Fourth Annual Conference on Carbon Capture & Sequestration

Developing Potential Paths Forward Based on the Knowledge, Science and Experience to Date

Session Title:

Advanced Conversion/Capture Concepts

CO_2 sequestration with ex-situ brine solutions and pH enhancing materials

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U.S. DOE NETL

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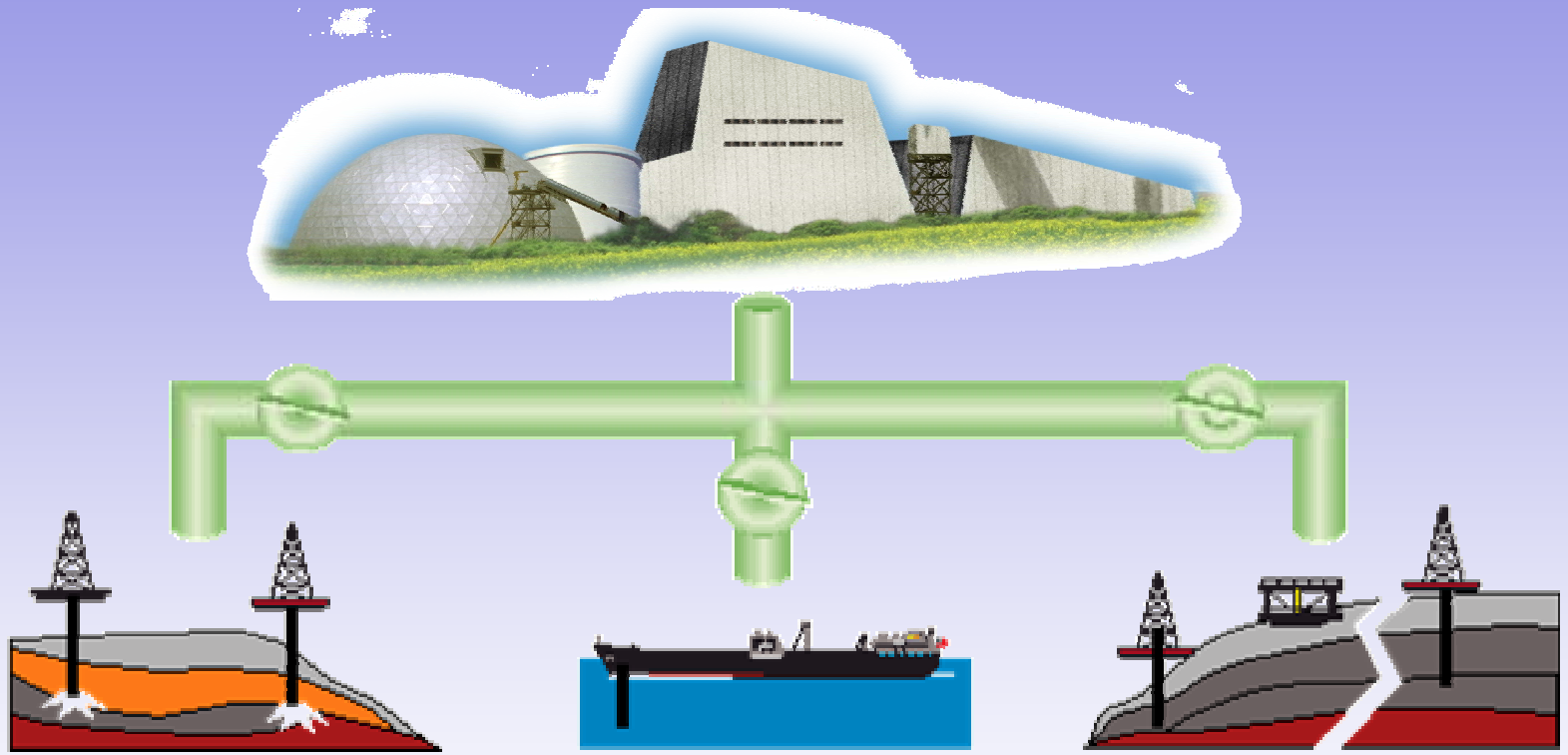
Direct Sequestration

Capture and Disposal of CO_2



Unmineable Coal Seams

Deep Ocean Injection

Depleted Oil / Gas Wells, Saline Aquifers

CO_2 can be trapped in saline aquifers

- **Hydrodynamic trapping :** traps the CO_2 into flow systems for geological periods of time
  - main concern : CO_2 leakage through imperfect confinement.
- **Solubility trapping :** traps the CO_2 in aqueous component (H_2CO_3, HCO_3^-, $CO_3^=$,and $CO_{2(aq)}$)
  - limited capacity
- **Mineral trapping :** convert CO_2 to carbonate minerals (e.g., calcite, dolomite, siderite) - extended time required for the formation of carbonates

