IPRO 346- Design of a Coal Desulfurization Process to Improve the Environment
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Team Members:

-Salil Benegal (CHEM)
-Anthony Doellman (PHYS)
-Greggory Kisiel (CHEM)
-Andrew Keen (CHE)
-James Maratt (CHE)
-Amy McDowell (CHE) (team leader)
-Adejoke Ogunride (CHE)
-Oscar Olmos (CHE)
-Myint Toe (CHEM)

Advisor- Professor Mohammed Reza Ehsani

What is the problem?

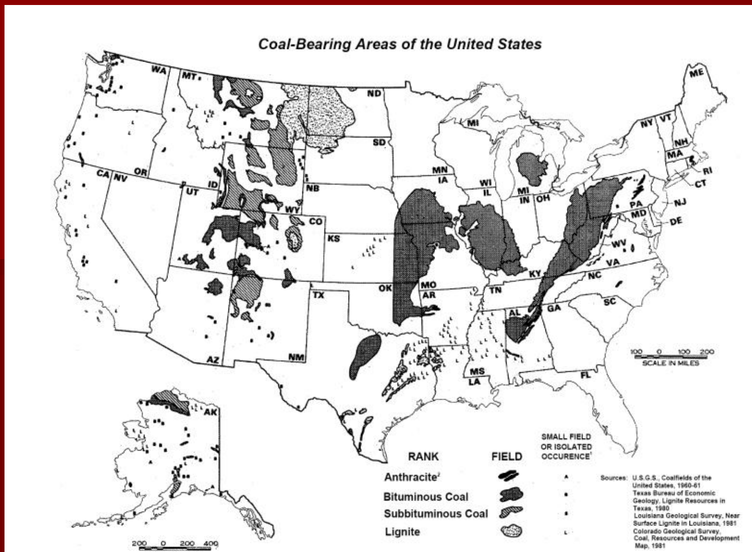


Image 1- US Coal Bearing Areas[1]

U.S. - Full of Coal

Coal - Full of Sulfur

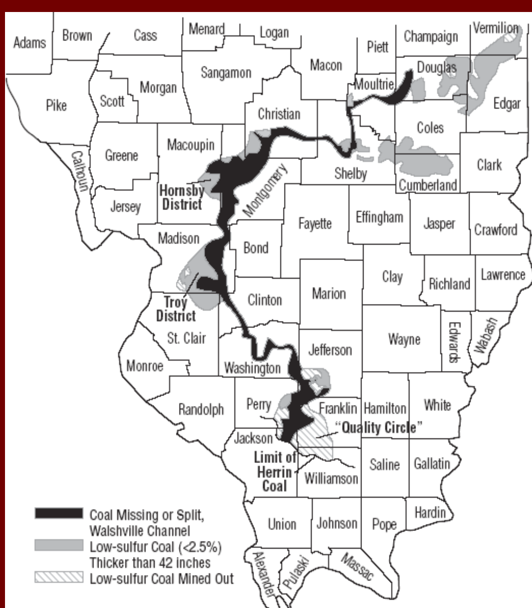


Image 2- Illinois Coal Bearing Areas[2]

- Sulfur
  - Causes acid rain
    - Alters pH of soil/water
    - Damages man-made structures and buildings
  - Increases difficulty and cost of producing steel
  - In coke, promotes brittle steel

[1]http://www.ket.org/Trips/Coal/AGSMM/agsmmwhere.html

[2]http://www.isgs.uiuc.edu/coalsec/Illinois-coalgeology.pdf

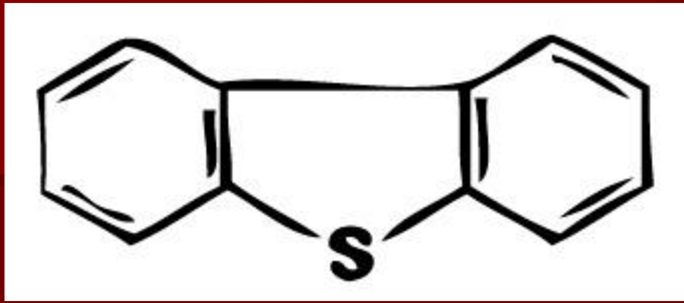
Sulfur in Coal

Inorganic Sulfur

- Mainly pyritic sulfur, a solid with the formula FeS_2 in two types of crystalline formation: Pyrite & Marcasite

Organic Sulfur

- Part of the chemical structure of the coal that cannot be removed by physical means



What is the solution?

- Objective:
  - Desulfurize coal pre-combustion to fit EPA standards
  - Produce coal for coking process

- Advantages to pre-combustion:
  - Reduces environmental contamination
  - Produces high purity coal for coke making

- Project Outline:
  - Research
  - Comparison
  - Modeling
  - Profitability analysis

EPA Standards

- EPA requires a removal of 2.5 lb SO_2/million BTU
  - For our process of 70 tons/hr, this equals a total sulfur removal of 81%

What is coke?

