ACERC Annual Conference

Prediction and Measurement of Carbonaceous Briquette Reactions in Carbon Dioxide

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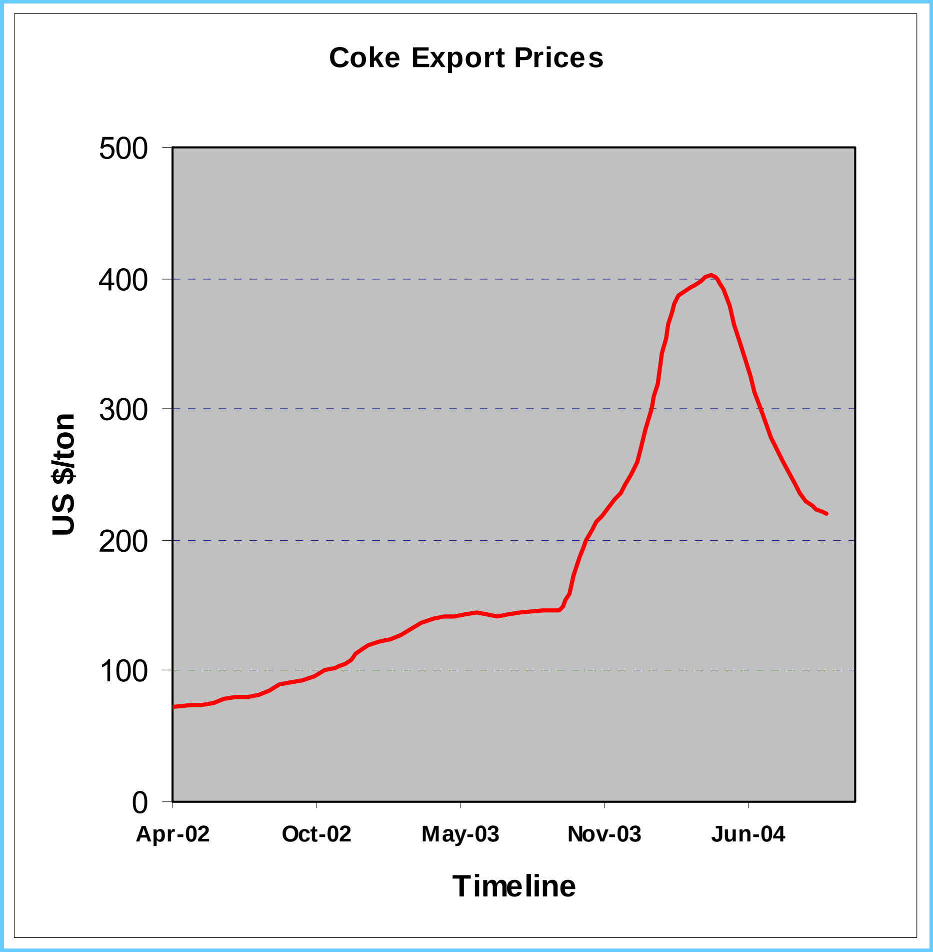
Background

- World met-coke squeeze
  - World met coke costs sharply higher ($220/tonne, FOB China)**
- Coal prices up
- Met coal supply down
- U.S. imports 4 million tons/yr and consumes 20 million tons/yr

** Met Coke World Summit 2004



Typical Met-Coke Requirements

Composition (%)		Strength, Reactivity, Size	
Ash	<10.5-12.5	Stability	>60
Sulfur	<0.6-1.0	CSR	>56-65
Alkali	<.02-.03	CRI	<25-30
Moisture	<1-5	Hardness	>68-70
Volatile Matter	<0.4-1.1	Size, %>5 cm	46
Phosphorus	<0.05		

CRI & CSR

- CRI – Coke Reactivity Index
  - Briquette % weight lost after 2 hr. reaction with 100% CO_2 at 1100°C
- CSR – Coke Strength after Reaction
  - Reacted coke tumbled 600 revolutions (30 min)
  - Determined by weight of briquettes retained on 3/8” sieve after tumbling

CRI<30 = >70% remaining after 2 hrs of reaction
CSR>60 = <40% of remaining mass less than 3/8”

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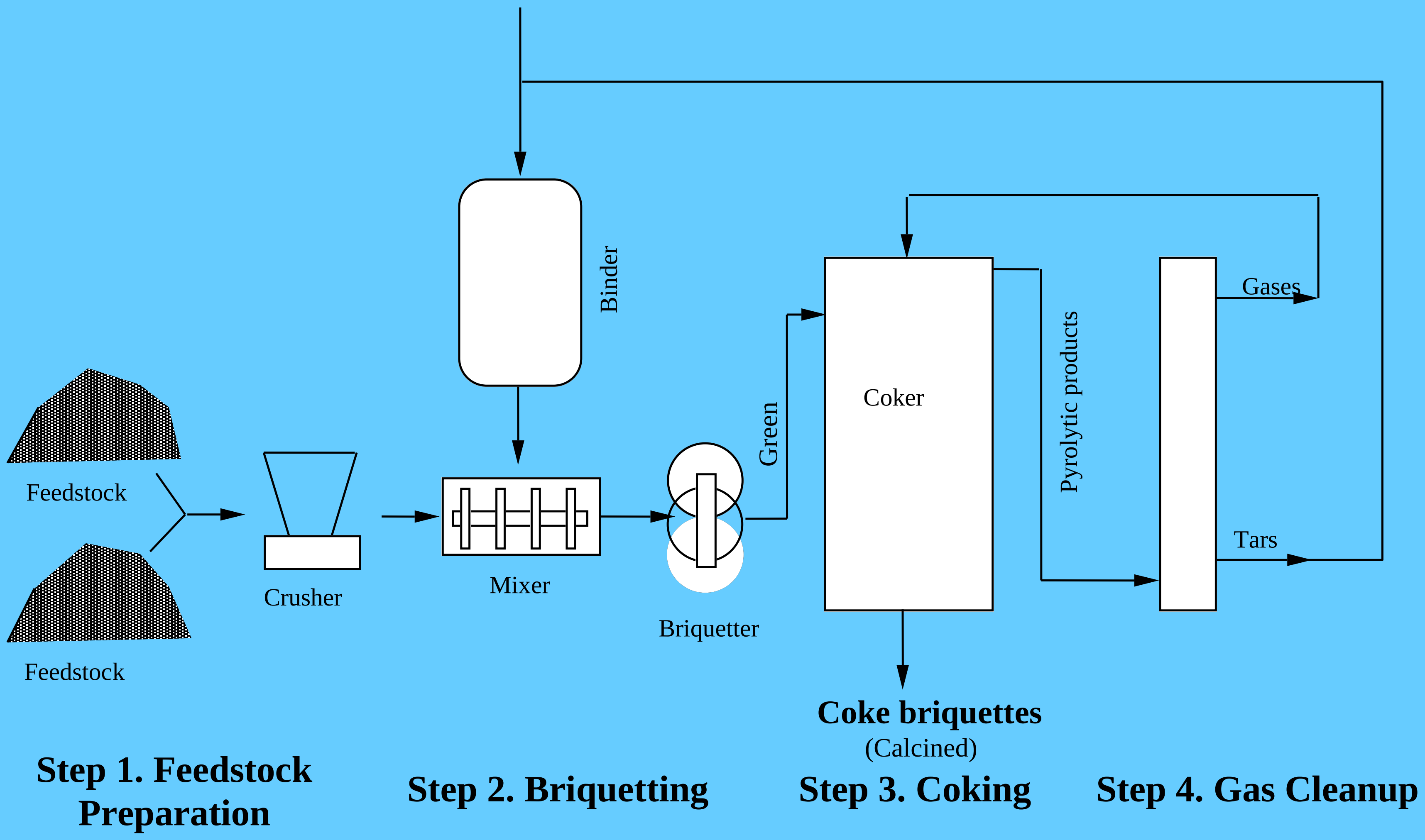
4 Step Coke Process



