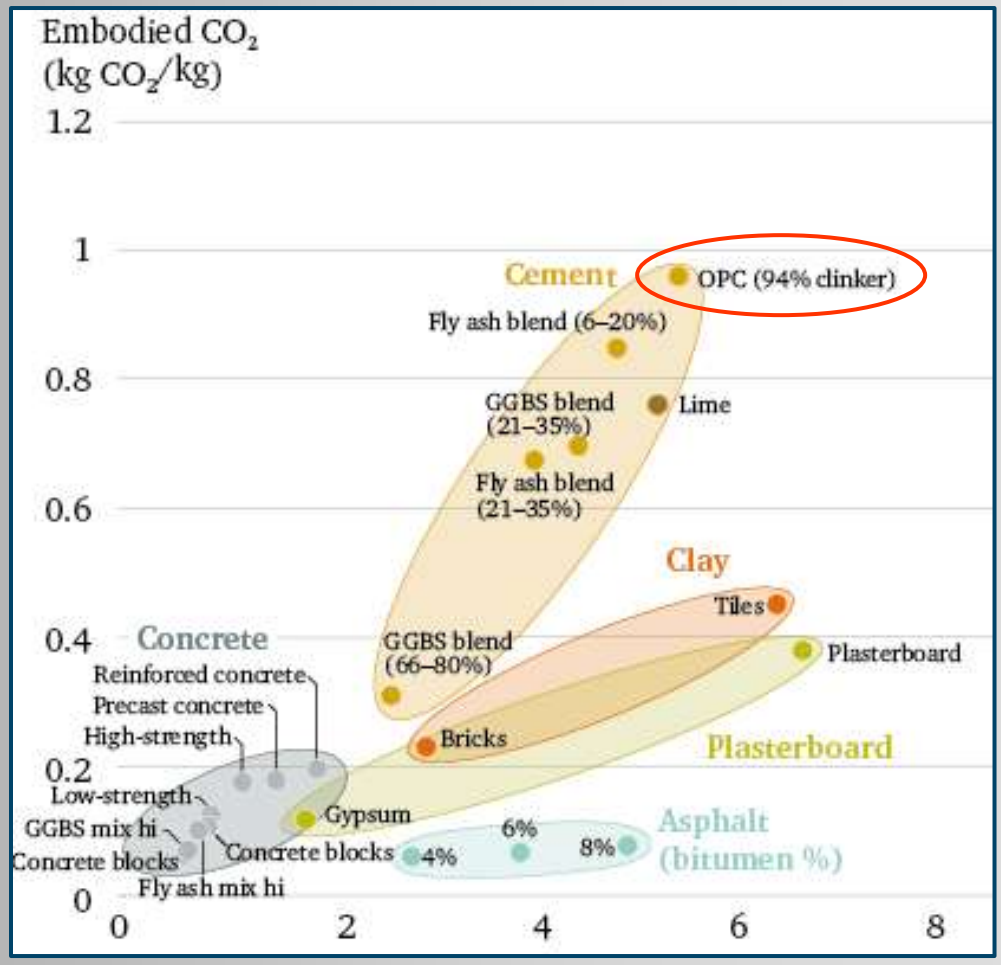
Portland Limestone Cement and Calcined Clay Stronger Together (and Less CO_2)

AWMA Coastal Plains Chapter
34th Annual Joint Florida/Alabama Technical Conference
Pensacola, Florida
June 16, 2023

Alvaro Linero, P.E.,
Linero Concrete Concepts, Tallahassee, Florida

Cement Industry is Big Energy User, CO_2 Emitter

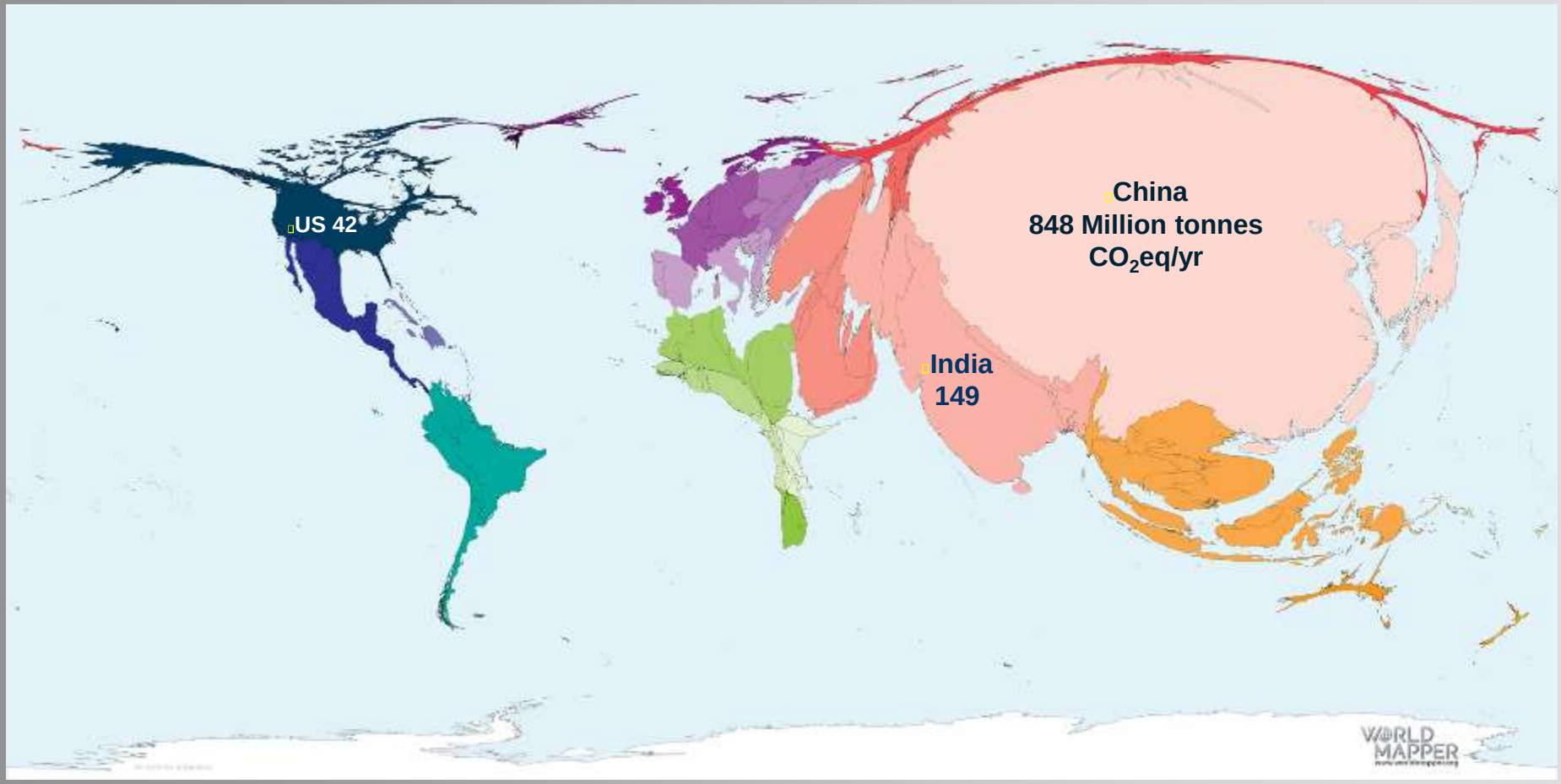
- Portland Cement (OPC) ~ 1 kg CO_2/kg Cement
- OPC is ~95% Clinker and 5% Gypsum
- Limestone ($CaCO_3$) is Main Raw Material
- Coal Ash, Iron Ore, Sand, Clay, Mill Scale
- $CaCO_3$ + Heat $\xrightarrow{\sim 1000^oC}$ CaO + CO_2(g)
- Coal is Main Calcining Energy Source
- Carbon (C) $\rightarrow$ Heat + CO_2(g)
- CaO, other Raw Materials Sintered ~2000ºC
- Coal is also Main Sintering Energy Source
- Grind with Gypsum to Delay Setting
- Blended Cements - Less Energy, Less CO_2
- Clay Products Contain Less Embodied CO_2
- Tires, Waste, Biomass Fuels "Reduce" CO_2



Embodied Energy (MJ/kg)

