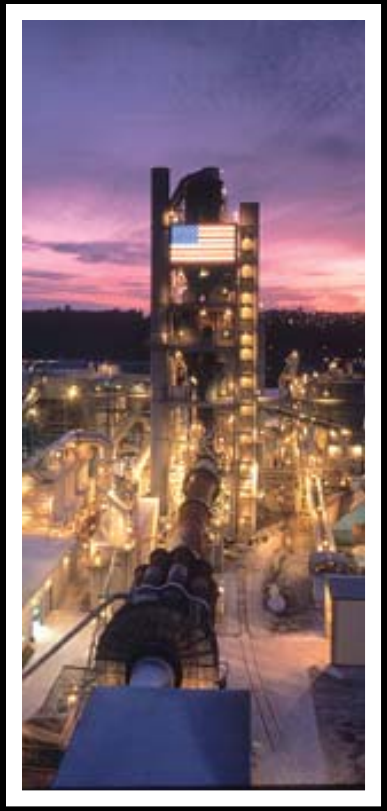
AMD Treatment Sludge

Raw Material for the Cement Industry

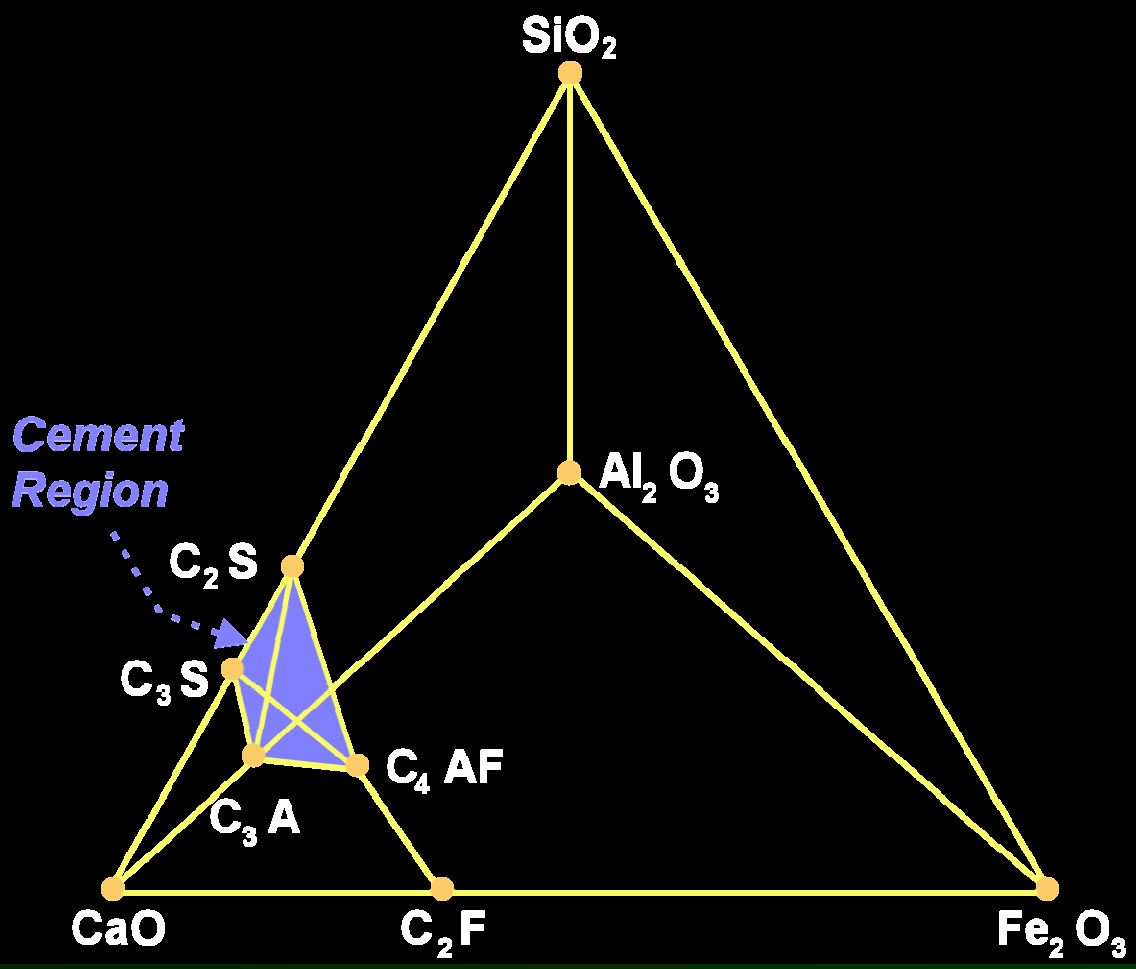


Dr. Michael Silsbee, Dr. Lykourgos Iordanidis, Dr. Boyd Clark, Norm Goodlin and Dr. Richard Lee

