Use of CCPs for Generating Carbon Offsets

by

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Reduce, reuse, and recycle for sustainable developments.

Minimize use of manufactured materials.

Maximize environmental benefits: clean air, clean water, and resource conservation.
Basic Approach

WASTE is wasted if you waste it, otherwise it is a resource. Resource is wasted if you ignore it and do not conserve it with holistic best practices and reduce societal costs. Resource is for the transformation of people and society.

Focus on turning brown fields into green fields – Opportunities for the Future.
Basic Approach

Recycle. Recycle as is.

Recycle without additional processing, (i.e., without adding any cost to it).

Avoided disposal leads to reduced GHGs.
Progression: 21st Century Solid Waste Management

Recycling, durable construction materials, sustainable infrastructures, sustainable management of resources (SMR), global climate change, reduced GHGs, improved air quality, CO2 reduction/sequestration/carbon offsets.
CLEAN AIR
CLEAN WATER
and
RESOURCE CONSERVATION
Spaceship Earth – La Bella Terra: Global Climate Change?
Production of one ton of portland cement releases approximately one ton of CO$_2$ and other greenhouse gases (GHGs) into the atmosphere. Therefore, for 2.2 billion tons of cement annually (2006), we produce 2.2 billion tons of GHGs (CO$_2$, water vapor, Methane, NOx, and CO).
Nitrous Oxide Emissions

For each ton of portland cement clinker, 3 to 20 lbs. of NOx are released into the atmosphere. Assuming 10 lbs of NOx per ton of clinker, this equals 11 million tons of NOx due to 2.2 billion tons of current (2006) clinker production.

Yomiuri Shimbun reported from Kobe, Japan that: “The Hyogo prefecture government (on Oct. 1, 2004) banned automobiles with emissions of nitrogen oxide (NOx) and particulate matter that exceed levels set in a law concerning these emissions from traveling in certain parts of the prefecture.”
Introduction

• Concrete is the world’s most consumed man-made product. World-wide about 18 billion tons of “concrete-equivalent” material is produced/year.

• To produce one ton of portland cement, 1.7 tons of raw materials are needed. Therefore each year, production of 2.2 billion tons of cement (2006) consumes 3.75 billion tons of raw materials.
Concrete is environmentally very friendly material.

As good engineers, we must use more of it in construction.
Portland Cement is not environmentally very friendly material.

As good engineers, we must reduce its use in concrete; and, we must use more of other cementitious materials.
Coal combustion products (CCPs) can be used to lower cement consumption, and, therefore, CO\textsubscript{2} & NO\textsubscript{x}, as well as water vapor and CO production.

CCPs can also facilitate the recycling of other industrial by-products, thereby conserving natural materials and reducing GHG emissions.
Need to Reduce CO$_2$ Emissions from Cement Clinker Production

- More efficient cement clinker production
- Reduce the production of cement clinker
  - Increased use of other cementitious materials (OCM)
  - Increased use of organic admixtures
SOLUTION

As good engineers, we must use more environmentally friendly other cementitious/pozzolanic materials in concrete.

Use fly ash (CCPs), g. b. f. slag, silica fume, natural pozzolans, rice-husk ash, wood ash, agricultural products ash, limestone/quarry fines, etc. (OCM).

Use more application specific high-quality, durable aggregates, and organic admixtures.

Use less water.
Carbon Dioxide Sequestration in Concrete and Other Cement-Based Materials
CO$_2$ Sequestration

• There exists an urgent need for reduction in CO$_2$ emissions and recycling of CO$_2$.

• An effective method for the recycling of CO$_2$ from the environment is to sequester it in lime- or cement-based (alkali-rich) products via the process of carbonation.
Carbonation of Concrete

(1) CO$_2$ ingress and diffusion in the cement paste matrix.