Source: Chatam House
https://www.chathamhouse.org/2018/06/making-concrete-change-innovation-low-carbon-cement-and-concrete

Worldwide Cement CO_2 Emissions

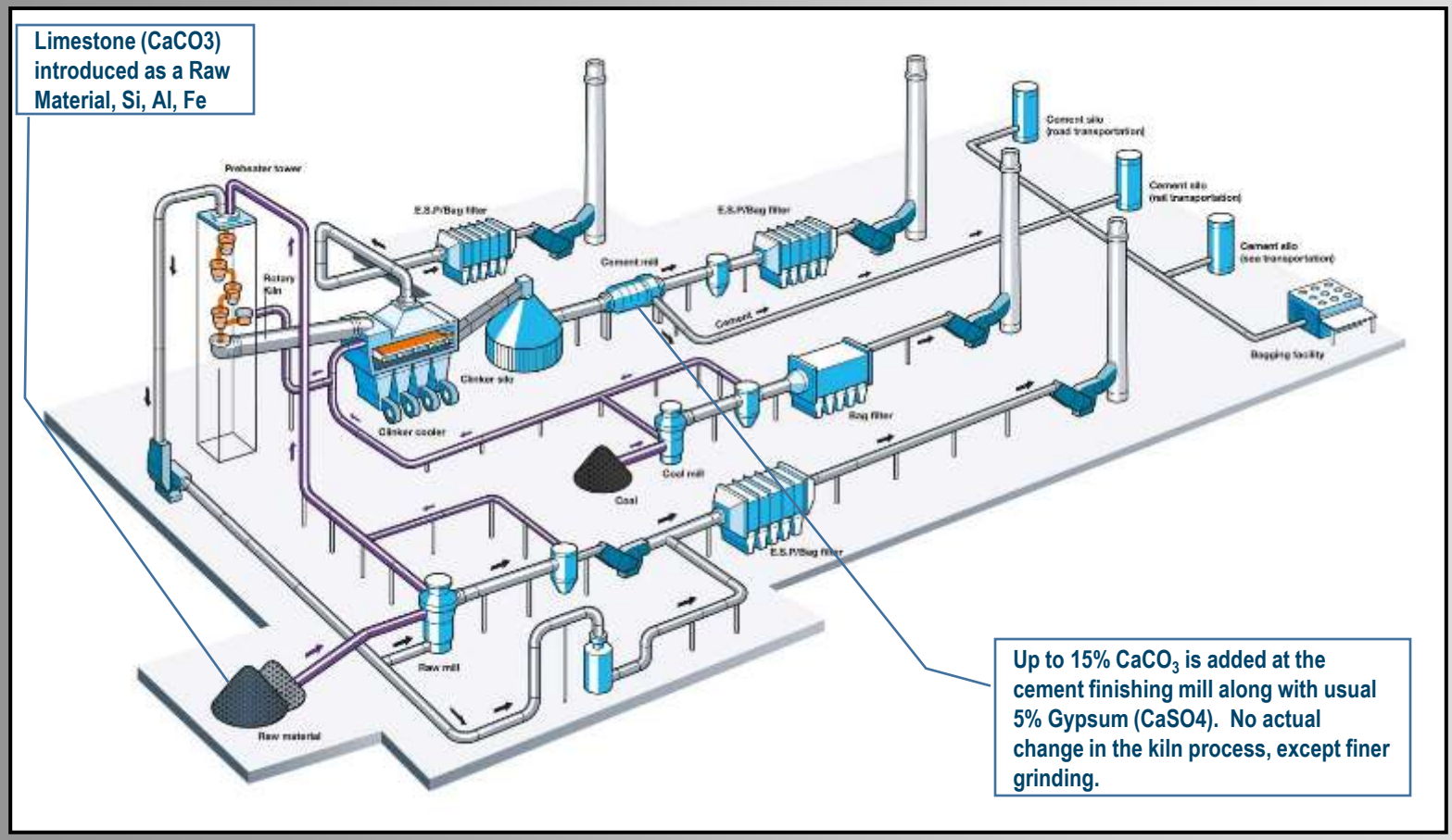


Country Sizes Exaggerated In Proportion to Respective Cement CO_2 Contributions

Might have been corrected for Waste Fuels

What is Portland Limestone Cement (PLC)?

- PLC is OPC with 15% Limestone Blended into Product at End of Process
- Extra Limestone is not Calcined, thus less Process and Fuel CO_2
- Wouldn't this be Poorer Cement based on Common Sense?



When Will PLC Hit the Market?

- **Now! Directives from Overseas Offices of All Cement Companies**
- **~6/2022, Companies Advised OPC No Longer Available by Yearend**

Benefits of PLC conversion

- Conversion has a positive impact on cement production in terms of volume and costs
  - Potential growth in cement production capacity of more than 10%.
  - The cost reduction compared to type I/II cement of around USD 2/ton in the mid-term.
- Accelerated conversion makes Argos an industry leader
  - Initial target - 30% by 2025
  - **Actual target - 100% by 2023**
- PLC accelerates the company's climate change targets and the industry's ambition to reduce its carbon footprint.

Source: Argos Investor Day. Cartagena June 15-16, 2022

How Does PLC Affect FDEP and Drillers?

- **FDEP Rules Require Use of OPC (Type I/II/III) for Water and Injection Wells**

> **62-532.200 Definitions for Water Well Permitting and Construction.**
> **(18) "Neat Cement Grout" means a mixture of water and Portland cement (American Concrete Institute Type I, Type II, or Type III); or a mixture of water and Portland cement of a type or kind approved by the permitting authority; or a mixture of water, Portland cement of a type or kind approved by the permitting authority, and an amount of those additives approved for use in cement grouts and approved by the permitting authority.**
>
> **62-532.500 Water Well Construction Standards.**
> **(i) Grouting and Sealing.**
> **1. All well casings seated into a consolidated formation shall be seated or sealed with neat cement grout.**
> **7. Alternate grouting methods and materials providing equivalent protection shall be approved in writing by the permitting authority.**

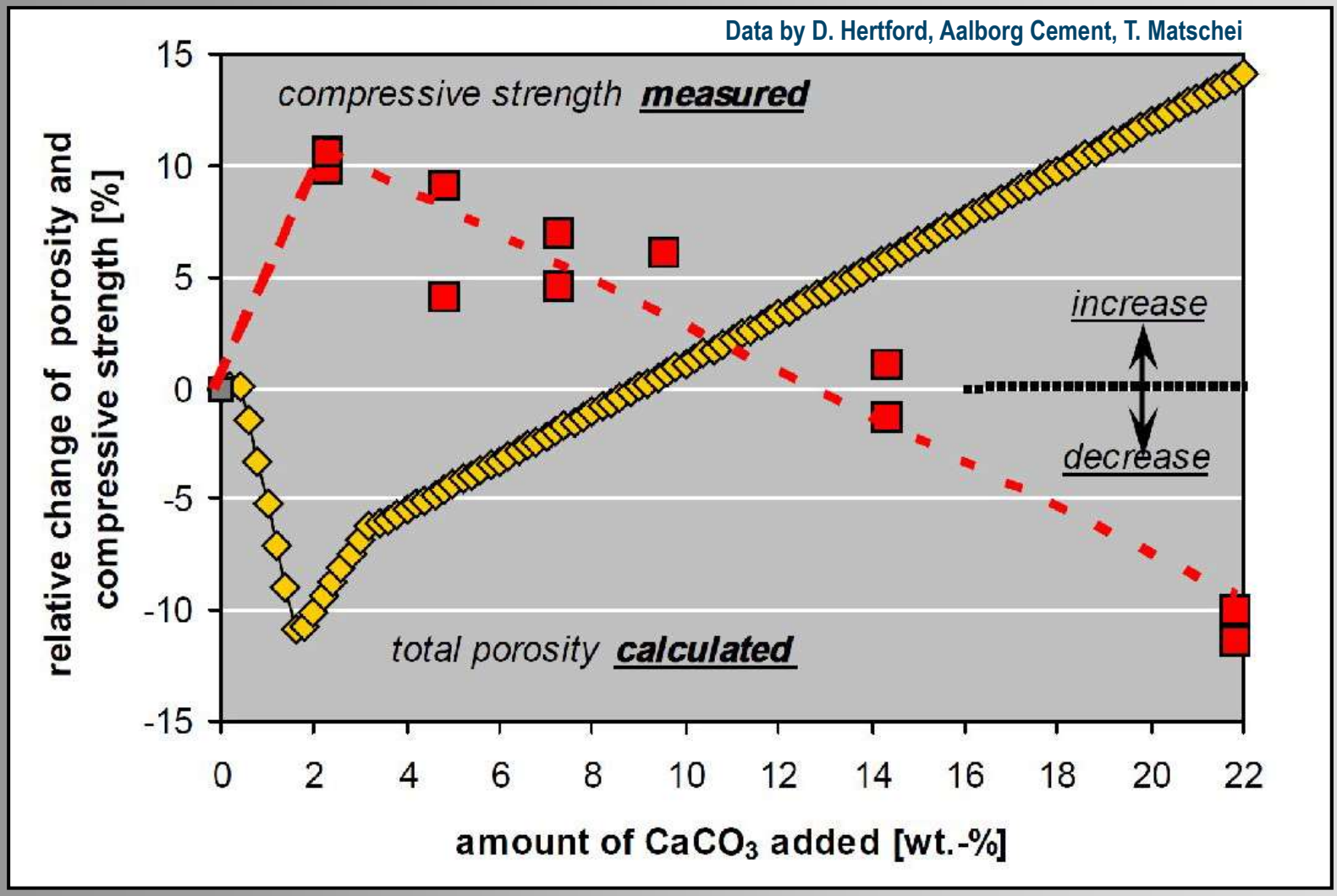
- **Cement Companies, Well Contractors Requested General Approval of PLC**
- **They Considered Prior Approvals by FDOT in Concrete Mixes as Sufficient**
- **No Clear Process to Approve Use of Cement Different than Type I/II/III OPC**
- **FDEP Considered and Ruled out Contract (UF), Lab Analysis (CTL)**
- **No Cement and Concrete Experts on Staff. Go to A. Linero and C. Fischler!**