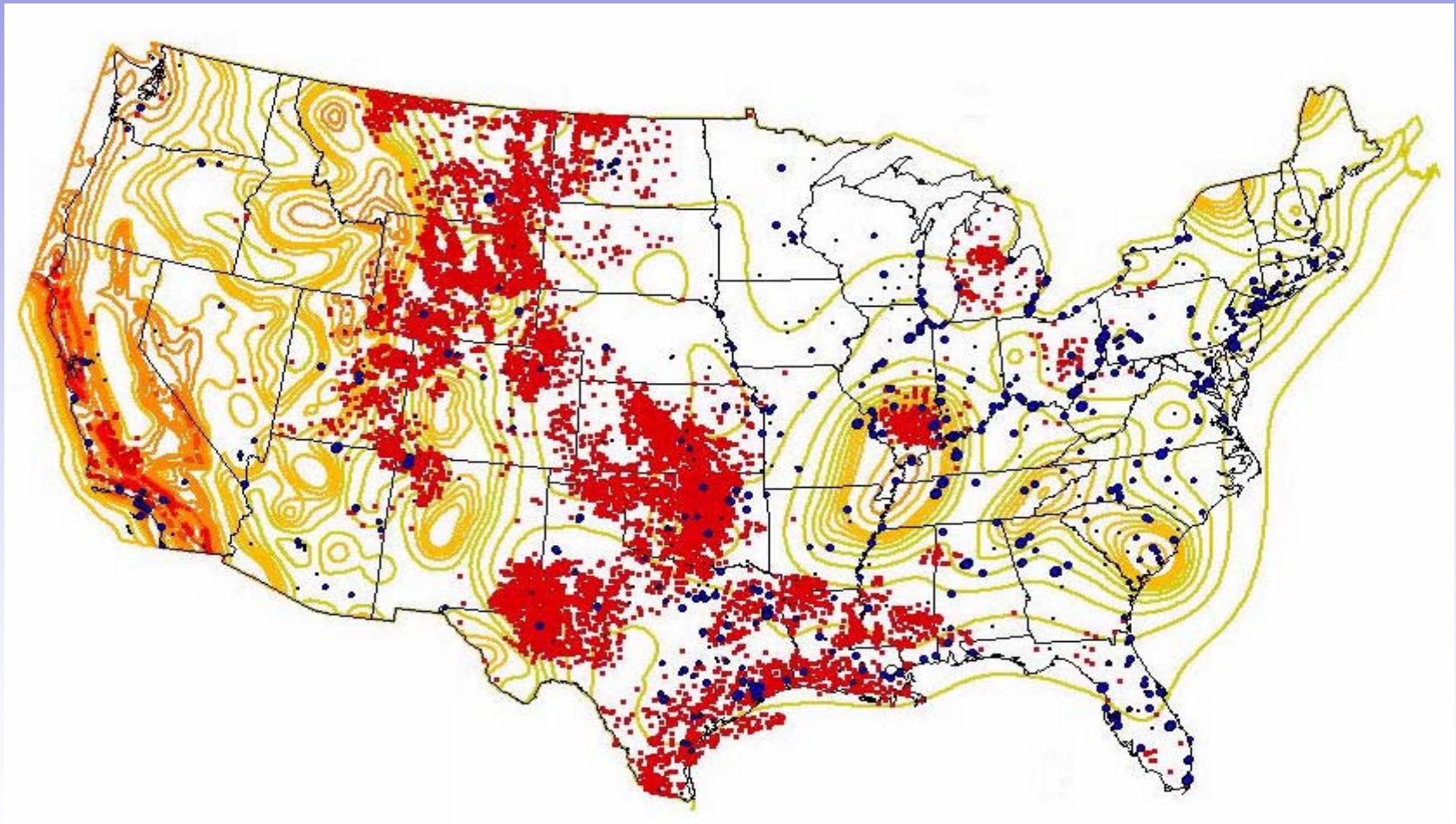
$$\mathbf{Ca^{++} + CO_3^{\,2-} \longrightarrow CaCO_3 \text{ (calcite)}}$$

$$\mathbf{Ca^{++} + Mg^{++} + 2\,CO_3^{\,2-} \longrightarrow CaMg(CO_3)_2 \text{ (dolomite)}}$$