Mine Water Treatment Technology Conference
August 15-18, 2005

Cement Forming Region in the System

$CaO\text{-}SiO_2\text{-}Fe_2O_3\text{-}Al_2O_3$



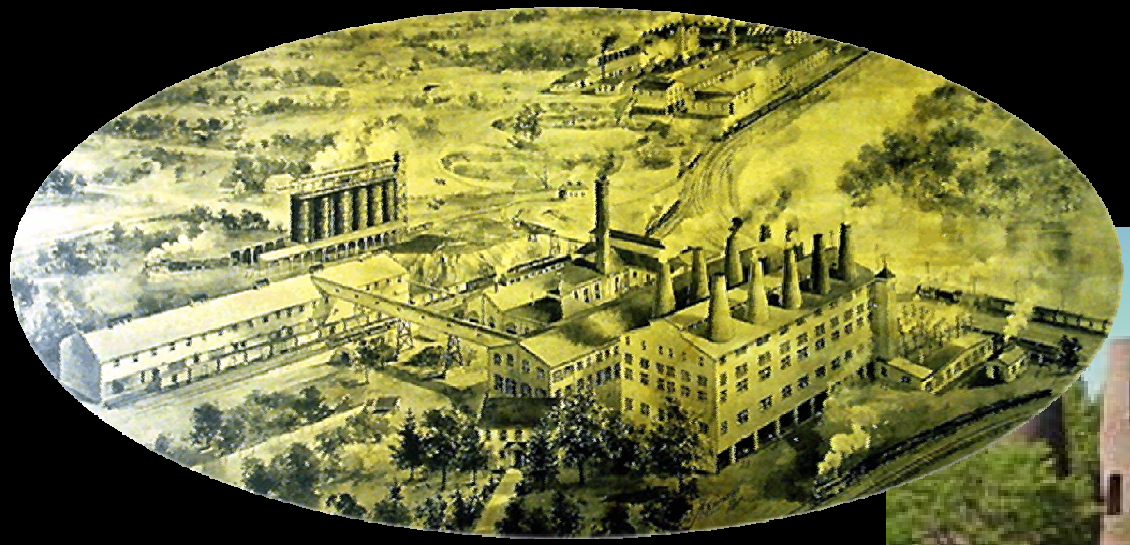
Industry Overview

Cement is a major industrial commodity.

- Manufactured commercially in at least 120 countries, cement is mixed with sand and gravel to make concrete.
- Concrete is used in the construction of buildings, roads, and other structures, as well as in other products and applications.
- The use of concrete as a residential building material is particularly important in countries where wood is not traditionally used for building or is in short supply.

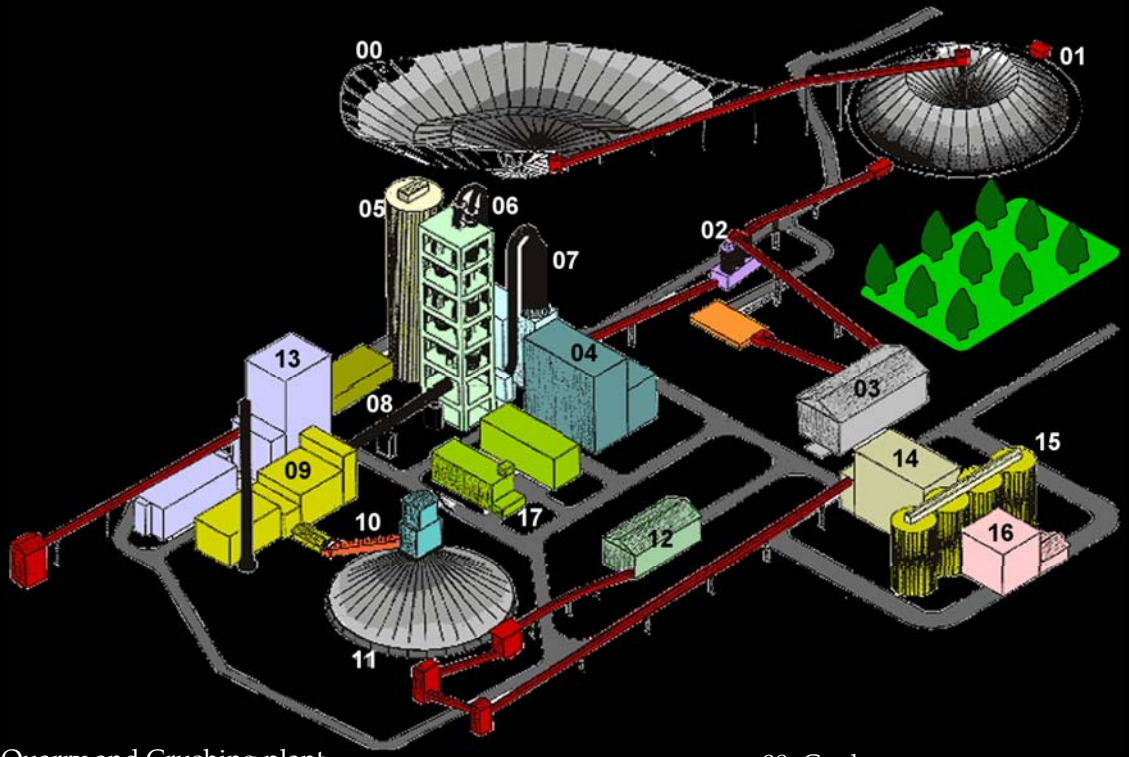
Source: http://unfccc.int/resource/ccsites/senegal/fact/fs030.htm