PLC Can be Designed as Strong as OPC

Cement Plant		Plant 1		Plant 2		Plant 3		Plant 4		Plant 5		Plant 6	
Cement		**OPC**	**PLC**	**OPC**	**PLC**	**OPC**	**PLC**	**OPC**	**PLC**	**OPC**	**PLC**	**OPC**	**PLC**
Limestone (%)		**1.4**	**8.6**	**4.7**	**13.2**	**2.2**	**14.0**	**1.8**	**10.0**	**2.0**	**10.1**	**3.70**	**14.5**
Loss on Ignition (%)		2.4	6.3	2.8	6.6	2.4	7.3	3.2	5.4	2.22	5.09	2.50	6.6
Blaine fineness (m^2/kg)		384	472	413	551	405	538	432	467	409	502	393	535
Strength (psi)	**1 day**	2180	2060	2400	2650	2084	2620	2000	2060	2380		2330	2310
	3 day	3720	3670	4080	4860	3758	4730	3480	3500	3960	3560	4230	4130
	7 day	4830	4660	5380	6130	4974	5730	4490	4510	4880	4440	5550	5270
	28 day	6280	5930	7210	7260	6364	6940	6160	6410	6140	5770	7370	7040
3-Day Heat of Hydration (calories/gram)		68	67	69	65	71	71	60.0	62.7	69	68.5	62	65
Tricalcium Aluminate (%)		7		8		6		6	6	7		7	

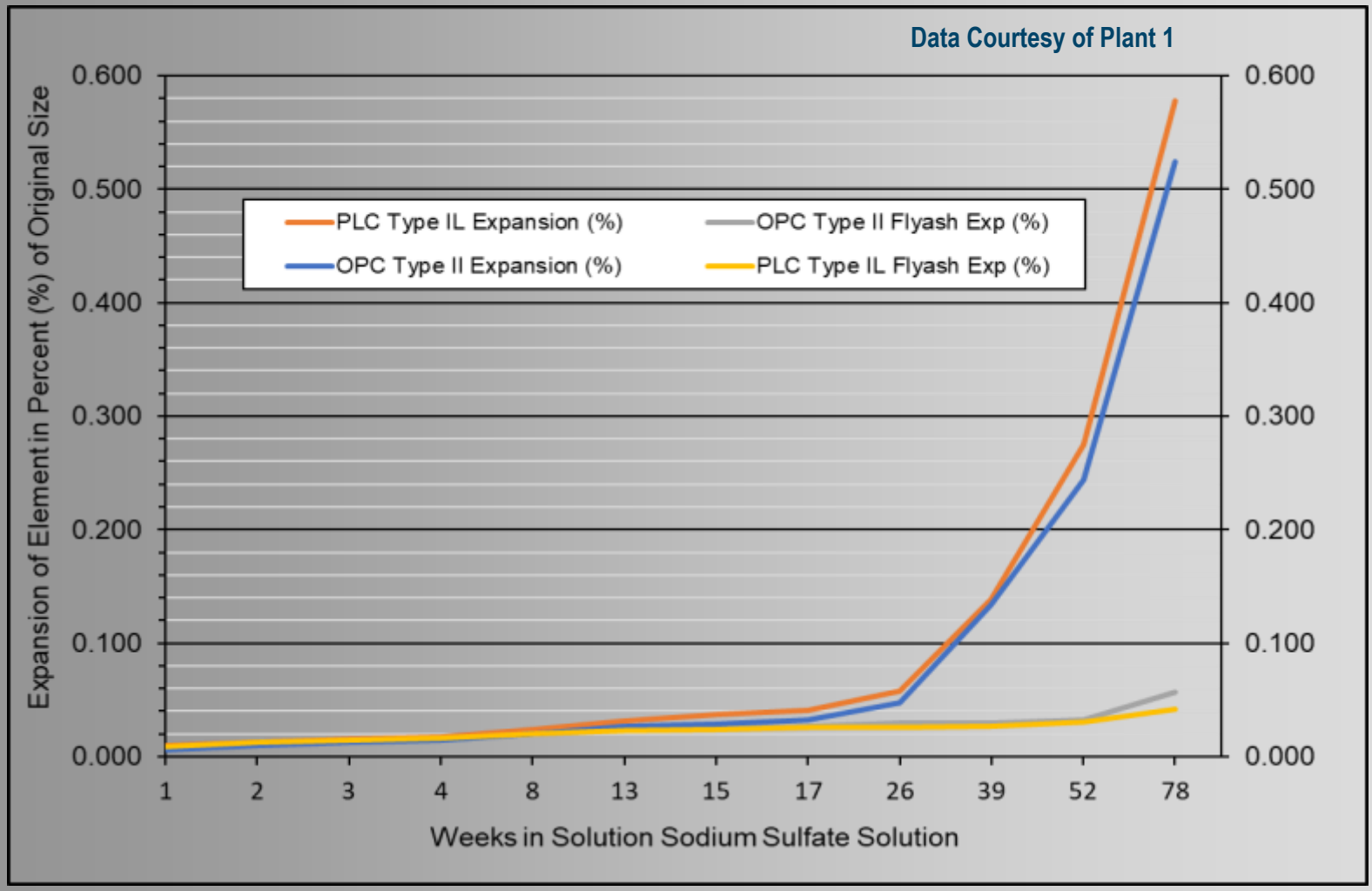
Data Compiled by Linero from Company Cement Mill Reports as Submitted to Florida DOT. 9/2022

Limestone Addition has Limits



- Initially Cement is Stronger with Limestone Addition. Back to Baseline by 12-14% Limestone Addition
- Porosity is Reduced. Back to Baseline by ~9% Limestone Addition. Low Porosity – SO_4, Cl, CO_2 Attacks!
- Finer Grinding Further Improves these Results up to a Point. Use Additives, Admixtures to Improve Handling

PLC vs OPC on Sulfate Resistance



- PLC Has Equal Sulfate Expansion Characteristics as OPC. Perform as Badly in Sulfate Environment
- Either Performs Much Better in when Combined with a Pozzolan like Fly Ash or Slag
- Both of these Pozzolans are or will Eventually be in Short Supply. Can Calcined Clay (CC) Help?

Getting the Approval Out to Stakeholders

- Prepared a White Paper
- Prepared a Report
- Prepared Letter and Report
- Letter and Graphics
- Letter Alone
- Memo Alone
- DEP Email 12/27/22 to DEP, WMDs
- Distributed in Response to Inquiries

During Review, Linero Resolves to Find Out What is Next!