$$\mathbf{Fe^{++} + CO_3^{\,2-} \longrightarrow FeCO_3 \text{ (siderite)}}$$

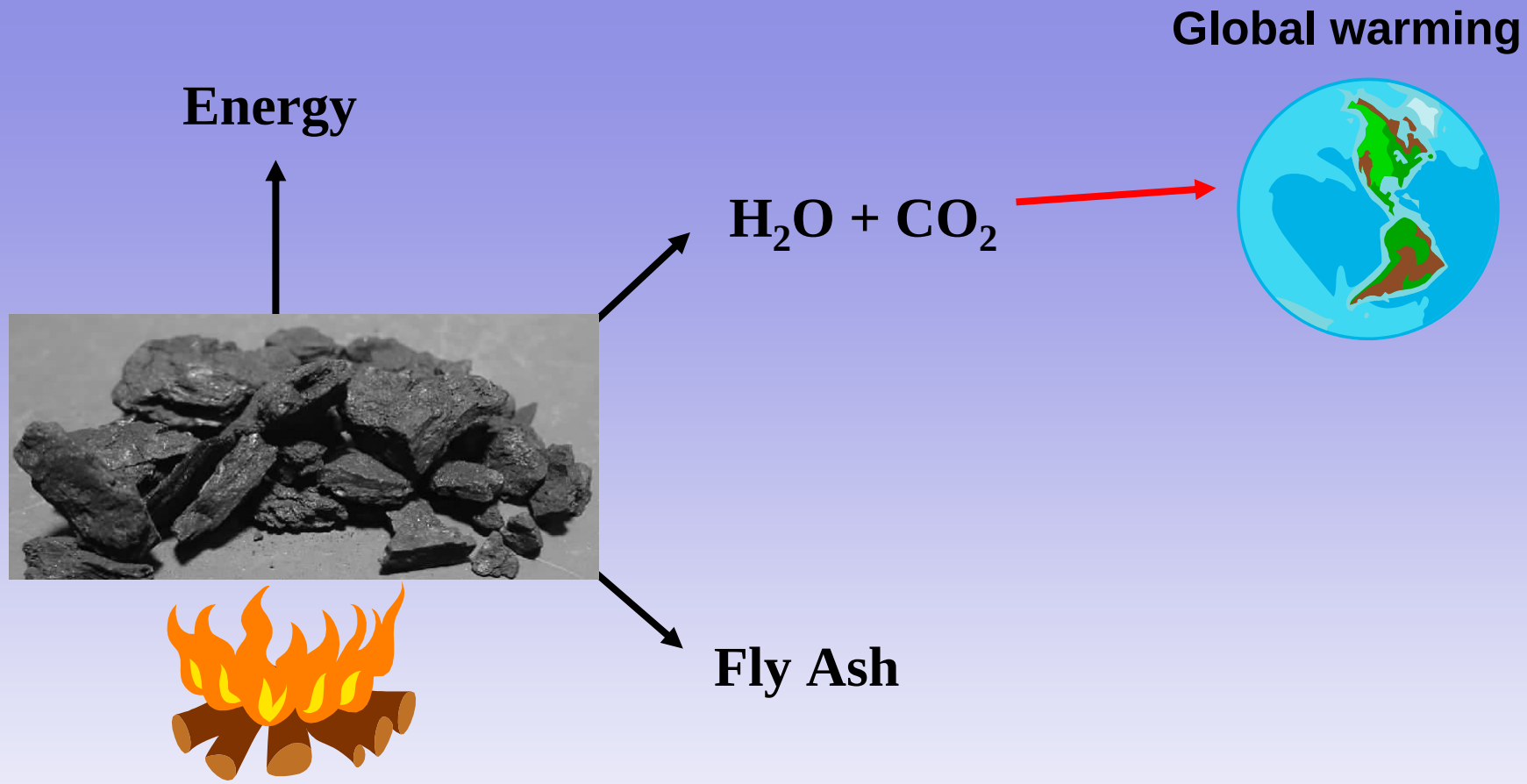
$$\mathbf{Mg^{++} + CO_3^{\,2-} \longrightarrow MgCO_3 \text{ (magnesite)}}$$

POWER PLANT LOCATIONS
BRINE WELL LOCATIONS
SEISMIC POTENTIAL



Saline Wastewater

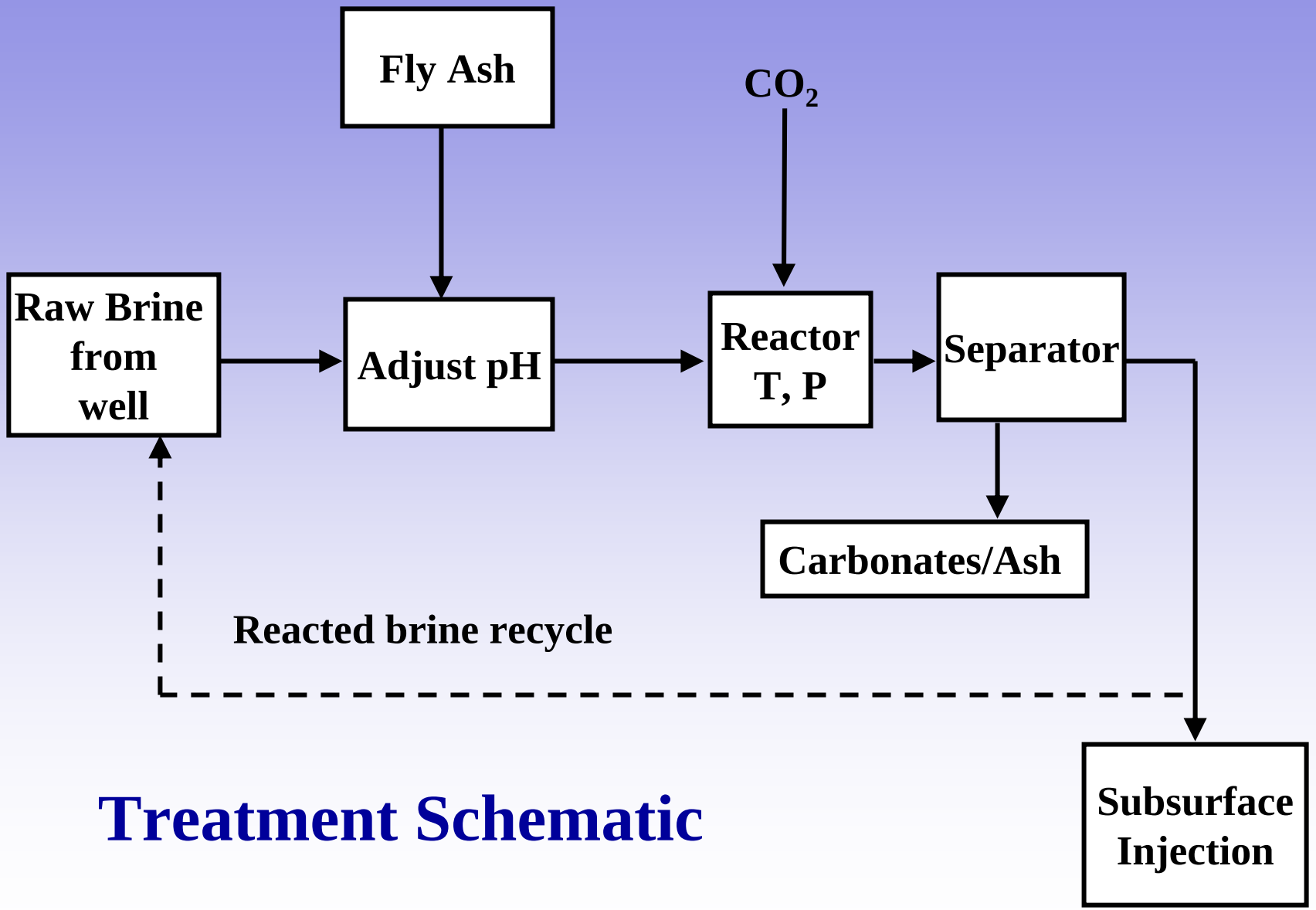
- **20-30 billion barrels/year of saline wastewater with the production of oil and gas in the USA.**
- **65% reinjected into reservoirs**
- **35% is treated/discharged into surface water**
- **Treatment cost of between $0.15 to 3.00/barrel reported**
- **Some saline wastewater are high in Ca, Mg, and Fe**
- **Mineral carbonate formation occurs at pHs of 7.8 or higher**
- **Most brines have a pH between 3 and 5, thus carbonate will not form even with presence of CO_2**