- A solid derived from low ash, low sulfur bituminous coal
- Coal carbonization - process for producing metallugical coke used in steel making blast furnaces
- Used in steel making blast furnaces

Desulfurization Methods

- 3 types of methods:
  - – Biological
  - – Physical
  - – Chemical

Biological Methods

- Mix microorganism with coal in a batch process
- Different organism options for various removal rates and types of sulfur removed

- Advantages
  - Low capital and operating costs
  - Less energy use
- Disadvantages
  - Sulfur removal rates are too slow
  - Low removal percentages (50-60% total sulfur)

Physical Methods

Flotation Method

- Flotation exploits the fact that coal has a specific gravity ~1.2-1.6 whereas pyrite is >2.
- By pulverization of coal particles, pyritic sulfur can be removed

High Gradient Magnetic Separation

- Based on differing magnetic properties of coal and pyrite
- Ground coal slurry solution is run through a magnet
- Pyrite and ash are attracted to steel while coal passes through
- Up to 90% removal of pyrite

Physical Methods

- Advantage:
  - Tend to be far more economical than their chemical or biological counterparts.
- Disadvantage:
  - Act exclusively on inorganic forms of sulfur in coal

Chemical Methods

Chemical Comminution

- Coal is treated with ammonia solution resulting in selective breakage for mineral liberation
- 80-90% less pyritic sulfur
- 50-60% less ash.
- No organic removal

Magnex Process

$$FeS_2 + Fe(CO)_5 \longrightarrow 2Fe_{1-x}S + 5CO$$

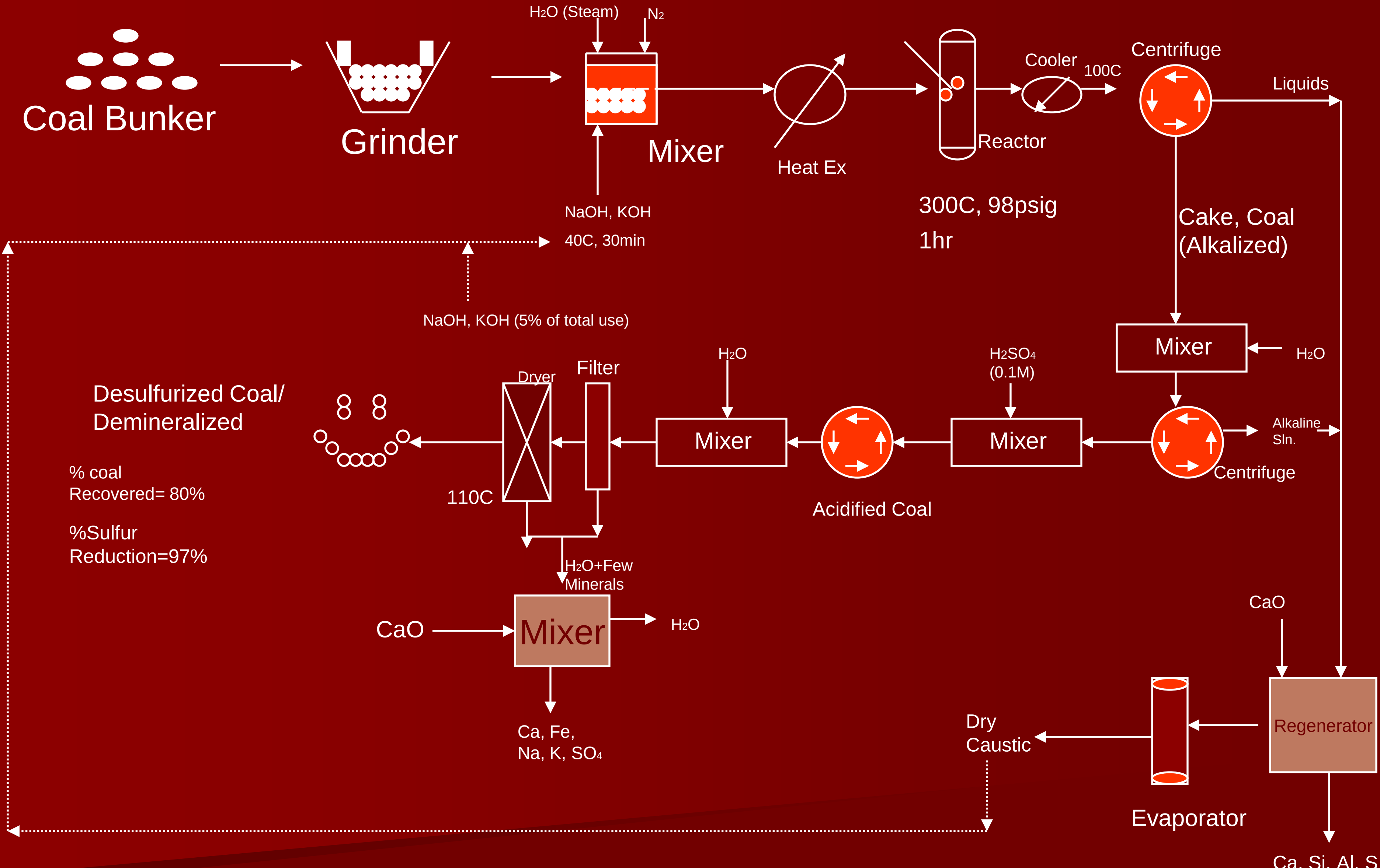
$$\text{Minerals} + Fe(CO)_5 \longrightarrow \text{Fe.Minerals} + CO$$

