Metrics for Screening CO₂ Utilization Processes

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> U.S. Department of Energy National Energy Technology Laboratory Carbon Storage R&D Project Review Meeting Developing the Technologies and Infrastructure for CCS August 20-22, 2013

Presentation Outline

- NETL's Carbon Storage Program
- Introduction of the metrics
- Review of the case study technology
- Application of metrics to the case study technology
- Discussion of metrics interpretation and grouping

NETL Carbon Storage Program

- The Carbon Storage Program contains three key elements:
 - Infrastructure
 - Global Collaborations
 - Core Research and Development:
 - Monitoring, Verification and Accounting (MVA)
 - Geologic Storage
 - Simulation and Risk Assessment
 - CO₂ Utilization

NETL Carbon Storage Program

- This analysis supports the CO₂ Utilization Focus Area of the DOE-NETL Carbon Storage Program for use in screening current and future utilization technologies:
 - Cement
 - Polycarbonate Plastics
 - Mineralization
 - Enhanced Hydrocarbon Recovery

Screening Metrics

- Developed a set of 12 metrics for use in screening utilization technologies, grouped into 5 categories:
 - Performance Metrics:
 - CO₂ Utilization Potential
 - CO₂ Utilization Efficiency
 - CO₂ Utilization Intensity
 - Energy Utilization
 - CO₂ Integration Reaction Rate

Screening Metrics

• Cost Metrics:

- Cost per Ton CO₂ utilized
- Product Marketability
- Incremental Cost Reduction

• Emissions Metrics:

- CO₂ Emissions Reduction
- CO₂ Avoided Potential
- Market Metric:
 - Product Supply-Demand
- Safety Metric:
 - Relative Safety and Environmental Benefits

- Technology in development targets (1) production of a Portland Cement substitute, and (2) utilization of CO₂ in carbonation chemistry as a binding phase
 - Traditional Portland Cement production:

 $5CaCO_3 + 2SiO_2 \rightarrow 3CaO \bullet SiO_2 + 2CaO \bullet SiO_2 + 5CO_2$

Tricalcium Silicate Die

Dicalcium Silicate

- Solidia Cement production:

 $CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2$ Solidia Cement

 Solidia Cement may also be mined as a naturally occurring mineral (Wollastonite)

• Cement processing comparison:

| | Traditional Portland Cement | Synthetic Solidia Cement |
|--|------------------------------|---|
| Cement Kiln Feed | 80 Limestone/20 Shale + Clay | 50 Limestone/50 Shale + Clay |
| Kiln Temperature (°C) | 1,500 | ~ 1,200 |
| Cement CO ₂ Emissions (ton CO ₂ /ton Cement) | 1.2 ¹ | 0.0 (natural Wollastonite) 0.77 (synthetic SC) |

¹Choate, William T. Energy and Emissions Reduction Opportunities for the Cement Industry. Columbia, MD : 2003.

- Utilization of CO₂ as a binding phase
 - Activation step for traditional Portland Cement Hydration
 - $2Ca_3SiO_5 + 7H_2O \rightarrow 3CaO \bullet 2SiO_2 \bullet 4H_2O + 3Ca(OH)_2 + 164.5 Btu$
 - Activation step for Solidia Cement Low-Temperature Solidification (LTS)

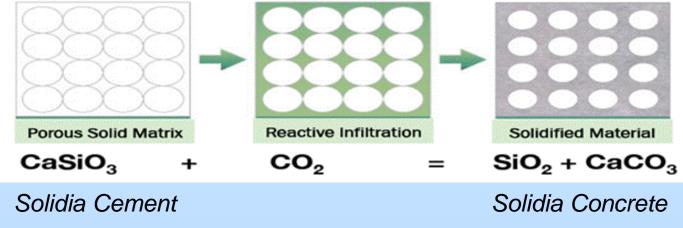
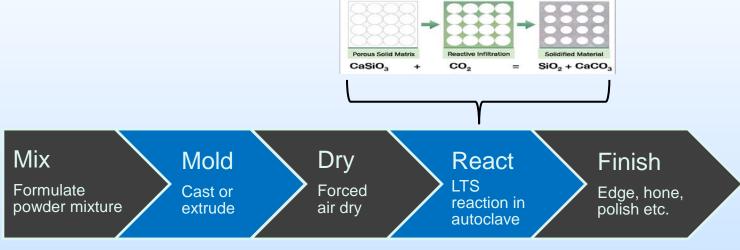


Image used with permission by Solidia

- Utilization of CO₂ as a binding phase (continued)
 - LTS reaction conditions:
 - Autoclave reaction vessel
 - Temperature: 90°C
 - Pressure: 20 psig
 - Reaction time: 19 hours
 - 65% carbonation translates to 0.25 tons CO₂/ ton cement (utilization)
 - Activation energy: 2.2 kcal/mol (7.87 Btu/mol)

• Complete system stages:



Images used with permission by Solidia

- Mixing, Molding, and Finishing stages mirror current concrete practice
- Dry and React stages total 22 hours

- Current performance/ path forward:
 - Total cycle emissions:
 - 0.77 (creation) 0.25 (carbonation) = 0.52 tons CO₂ / ton Solidia Concrete (net)
 - Mechanical strength properties compare/ exceed
 Portland Cement equivalent
 - Structural enhancements: increased thickness, rebar
 - Transition to 'flue gas-like' CO₂ source
 - Move towards optimized ambient LTS reaction conditions

Calculation Basis

- Reference case for CO₂ supply:
 - Supercritical PC plant: 550 MW-net
 - Conventional amine capture technology
 - Available CO₂: 4.5 M tons/year (85% on-stream factor)
 - Allows for CO₂ available at pressure; no required cost addition
 - Implicit assumption is co-location; no explicit assumption about CO₂ distribution network

• Production evaluation basis:

- 2011 U.S. Portland Cement production of 74.6 M tons
- Of concrete production: ~80% cast in place, ~20% precast
 - Assumption is 100% of concrete/cement market is accessible

Application of Metrics to Case Study

| Performance Metrics | Solidia |
|--|--|
| CO_2 Utilization Potential ^a – Amount of CO_2 utilized to meet product market demand relative to amount of CO_2 emitted or captured from the reference | 413% |
| CO_2 Utilization Efficiency – Amount of CO_2 utilized per unit amount of CO_2 fed to the utilization process | 24.6% |
| CO_2 Utilization Intensity – Amount of CO_2 utilized per unit amount of the desired product | 0.25 ton CO_2 / ton S Cement 0.28 ton CO_2 / ton S Concrete |
| Energy Utilization Metric – Net amount of energy required per unit amount of CO_2 utilized (kW-net/(ton CO_2/hr)) | _ |
| $\label{eq:constraint} \begin{array}{ c c c } \textbf{CO}_2 \ \textbf{Integration Reaction Rate} & - \ \textbf{Molar rate of CO}_2 \\ \textbf{utilized per unit of reactor volume (Ib}_{mol} \ \textbf{CO}_2 / \textbf{gal-yr)} \end{array}$ | - |

^a – Based on CO₂ available from 550 MW-net PC plant

Application of Metrics to Case Study

| Cost Metrics | Solidia |
|--|---|
| Product Marketability Metric – Cost to make a unit amount of the desired product relative to the market value of that product | <100% ª |
| Incremental Cost Reduction Metric – Incremental cost reduction of the new utilization process over the traditional process cost (percent) | _ |
| Cost/Ton CO₂ Utilized – Annualized capital and operating cost of the utilization system relative to the tons of CO_2 utilized annually (\$/ton CO_2) | _ |
| Emissions Metrics | Solidia |
| CO₂ Emission Reduction Metric – Amount of CO ₂ emitted per unit amount of product in the new utilization pathway relative to the traditional pathway | 35.8% Cement Only 56.7% for Concrete |
| CO_2 Avoided Potential ^b – Amount of CO_2 avoided by the proposed technology over the traditional technology relative to the amount of CO_2 emitted from the reference plant | 711% |

^a – Approximate, based on discussion with Solidia

^b – Based on CO₂ available from 550 MW-net PC plant

Application of Metrics to Case Study

| Market Metric | Solidia |
|--|------------------------------|
| Product Supply-Demand Metric – Percentage of market that may be satisfied with the proposed technology, considering feedstock or other requirements | 100% ª 60.3% ^b |
| Safety Metric | Solidia |
| Relative Safety and Environmental Benefits Metric – Ranking of the safety of raw materials and processing conditions, including any environmental benefits, of the new utilization pathway relative to those of the traditional pathway (using NFPA category hazard values 0-4; Improved, No Change, or Reduced, over traditional process) | Improved |

^a – Based on synthetic SC production

^b – Based on natural SC production (Wollastonite reserves)

Metric Interpretation and Use

- Use of metrics is dependent on the end goal of the developer:
 - Is the scale large and is the goal to maximize CO_2 utilization?
 - Focus on Utilization Efficiency/ Potential/ Intensity
 - Is the scale small and is the goal to produce a product capable of offsetting the cost of implementing capture?
 - Focus on Integration Reaction Rate/ Cost per ton CO₂ Utilized/ Product Marketability
 - Are the traditional process operating characteristics or chemistry such that improvements in process safety outweigh marginal product economic gains?
 - Focus on Relative Safety and Benefits

Acknowledgements

This study was performed under the Energy Sector Planning and Analysis contract for the United States Department of Energy (DOE Contract Number DE-FE0004001).