Coplay Company Cement Kilns



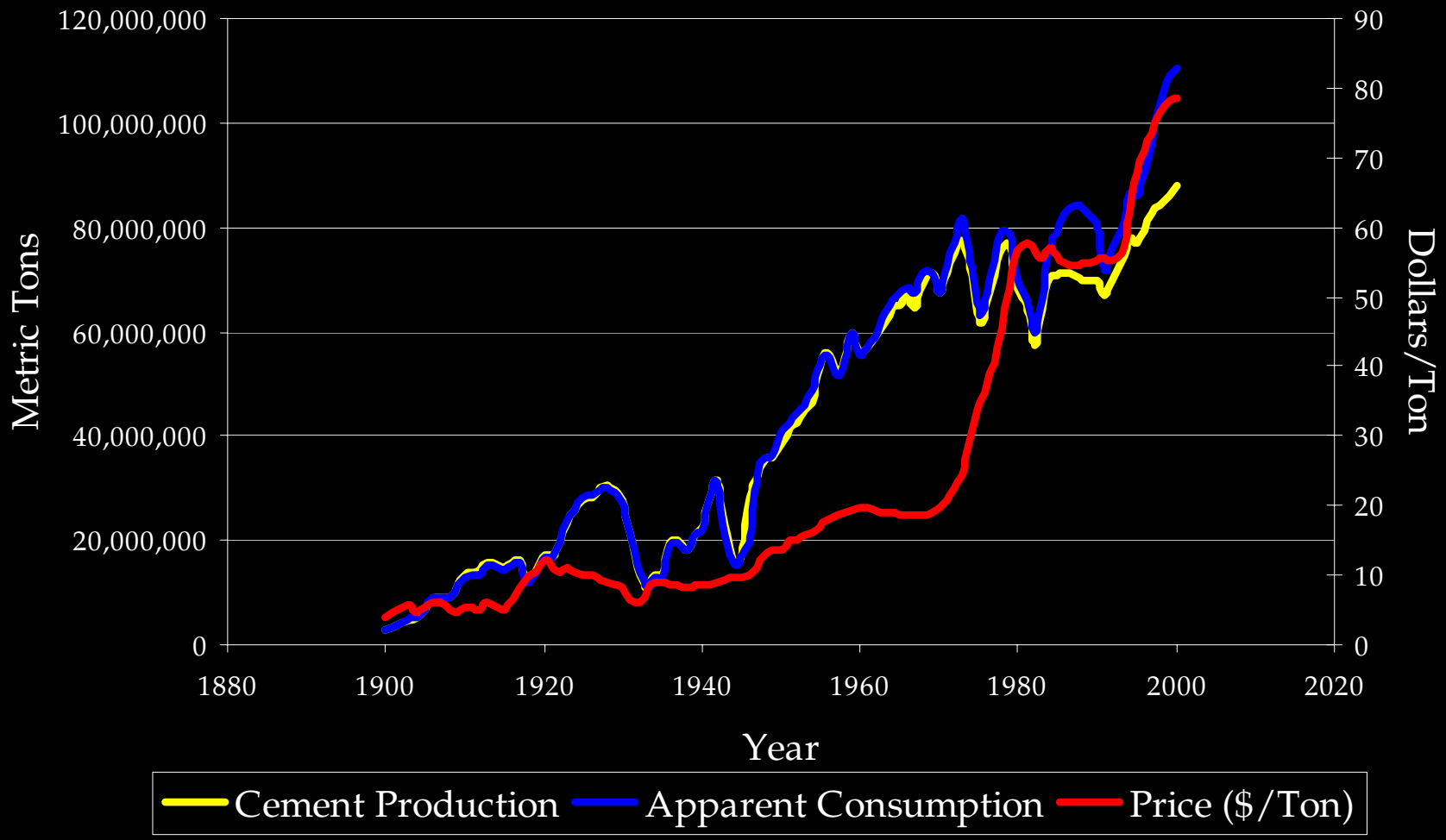
Photograph courtesy of Sue Pridemore

Cement Plant



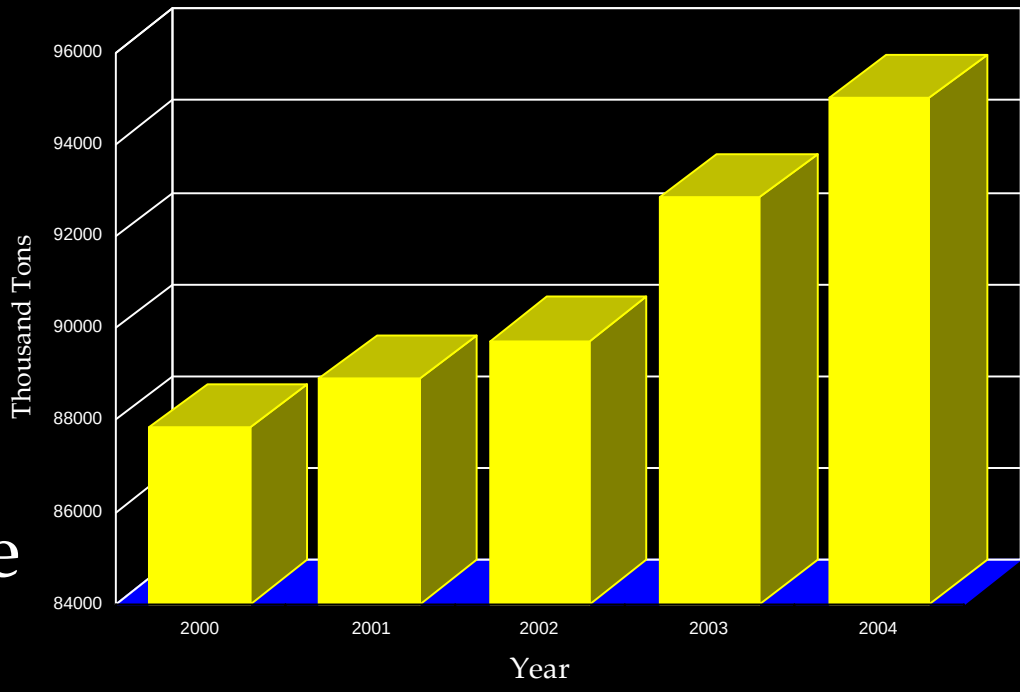
00. Limestone Quarry and Crushing plant
01. Limestone Stockpile
02. Additives Hopper
03. Additives Storage
04. Raw Mill Building
05. Blending and Storage Silo
06. Preheater
07. Gas Conditioning Tower and ESP
08. Kiln
09. Cooler
10. Deep Bucket Conveyor
11/12. Clinker/Gypsum Storage
13. Coal Mill Building
14. Cement Mill and Bag House
15. Cement Storage Silo
16. Packing & Dispatch
17. Central Control Room

Yearly Production



U.S. Cement Production

