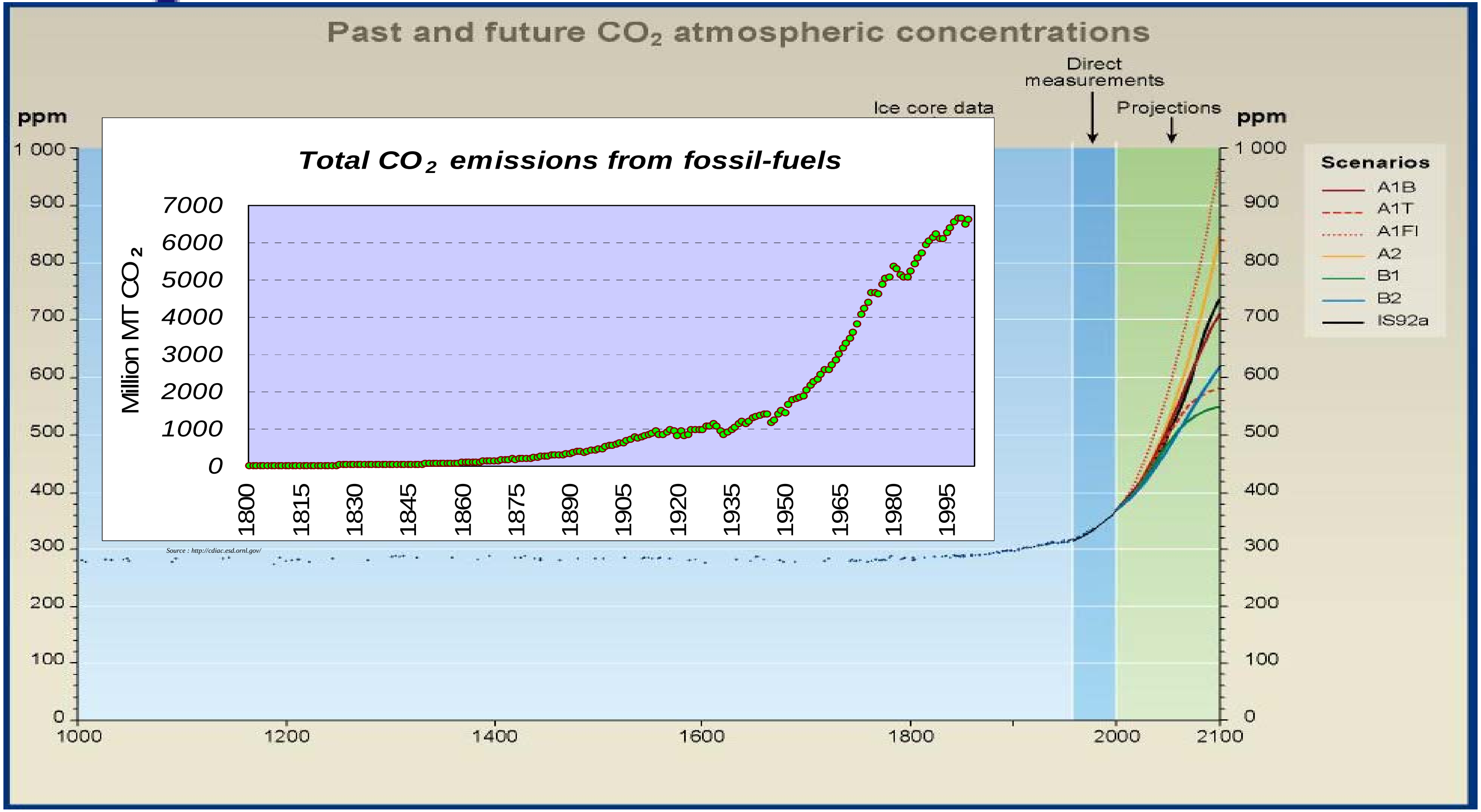
SEM-EDS Surface Composition

Experiment	Reason	Concentration
21	Baseline	2M H_2SO_4
22-1	2-stage	2M H_2SO_4
22-2		2M H_2SO_4
23-1	2-stage	1M H_2SO_4
23-2		1M H_2SO_4
24	24 hours	2M H_2SO_4
25-1	3-stage	2M H_2SO_4
25-2		1M NaOH
25-3		2M H_2SO_4
26	50 C	2M H_2SO_4