- **121 Million tons of combustion byproduct generated per year - only 33% used**
- **Some fly ashes (Class C ashes) have high CaO and MgO.**
- **FGD ash also has high CaO**
- **These ashes are alkaline in nature**

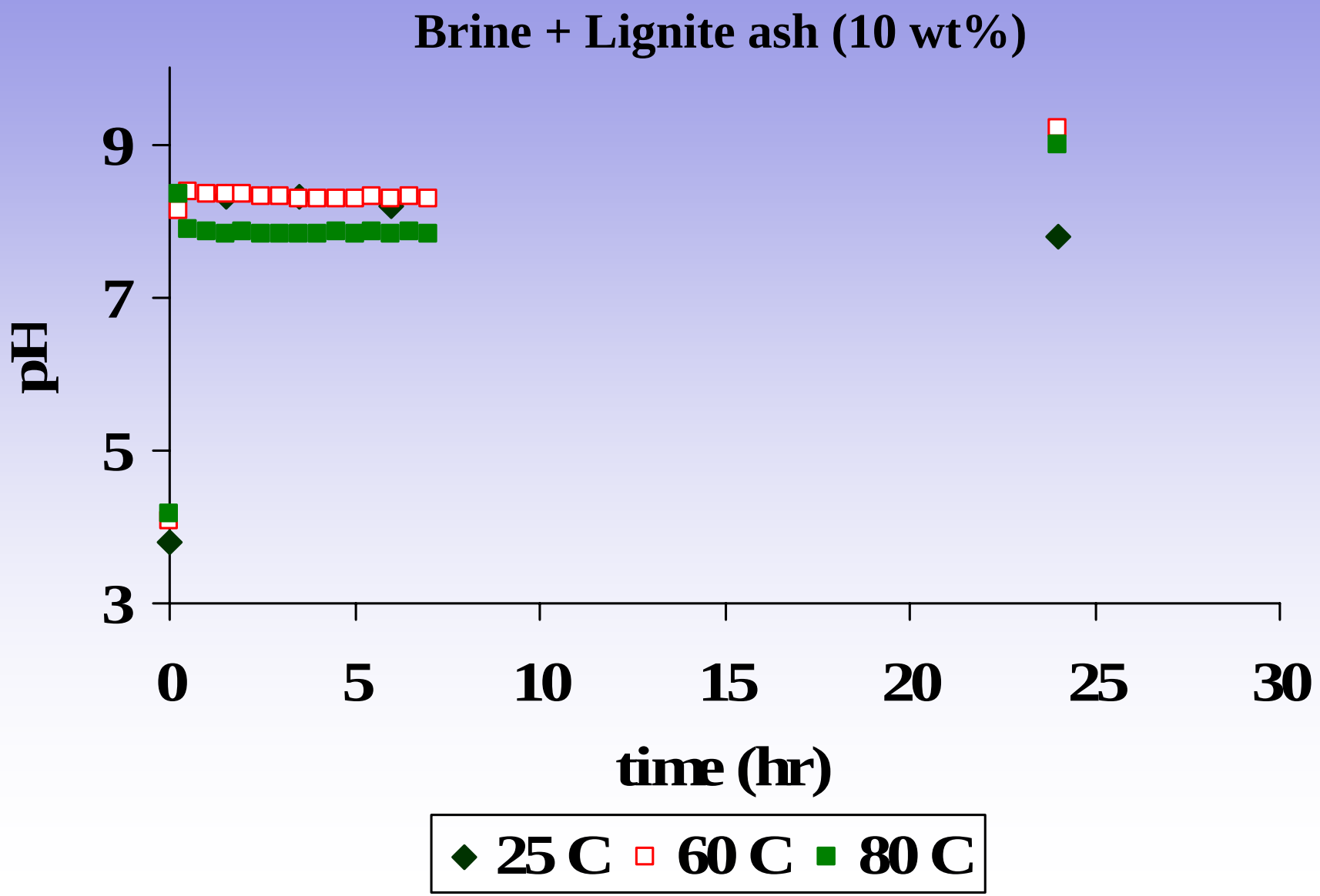
Treatment Concept

- **Brine + fly ash + CO_2 for CO_2 sequestration**
- **Fly ashes can be used as caustic material to adjust brine pH**
- **Ca, Mg, and Fe in brine as well as Ca/Mg from fly ash react with CO_2 to produce mineral carbonates**
- **The reacted brine can be reinjected into the ground for further trapping of CO_2**