(2) CO$_2$ dissolution in the pore solution for formation of carbonic acid (H$_2$CO$_3$) and reaction with calcium hydroxide to form calcium carbonate:

\[
\text{Ca(OH)}_2 + \text{H}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{H}_2\text{O} \\
[\text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3]
\]
Carbonation of Concrete (cont’d)

(3) Reaction with silicates and aluminates (more difficult):

- $3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O} + 3\text{CO}_2 \rightarrow 3\text{CaCO}_3 + 2\text{SiO}_2 + 3\text{H}_2\text{O}$

- $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 13\text{H}_2\text{O} + 4\text{CO}_2 \rightarrow 4\text{CaCO}_3 + 2\text{Al(OH)}_3 + 10\text{H}_2\text{O}$
Effects of Carbonation on Concrete

- Consumption of water and CO$_2$
- Pore refinement/densification due to precipitation of CaCO$_3$ inside the pores of the cement paste matrix
- Increase in weight
- Increase in strength
- Improved surface hardness
- Reduction in pH (reinforcing steel could become vulnerable to corrosion)
CO$_2$ Sequestration Experiments
Concrete Mixture Proportions

- **Class C fly ash** was used as a partial replacement of cement.

- Concrete mixtures (regular and/or no-fines/porous) were **non-air entrained** and some were **air entrained**.
Demolding and Curing

• Approximately 24 hours after casting, specimens were removed from molds.

• Immediately, they were put in three types of curing environment
  – Moist-curing room: 100% RH & 0.15% CO₂
  – Drying room: 50% RH & 0.15% CO₂
  – CO₂ chamber: 50% RH & 5% CO₂.
CO$_2$ Chamber
Inside of CO\textsubscript{2} Chamber
Strength

- The concrete specimens cured in the **drying room** developed the **lowest strength**. In the drying room, there was little or no gain in compressive strength after the 28-day age; and, the concrete containing 35% fly ash showed the lowest compressive strength in this environment.

- The **CO₂ chamber** was as effective as the moist-curing room in developing the compressive strength of concrete containing 0% to 35% fly ash.
Abrasion testing: using rotating cutters for six minutes under a load of 197 N
In both the moist-curing room and the CO$_2$ chamber, the abrasion resistance of concrete improved with age.
Testing for Depth of Carbonation of Concrete

Pink: considered non-carbonated.
No discoloration: considered carbonated.
Depth of carbonation of concrete mixtures containing 35% fly ash, measured at 28 days

F35-M  F35-D  F35-C
Depth of Carbonation

• Concrete made with or without fly ash, cured in the moist-curing room (100% RH and 0.15% CO₂) did not show carbonation at 3, 7, 28, and 91 days.

• In the drying room (50% RH and 0.15% CO₂), concrete carbonated to some extent.

• Concrete cured in the CO₂ chamber showed much higher carbonation than the concrete cured in the drying room.
Amount of CO2 Sequestered

- Typically Class C fly ash would sequester about 6% CO2 by weight. Therefore, 100 tons of fly ash would capture about six tons of CO2.
- Similarly 100 tons of portland cement would capture up to about 15 tons of CO2.
- Of course, Ca(OH)2 and other hydroxides present in the cement hydration products are necessary for mineralization of CO2 to carbonate minerals.
- 100 tons of cement would produce up to about 25 tons of Ca(OH)2 and other hydroxides, more than enough to transform 15 tons of CO2.
Carbon Dioxide Sequestration in Foamed Controlled Low-Strength Materials
Background

• Carbonation
  – Calcium Hydroxide + Carbon Dioxide
  – Produces Calcium Carbonate

• Class C fly ash in CLSM would provide a source of calcium hydroxide for the carbonation reaction.

