FGD Gypsum Utilization: Wallboard, Cement Manufacturing, and Agricultural Applications

Bruce Ramme

Presented at the UWM-CBU Workshop on Green Construction Materials Using Coal Combustion Products
May 1 - 2, 2008
Milwaukee, Wisconsin
Coal Combustion Products Utilization
CCP Utilization (tons)

- Concrete: 261,000 tons
- Ash Fuel: 106,000 tons
- Sub-Base (Bottom Ash): 101,000 tons
- Cement Raw Feed: 92,000 tons
- Manufactured Aggregate: 75,000 tons
- Wallboard Manufacturing: 70,000 tons
- Stabilization (Soil & Asphalt): 43,000 tons
- Miscellaneous: 17,000 tons
P4 – FGD Gypsum (CaSO$_4$)
Pleasant Prairie Power Plant
Environmental Improvements & Innovation

New 450' chimney located near scrubbers and designed to accommodate separate flue gas streams from each plant unit.

Existing chimney will be removed in 2008.

Selective catalytic reactor (SCR) installed on Unit 2. Second SCR being installed in Unit 1. Each SCR reduces nitrogen oxide (NOx) emissions by 85-90 percent.

Wet flue-gas desulfurization systems (scrubbers) being installed in both units. Will reduce sulfur dioxide (SO2) emissions by 90-95 percent.

Ash fuel blending system used for adding bottom ash and ash recovered from landfills.

Fly ash silos. 100 percent of ash from Pleasant Prairie is beneficially used.

Location of Eco-Pad pavement containing 100 percent recycled content in-situ mixed concrete.

Dry fly ash reburn system to blend recovered high-carbon fly ash with coal as fuel.
ALSTOM Carbon Capture Pilot Test System arranged in side stream (slip stream) arrangement on plant discharge to stack

First field pilot installation at power plant

Information available at www.we-energies.com
Lime(stone) Forced Oxidation Wet Flue Gas Desulfurization Process
Historical Uses of Gypsum

- Used for over 2000 years by Chinese to coagulate soy milk to make Tofu
- Egyptians used in cement 9000 years ago.
- Greeks and Romans used with volcanic pozzolans to make concrete
- Europeans used gypsum for fertilizer values in 18th Century and brought its use to the USA
- Jefferson and Franklin were among the promoters
- Gypsum use in agriculture in the USA has largely been forgotten except in specialty crops.
Gypsum Products
<table>
<thead>
<tr>
<th>Other Uses of Gypsum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Erosion Control</td>
</tr>
<tr>
<td>Filler for Polymers and Chemicals</td>
</tr>
<tr>
<td>Pottery</td>
</tr>
<tr>
<td>Art Statuary</td>
</tr>
<tr>
<td>Metal Casting Plaster</td>
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<tr>
<td>Surface Enhancer</td>
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<tr>
<td>Machinable Media</td>
</tr>
<tr>
<td>Food Pharmaceutical</td>
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</table>
FGD Gypsum Production and Use

- **2006 Production**
  - ACAA National = 12,100,000 tons

- **2006 U.S. Reported Utilization (79.02%)**
  - Wallboard = 7,579,187 tons
  - Concrete = 1,561,489 tons
  - Cement = 264,568 tons
  - Agriculture = 168,170 tons (99.5%)
  - Other = 7,614 tons
Other FGD Materials (Not Gypsum)

- 2006 Production Other FGD Materials
  - ACAA National = 18,088,000 tons

- 2006 U.S. Reported Utilization (5.9%)
  - Misc./Other = 338,797 tons
  - Mining = 316,707 tons
  - Blasting Grit/Roofing = 232,765 tons
  - Structural Fills = 131,821 tons
  - Concrete, CLSM, etc. = 49,392 tons
  - Agriculture = 846 tons (0.5%)
FGD Gypsum Production and Use

- **2007 We Energies Production**
  - PPPP = 73,000 tons

- **2007 Utilization - 100%**
  - Wallboard = 73,000 tons
  - Concrete = R&D at CBU in Progress
  - Cement = Discussions in Progress
  - Agriculture = Exemption in Place

- **Future – Oak Creek Power Plant Units**
Wallboard Manufacturing
Melnik Plant, Bulgaria
Palatka, Florida
Gypsum in Cement Manufacturing
Cement Manufacturing