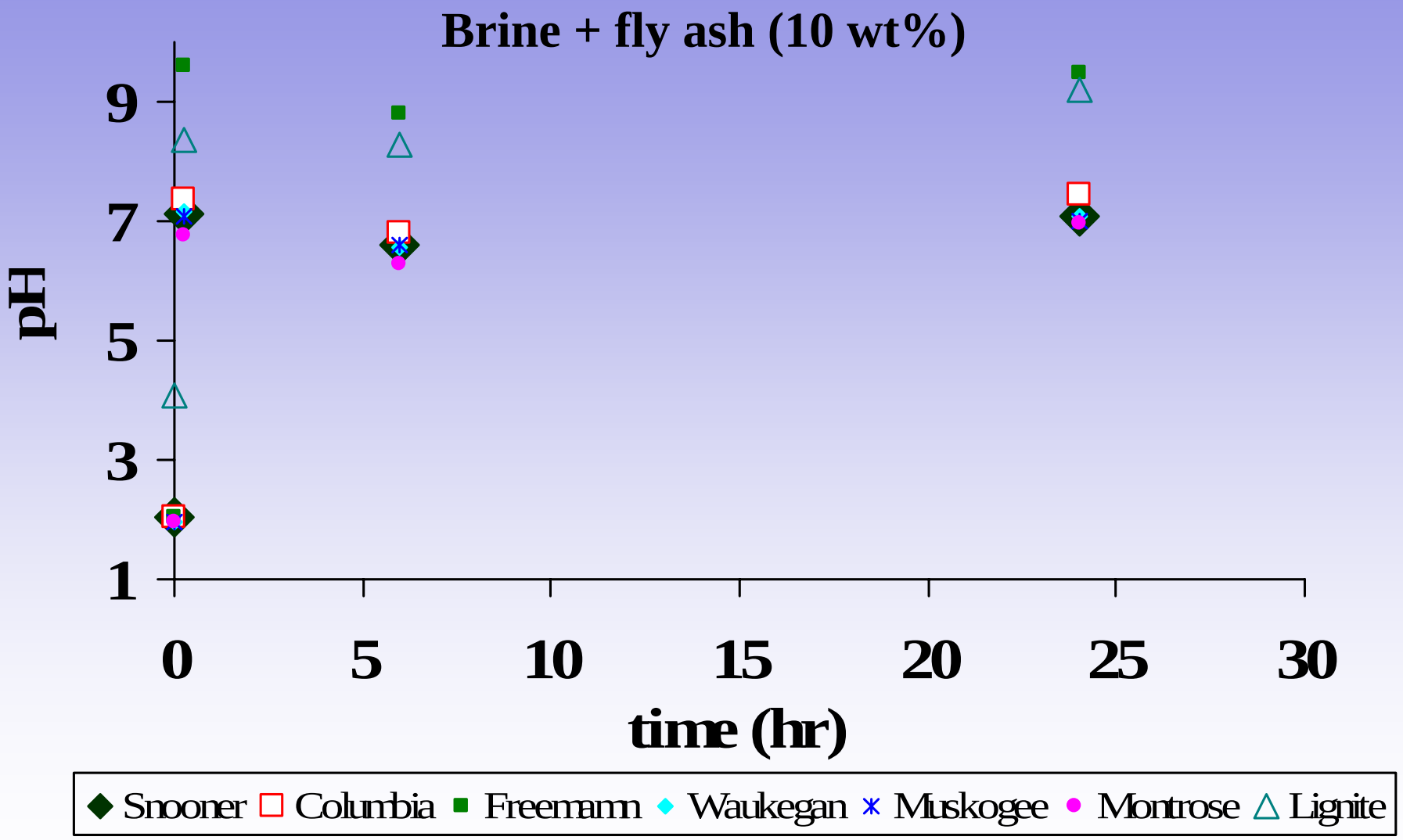


Treatment Schematic

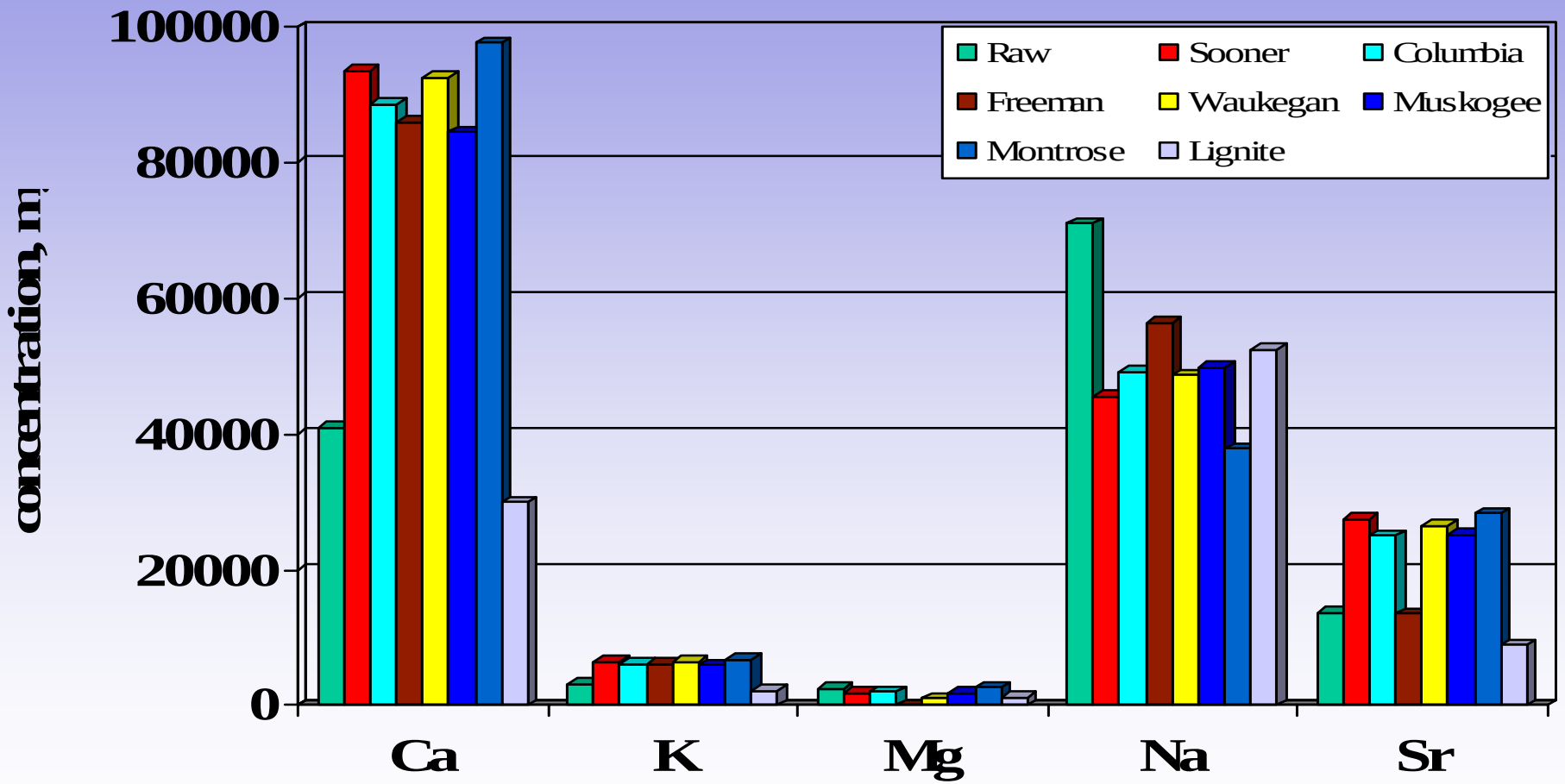
Brine pH adjustment as a function of temp.