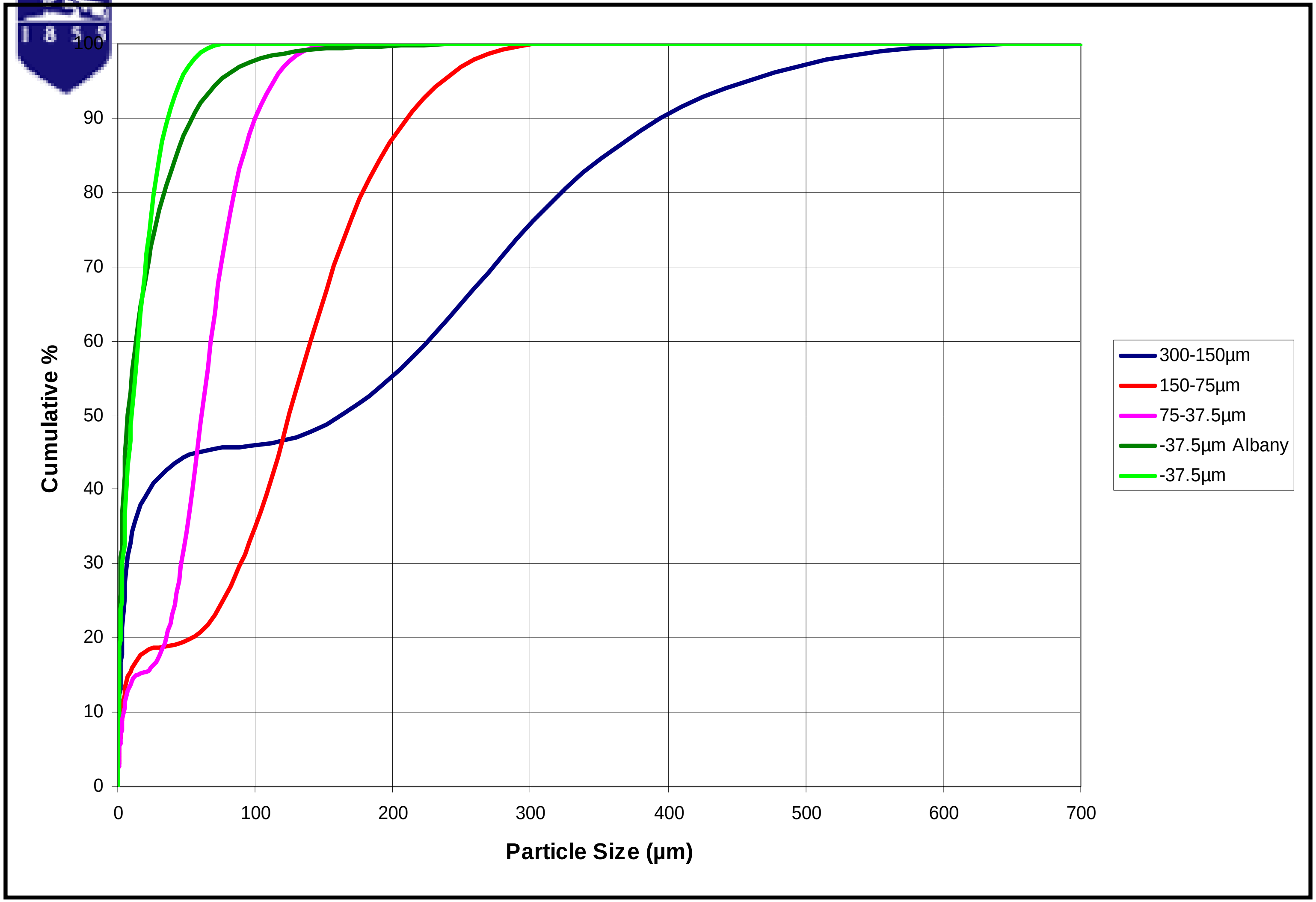


CO_2 Emissions