Steps in the Cement Making Process:

1. Quarrying
2. Raw Milling
3. Dust Collecting & Recyling
4. Proportioning
Gypsum in Cement Manufacturing

- Gypsum is used to control the time of set in Portland cement manufacturing.
- Gypsum has a retarding effect.
- Addition rate is typically 2% to 5% depending on clinker chemistry and cement type being manufactured.
- Natural Gypsum and FGD Gypsum are both commonly used.
Gypsum in Agriculture

Nutrient application guidelines for field, vegetable, and fruit crops in Wisconsin

Carrie A. M. Laboski
John B. Peters
Larry G. Bundy
Commercial Products Comparison
<table>
<thead>
<tr>
<th>Trace element</th>
<th>FGD Gypsum ¹</th>
<th>Mined Gypsum ¹</th>
<th>P4 Gypsum</th>
<th>National Background-Soil ¹</th>
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<tbody>
<tr>
<td>Antimony</td>
<td>2.0-9.1</td>
<td>0.02-0.28</td>
<td>0.28</td>
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<tr>
<td>Arsenic</td>
<td>0.6-4.0</td>
<td>0.19-3.0</td>
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<tr>
<td>Cadmium</td>
<td>0.2-1.2</td>
<td>&lt;2-0.5</td>
<td>0.36</td>
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<td>Chromium</td>
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<td>8.7-30.5</td>
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<td>Lead</td>
<td>0.8-12.0</td>
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<td>14.5</td>
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<td>Mercury</td>
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<td>0.00044-0.025</td>
<td>1.0</td>
<td>0.039</td>
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<td>Molybdenum</td>
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<td>Selenium</td>
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<td>Vanadium</td>
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<td>Zinc</td>
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<td>13.1-27.5</td>
<td>8.0</td>
<td>36.8</td>
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</table>

¹-From: P. Grevall, USEPA. Presentation at Agricultural & Industrial Uses of FGD Gypsum Workshop. October 23, 2007
### Leachate Trace Elements (mg/l) in P4 FGD Gypsum, Mined Gypsum, Ammonium Sulfate and Aluminum Sulfate

<table>
<thead>
<tr>
<th>Parameter</th>
<th>P4 Gypsum</th>
<th>Mined Gypsum</th>
<th>Ammonium Sulfate</th>
<th>Aluminum Sulfate</th>
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<tbody>
<tr>
<td>Aluminum</td>
<td>0.33</td>
<td>0.75</td>
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<td>Antimony</td>
<td>0.00022</td>
<td>0.00058</td>
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<tr>
<td>Arsenic</td>
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<td>&lt;0.0026</td>
<td>&lt;0.0026</td>
<td>&lt;0.026</td>
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<td>Barium</td>
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<td>Beryllium</td>
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<td>Boron</td>
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<td>Cadmium</td>
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<td>Chloride</td>
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<td>Chromium</td>
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<td>0.012</td>
<td>&lt;0.032</td>
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<td>Copper</td>
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<td>Cyanide</td>
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<td>Fluoride</td>
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<td>Iron</td>
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<td>1.7</td>
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<tr>
<td>Parameter</td>
<td>P4 Gypsum</td>
<td>Mined Gypsum</td>
<td>Ammonium Sulfate</td>
<td>Aluminum Sulfate</td>
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<tr>
<td>-----------------</td>
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<td>--------------</td>
<td>------------------</td>
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</tr>
<tr>
<td>Lead</td>
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<tr>
<td>Manganese</td>
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<td>Mercury</td>
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<td>&lt;0.000012</td>
<td>&lt;0.000012</td>
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<tr>
<td>Molybdenum</td>
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<td>0.0061</td>
<td>0.0079</td>
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<tr>
<td>Nickel</td>
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<td>0.014</td>
<td>0.017</td>
<td>0.038</td>
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<tr>
<td>Nitrate-Nitrite</td>
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<td>0.68</td>
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<td>Phenolics</td>
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<td>Selenium</td>
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<td>&lt;0.046</td>
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<td>Silver</td>
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<td>&lt;0.00065</td>
<td>&lt;0.0065</td>
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<tr>
<td>Sulfate</td>
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<td>35300</td>
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<tr>
<td>Thallium</td>
<td>0.00015</td>
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<tr>
<td>Zinc</td>
<td>0.0029</td>
<td>0.022</td>
<td>0.02</td>
<td>0.6</td>
</tr>
</tbody>
</table>
Runoff Causing Soil Erosion and Removal of Chemicals
Effect of Degradation by Erosion on Crop Productivity
Rainwater is Naturally Distilled
Raindrop Impact has Physical and Chemical Effects on the Soil Surface
This Leads to Surface Sealing
Loss of Yield
Offsite Water Quality Problems
Effect of Gypsum on Erosion