Variables

Feedstock

- Carbon Types
- Blend %'s
- Feedstock Properties
- Particle Sizes

Process

- Briquette Size
- Briquetting Pressure
- Coking Temp Ramp
- Coking Time

Research Objective

Devise a method for guiding the development of briquetted met-coke products

- Reduce Time
- Improve Quality
- Make Use of More Feedstocks

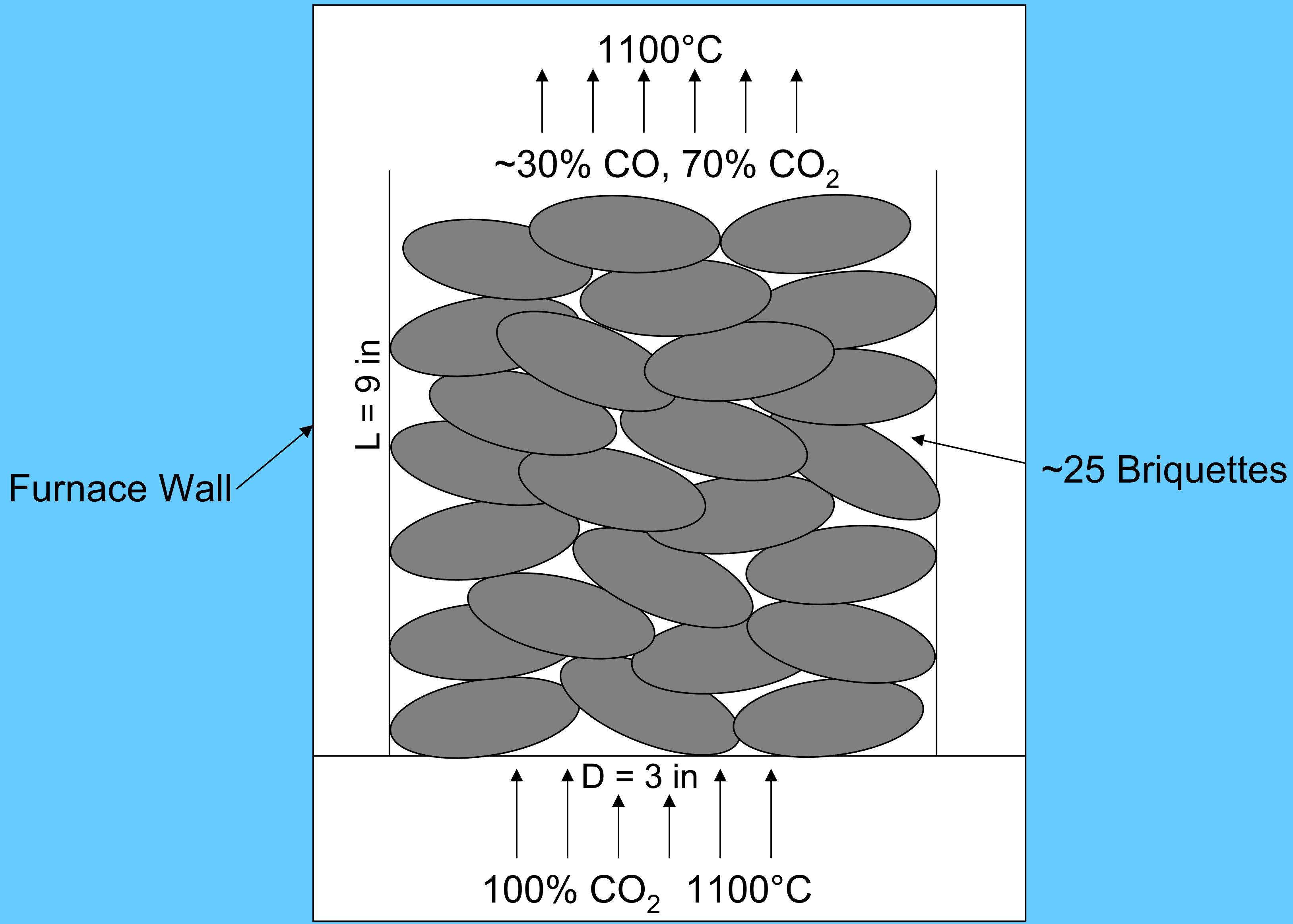
Tested Briquette Formulations

Case	Non-Coking Coal	Non-Coking Coal Char	Coking Coal	Pet Coke	Tar
1	40	40	0	10	10
2	0	40	40	10	10
3	0	0	40	50	10

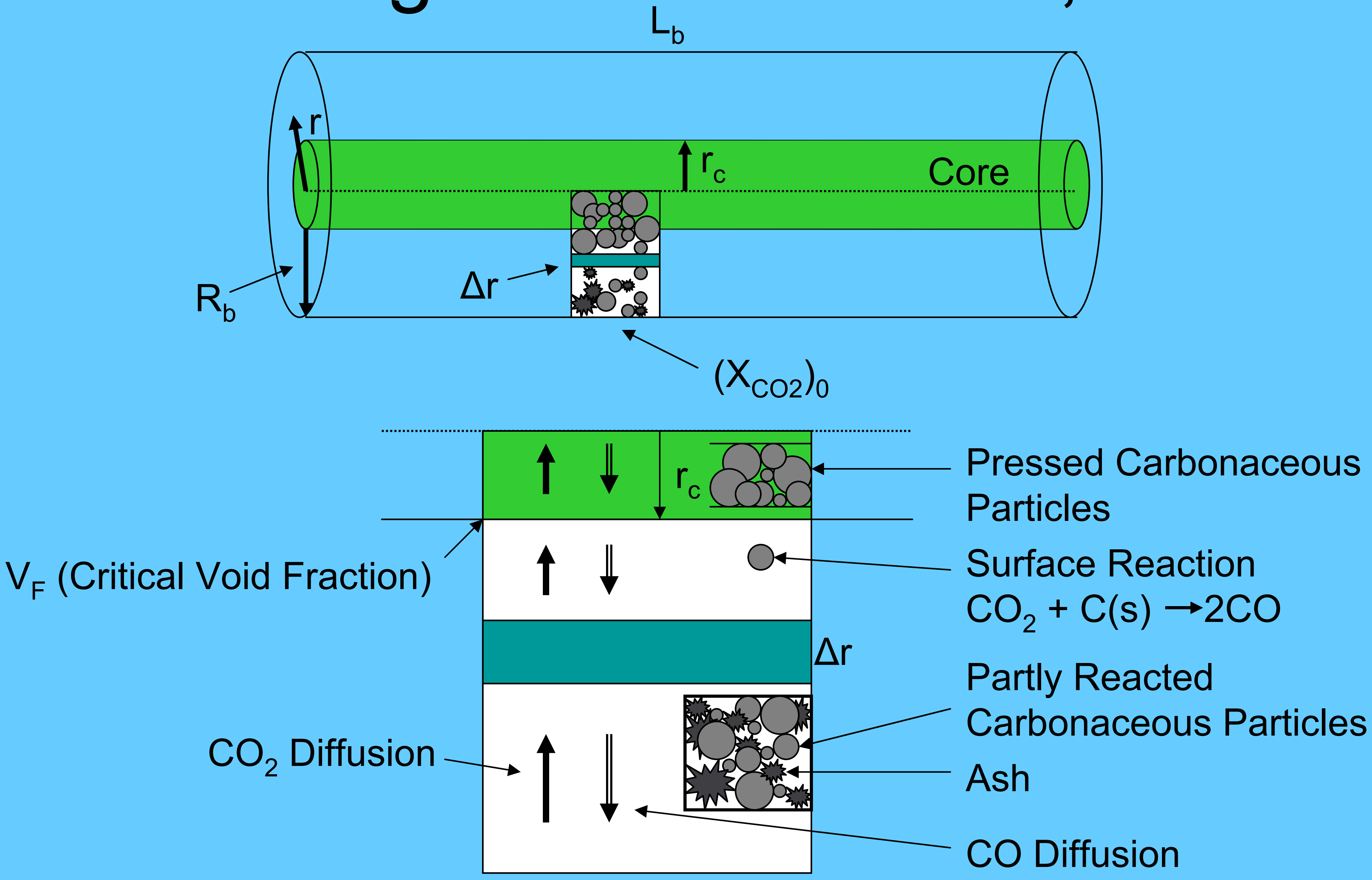
Task 1: Model Briquette Reaction Process