• Use of a CLSM mixed with foam containing carbon dioxide should increase the rate of carbonation.
Foam Generator

Center for By-Products Utilization
Split Test Cylinders Treated With Phenolphthalein Solution
Measurement of Depth of Carbonation
Carbonation of Mixture FS-3, 7-Days
Carbonation of Mixture FS-3, 28-Days

Center for By-Products Utilization
Carbonation of Mixture FS-3, 56-Days
Carbonation of Mixture FS-3, 91-Days
Summary

• Rate of CLSM carbonation was highest when carbon dioxide was used with the foam.
• Similar carbonation rates for CLSM when using compressed air or the mixed gas in the foam.
• CO₂ can be sequestered inside foamed CLSM made with fly ash.
Reduction of CO$_2$ Emissions by Increased Use of Fly Ash

Replacing 15% of 2.2 billion tons of cement worldwide by Supplementary Cementitious Materials (SCM) will reduce CO$_2$ emissions by 330 million tons.
Recycling of Coal Combustion Products (CCPs) for Use with Other Industrial By-Products in Sustainable Construction Practices for Generating CO2 Credits
USE OF COAL FLY ASH WITH WOOD ASH IN CONCRETE

Wood ash is generated by the pulp and paper industry, saw mills, and wood products industry.
MICROGRAPH OF WOOD FLY ASH
Wood Ash Concrete Test Results

- 28-day compressive strength approximately 33 MPa.
- 365-day compressive strength over 42 MPa.
Use of Fly Ash with Foundry Sand in Concrete

Mined foundry sands are silica sand of graded size used for making molds. Sand mold is made to cast a hollow shape in which molten metal is poured to produce a cast-metal product. Sand in the mold is bonded by clay (green sand) or chemicals (clay-bonded and chemically-bonded).
Foundry Sand

In modern foundry practice, sand is typically reused through several production cycles. Typically 10% or so of sand is discarded during each reuse cycle. Such sand is available for other recycling options. Wisconsin alone produces over 500,000 tons of foundry by-products.
Materials

Three types of sand
- Regular Concrete Sand (RCS)
- Used Foundry Sand (UFS)
- Clean Foundry Sand (CFS)

Type I Cement (ASTM C 150)
Class C Fly Ash (ASTM C 618)
Conclusions

• Inclusion of fly ash improved compressive strength of concrete mixtures containing up to 40% foundry sand (used or clean).

• All concrete mixture with up to 40% foundry sand and up to 25% fly ash outperformed the reference mixture.
BOTTOM ASH for STRUCTURAL FILL

- Irregular shape of bottom ash (usually conditioned to contain 10% moisture) locks in place and shows better support than sand.
- Shows better drainage compared with sand.
- Concrete pavement is placed on top of a bottom ash layer.
Recycling of CCPs in Permeable Roadway Base Construction
• A loss in pavement support occurs, leading to early failure of the pavement.

• This failure can be avoided by using free-draining pavement base.
• To meet current and future EPA air-quality standards, utilities are utilizing low-NO\textsubscript{X} burners to reduce NO\textsubscript{X} emissions and flue-gas desulfurization (FGD) to reduce SO\textsubscript{X} emissions.

• FGD materials are high-sulfite and/or sulfate products, and low-NO\textsubscript{X} burners generate high-carbon CCPs.
• Most of FGD materials and/or high- or variable-carbon CCPs are landfilled at high disposal costs and potential future environmental liabilities to the utilities.

• Permeable base materials for highways, roadways, and airfield pavements would be a high-volume application for these types of CCPs.
Permeable-Concrete Base Course

• It is estimated that the use of a porous base would increase pavement service life by up to 70% for concrete and asphaltic pavements.
Concrete Masonry Bricks, Blocks, and Paving Stones Made With Class F and Class C Fly Ash and Bottom Ash
Manufacturing of concrete products for growth of grass, shrubs, plants, walls for ivy/vines, as well as for replenishing ground water, etc.
• When fly ash is used as a partial replacement of cement (~30%), this can improve the strength, abrasion resistance, and resistance to freezing-and-thawing of concrete masonry units.

• Fly ash can also be used with foundry sand to improve strength and durability of bricks, blocks, and paving stones.
• When bottom ash is used as a partial replacement for sand, this lowers the weight of concrete blocks, improving worker safety and construction speed.
FGD Gypsum in the Manufacture of Wall Board

• Wet scrubbing of flue gas using limestone gives off CO$_2$. However, use of FGD gypsum has the following benefits:

• Energy savings from mining and crushing natural gypsum.

• A purer form than natural gypsum.

• Transportation cost to gypsum wallboard plants may be reduced.