- Runoff (mm)
- Soil Loss (g/10 sq m)
- SRP (mg/sq m)
Soluble Electrolyte Sources

- Calcium Sulfate exists in several stable mineral forms
- Gypsum (CaSO₄-2H₂O) 2.41 g/L
- Anhydrite (CaSO₄) 2.09 g/L
- Bassanite (2CaSO₄-H₂O) 3.00 g/L
- Hannebachite (2CaS0₃-H₂O) 0.04 g/L
- Calcite (CaCO₃) 0.14 g/L
Ca Effect on Flocculation

Ca/Mg Ratio has been found to be important in clay flocculation
Soil Structural Differences (Control left Gypsum on right)
Conventional No-tillage on Vertisol in Villadiego, MX
Nu-Till System with Gypsum application, Villadiego, MX
Root Growth Increase with Gypsum, Corn South Dakota
Gypsum Application on Left w/o on Right
Random Corn Ears Amended with Gypsum on Left and Control, Colorado
Spreader Application to Soil
Key DNR Exemption Conditions for PPPP FGD Gypsum

- P4 FGD Forced Oxidation Gypsum Only
- Not for Filter Cake
- Effective for 5 years
- Characterization – Metals in NR 538, pH, Nutrient Contents, Salt Contents
- Re-characterized with System Changes
- Information & Guidance for Customers
- Application Rates & Agency Reporting
Key DNR Exemption Conditions for PPPP FGD Gypsum

- Application Rates Cannot Cause Detrimental Effects to Soil or Water
- Best Management Practices for Use
- Use Accepted Agricultural Practices
- Outdoor Storage for One Year or Less
- Prevent Excessive Dusting
- Best Management Practices to Prevent Runoff
- Hauling per NR 538
- Annual Reporting
- Agricultural Regulations and Permitting
Wisconsin Nutrient Application Guidelines for Gypsum

- Nutrient Application Guidelines
  - Field
  - Vegetable
  - Fruit Crops
Additional References

Conference Presentations

http://www.fgdproducts.org/fgd_products_website_013.htm

UW Extension Publications


http://learningstore.uwex.edu/pdf/A3588.pdf
Anticipated Benefits

- Improve soil properties for increased crop production (soil test-justified applications).
- Reduce silt loading in runoff from fields (gypsum enhances water permeability).
- Lower cost gypsum for region’s agricultural producers.
- Lower fuel usage and emissions with shorter haul distance for “locally produced” commodity.
- Reduced mining and associated impacts elsewhere.
- Preserves natural gypsum supplies for use by future generations.
Conclusions

- FGD Gypsum is a Commodity
  - Co-Product of Electric Power Generation
- Proven for Wallboard and Cement Manufacturing
  - Conserves Energy (Raw Material Processing)
  - Sustainability in Conserving Natural Resources
- Agricultural Benefits = Future Growth
  - Reduces Erosion and Improves Infiltration
  - Greater Roots Volume and Plant Efficiency
  - Electrolyte Source and Calcium Benefits
  - New Resource for Wisconsin Farmers
Current Research Challenge !
Filter Cake (Not FGD Gypsum)

- Although mercury leachability is very low, bulk concentrations are higher than the gypsum itself.

- R&D on other (non-ag) beneficial utilization methods for this low-volume byproduct.

- Presently investigating the potential for use in conjunction with crushed stone or recycled concrete to create a “hard-pan” like composite pavement base material.
Filter Cake Test Data

- Max. Dry Density = 57 lb/ft³
- Optimum Moisture = 72%
- Liquid Limit = 123%
- Plastic Limit = 65%
- Plasticity Index = 59%
- Specific Gravity = 3.08
- Grain Size = 96.6% passing a #200 Sieve
- Permeability = $2 \times 10^{-8}$ cm/sec
Questions ???