- The largest cement-producing states are California, Texas, Pennsylvania, Michigan, Missouri, and Alabama. Together these states account for 50% of the annual U.S. cement production.



Portland Cement

- The basic ingredients of cement, is a closely controlled chemical combination of:
  - Calcium
  - Silicon
  - Aluminum
  - Iron
  - Other Ingredients

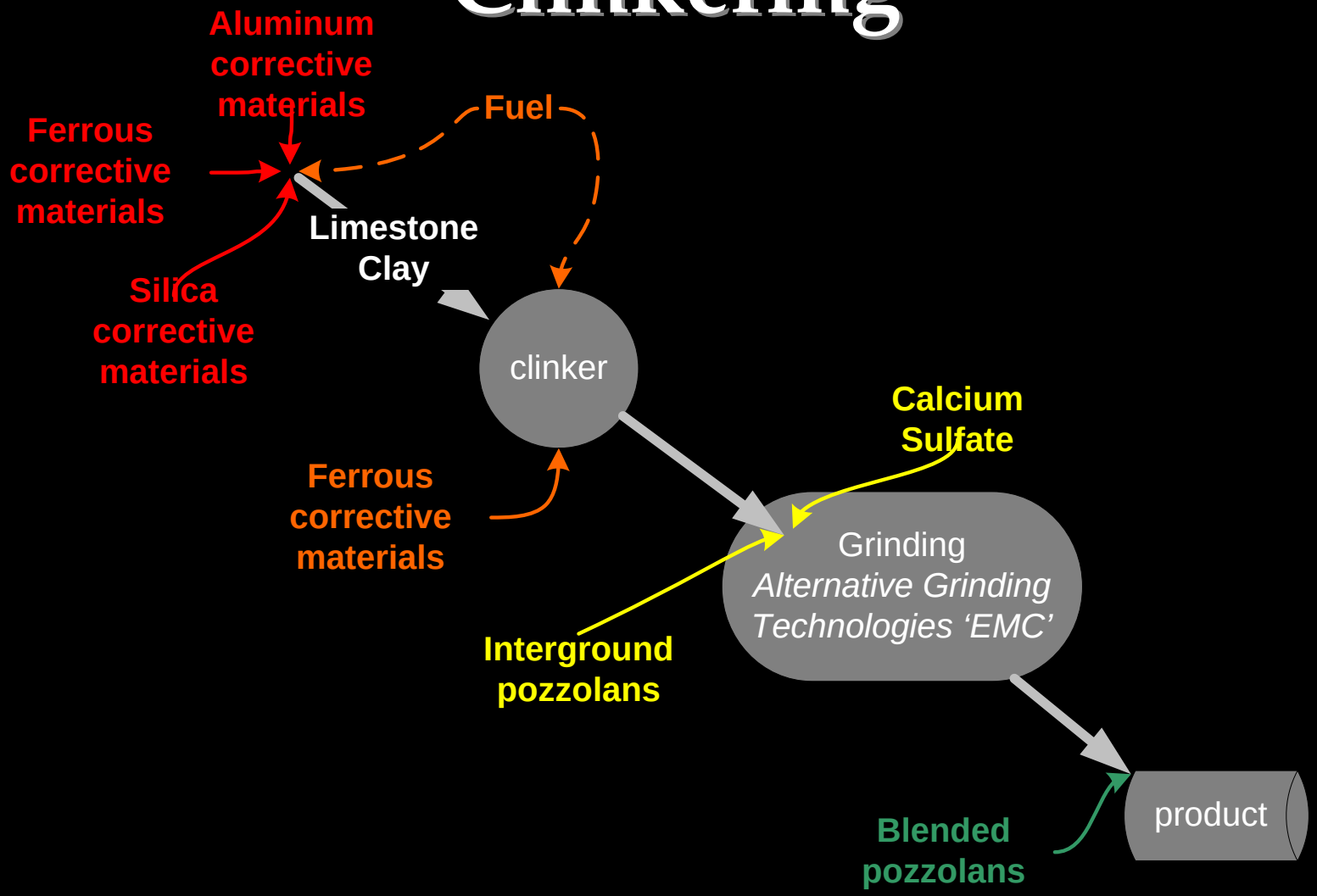
Portland Cement

- Gypsum is added in the final grinding process to regulate the setting time of the concrete.
- Lime and silica make up about 85% of the mass. Common among the materials used in its manufacture are limestone, shells, and chalk or marl combined with shale, clay, slate or blast furnace slag, silica sand, and iron ore.