From: Fischler, Cindy
Sent: Tuesday, December 27, 2022 10:52 AM
To: Wesley Curtis <WCurtis@sjrwmd.com>; Mike Turner <mturner@sjrwmd.com>; Bill Adams <badams@sjrwmd.com>; David Arnold (david.arnold@swfwmd.state.fl.us) <david.arnold@swfwmd.state.fl.us>; Elizabeth M. Fernandez <Elizabeth.Fernandez@swfwmd.state.fl.us>; David King <david.king@srwmd.org>; Zwanka, Warren <Warren.Zwanka@srwmd.org>; Megan Seward <megan.seward@nwfwater.com>; Tom Brown <tom.brown@nwfwater.com>; Lyle Hatchett@nwfwater.com; Selina Potter <Selina.Potter@nwfwater.com>; Richard Ilsley <rilsley@swfwmd.gov>; Miller, Deneale <Deneale.M.Miller@FloridaDEP.gov>; Evans, Bill <Bill.Evans@FloridaDEP.gov>; Ates, Katie L. <Katie.L.Ates@FloridaDEP.gov>; Bazewicz, Rebecca <Rebecca.Bazewicz@FloridaDEP.gov>; Martin, Robert L. <Robert.L.Martin@FloridaDEP.gov>; Kallemeyn, Thomas <Thomas.Kallemeyn@FloridaDEP.gov>; Hornick, Neil <Neil.Hornick@FloridaDEP.gov>; Desai, Anil <Anil.Desai@FloridaDEP.gov>; Lewis, Christopher J <Christopher.J.Lewis@FloridaDEP.gov>; Burson, Lu <Lu.Burson@dep.state.fl.us>; Peck, Erica <Erica.Peck@FloridaDEP.gov>; Kautz, Lance <Lance.Kautz@FloridaDEP.gov>; Starrach, Gabriele <Gabriele.Starrach@FloridaDEP.gov>; Moon, Nelin <Nelin.Moon@FloridaDEP.gov>; Newburg, Deanna <Deanna.Newburg@FloridaDEP.gov>; Fishkin, Len <Len.Fishkin@FloridaDEP.gov>; Davis, Jacob N <Jacob.N.Davis@FloridaDEP.gov>; Hardie, Gary <Gary.Hardie@FloridaDEP.gov>
Subject: Portland Limestone Cement

Hello everyone,

The Department received information that the cement industry has stopped producing Type I/II cement, which was previously approved by the Department for use in well construction. The cement industry throughout the nation will now be producing Portland Limestone Cement (PLC), also known as Type IL as the replacement. This Type IL has a higher limestone content (5% - 15%).

In response to the discontinuation of the Type I/II cement, the Department has reviewed data regarding the Portland Limestone Cement (PLC)/Type IL for replacement suitability. As a result of the Department's review of the of PLC/Type IL cement, the Department issues the following approvals:

- The Department considers and approves PLC/Type IL cement with a limestone content between 5% and 15% as acceptable for use in well construction permitting. The PLC Type II must still meet the respective standards listed in the American Society for Testing and Materials (ASTM), ASTM C595M-21.
- The Department considers and approves PLC/Type IL cement with a limestone content between 5% and 15% and with a specification of moderate sulfate (MS) resistance or better as acceptable when cementing Class I and Class III UIC wells as described in subsection 62-528.410(5) F.A.C. The exact designation shall be PLC Type II (5-15%) (MS) or better in accordance with ASTM C595M-21.
- The Department considers and approves PLC/Type IL (5-15) (MS), used in conjunction with a Department approved pozzolanic secondary cementitious material (SCM), as acceptable as part of the well construction permitting. Pozzolanic SCM, such as calcined clay, silica fume or other environmentally friendly (non-coal ash) material are also effective for resistance to sulfate, chloride, and other forms of attack on cement and concrete.

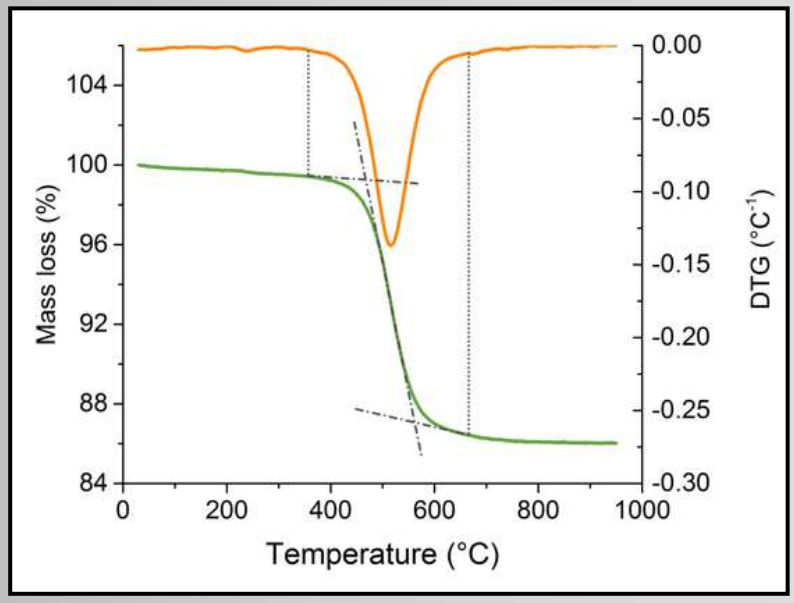
Please utilize the above Department approvals in your decision making process when reviewing permit applications for cement requirements for either Water Well Permitting and Construction Requirements pursuant and 62-532.200(18), Florida Administrative Code, or for permit applications associated with Underground Injection Control (UIC) Class I and III injection and monitoring wells pursuant to 62-528.410(5) and 62-528.420(5) Florida Administrative Code.

If you have questions, please contact Cindy Fischler at Cindy.Fischler@FloridaDEP.gov or 850-245-8558.

Cindy Fischler M.S., P.G.
Environmental Administrator Aquifer Protection/Underground Injection Control
Florida Department of Environmental Protection
Aquifer Protection Program
Division of Water Resource Management
2600 Blair Stone Rd. MS 48530
Tallahassee, FL 32399
Cindy.Fischler@floridadep.gov
Phone (850) 245-8558

What is Calcined Clay (CC)?

- Kaolinitic Clay*, Heated to ~ 750ºC
- 50% Purity, not the High Value Stuff
- Mass Loss, Bound Water is Released
- Disordered High Surface Area Structure
- Low Temperature vs Cement Calciner/Kiln
- No Process CO_2 and Less Fuel CO_2
- Reactive Pozzolan, Source of Si and Al