Calculate briquette mass loss(r,t) and void fraction(r,t) to establish residual briquette core and hence CRI and CSR

Reactor Schematic



Schematic of Idealized Briquette Being Modeled at time, t.



Key Assumptions

• Geometric	Cylinders, 1-D, Quasi-steady
• Gas Phase	CO and CO_2
• Solid Phases	Spheres, Sizes
• Kinetic	C-CO_2 1st order surface reaction, inert ash
• Transport	$D_{CO\text{-}CO2}$ α void fraction
• Boundary Conditions	Surface CO_2, pressure, and briquette temperature constant
• Briquette Strength	Residual solid breaks off at critical void fraction during tumbling

Basic Briquette Model Equations

(1) $$\frac{1}{r}\frac{d}{dr}\left[\left(\frac{rcV_f D_{CO-CO_2}}{1+X_{CO_2}}\right)\frac{dx_{CO_2}}{dr}+R_{CO_2}\right]=0$$

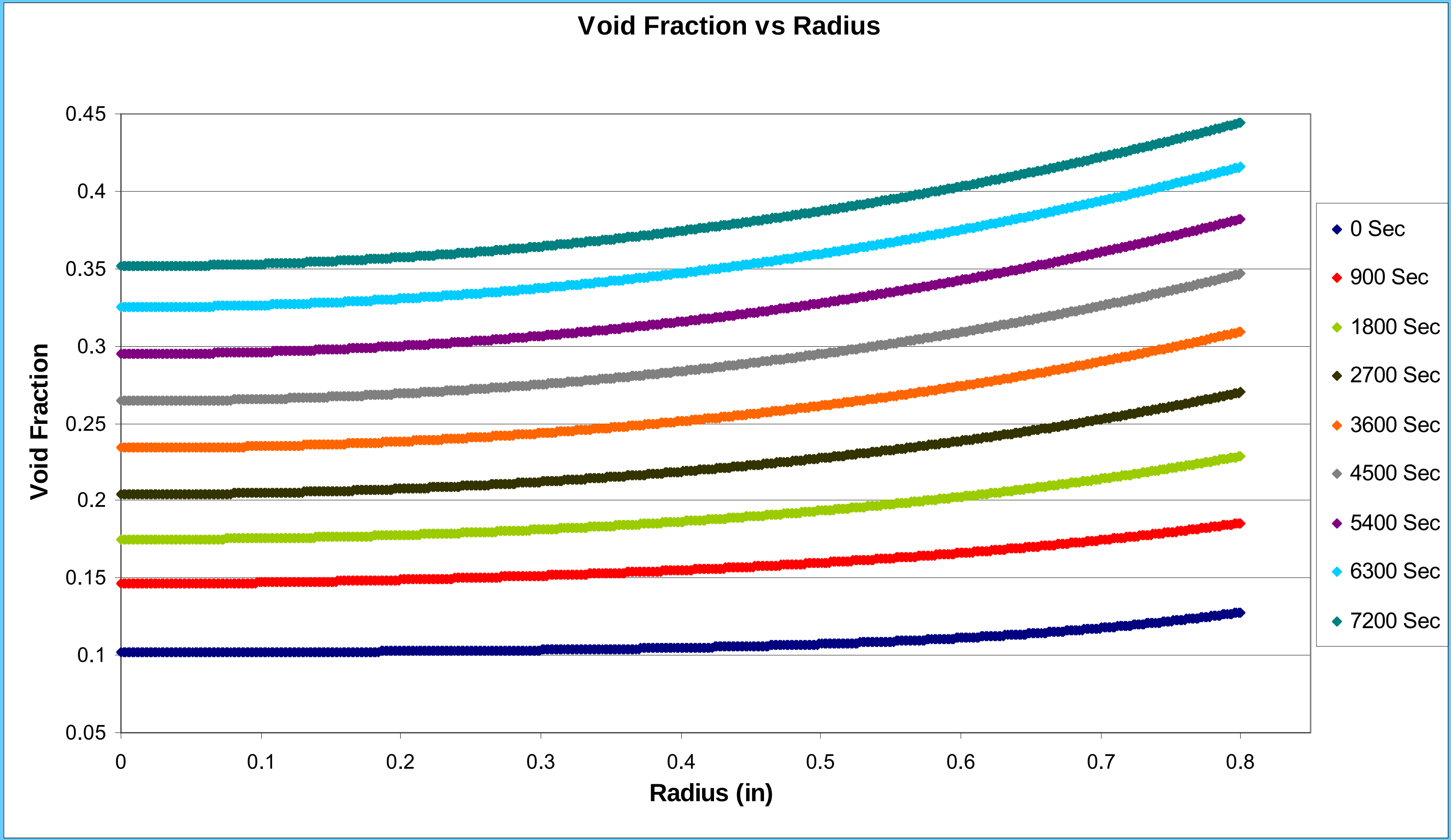
(2) $C(s) + CO_2 \rightarrow 2CO$; $N_{CO} = -2N_{CO2}$