Raw Materials

- The raw materials sometimes have the desired composition but may require the addition of:
  - Clay
  - Limestone
  - Iron Ore
  - Bauxite
  - Recycled Materials

Clinkering


Aluminum corrective materials
Ferrous corrective materials
Fuel
Limestone
Clay
Silica corrective materials
clinker
Calcium Sulfate
Ferrous corrective materials
Grinding
Alternative Grinding Technologies 'EMC'
Interground pozzolans
product
Blended pozzolans

Role of Iron

- In the hottest part of the kiln, known as the "burning zone", the material temperature reaches 1450 - 1500°C.
- A degree of melting is achieved, sufficient to cause the material to cohere into small balls or lumps of clinker.
- Between 20% and 30% of the material is normally molten at this temperature.
- The liquid is composed principally of alumina and iron oxide, which act as fluxes in the formation of the calcium silicates.
- The product after cooling, consists essentially of crystals of C_3S and C_2S embedded in a matrix of interstitial material containing the aluminate and ferrite phases.

Final Product

- In order to achieve the desired setting qualities in the finished product, about 2% gypsum is added to the clinker and the mixture is very finely pulverized. This powder is ready for use and will react with the addition of water.

Product Chemical Composition

- The finished cement has approximately the following composition:
  - Calcium Oxide (64%)
  - Aluminum Oxide (5.5%)
  - Silicon Oxide (21%)
  - Ferric Oxide (4.5%)
  - Magnesium Oxide (2.4%)
  - Sulfate (1.6%)
  - Loss of Ignition, Mostly Water (~1%)

Product Chemical Parameters

Silica Modulus = $\frac{SiO_2}{Al_2O_3 + Fe_2O_3}$ (2.3-3.5)

Alumina Modulus = $\frac{SiO_2}{Al_2O_3}$ (~1.6)

Lime Saturation Factor = $\frac{100CaO}{2.8\ SiO_2 + 1.18\ Al_2O3 + 0.65\ Fe_2O_3}$ (92%-96%)

Main Constituents in a Typical Portland Cement

Chemical Name	Chemical Formula	Shorthand Notation	Percent by Weight
Tricalcium Silicate	$3CaO \cdot SiO_2$	C_3S	50
Dicalcium Silicate	$2CaO \cdot SiO_2$	C_2S	25
Tricalcium Aluminate	$3CaO \cdot Al_2O_3$	C_3A	12
Tetracalcium Aluminoferrite	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	C_4AF	8
Gypsum	$CaSO_4 \cdot H_2O$	CSH_2	3.5

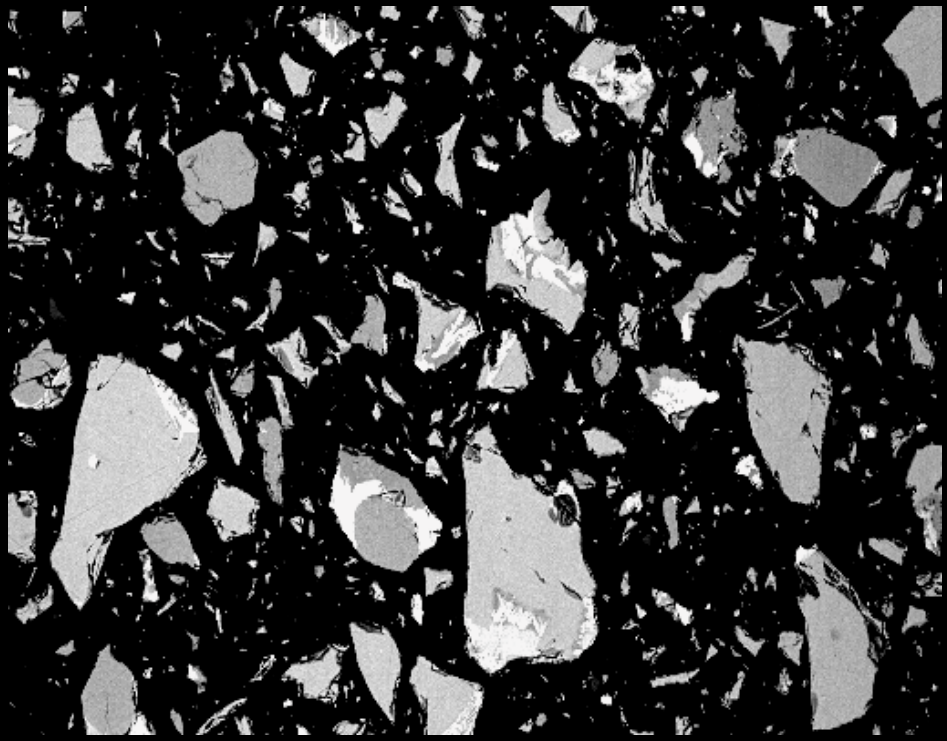
Source: Mindess and Young, 1981

Product Phase Composition

- C_3S ("alite")
  - Gives cement/concrete most of its early strength developing qualities.
- C_2S ("belite")
  - Hydrates more slowly than C_3S and provides concrete's late strength.
- C_4AF
  - No significant hydraulic properties, but melts at low temperatures promoting other reactions.
- C_3A
  - Responsible for workability and aids kiln burning as a flux that melts, assisting in reactions of other compounds.