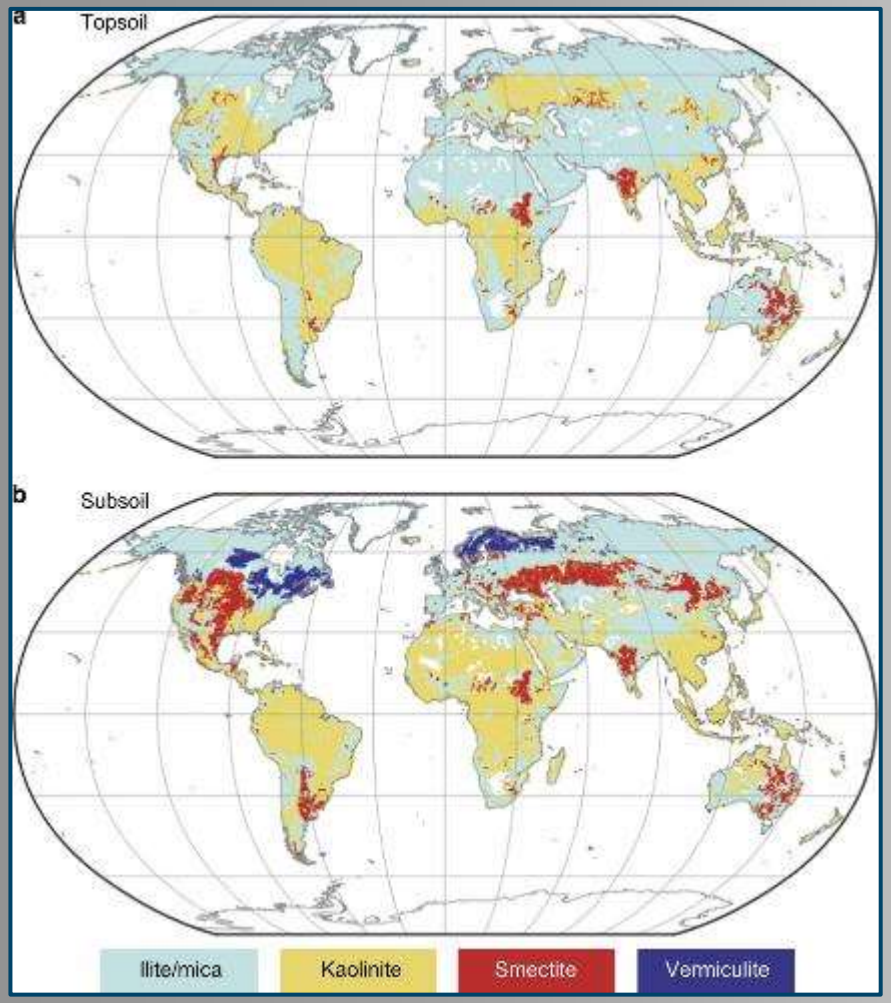


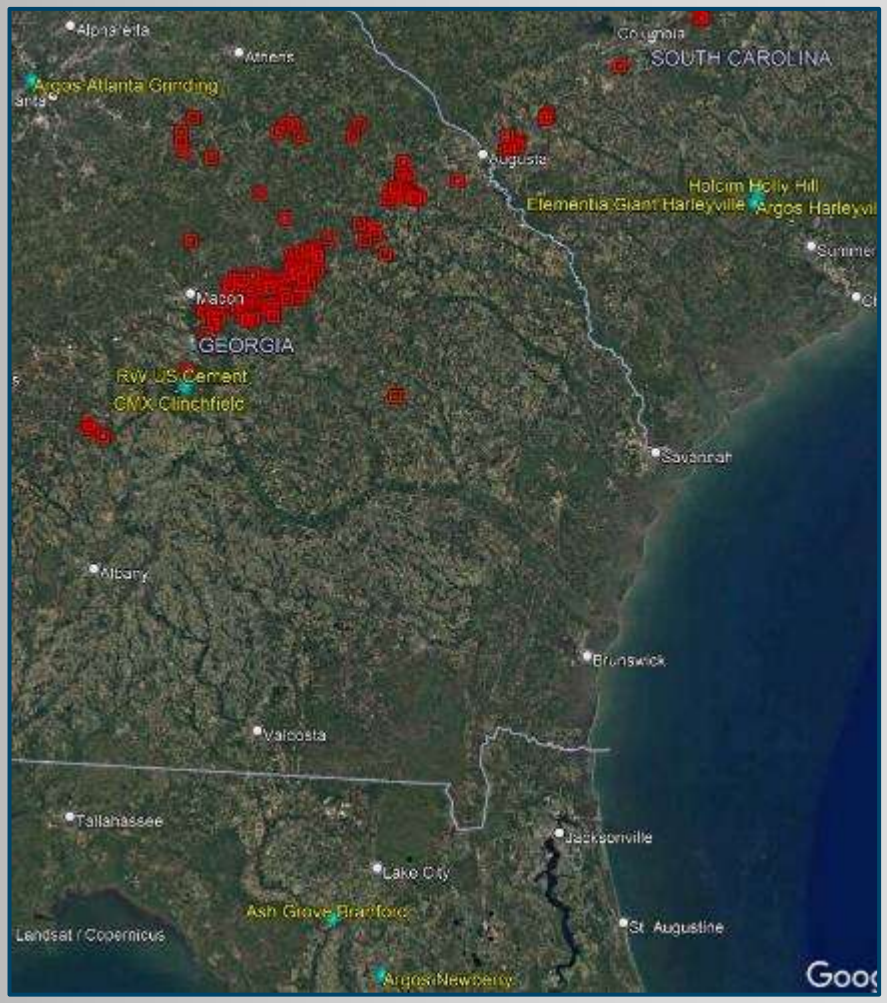
From Presentation by K. Scrivener of LC3 Project, Lausanne

- Added to OPC, Combines with Portlandite (CaO) to Form More CSH Crystals
- In PLC Combines with $CaCO_3$ to Form Carboaluminates and Retain CO_2
- Replace Fly Ash, Slag as these Secondary Cementitious Materials are Exhausted
- Better to Use CC than Fly Ash as SCM when Drilling Wells through USDW

**Can Also Consider Montmorillonite and Ilite, but these are Not as Useful as Kaolinite*

Where Are Useful Clays Found?



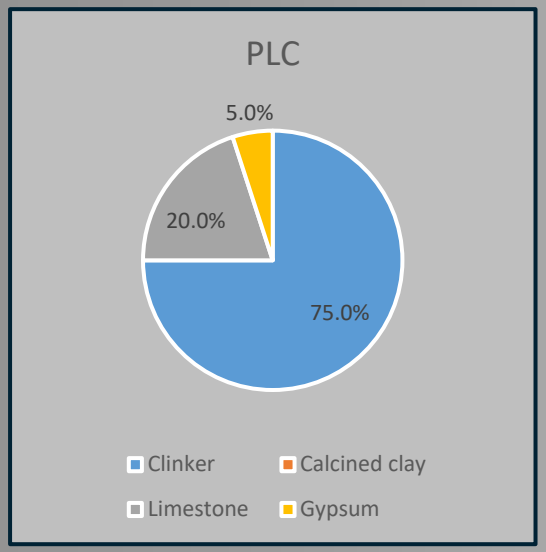


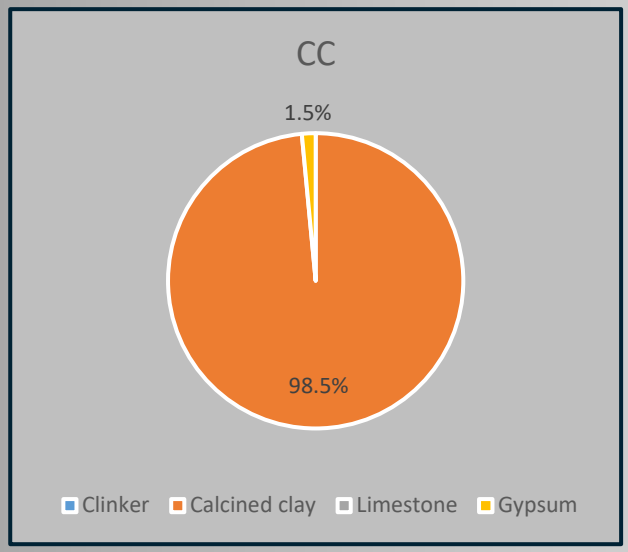
Clays Everywhere! A. Ito, R. Wagai, Nature, 2017

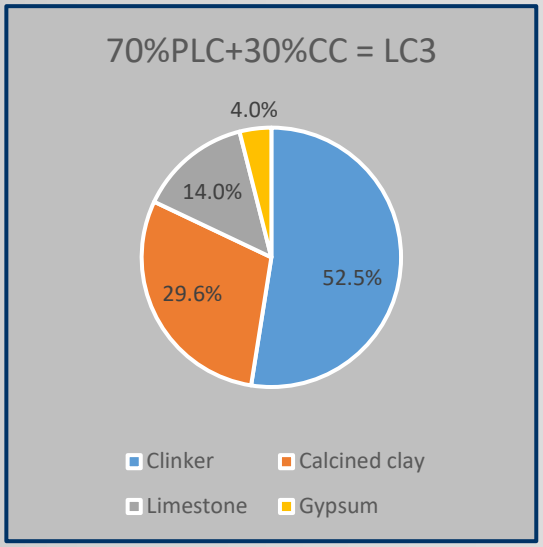
Ceramic Quality Kaolin Mines in Georgia, S. Carolina

There are Extensive Railroad Network, Cement Plants and Many Ready-Mix Plants in Southeast USA