- Magnex process uses a chemical reaction to convert weakly magnetic pyrite and nonmagnetic mineral into paramagnetic material
- No organic removal

Chemical Methods

Molten Caustic Leaching

- Molten caustic leaching (MCL), uses strong bases at high temperatures to dissolve sulfur off of coal
  - Common bases: $NaOH$, KOH
- Pyritic sulfur released at 150˚C
- Organic sulfur released is released at 200˚C
- Removal:
  - 90-95% pyritic sulfur
  - 70-90% organic sulfur
  - 90-99% of ash.



Cost of processing coal = $21.05/ton

Diagram 1: Molten Caustic Leaching Process

Chemical Methods

Oxydesulfurization

- Uses high temperature and pressure along with steam and air to remove sulfur from coal
- Takes place in a fluidized bed reactor
- Removes 70-90% of total sulfur in coal
- Main advantage is the use of air over chemicals

Process Flow Diagram

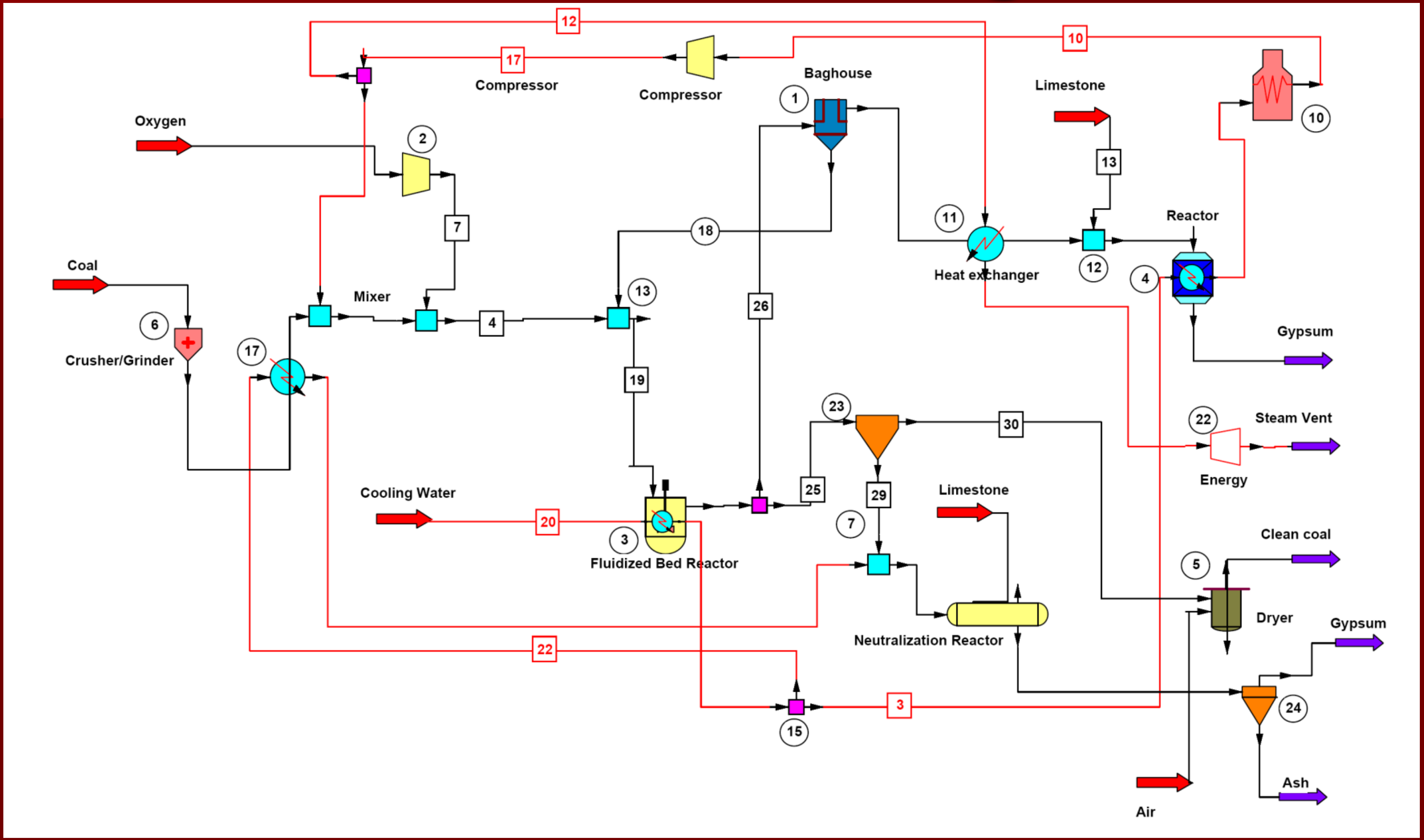


Diagram 2: Oxydesulfurization Process

Simplified Process Flow Diagram

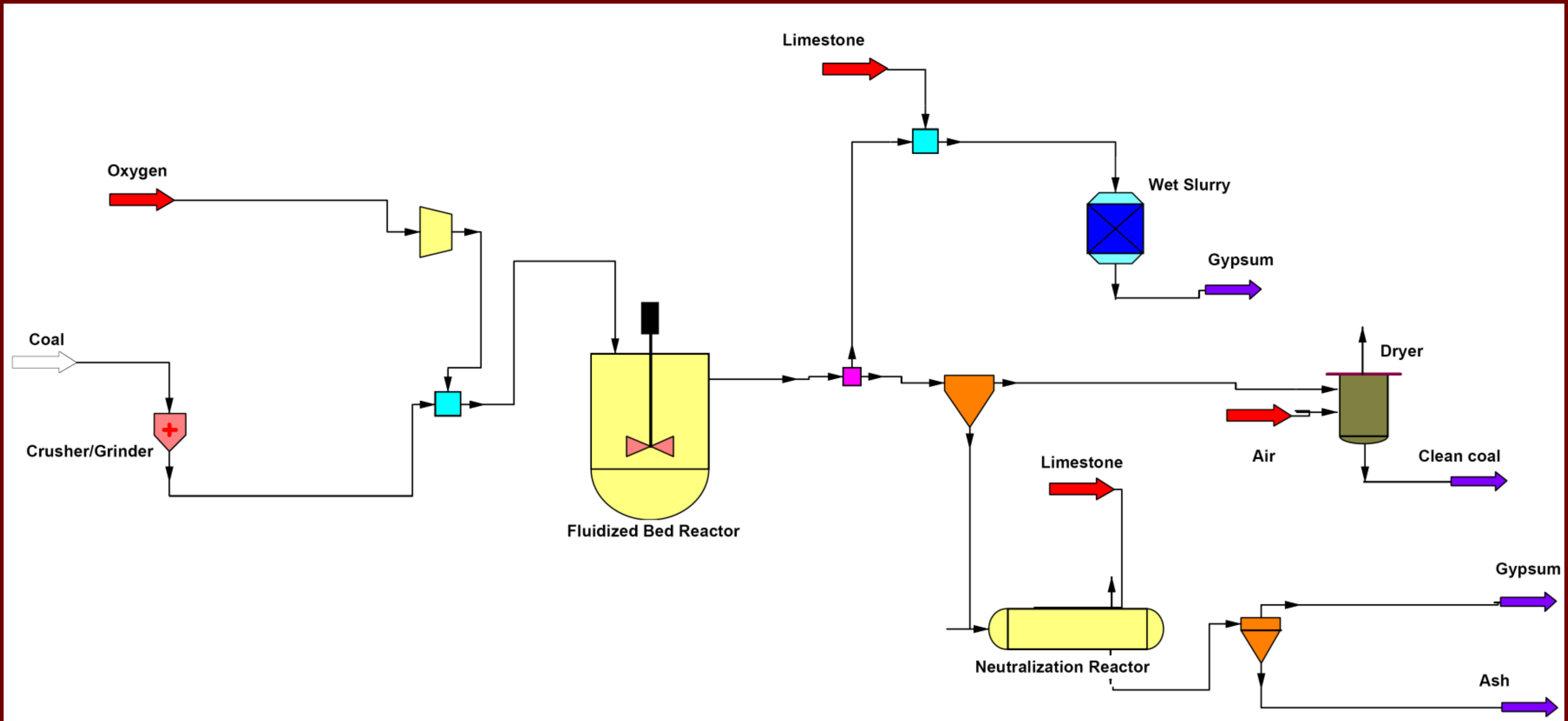


Diagram 3: Simplified Oxydesulfurization Process

Main Reactor (Fluidized Bed)