Portland Cement

- Backscattered electron image of a typical Type I



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Colorized Image

Legend

Tricalcium silicate

Dicalcium silicate

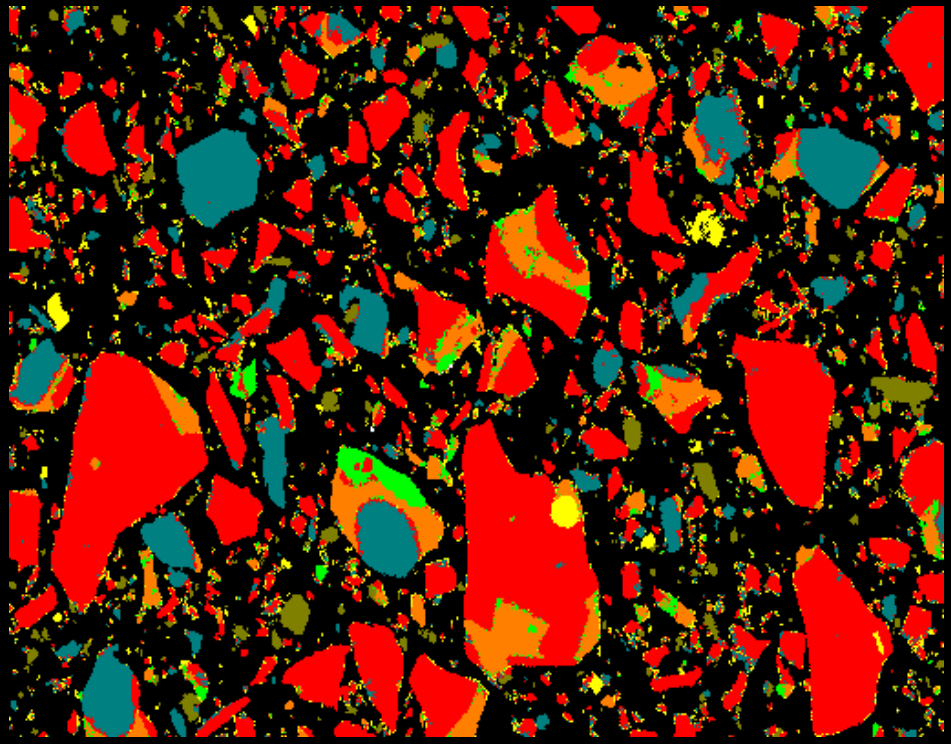
Tricalcium aluminate