Combining PLC with CC Yields LC3

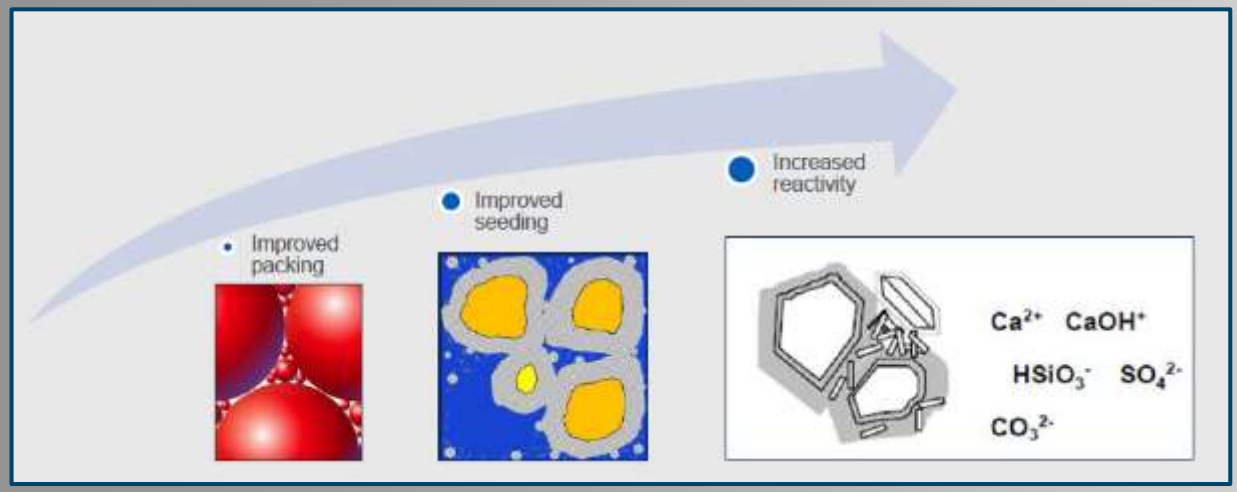




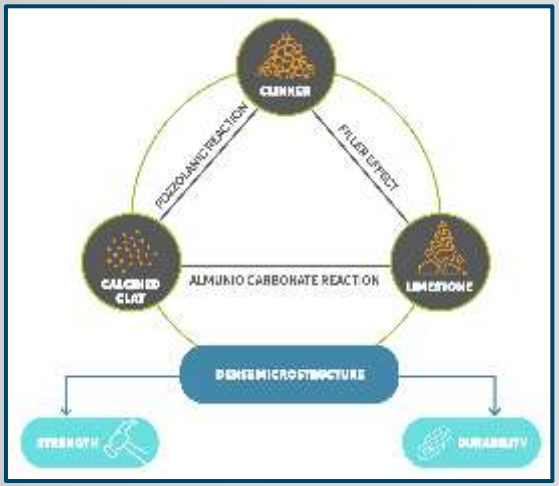


- Limestone Calcined Clay Cement (LC3) Can be made at an Existing Cement Plant
- Separately make Limestone Calcined Clay (LC2) and add to OPC to Make LC3
- More Practical Option in U.S. is to Mix CC as an SCM with PLC at Ready-Mix Plant
- Thus, CC Would be in Direct Competition with Fly Ash, Slag, Ground Glass, Etc.

PLC and CC – Stronger Together



Slide and *Comment, A. Dorsey, Ash Grove Presentation, LC3 Day, March 28, 2023

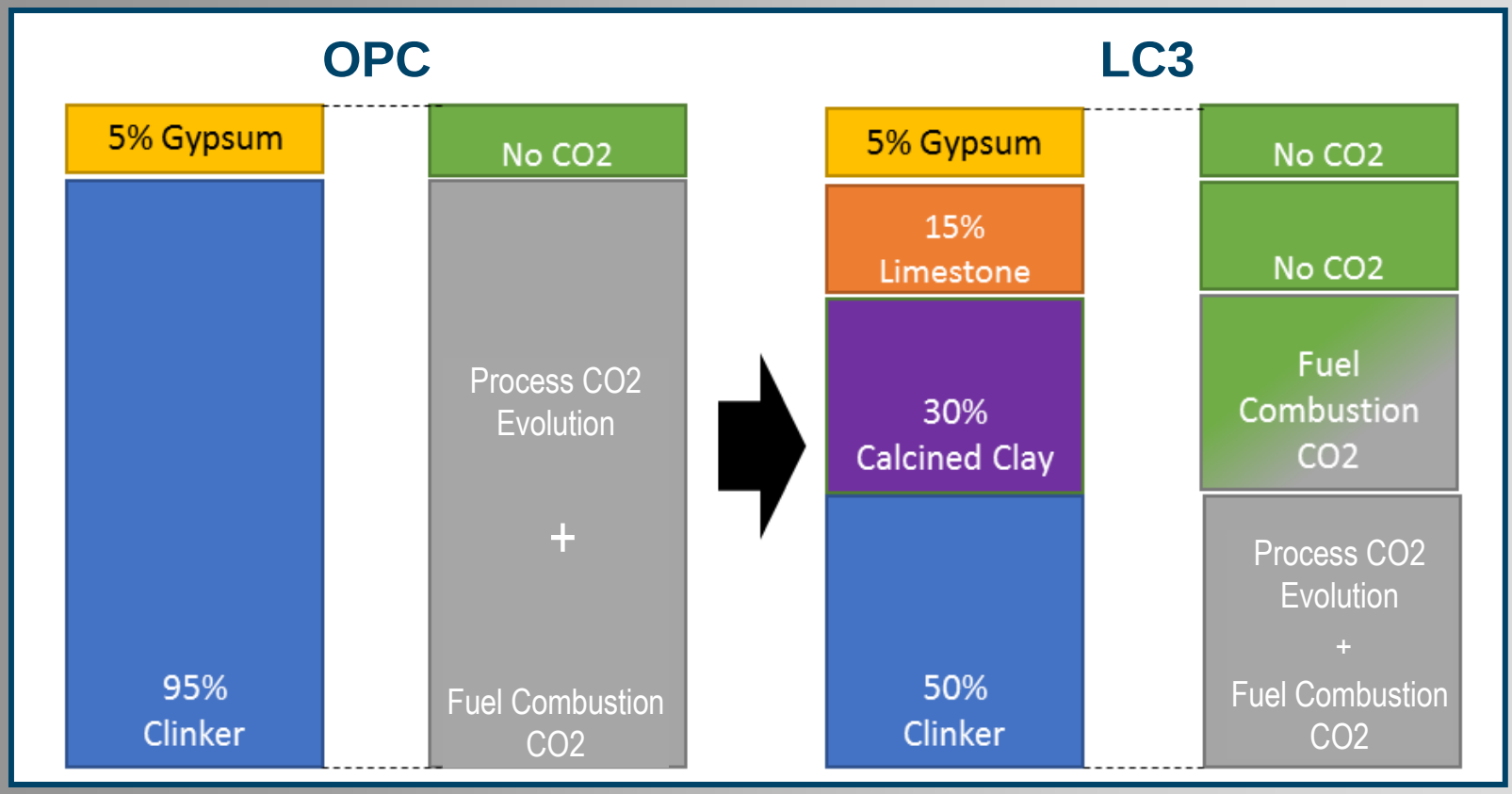


Slide F. Martirena, LC3 Project

- Improved Packing by Finer Particles Reduces Porosity and SO_4, Cl, CO_2 Attack
- More Nucleation Sites for Additional Crystal Formation and Strength
- Strong Pozzolanic Reaction and Permanent Incorporation of Limestone CO_2
- Less Embodied Energy and CO_2 Emissions than Ordinary Portland Cement
- Some Extra Electric Energy for Grinding the PLC
- Good Long-Term Solution to Diminishing Fly Ash and Slag
- Reasonable Way to Reduce CO_2 Emissions from Cement without Sequestration