(3) $$R_{CO_2}=\left[\sum_{f_i}\sum_{p_j}k_i A_{ij}\right]cX_{CO_2}$$

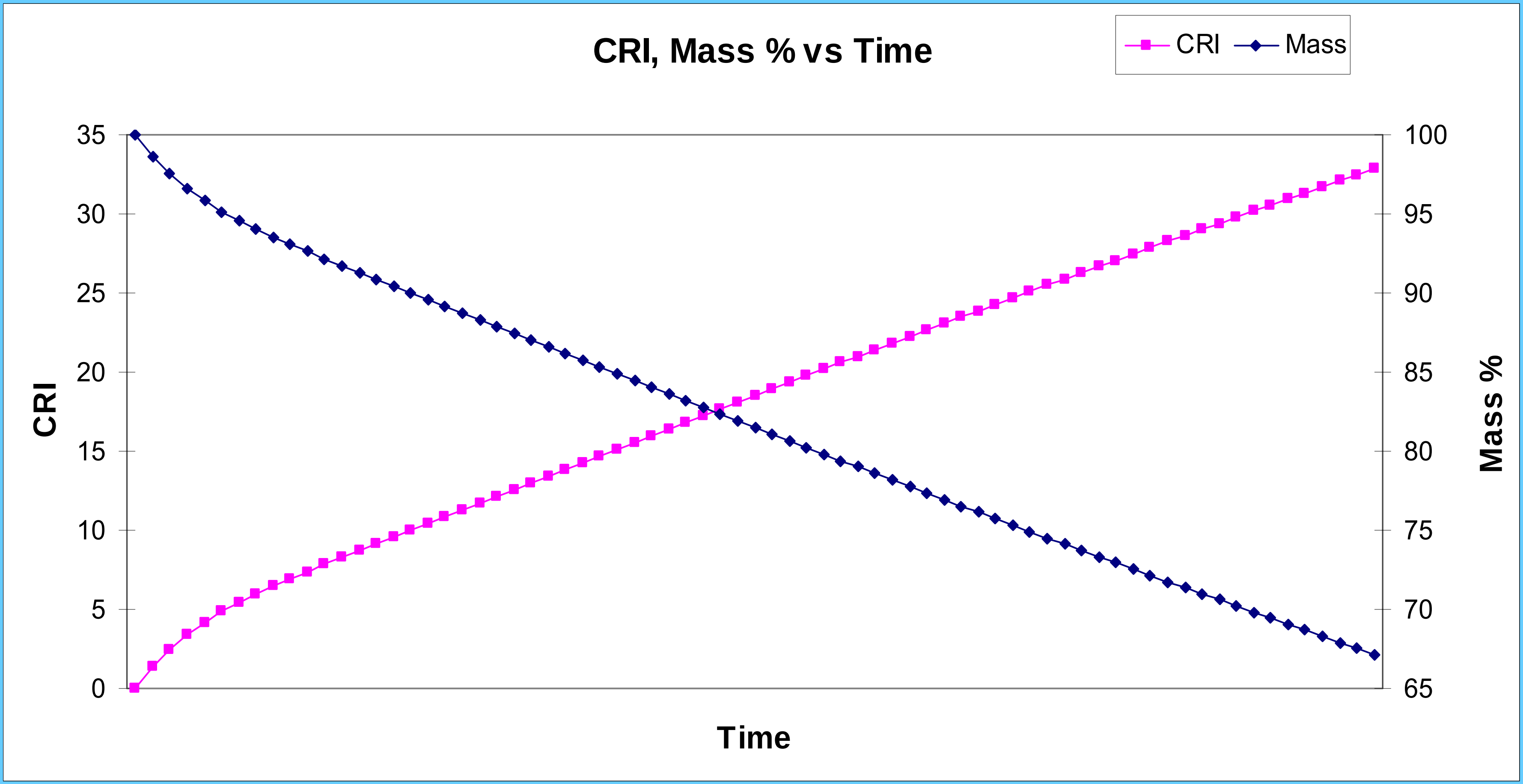
f = number if feedstocks

p = number of particle sizes/feedstock

Predicted Void Fraction



Predicted CRI & Mass %



Task 2: Measure Briquette Properties

Evaluate briquette structure and properties to relate to predicted and measured CRI and CSR

Properties Being Measured (Phase 1) for Three Briquette Test Formulations

Composition %
- Ash
- Moisture
- Volatile Matter
- Fixed Carbon
- Sulfur

Structural
- Apparent Density
- Void Fraction
- Size
- SEM

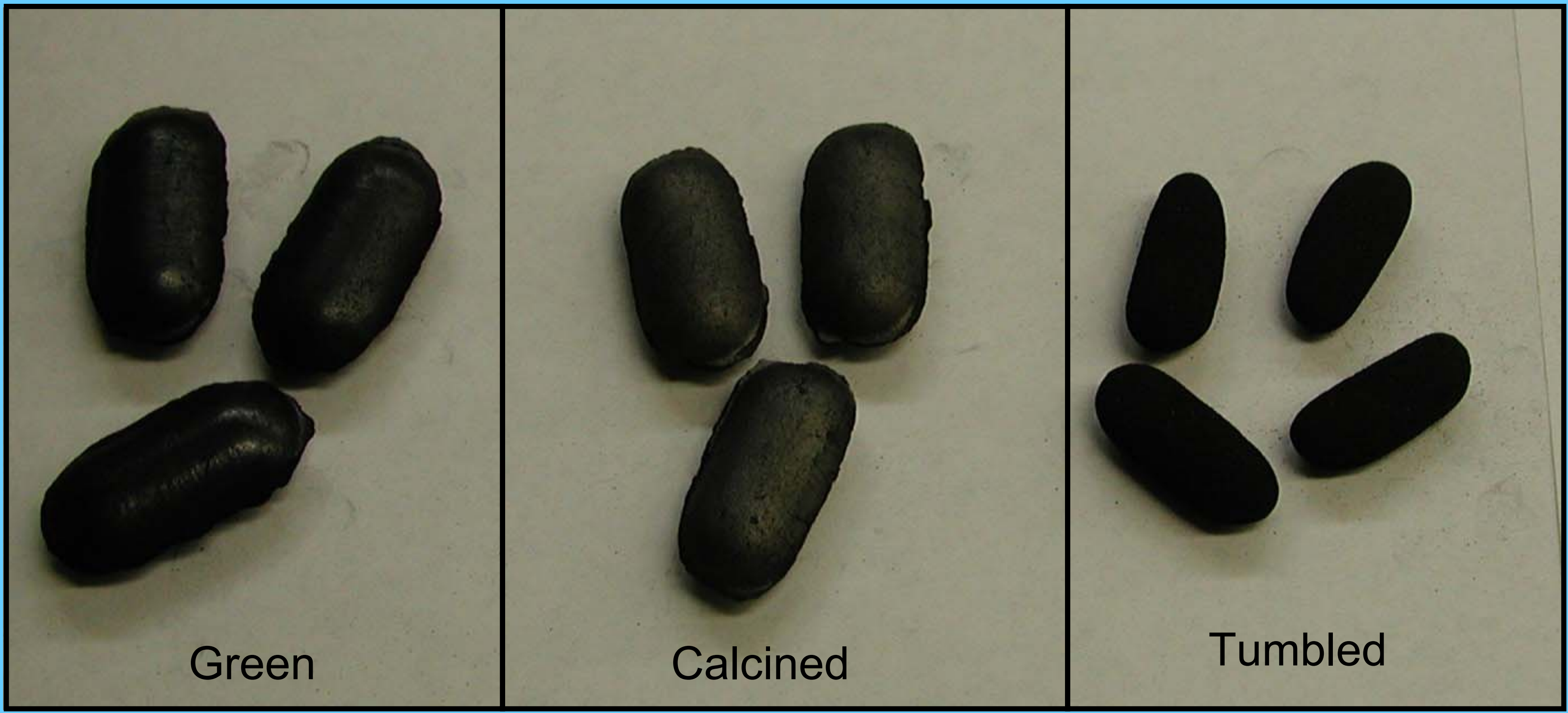
For Three Process Steps: Green, Calcined, and Tumbled

Green Briquette Composition

Composition %	Case 1	Case 2	Case 3
Moisture	2.2	1.3	1.5
Volatile	28.1	21.4	17.0
Ash	3.3	3.9	2.3
FC	66.4	73.4	86.4
Sulfur	0.70	0.80	1.03