Brine pH adjustment using various ash sources



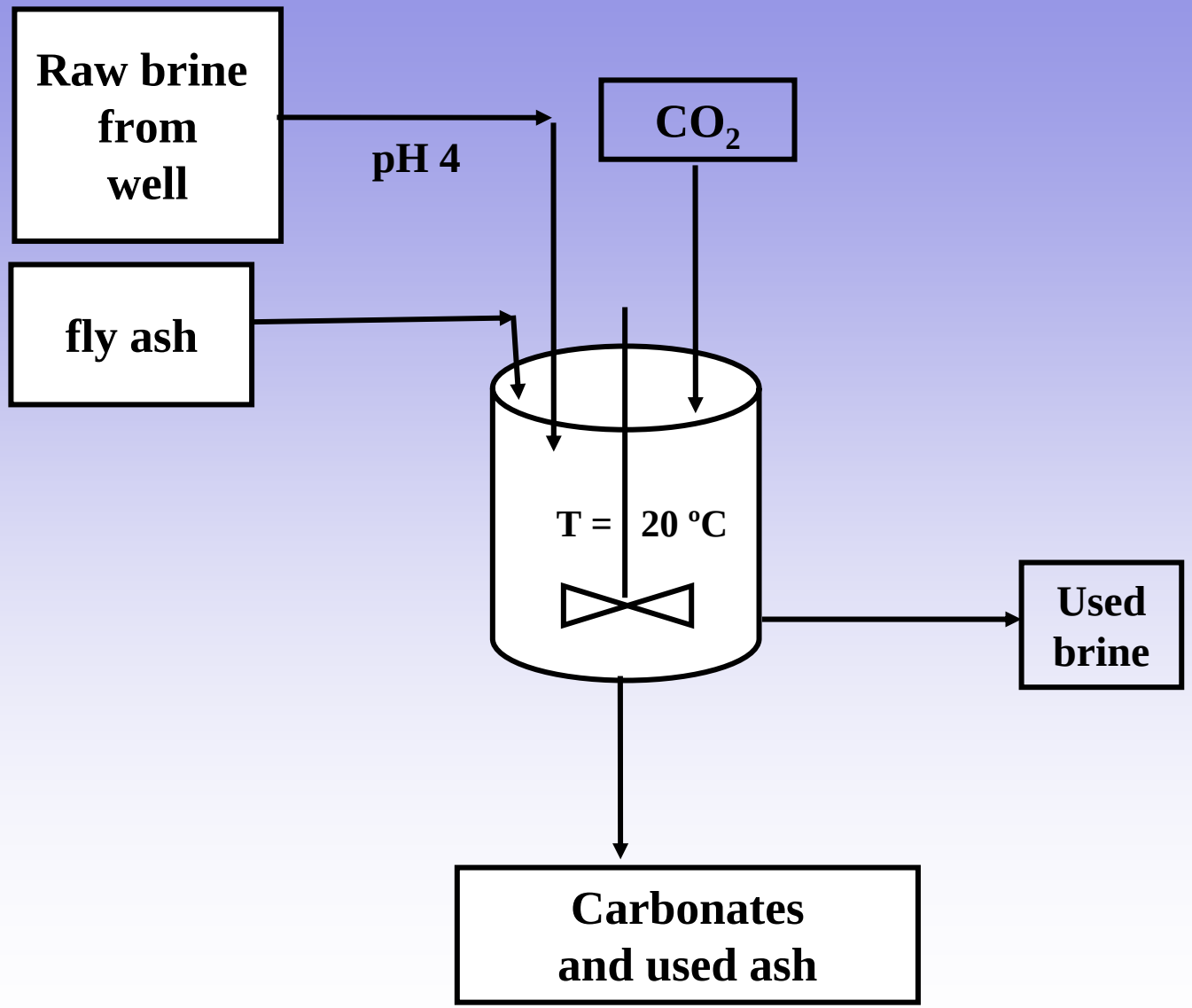
Reactant Mixtures:
Oriskany Brine and 10 wt. % Ash