** It was also found that Quartzite can be made less troublesome and more reactive during Clay Calcination*

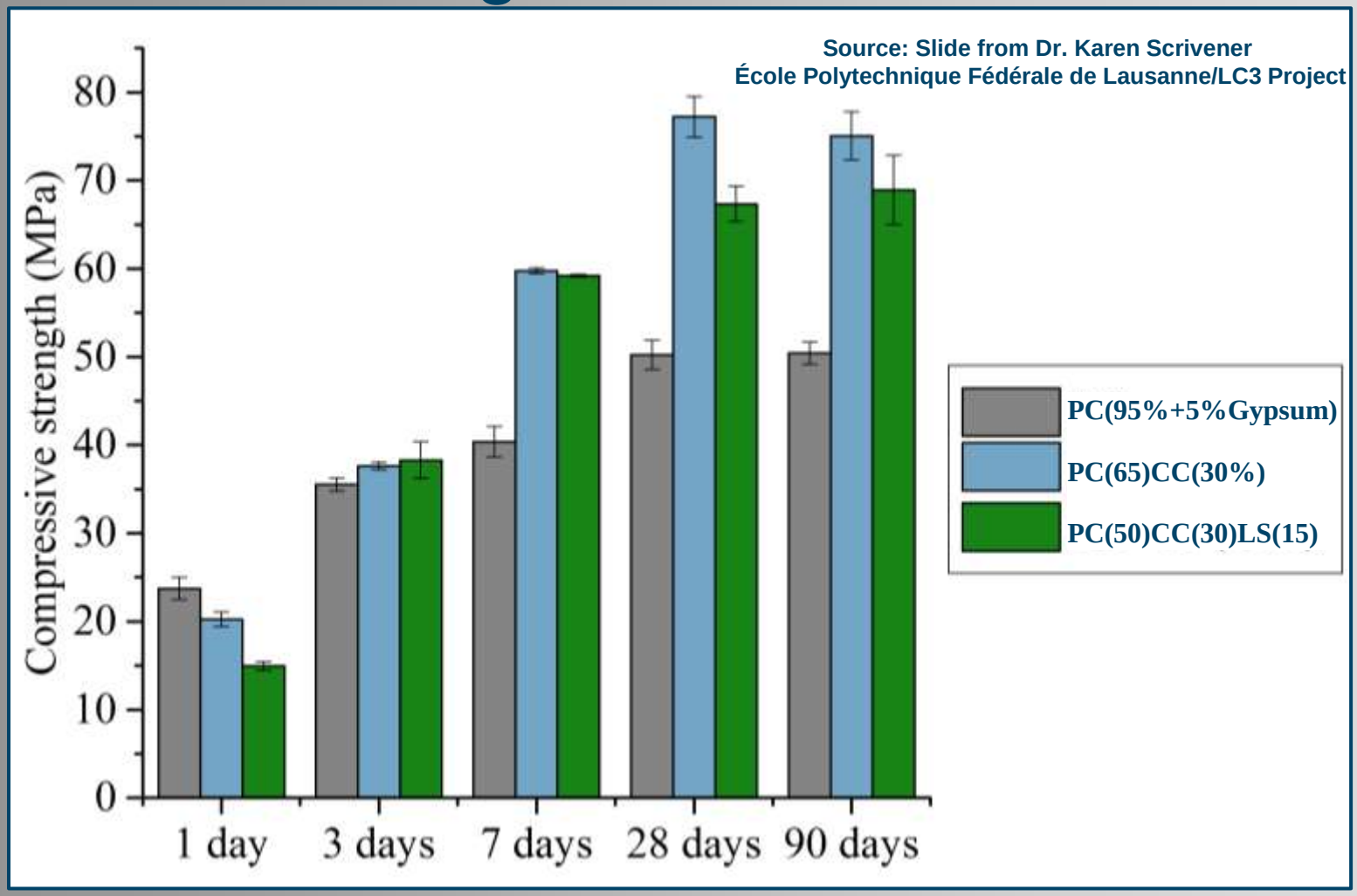
How PLC (OPC + Limestone + CC) Reduces CO_2



Slide F. Martirena, LC3 Project

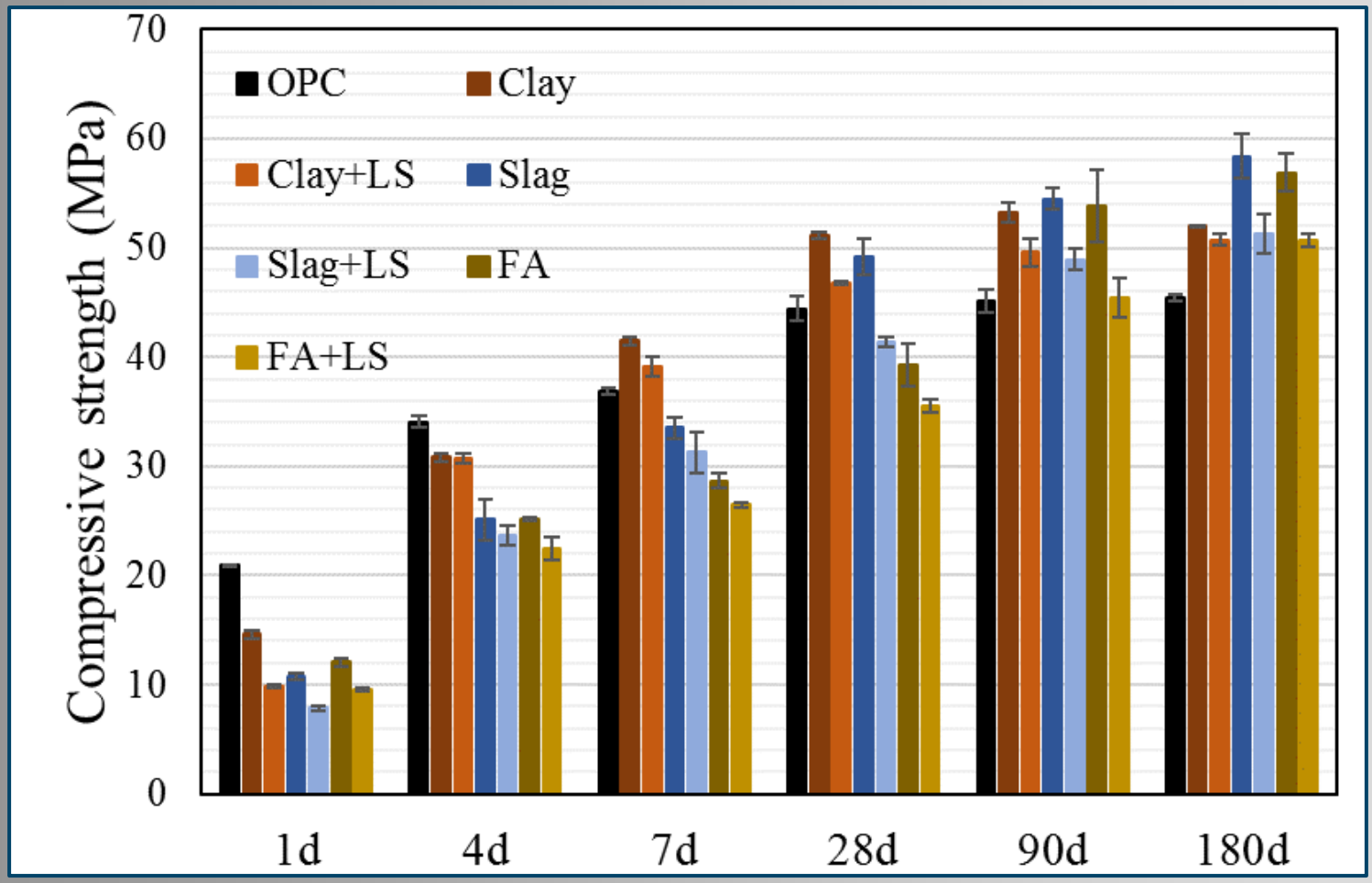
- LC3 Contains Significantly less Embodied Energy and CO_2 Emissions than OPC
- Drying and Dehydroxylation of CC Emits no CO_2 and Less Fuel CO_2 due to Lower Temperature
- Limestone Addition Emits no CO_2 and No Fuel CO_2. Some Extra Grinding Electric Energy

Effect of Adding CC and Limestone to OPC



- By Day 3 Additions of Calcined Clay and Limestone to Make LC3 Yield Cement of Equal Strength to OPC
- Beyond 3 Days the Strengths of the "Stronger Together" Formulations Are Greater than OPC
- Can Add Quite a bit of Uncalcined Limestone and Maintain a Very Good Strength Profile and Lower CO_2

Comparison of LC3 with Other Systems



- OPC is Portland Cement Alone, Including 5% Gypsum
- Binary Systems (e.g., OPC plus an addition) are 70% OPC and 30% CC, Slag or Fly Ash
- Ternary Systems (e.g., OPC plus 2 additions) are 50% OPC, 15% Limestone and 30% of Slag or Fly Ash

Source: Slide from Dr. Karen Scrivener at École Polytechnique Fédérale de Lausanne/LC3 Project

Where Has This Been Done?