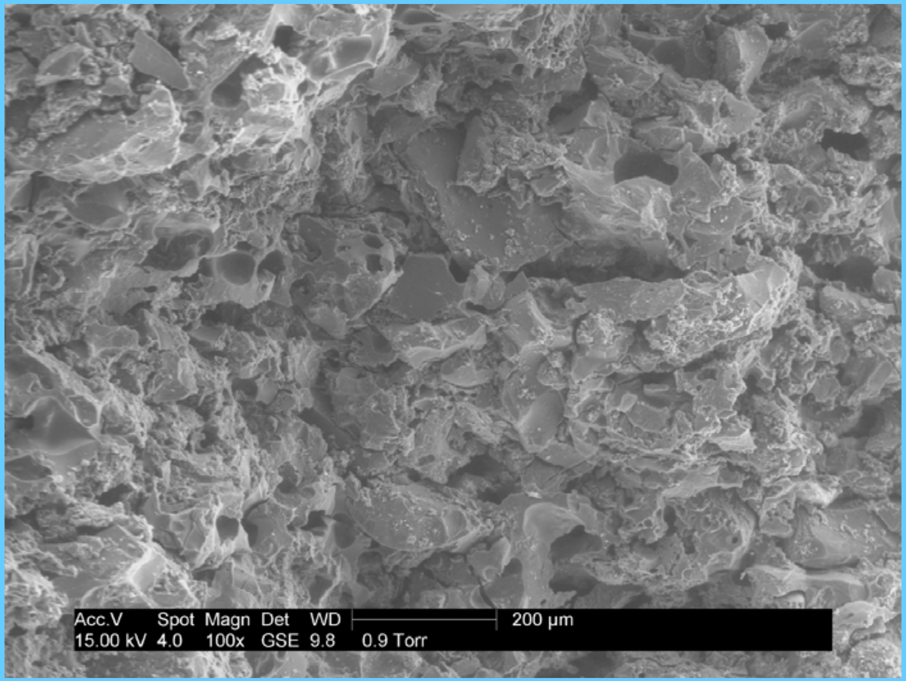
Briquette Photos

Formulation 2

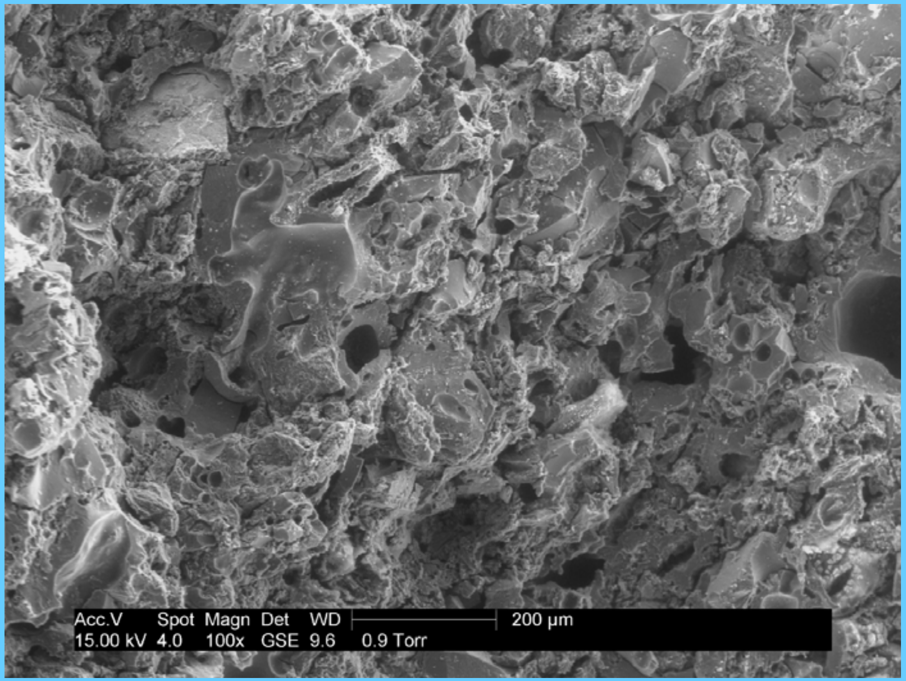


SEM Results

Formulation 1



30 min



90 min

Task 3: Measure Briquette Reaction Rates (CRI)

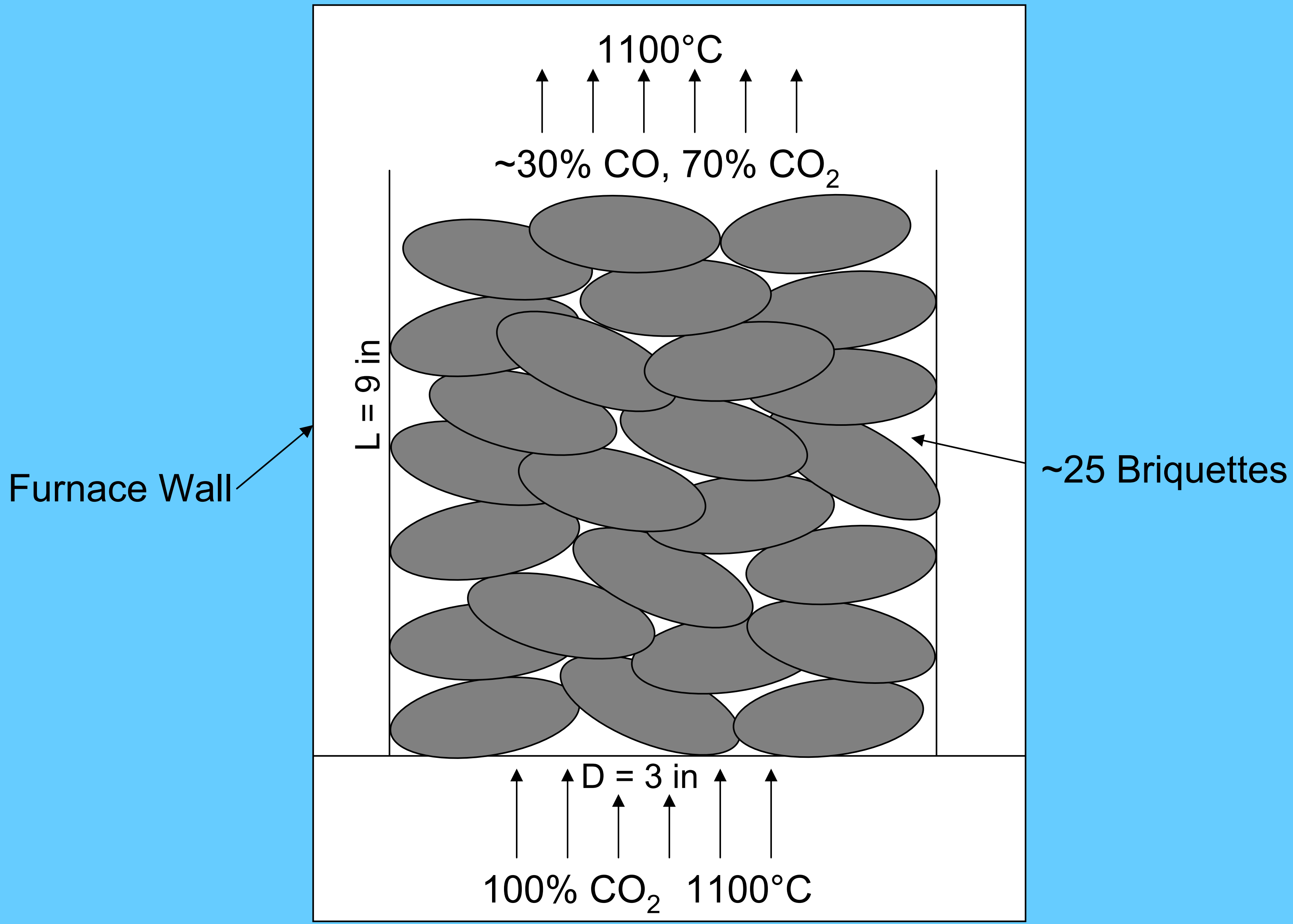
Measure extent of briquette reaction(t) in CO_2 with ASTM-D5341-93a (CRI) to produce briquettes for strength test