Experimental study

- **Brines tested (Oriskany Formation, Indiana, PA)**
- **Caustic material - lignite fly ash, Columbia fly ash, Freeman coal ash (10 wt. % solids)**
- **1/2 liter and 1 liter autoclave**
- **Typical reaction conditions:**
  - **25 °C, 200 psi CO_2, 1 hr**

Treatment concept using fly ash



Representative Experiment (Columbia lignite/brine/CO_2 sequestration)

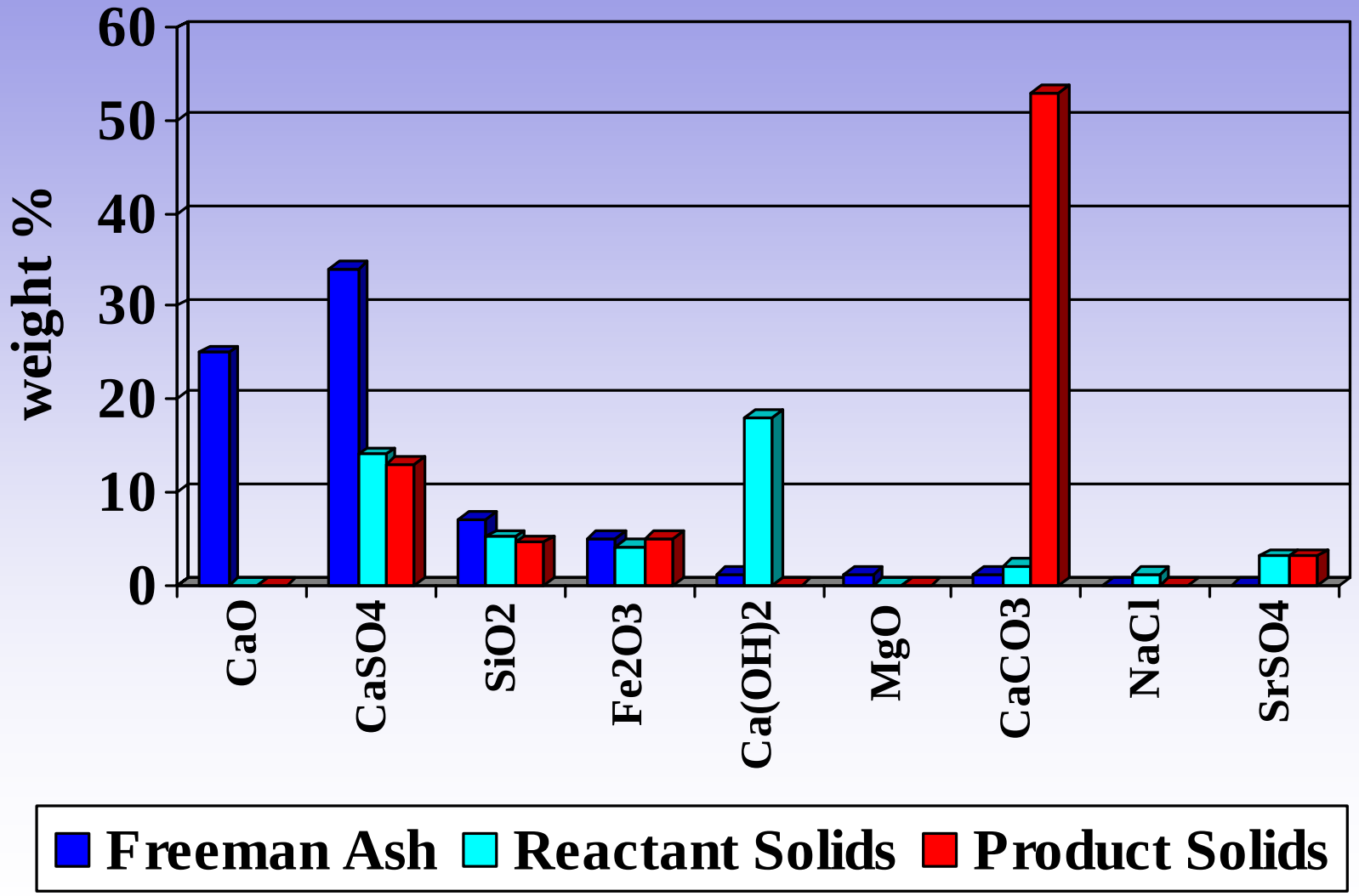
- 10% lignite in brine for 1 hr (pH 3 to 8.84)
- Brine + CO_2 at 20 ^oC with 200 psi of CO_2 for 2 hours
- Consume 0.306 moles CO_2/liter reactant
- Solid weight gain 9.94 grams/liter reactant
- 33% $CaCO_3$, 3% Fe_2O_3, 5% FeS and 2% NaCl product