The authors wish to acknowledge the following individuals who contributed to the study:

Vladimir Vaysman, WorleyParsons James Simpson, WorleyParsons Richard Riman, Solidia Technologies

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Backup Slides

CO₂ Utilization Potential

 $CO2 \ Utilization \ Potential (\%) = \frac{tons \ CO2 \ utilized \ to \ meet \ market \ demand}{tons \ CO2 \ available \ from \ reference \ plant} \ x \ 100$

$$= \frac{18.6 M tons CO2 / year utilized}{4.50 M tons CO2 / year available} x 100$$

= 413%

• Equivalent to 4.1 of the reference plants' CO2 streams utilized

CO₂ Utilization Efficiency

 $CO2 \ Utilization \ Efficiency (\%) = \frac{tons \ CO2 \ utilized \ (in - out)}{tons \ CO2 \ fed \ to \ process} x \ 100$

$$= \frac{(145.0 - 109.3) M \text{ tons } CO2 / \text{year utilized}}{145.0 M \text{ tons } CO2 / \text{year fed to process}} x 100$$

• Based on a single pass of the process (no CO2 recycle)

CO₂ Utilization Intensity

CO2 Utilization Intensity =

tons CO2 utilized tons product produced

x % Carbonation

= <u>44.01 ton CO2</u> 116.16 ton Solidia Cement x 65%

= 0.25 ton CO2 / ton Solidia Cement

 $CO2 \ Utilization \ Intensity = \frac{tons \ CO2 \ utilized}{tons \ product \ produced} x \ \% \ Carbonation$

 $= \frac{44.01 \text{ ton } CO2}{100.08 \text{ ton Solidia Concrete}} \times 65\%$

= 0.28 ton CO2 / ton Solidia Concrete

CO₂ Emission Reduction

 $CO2 \ Emission \ Reduction (\%) = \frac{tons \ CO2 \ emitted \ in \ traditional \ - \ tons \ CO2 \ emitted \ in \ new \ pathway}{tons \ CO2 \ emitted \ in \ traditional \ pathway} x \ 100$ $= \frac{1.2 \ tons \ CO2 \ emitted \ in \ traditional \ cement} x \ 100$ $= \frac{tons \ CO2 \ emitted \ in \ traditional \ cement}{1.2 \ tons \ CO2 \ tons \ CO2 \ tons \ CO2 \ emitted \ in \ new \ pathway} x \ 100}{tons \ CO2 \ tons \ CO2 \ tons \ CO2 \ tons \ CO2 \ tons \ CO2 \ emitted \ in \ traditional \ pathway} x \ 100$ $= \frac{tons \ CO2 \ emitted \ in \ traditional \ - \ tons \ CO2 \ emitted \ in \ new \ pathway}{tons \ CO2 \ emitted \ in \ traditional \ tons \ CO2 \ emitted \ in \ new \ pathway} x \ 100$ $= \frac{tons \ CO2 \ emitted \ in \ traditional \ - \ tons \ CO2 \ emitted \ in \ new \ pathway}{tons \ CO2 \ emitted \ in \ traditional \ pathway} x \ 100$ $= \frac{tons \ CO2 \ emitted \ in \ traditional \ - \ tons \ CO2 \ emitted \ in \ new \ pathway}{tons \ CO2 \ emitted \ in \ traditional \ pathway} x \ 100$

= 56.7% for Solidia Concrete

CO₂ Avoided Potential

CO2 Avoided Potential (%) =

tons of CO2 avoided to meet market demandx 100tons of CO2 available from reference plantx 100

= <u>89.6 M tons PC CO2 emitted/year - 57.5 M tons SC CO2 emitted/year</u> x 100 4.50 M tons CO2 / year available

= **711%**

• Equivalent of 7.1 reference plants' CO2 streams avoided

Product Supply-Demand Metric

• Synthetic SC production can meet PC market production, thus Product Supply-Demand Metric is 100% (CO2 supply is not limiting)

Product Supply-Demand Metric (%) =

tons per year of product that can be produced tons per year of market demand for that product x 100

= <u>45.0 M tons / year of natural SC (Wollastonite)</u> x 100 74.6 M tons / year of PC production

= 60.3% based on limited Wollastonite reserves

Relative Safety and Benefits

• Example of Relative Safety and Benefits

- Traditional Process: Partial Oxidation of Propylene
- Proposed Process: CO₂ Reforming with Ethylene
- NFPA Feedstock Analysis:

| Category | Propylene | Ethylene |
|--------------|-----------|----------|
| Health Risk | 1 | 3 |
| Flammability | 4 | 4 |
| Reactivity | 1 | 2 |

0 – No Risk 4 – Very High Risk

• Cost:

| | Propylene (\$/ton) | Ethylene (\$/ton) |
|--------------|----------------------|----------------------|
| March (2012) | \$1,520 ¹ | \$1,010 ¹ |
| May (2012) | \$1,3201 | \$1,069 ¹ |

• **Result:** Ethylene feedstock poses higher Health and Reactivity risks, but the nature of the overall proposed process is safer, and ethylene provides an economic benefit as a starting material over propylene

Bituminous Baseline Case 12: SC PC