- Test Program
- Briquette Photos
- Reaction Data
- Observations

CRI – Briquette % weight lost after 2 hr. reaction with 100% CO2 at 1100°C

CRI<30 = >70% remaining after 2 hrs of reaction

Reactor Schematic



Test Conditions

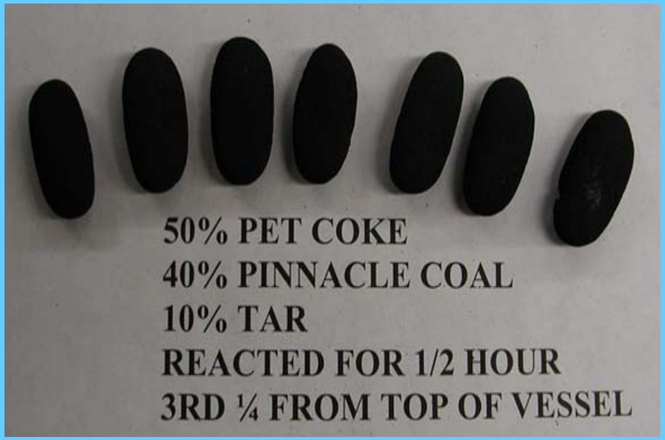
• Pressure	Ambient
• CO_2 Mole Fraction	1.0 (Reactor Base)
• Briquette Mass	ca. 6 grams
• Time	0, 0.5, 1, 1.5, 2 hrs