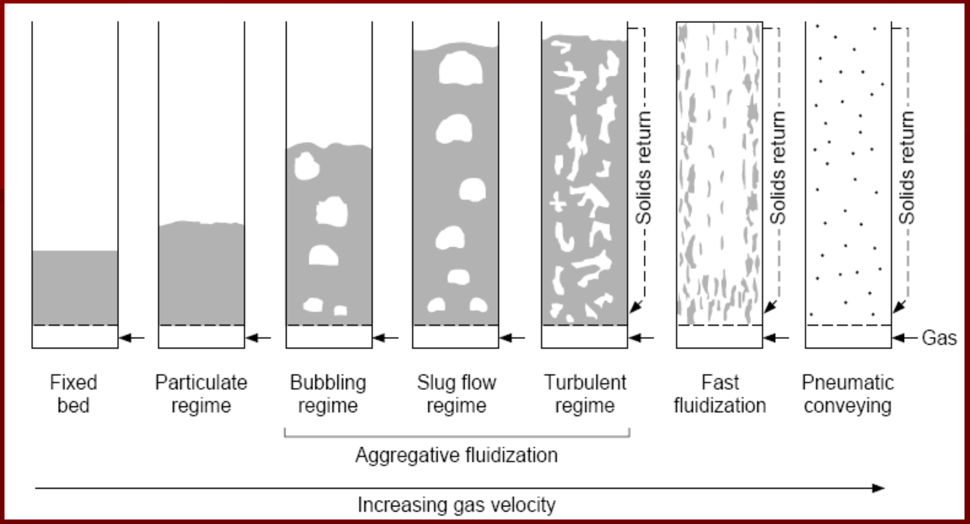


Image 3: Fluidization Regimes- Perry's Handbook, Ch17 pg 4

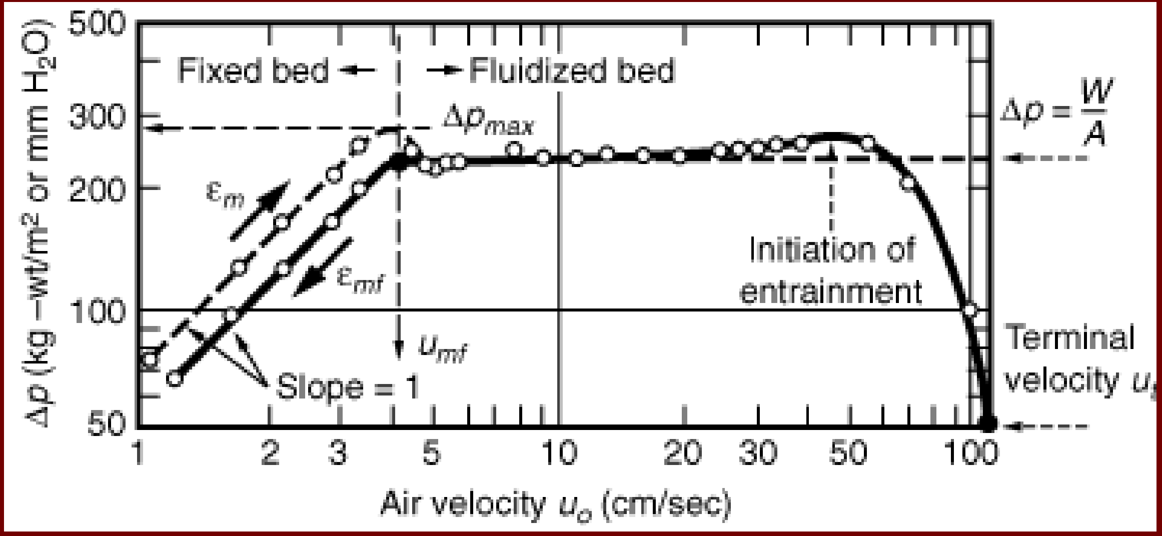


Image 4: Fluidization Graph - Kunii & Levenspiel *Fluidization Engineering*

- Pressurized gaseous medium of air and steam passes through coal particles
- Oxygen binds with sulfur on coal and is removed as SO2

Calculations

- U_{mf} - Minimum fluidization velocity
  - Calculated using correlation by Wen and Yu
  - Takes into account particle size distribution and spherocity

$$U_{mf} = \frac{\mu \mathrm{Re}_{mf}}{\rho_f d_p}$$

$$\frac{\Delta P}{h} = \rho_g U^2 \left[\frac{150(1-\varepsilon)}{\mathrm{Re}_d \, \psi} + \frac{7}{4} \right] \frac{1-\varepsilon}{\psi d_p \varepsilon^3}$$

$$\mathrm{Re} = (1135.7 + 0.0408 * Ar)^{0.5} - 33.7$$

$$Ar = \frac{d_p{}^3 \rho_f (\rho_s - \rho_f) g}{\mu^2}$$

Calculated Values:

$$U_{mf} = 33 cm/s$$

$$\mathrm{Re} = 62.4$$

$$Ar = 1.06x10^7$$

$$\Delta P = 1.49 psi$$

Reactor Size:

$$A = \frac{weight * gravity}{pressure} = 60.59 m^2$$

$$r = 4.6m$$

$$h = 8m$$

Perry's Handbook, Ch17 pg 4

Calculations (Kinetics)