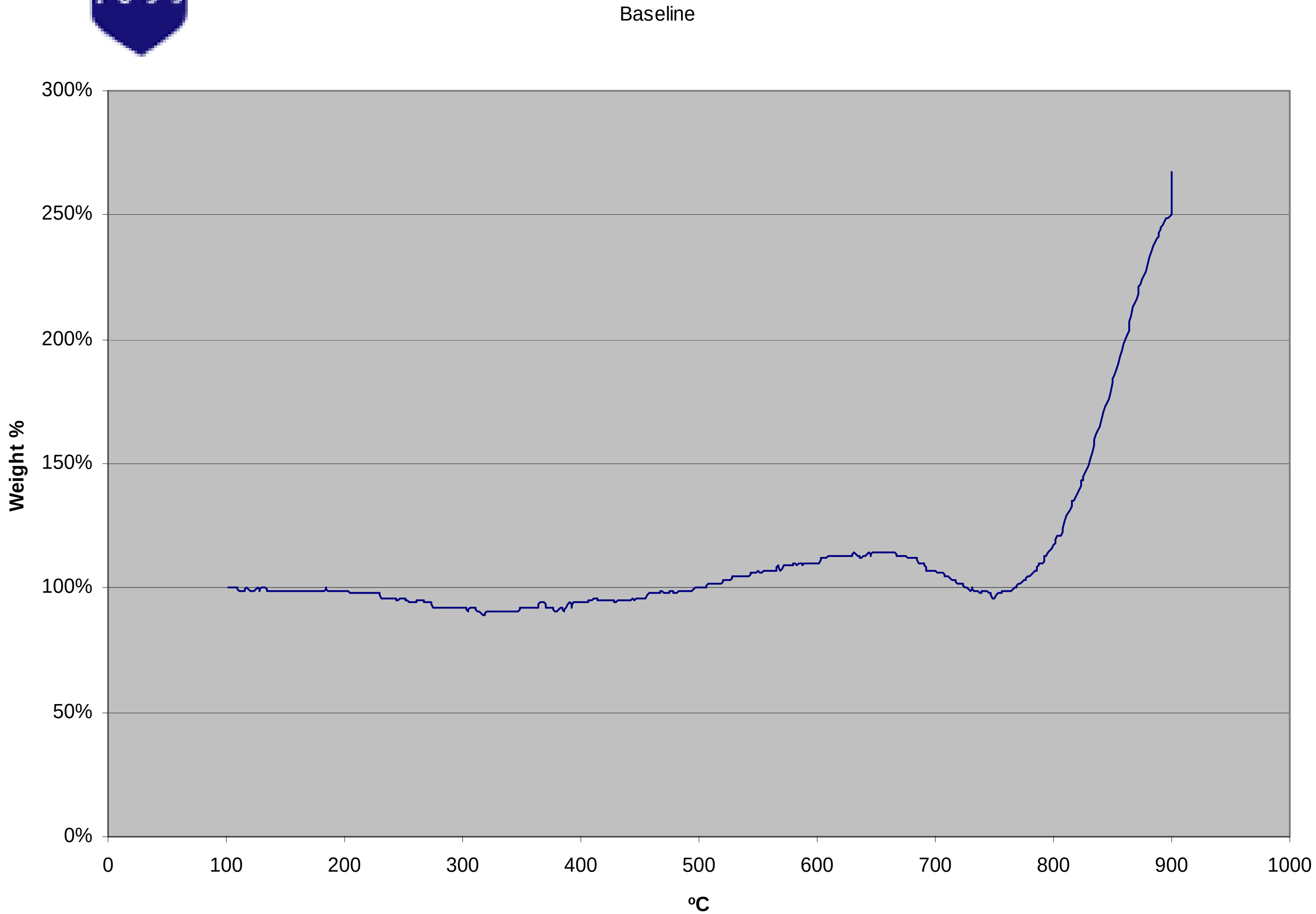
[source IPCC,2001]