Briquette Photos

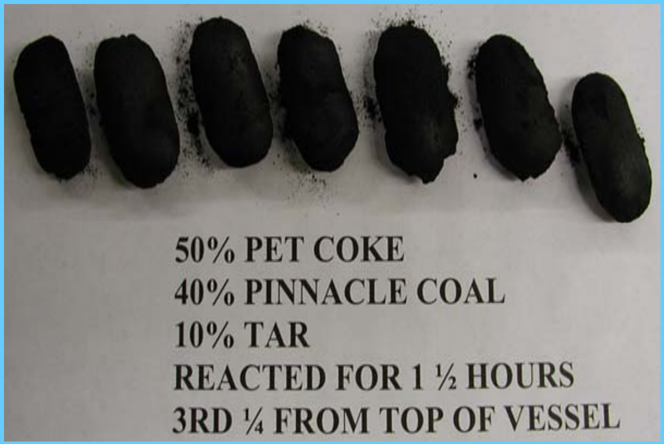
Formulation 3

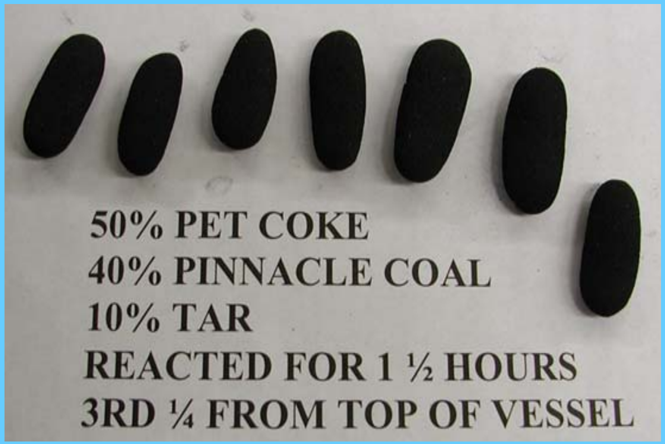
After Reaction | After Tumbling

0.5 hrs



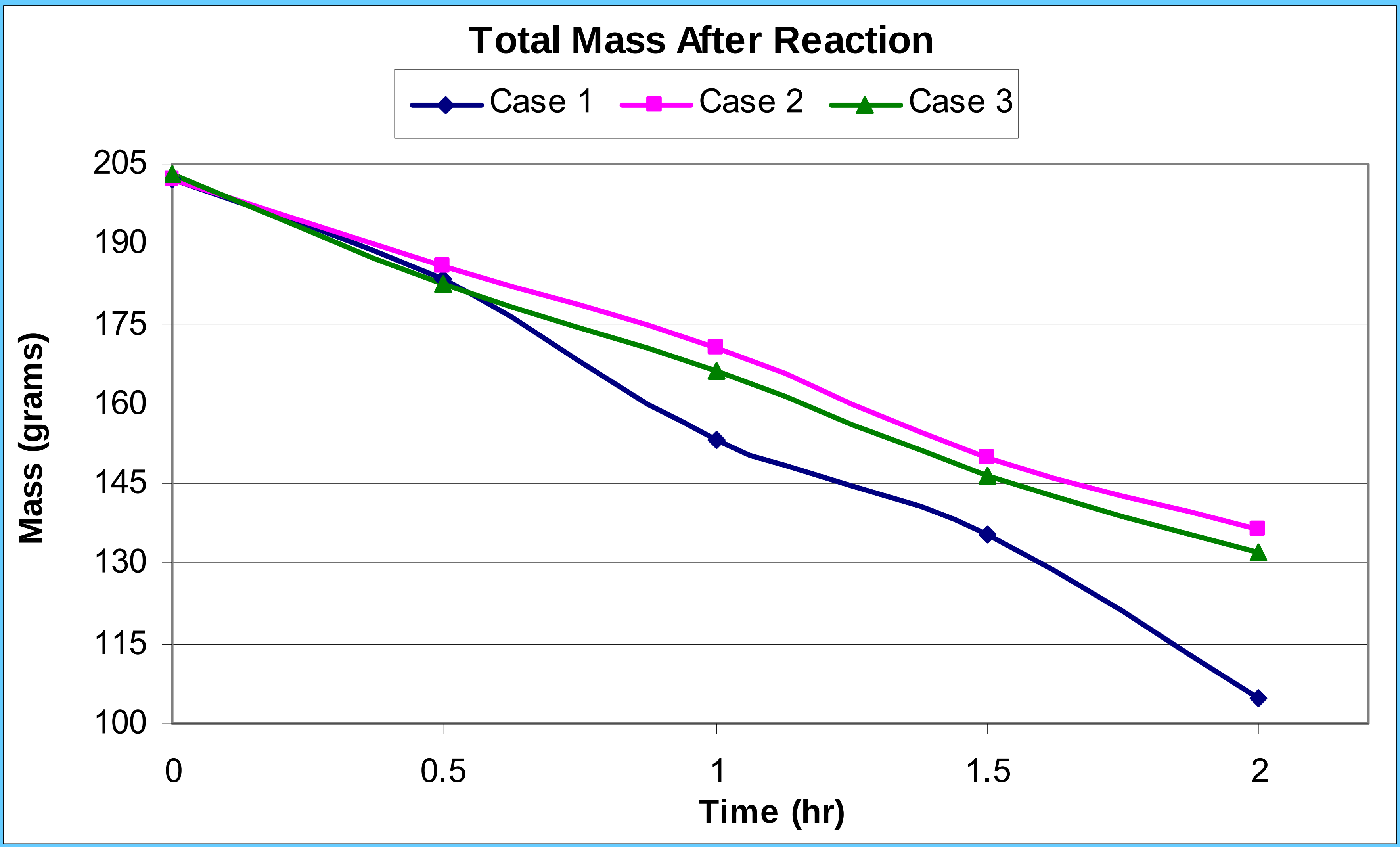
1.5 hrs



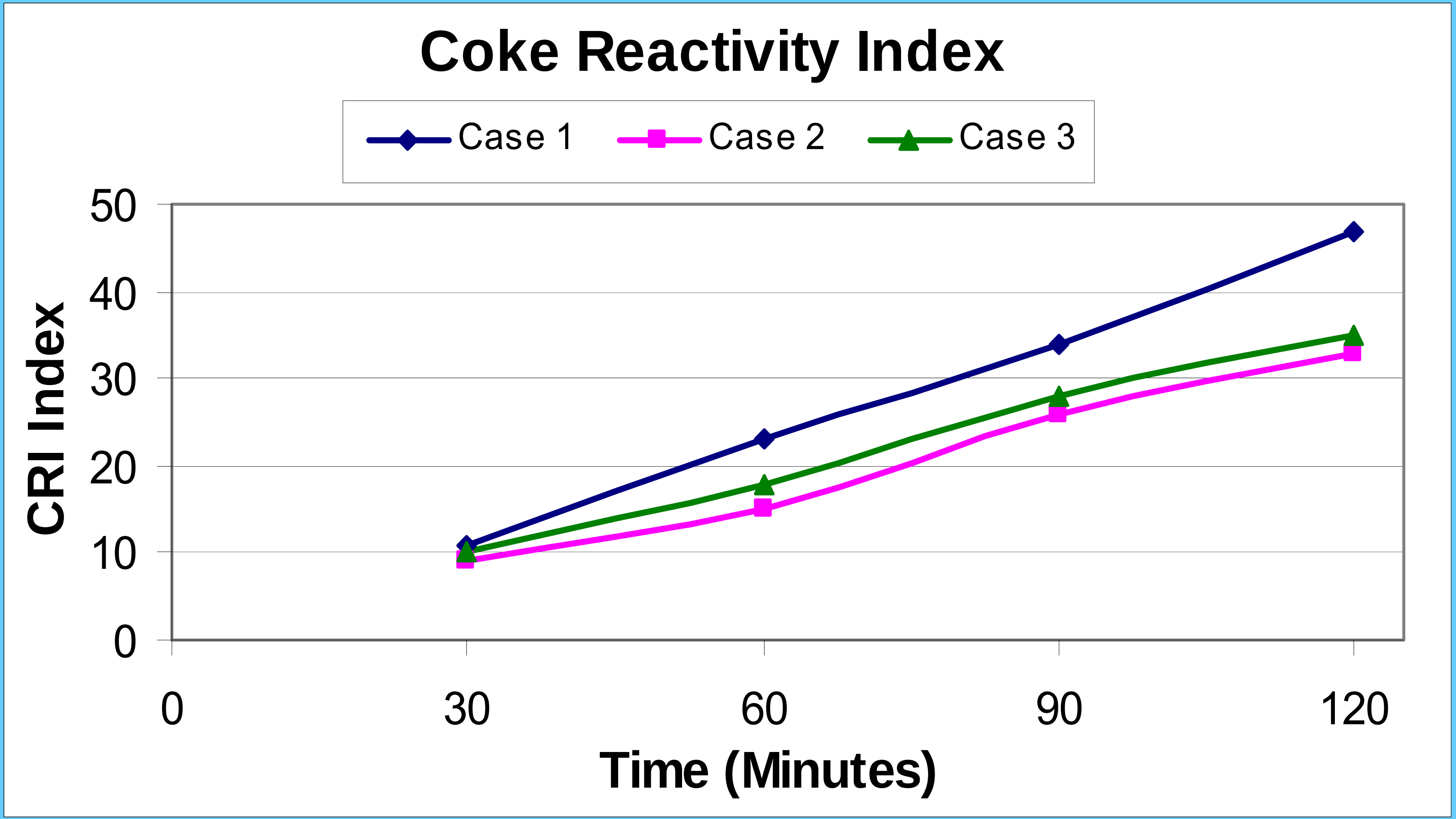


Mass Loss

After Reaction Before Tumbling



CRI Data



Coke Reactivity Index
Case 1
Case 2
Case 3
CRI Index
50
40
30
20
10
0
0
30
60
90
120
Time (Minutes)

Task 4: Measure Briquette Strength After Reaction (CSR)

Measure residual briquette core size through ASTM-5341-93a to provide data base for model comparison with predicted CRI and CSR

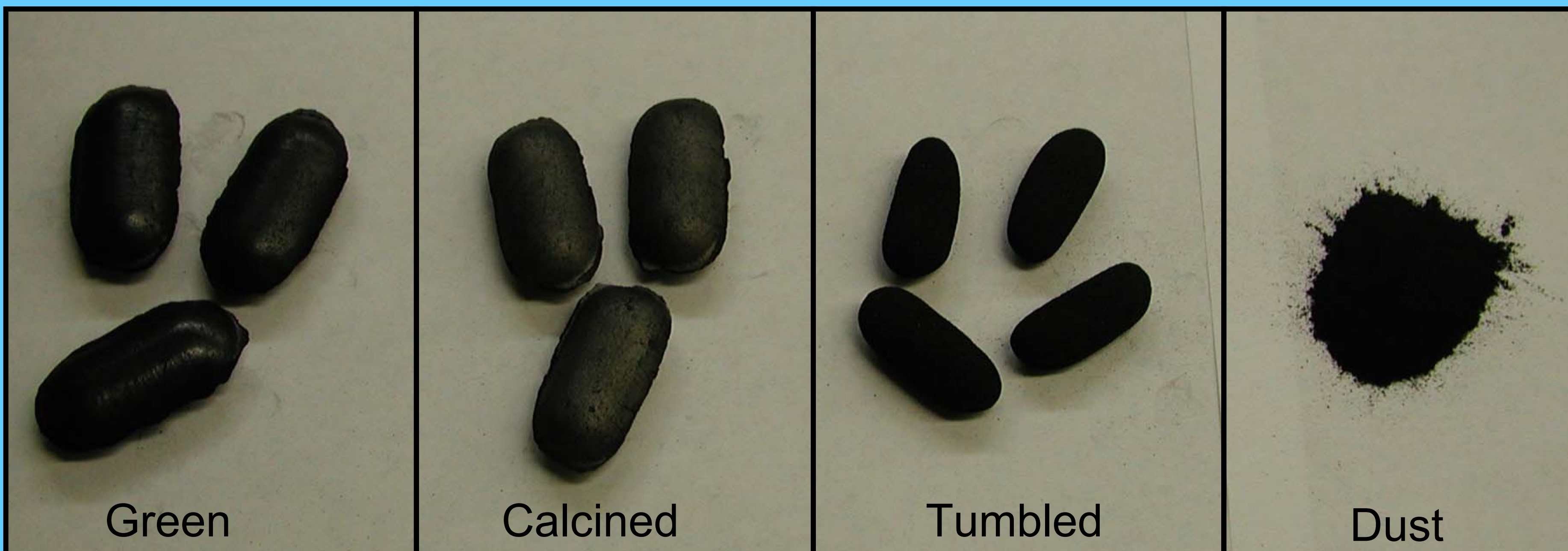
- Test Method
- Test Data
- Observations

CSR – Reacted coke tumbled 600 revolutions (30 min). Determined by weight of briquettes retained on 3/8” sieve after tumbling

CSR>60 = <40% of remaining mass less than 3/8”