Fly ash alone with brine can sequester CO_2 in the form of carbonate

Oriskany Brine + Freeman FGD Byproduct (10 wt%)

25 ºC, 200 psi CO_2, 1 hr,

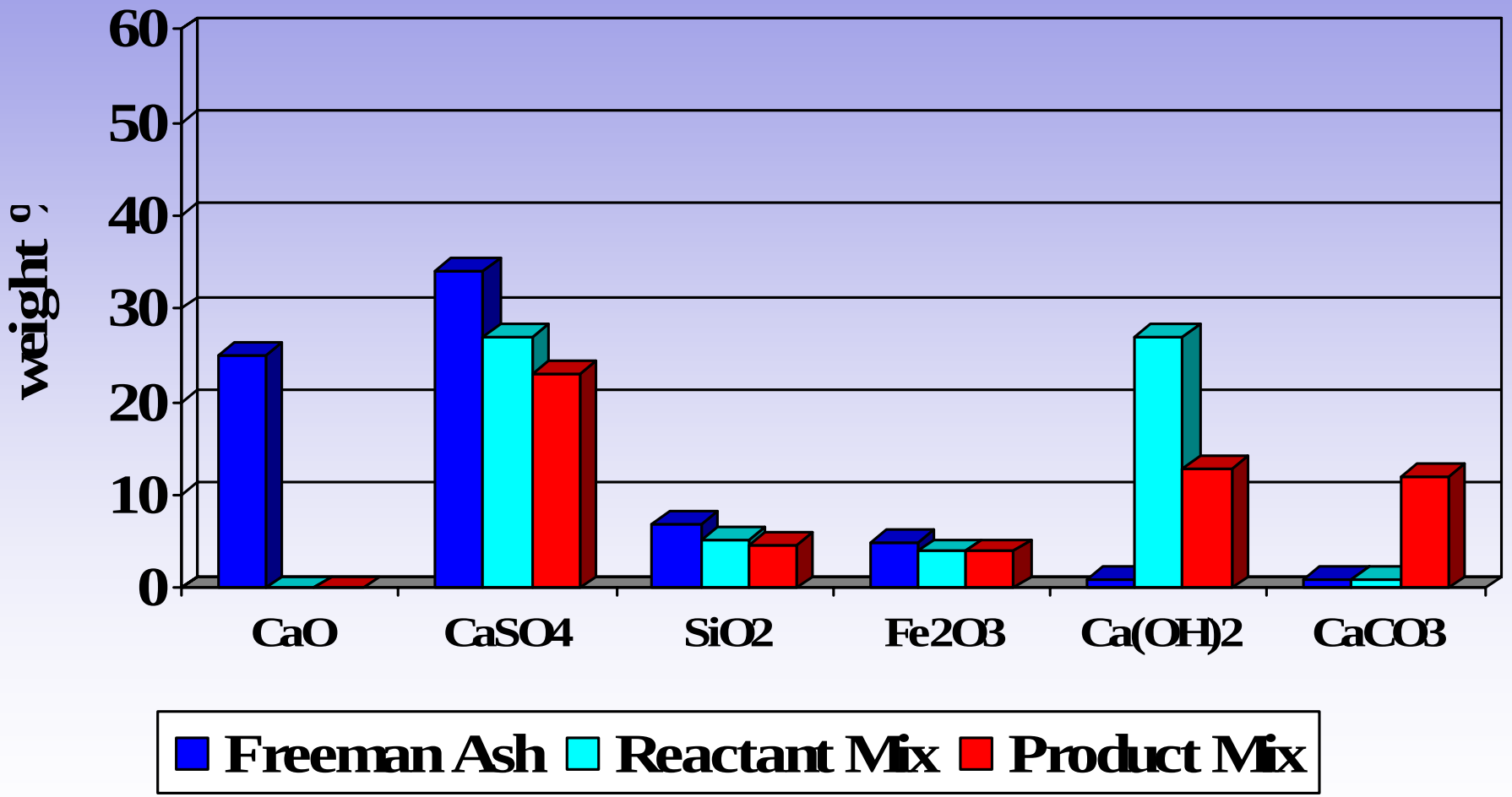
0.533 mole/L CO_2, weight gain 13.8 g/L



Water + Freeman FGD ash 10 wt%

25 °C, and 200 Psi CO_2, 1 hr

0.53 mole CO_2/liter, weight gain 8.8 g/liter



FGD ash alone with brine can sequester CO_2 in the form of $CaCO_3$. The Ca from brine further enhancing the amount of $CaCO_3$ formed

Summary

- **Demonstrated the feasibility of using CaO-rich industrial byproduct as the caustic material for brine carbonation**
- Total Sequestration and Mineral Trapping Capacity:
  - Lignite/Brine/CO_2 - 0.306 M CO_2, 10.7% mineral trapping as $CaCO_3$
  - FGD/Brine/CO_2 - 0.533 M CO_2, 13.2% mineral trapping as $CaCO_3$
  - FGD/H_2O/CO_2 – 0.530 M CO_2, 1.83% mineral trapping as $CaCO_3$
- **The reaction conditions are mild (20 ºC, 200 psi of CO_2 within hours)**
- **Process achieves formation of $CaCO_3$ for the permanent sequestration of CO_2**
- **Ca-bearing brine addition promotes precipitation of $CaCO_3$**
- **Combination of solubility and mineral trapping of CO_2 for longer term sequestration of CO_2**

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Questions?

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