Tetracalcium aluminoferrite

Gypsum

Free lime

Potassium sulfate



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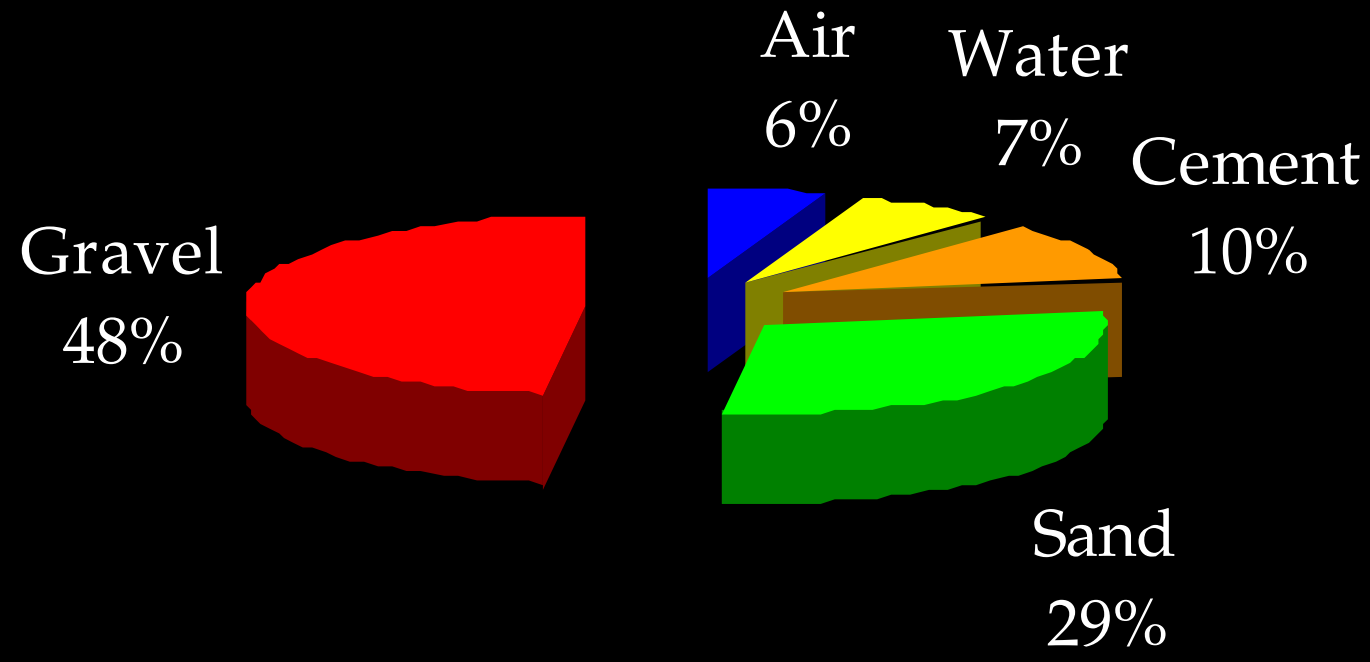
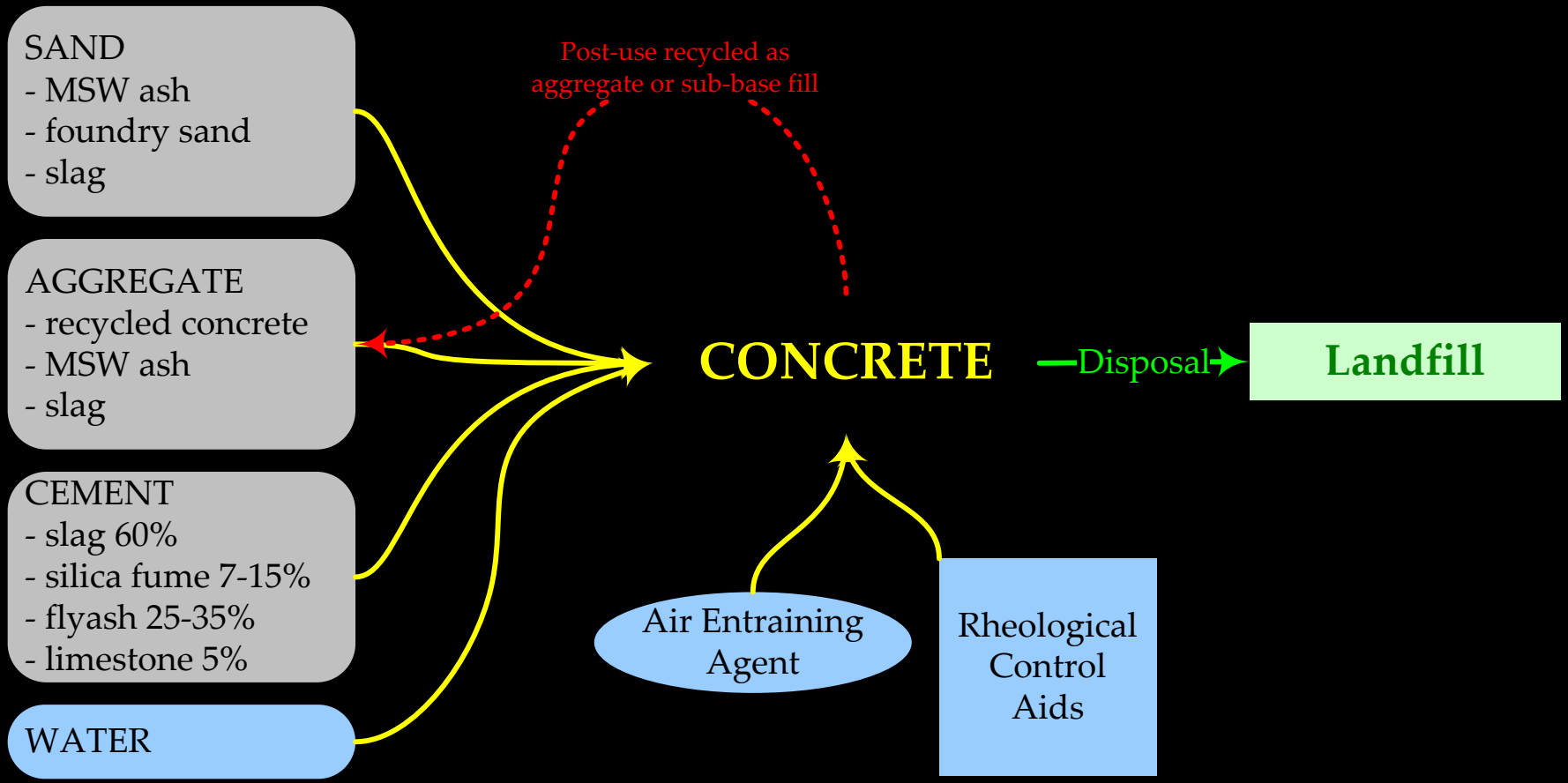
Typical Concrete Composition