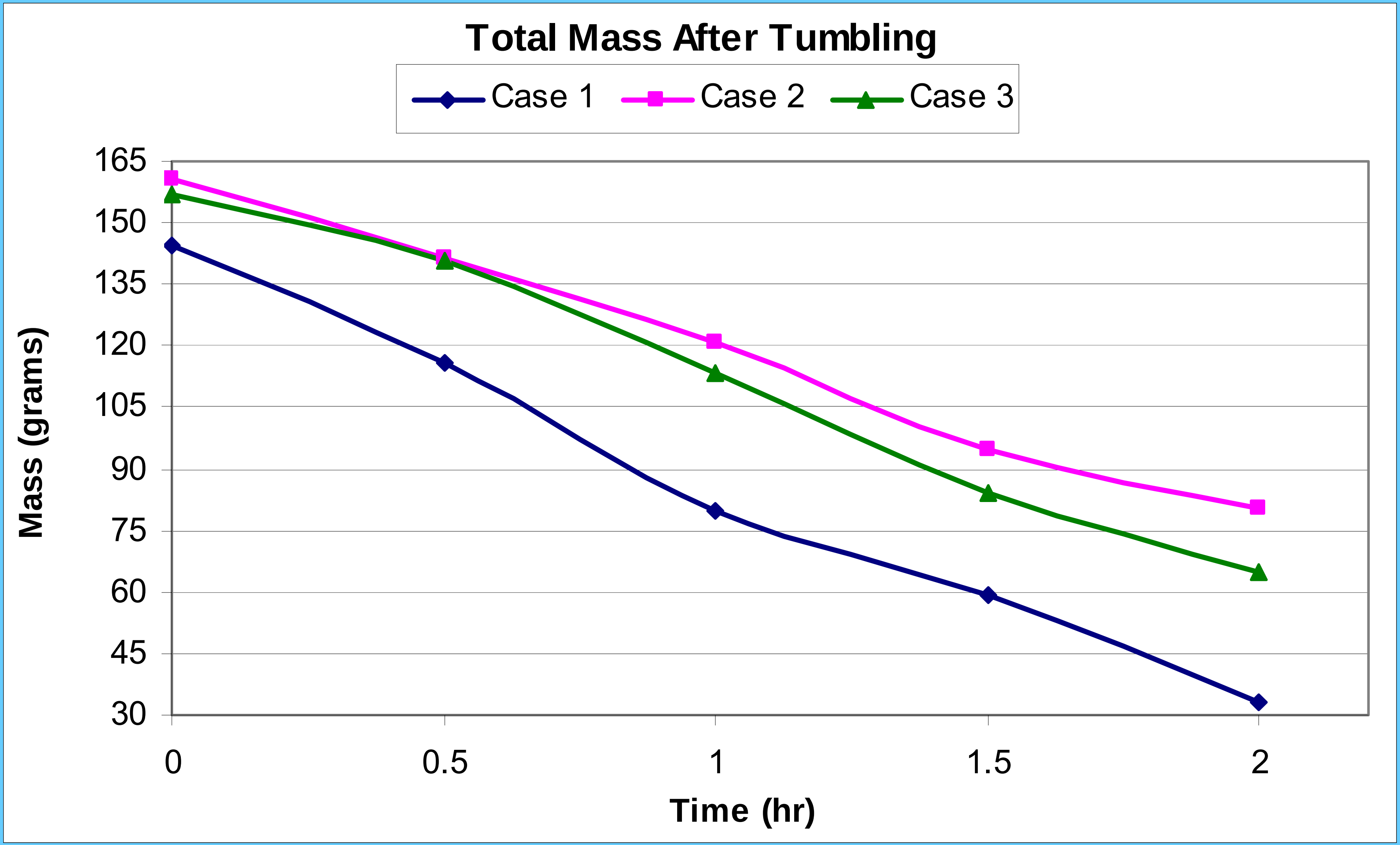
Tumbled Briquette Photos

Formulation 2

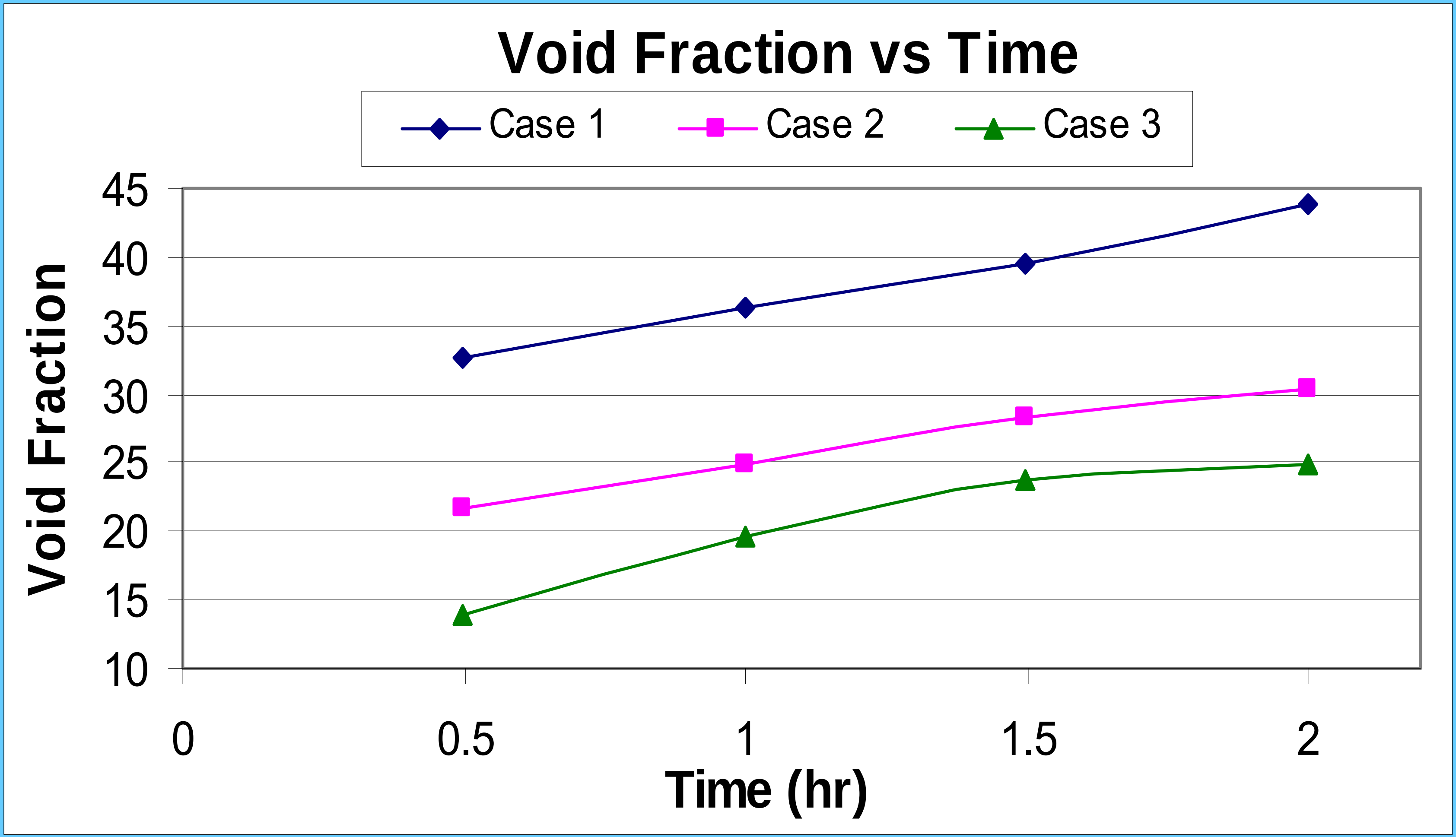


Mass Loss

After Reaction and Tumbling



Residual Core Void Fraction Data



Initial Observations

- Model Predicts Smoothly Changing Mass Loss and Void Fraction
- Initial Void Fraction-Important and Highly Variable
- Void Fraction Varies Nearly Linearly with Time
- No Evidence of a Single Critical Void Fraction
- Void Fraction not the Only Factor
  - Fluidity
  - Surface Reaction