Pyritic Sulfur

$$FeS_2 + 2O_2 \longrightarrow FeSO_4 + S$$

$$FeS_2 + \frac{7}{2}O_2 + H_2O \longrightarrow Fe^{2+} + 2SO_4 + 2H^+$$

$$FeS_2 + \frac{15}{4}O_2 + \frac{1}{2}H_2O \longrightarrow Fe^{3+} + 2SO_4^{\ 2-} + H^+$$

$$FeS_2 + \frac{15}{4}O_2 + 2H_2O \longrightarrow \frac{1}{2}Fe_2O_3 + 4H^+ + 2SO_4^{\ 2-}$$

$$-r_{FeSO_2} = K_p C_{FeS_2}^{\ \ 2}$$

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$$\frac{dC_{ps}}{dt} = -K_p C_s^{\ 2}$$

$$r_{FeS_2} = \sum_{i=1}^{4} r_{i_{FeS_2}} = -4K_p C_{FeS_2}^{\ \ 2}$$

$$K_p = 1.14X10^4 * \exp\left[\frac{-46.5X10^6 \frac{J}{kmol}}{RT}\right]$$

Modeled as a batch reactor:

% Desulfurized Pyritic Sulfur = 99.5%

Calculations

Elemental sulfur

$$S + \frac{3}{2}O_2 + H_2O \longrightarrow 2H^+ + 2SO_4^{\ 2-}$$

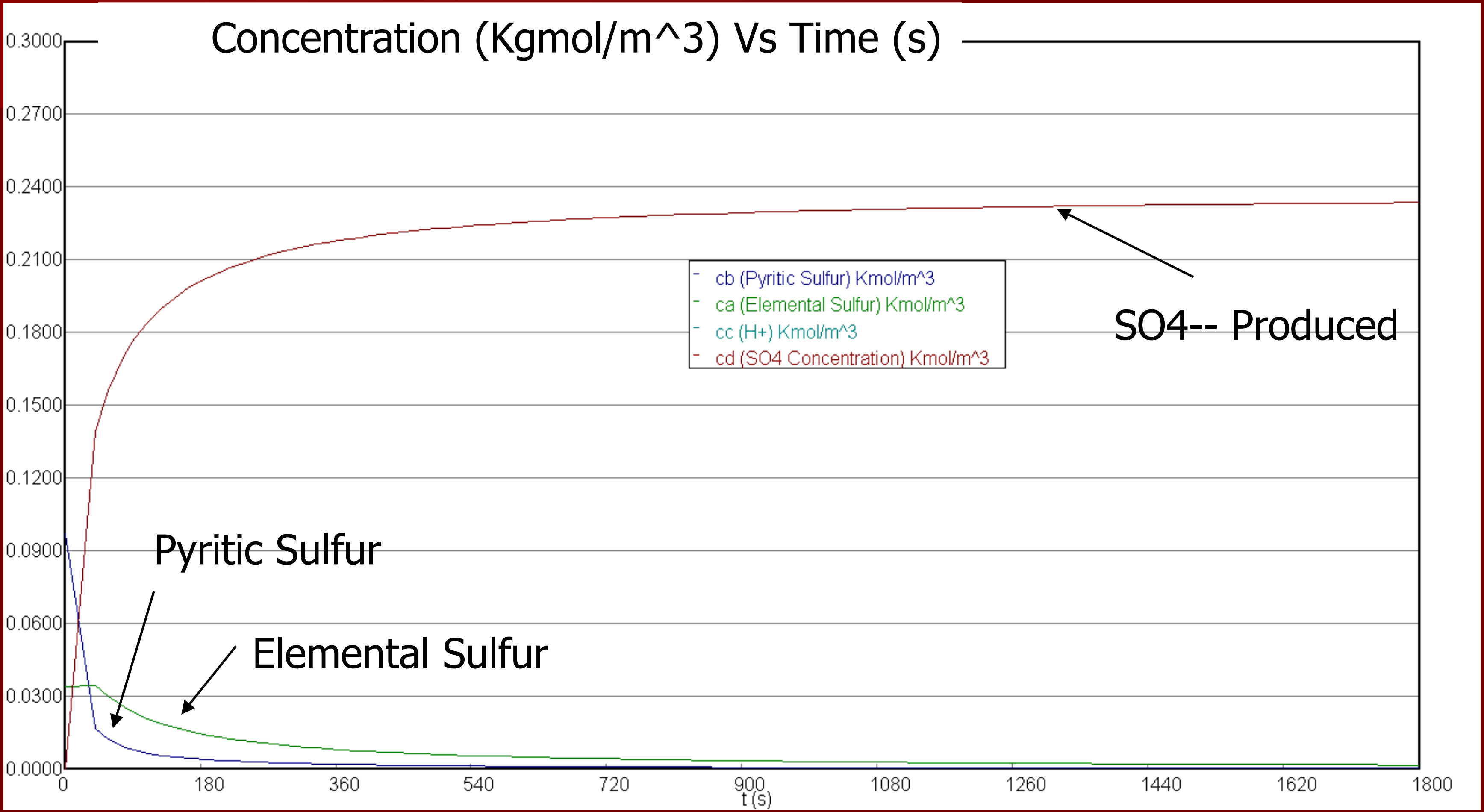
$$\frac{r_{5S}}{-1} = \frac{r_{5O_2}}{-\frac{3}{2}} = \frac{r_{5H_2O}}{-1} = \frac{r_{H^+}}{2} = \frac{r_{SO_4^{\ 2-}}}{2}$$

$$\frac{dC_{elemS}}{dt} = -K_p C_s^{\ 2}$$

Modeled as a batch reactor:

% Desulfurized Elemental Sulfur = 94.7%

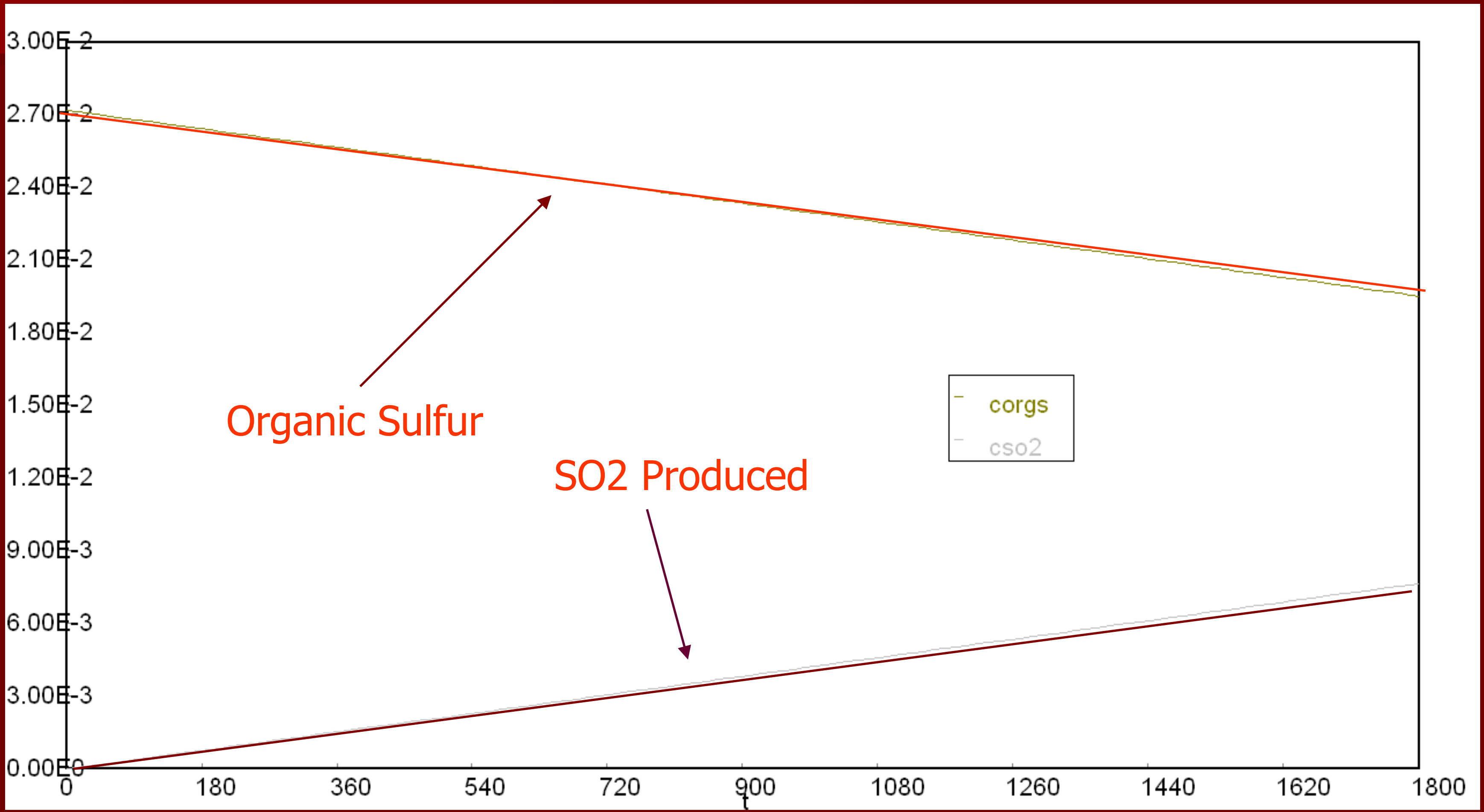
Inorganic Sulfur & Elemental Sulfur



Graph 1: Inorganic and Elemental Sulfur Change in Concentration Over Time

Organic Sulfur

Organic Sulfur (kgS/kgcoal), SO2 production (kgSO2/Kgcoal)