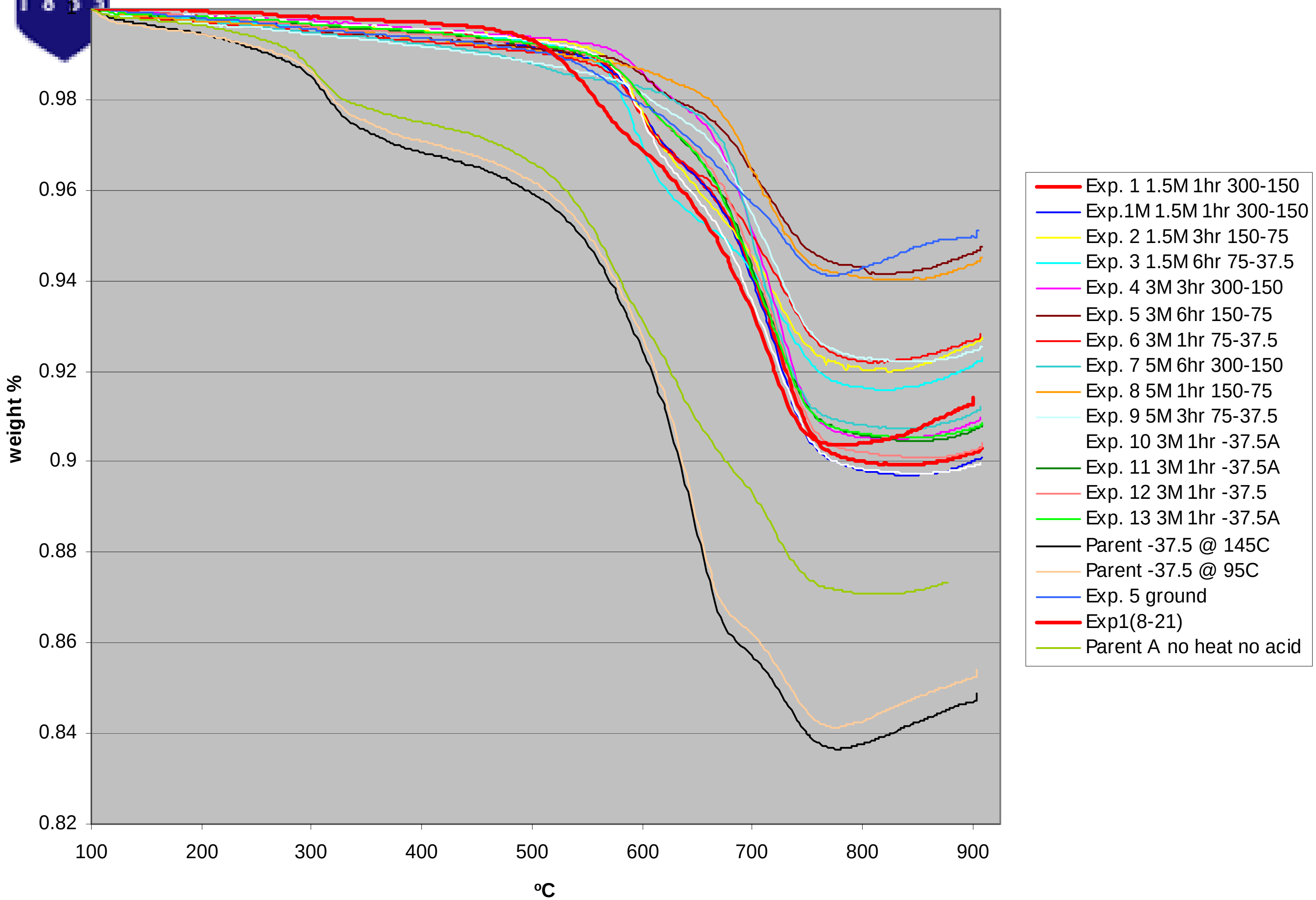
Particle Size Analysis



Baseline/Drift



Complete TGA Results



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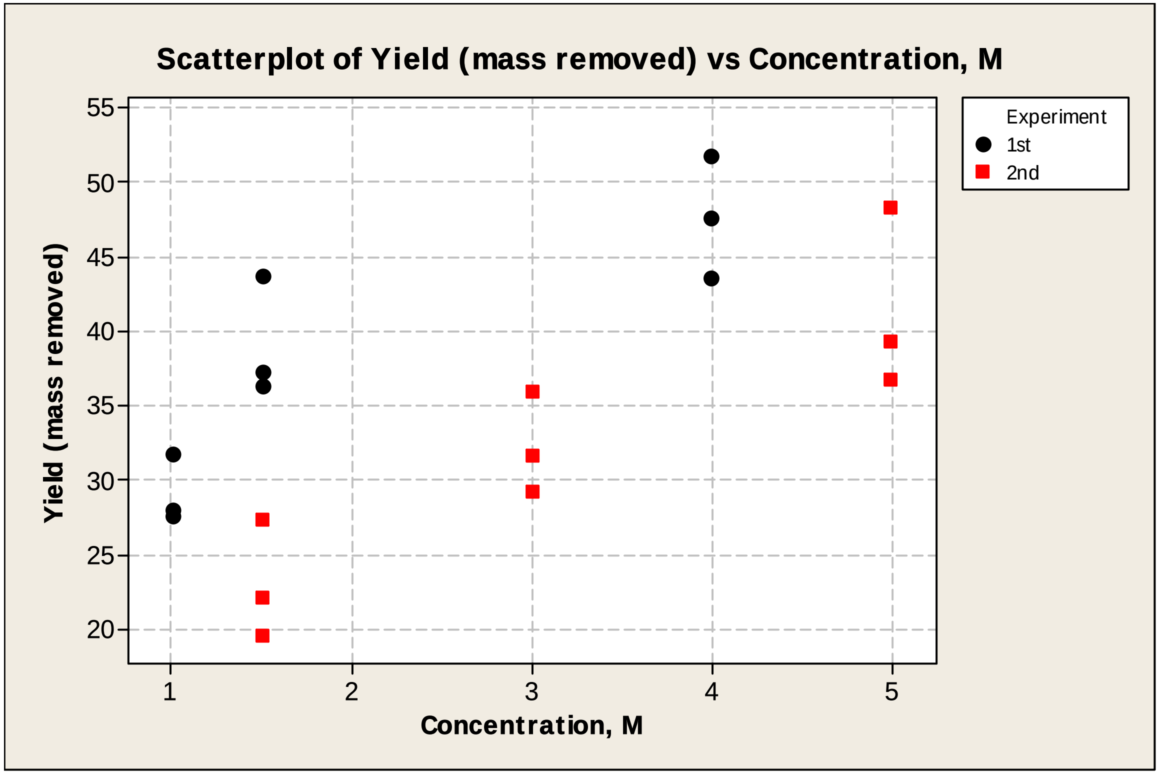
Experimental Results

						ICP Solids, %			ICP Solutions, ppm		
Exp	Conc	Size	Time	Yield	TGA	MgO	CaO	SiO2	Mg	Ca	Si
1	1.5	163	1	19.6	10	34.5	0.03	49.3	8728	560	146
2	1.5	125	3	22.04	7.97	26.7	7.52	43	9539	541	157
3	1.5	61	6	27.39	8.39	28.9	5.36	44.3	8160	499	158
4	3	163	3	31.68	9.47	32.7	0.04	54.4	9255	252	21
5	3	125	6	29.26	5.7	20.7	8.84	46.9	9751	251	60
6	3	61	1	35.86	7.78	24.1	5.38	49.4	10556	261	62
12	3	10	1	38.48*	9.79	29.2	0.07	55.1	9170	247	70
13	3	10	1	37.87	9.38	26.8	0.02	57.1	9627	72	86
7	5	163	6	39.23	9.18	27.5	0.01	59.3	6825	65	11
8	5	125	1	36.73	5.93	14	11	48.5	10385	80	21
9	5	61	3	48.22	7.71	17.7	2.84	62.7	12827	76	29
		163				41.3	0.98	38.9			
		125				33.7	10.6	34.1			
		61				38.6	6.64	33.6			

$$\text{Reaction Yield} = \frac{\text{Mass Removed}}{\text{Mass Initial}} \times 100\%$$



Scatterplot of Yield (mass removed) vs Concentration, M
Yield (mass removed)
55
50
45
40
35
30
25
20
1
2
3
4
5
Concentration, M
Experiment
1st
2nd