- Brazil in 1990s (Energy Crisis)
- India, Cuba, Colombia in Cooperation with the LC3 Project
- Cameroon Flash Calciner 2020
- Ivory Coast Rotary Kiln 2020
- Argentina Kiln Conversion (Illite)
- Ash Grove, Duracem 1990s*
- Ash Grove, Nebraska 2020

Abidjan, Ivory Coast Where Limestone is in Short Supply

* Duracem was Developed to Deal with Damaging Alkali Silica Reactions with Aggregates that cause Gelling and Swelling in Concrete

CC Production Know-How – Examples

Refurbished Kilns

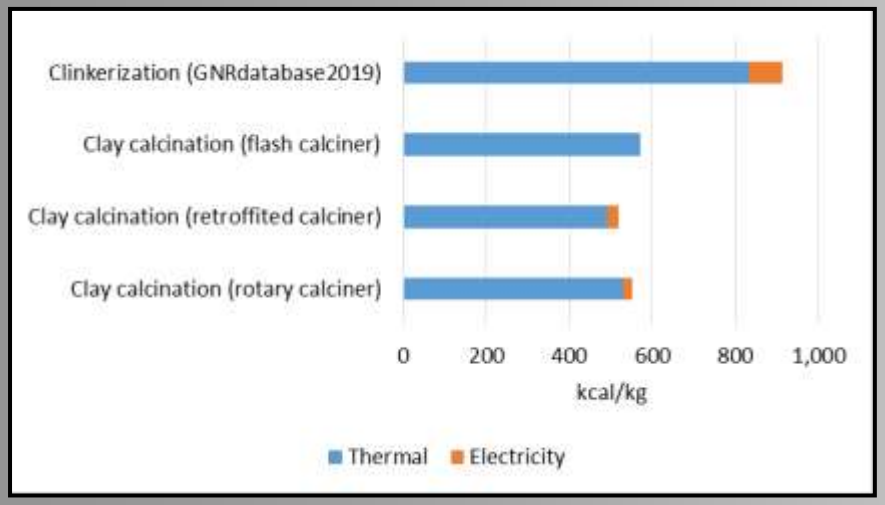
New Rotary Kiln

Flash Drying, Refurbished Kiln
Dehydroxylation

Data From Some Existing Clay Calciners

Location	Company	Technology	Capacity (tonnes/yr)	Heat (kcal/kg)	Electricity (kW-h/tonne)	Moisture Clay (%)	Fuel
Rio Claro, Colombia[1]	Argos	Flash Hybrid	450,000	570	Not Available	25	Coal
Porto Velho, Brasil[2]	Votorantim	Retrofit	300,000	490	25	Not Available	Not Available
Abidjan, Ivory Coast[3]	IPIAC-Nery	Rotary	250,000	529	20	30	Fuel Oil
Santa Clara, Cuba[4]	IPIAC-Nery	Rotary Pilot Plant	1,188	600	22	30	Fuel Oil
Jiaozuo, China[5]	Sinoma	Rotary Dryer	405,000	400	Not Available	15	Not Available

1. Dynamis and Loesche, *Reshape your Footprint*. Calcined Clay and grinding. Presented in LC3 Day, Costa Rica March 26-29th 2023.
2. Parashar et al. *Overview of the Use of Calcined Clays in Cementitious Materials*: Case Studies. 2023. In process of publication.
3. Putin, A., IPIAC´s Technology. Presentation, LC3 Day in Costa Rica March 26-29th 2023.
4. Dynamis and Loesche, *Reshape your Footprint*. Calcined Clay and grinding. Presented in LC3 Day in Costa Rica, March 26-29th 2023.
5. Sinoma International Engineering CO, LTD, *Development of Key Technology & Equipment for Calcined Clay of Sinoma*. Presentation, LC3 Day in Costa Rica March 26-29th 2023.



- **Typical Clinker Production Energy Values are 834 kcal/tonne and 72 kWh/tonne clinker**
- **CC Heat and Electric Consumption are Significantly Less than Typical Clinker Values**
- **Thus, much Less Fuel CO_2**
- **No Drying/Dehydroxylation CO_2 Release from Clay.**
- **To the Extent that CC Replaces Clinker, there will be Corresponding Heat and CO_2 Emission Reductions. Same Applies to Limestone Additions**

Data on Slide Compiled 2023 by Sofia Sanchez Berriel, LC3 Project

Financial Attractiveness of LC3

Scenario 1: Produce 1 million tonnes/yr of LC3 at Existing Integrated Cement Plant (300,000 tonnes/yr of Calcined Clay)				
Calciner Type	CAPEX ($millions)	Clay availability (km)	LC3 Production Cost ($US/tonne)	Attractiveness (% IRR)
Flash Calciner	10.3	10 / 200	23.4 / 27.3	63 / 22
Rotary Kiln	6.6	10 / 200	24.2 / 28.1	87 / 24
Scenario 2: Produce 413,000 tonnes/yr LC3 at Existing Grinding Station (124,000 tonnes/yr Calcined Clay)				
Calciner Type	CAPEX ($millions)	Clay Availability (km)	LC3 Production Cost (US$/Tonne)	Attractiveness (% IRR)
Flash Calciner	8.15	10 / 200	32.1 / 36.0	75 / 55
Rotary kiln	6.1	10 / 200	32.6 / 36.5	98 / 71
Scenario 3: Produce 413,000 tonnes/yr LC3 at Greenfield Grinding Station (124,000 tonnes/yr of Calcined Clay)				
Calciner Type	CAPEX ($millions)	Clay Availability (km)	LC3 Production Cost (USD/Tonne)	Attractiveness (% IRR)
Flash calciner	27.0	10 / 200	32.1 / 36.0	17 / 9
Rotary kiln	26.0	10 / 200	32.6 / 36.5	17 / 9

Source: 2019 Financial Attractiveness by LC3 Project https://lc3.ch/financial-attractiveness-of-lc3/

Comparison would be Against Ordinary Portland Cement at $30/tonne if produced in a cement plant, and $47/tonne if produced with imported clinker. Assumes Continued Use of Coal as Fuel.

Summary

Use of 15% Limestone to Make PLC Really is the Down Payment for Lower CO_2 Emissions from Cement/Concrete

Most Cement Companies in U.S. do not Want to Invest Capital Right Now to Convert all the way to LC3

But the Same Companies are Doing it Overseas and Really are Interested in Doing this In the U.S.

Owners of U.S. Kaolin Mines are not as Inclined to offer CC; not as Profitable as Metakaolin and other Products

Owners of some Kaolin Mines also Market Fly Ash and other SCM. CC Might Reduce Value of such Products

CC is Sustainable and Offers Alternative to Fly Ash and Slag Scarcity and their Ultimate Price Increases

As DOTs and Builders See LC3 as Good Cement and Concrete and Lower CO_2 they will Gravitate to it

Look to Possible Importation of CC from other Countries to Compete with Fly Ash and Slag

Look to Possible Grant(s) from DOE under Inflation Recovery Act to Kick Start with Incentives and Subsidies

IRA and Provides for Multi-million-dollar Demonstration Projects, 2% Incentives to Use Alternatives like LC3

Up to a Point, IRA/DOE will reimburse Users the Entire Added Cost to Use such Alternative

Ash Grove, Louisville NE is already producing and trying out CC (possibly at a Google Center)

Ash Grove, Foreman AR received a 15,000,000 Grant from DOE for Front end engineering Design for CCS

Let's See if anyone gets a Grant to Construct an LC3 Plant!

OPC, Limestone and CC are Stronger Together as LC3, Emit Less CO_2 and Require Less Energy to Produce

Questions? Contact Information

Alvaro Linero, P.E.,
Linero Concrete Concepts, Tallahassee, Florida
aaalinero@gmail.com
850-591-7364

Sofía Sánchez Berriel, PhD., UCLV
martirena@uclv.edu.cu

Fernando Martirena H., D.Sc. UCLV
ssbma87@gmail.com