Graph 2: Organic Sulfur and SO2 Change in Concentration Over Time

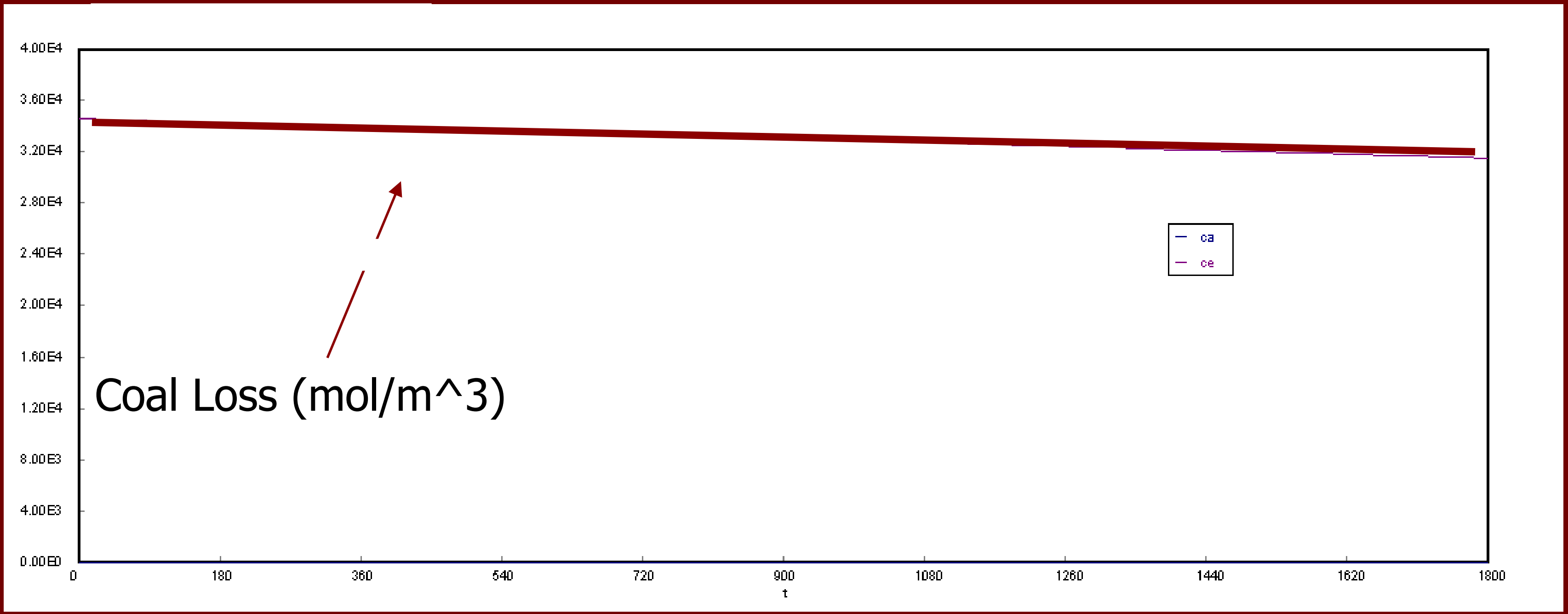
Calculations

Oxidation of Carbon

$$\frac{dC_c}{dt} = -K_0$$

$$K_0 = 2.88X10^{37}\exp\left[\frac{-380X10^6 \frac{J}{kmol}}{RT}\right] \left[\frac{mol}{m^3.s}\right]$$

$$\%C\_recovered = \frac{31670\frac{mol}{m^3}}{34640\frac{mol}{m^3}} * 100 = 91.42\%$$



Time (s)

Economic Analysis

Production Basis: 554,400 tons/year clean coal

Cost of Cleaning Coal (includes cost of raw coal)	$88/ton
Total Sales	$98/ton
Pre-tax Earnings	$10/ton
Total Cleaning Cost	$48,902,410/year
Total Sales	$54,070,290/year

Economic Analysis

Total Cost of Equipment	$6,656,840
Total Capital Investment	$14,346,725
Pre-tax Earnings	$5,167,879
Return on Investment	23%
Payback Period	2 years

Safety Analysis

- Critical aspects:
  - High pressure considerations for reactor design
  - Operating pressure maintenance to prevent combustion
  - Fluidized bed effluent is harmful to operators
  - Bleed valve on fluidized bed necessary to unload coal safely
- Non-critical aspects:
  - Water cleansing and disposal
  - Periodic acid neutralization in the entire system to prevent corrosion in points of accumulation

Feasibility of Process

- Method is feasible, but not mainstream
- Meets EPA Standards – 86% sulfur removal
- Necessary for higher quality steel production
  - Successful ash and sulfur removal drastically improves product quality
  - Solid state of coke makes forms of post-combustion undesirable
- Organic sulfur removal can still be improved without significant changes in operating conditions

Acknowledgements

- Professor Mohammed Reza Ehsani
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Questions?