• Less H$_2$S gas by reducing landfilling of gypsum.
Shingles

- Fly ash has been used in the industry as inert filler to extend an asphaltic base in the manufacture of roofing shingles.

- Cyclone boiler slag can be used for roofing granules.

- Bottom ash can be used in lieu of sand and aggregates.
Raw Materials for Portland Cement Manufacture

- **Calcium carbonate, 80 – 85%**
  - Limestone, chalk, sea shells, lime mud from a paper mill, etc.

- **Silica**
  - Clay, sand, fly ash, foundry dust, spent catalyst, etc.

- **Alumina**
  - Fly ash, clay, bauxite, aluminum dross, etc.

- **Iron**
  - **Bottom ash, mill scale from a steel plant, iron ore, etc.**

Information from Jeff Grant, CEMEX/Kosmos Cement
Use of Fly Ash and Bottom Ash in Portland Cement Manufacture

• There are locations where deposits of traditional raw materials near cement plants are running low or have been used up.

• It is very costly to build a new cement plant ($300+/- million per million ton capacity).

• Fly ash and bottom ash can be used to minimize the need to mine and transport virgin raw materials.

• Depending on the chemical composition, a mixture of fly ash and sand has been used to replace clay.
Blended Cement

• Hydraulic cement
• Consisting of portland cement + one or more inorganic constituents
• Produced by inter-grinding or blending, with or without functional additions (such as powder additives, alkalies, dry-organics, and other similar materials)
Constituents

(1) Portland cement clinker.

(2) Mineral additives:
   – Fly ash;
   – Clean-coal Ash;
   – Blast furnace slag;
   – Natural pozzolans;
   – Silica fume;
   – Others: RHA, wood ash, non-ferrous slag, etc.

(3) Functional additives.
Why Blended Cements

• Technical reason
  Durability of portland cement concrete

• Ecological reason
  Reducing green gas emission
  Reduction of energy consumption
  Increasing use of low-rank coal ash

• Quality control reason
  Change the quality control from field to manufacturing plant

• Economical reason
  Overall savings due to blended cements
Blended Cements

- Concrete produced from blended cements with 40% (20% Class C fly ash + 20% FGD) and 60% (30% Class C fly ash + 30% FGD) mineral additives had higher strength and durability than the control concrete.
Conclusions

• With 80% (20% Class C fly ash + 60% FGD) mineral additives, the concrete had equivalent strength development and resistance to freezing-and-thawing as the control concrete, and it had higher resistance to alkali-silica attack and sulfate attack.
Use of CCPs for Generating Carbon Offsets

- **CO₂ Sequestration**
  - In concrete made with CCPs
  - In CLSM (flowable fill) made with CCPs

- **Green Building Materials**
  - Fly ash for use with by-products from other industries
  - Bottom ash for structural fill
  - Flowable fill (CLSM)
  - Permeable base

- **Concrete Products**
- **Wallboard**
- **Portland Cement and Blended Cement**
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Spaceship Earth – La Bella Terra

Center for By-Products Utilization
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Ponded Coal Ash and Quarry Fines in Flowable Slurry
Ponded Coal Ash

• Wet-collected fly ash and bottom ash

• Characterization
  – High moisture content (10-50%)
    • Variable depending on storage, location, weather, etc.
  – Wide range of particle sizes
    (< #200 to 3/8-in.+)
    • Pre-sieve prior to use for some applications
  – High LOI (45-50%)
Ponded Coal Ash

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Quarry Fines

- Typical by-product of quarries
  - Sent to landfills

- Characterization
  - Finer than standard concrete sand
Quarry Fines
Summary – Use of Ponded Ash and Quarry Fines in CLSM

- Increasing the amount of coal ash in CLSM decreases the permeability of the CLSM – less likely to be susceptible to leaching
Conclusions:

CLSM: A Sustainable Material

CLSM not only uses large amounts of recyclable materials, e.g., foundry sand, glass, wood ash, quarry fines, and ponded ash in the CLSM manufacture but it can also be later excavated and re-used.