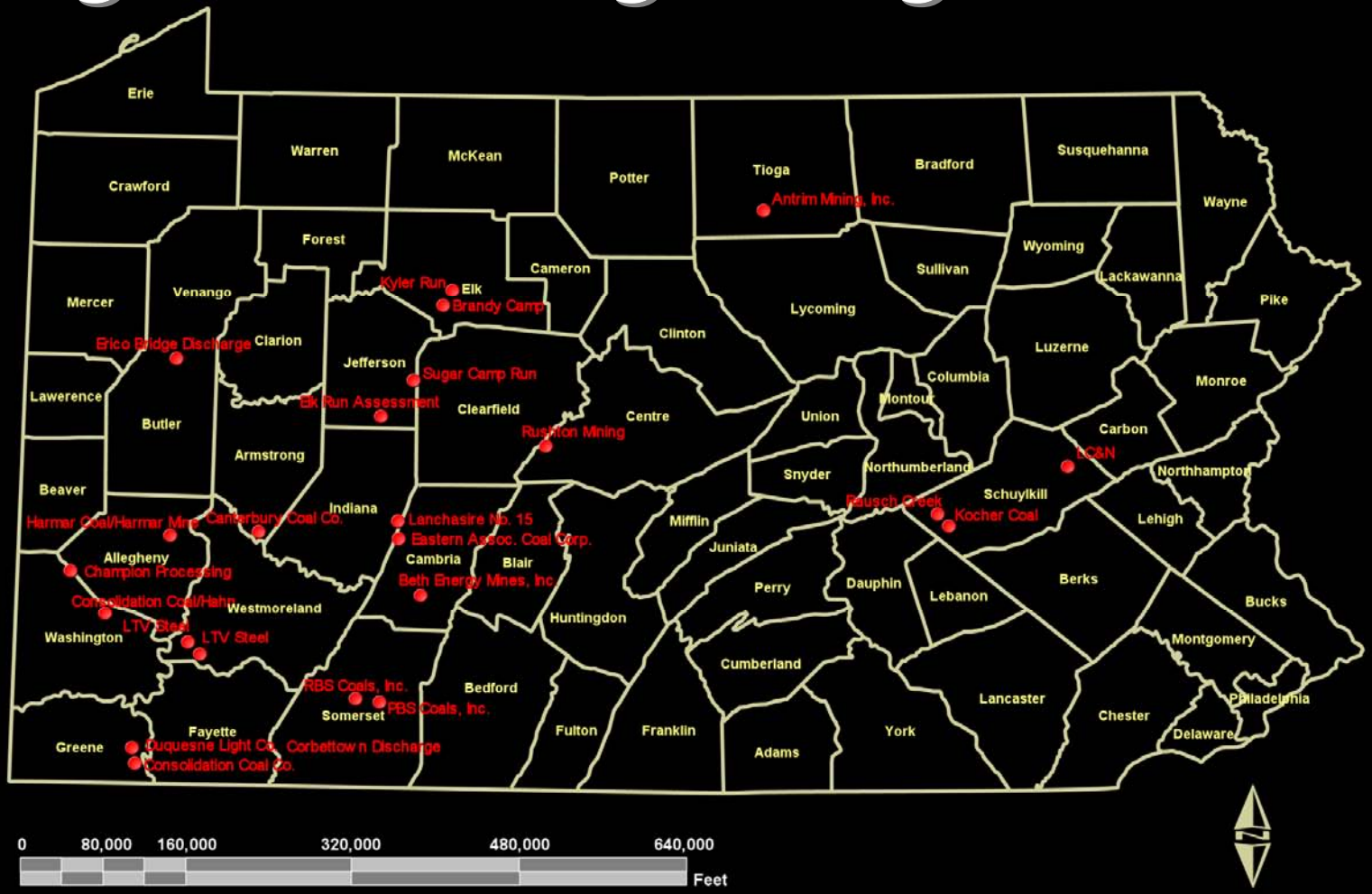
Concrete Mix Options



Waste Materials in the Cement Industry

- Spent potliner wastes
- Foundry sands
- Slags
- Fly ash
- Tire derived fuels
- Solvents
- Abrasives
- Contaminated soils
- Used grease
- By-product gypsum
- Soots and dust
- **Sludges**
- Pickling wastes
- Rubber
- Used solvents
- Oil
- Meat and bone meal
- Wood waste

High Producing Sludge Locations



Cement Producers in PA

- LaFarge Corporation (Whitehall)
- Medusa Cement Company (Wampum)
- Giant Cement Holding, Inc. (Bath)
- Essroc Materials (Nazareth & Bessemer)
- Kosmos Cement Co. (Pittsburgh)
- Armstrong Cement & Sup. Corp. (Cabot)
- Lehigh White Cement (York)
- Lehigh Cement (Evansville)

Trial Underway

- 100 tons of AMD treatment sludge from DEP's Rauch Creek plant will be moved into a cement plant in Eastern PA.
- The trial will take place within the next few weeks.
- Upon successful completion of the trial plans are to go into production and to expand to other plants.

Summary

- Chemistry restrictions in cement industry are more flexible that many other applications
- Preliminary assessment indicates that the use of AMD sludge in the cement industry is feasible
- Potential for expansion to other plants exists
- Major issues may not be chemistry
- Limitations
  - Water Content, Trucking, Handling, Perception

Summary

- Sink for thousands of tons of AMD iron per year
- Applied for patent
  - U.S. Provisional Patent Application relating to "Methods of Making Portland Cement Using Acid Mine Drainage Sludge and Associated Compositions"


Questions?