Biosilica - A Sustainable Low Carbon Supplementary Cementitious Material For Concrete

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NRMCA Concrete Innovations Session 15: Innovative Cements

September 13th, 2023

Courtesy: Some images/data from online resources are shown for demonstration purpose only.

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Acknowledgements

- NSF SBIR
- USDA
- ChK Group (Dr. Rajan Vempati)

PCA Roadmap to Carbon Neutrality

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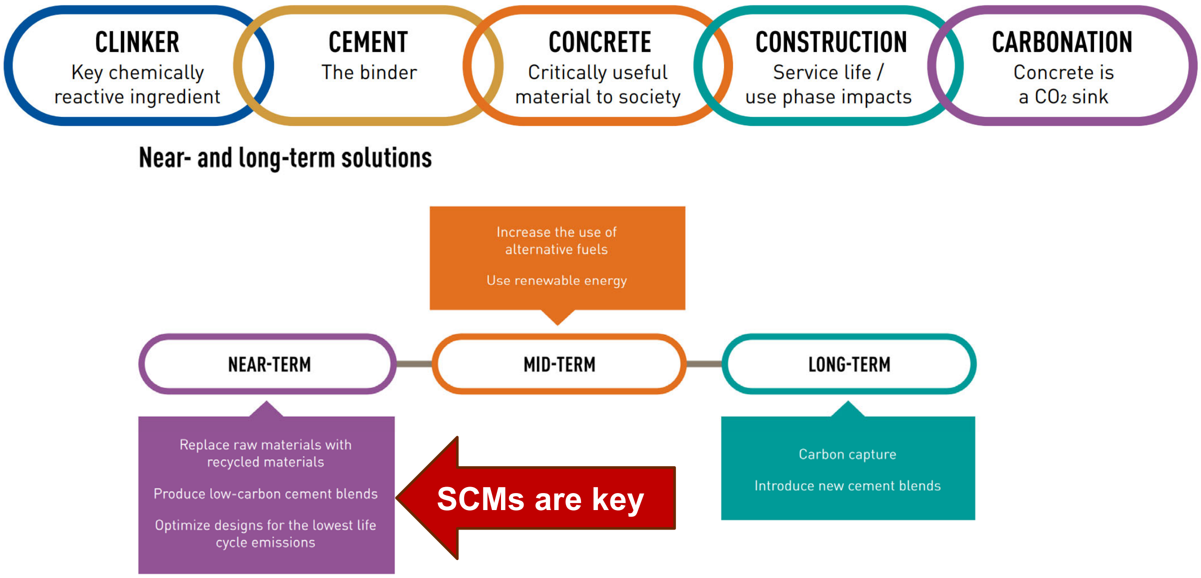

PCA Roadmap to Carbon Neutrality, October 2021

Overview

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- What are supplementary Cementitious Materials (SCMs)?
- Need for alternate, low-carbon sources of SCMs
- Biomass-based SCMs
- Potential for scalability of biomass-based SCMs in the US and around the world
- Rice Husk Ash (Biosilica)
- Role of Biosilica in Improving Properties of Concrete
- Conclusions

Traditional Supplementary Cementitious Materials (SCMs)

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- Fly ash – Class F and Class C
- Slag – Grades 80, 100 and 120
- Silica Fume
- Meta-Kaolin
- Natural Pozzolans – Class N

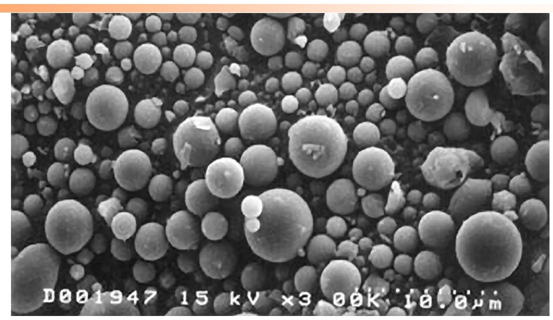
Cement hydration

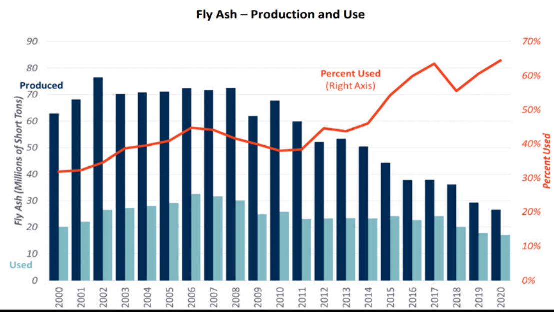
Reactive Si or Al-Si + CH + H → C(A)SH gel

SCMs or Pozzolans

Lower Carbon Footprint

Improved Strength & Durability





https://acaa-usa.org/wp-content/uploads/2021/12/News-Release-Coal-Ash-Production-and-Use-2020.pdf

Need for Alternate SCMs

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- Natural Pozzolans and Calcined Clays (ASTM C618 – Class N)
- Harvested Ash, Ground Bottom Ashes and Other CCPs (ASTM C618)
- Ground Glass Pozzolans (ASTM C1866 – Type GS and GE)
  (Concrete Innovations Webinar No. 9, Nov. 2022)
- Biomass ashes
- Blended Supplementary Cementitious Materials (ASTM C1697)

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Biomass Availability in the United States

Biomass Ash:

- **Mineral residue from combustion of biomass** can potentially yield valuable material with a composition that is suitable to used **as an SCM with Portland cement in concrete**.
- The composition of the biomass ash will depend on:
  - Source and nature of the biomass
    - Forests
    - Wastes
    - Agricultural Residues
    - Energy Crops
  - Combustion process
  - Post-combustion processing
- Availability of biomass ash is regional

Feedstock	Available Biomass (million dry tons)	
	UCS Analysis	Updated ORNL Analysis (base case 1% yield increase)
Energy Crops	400	400
Agricultural Residues: Primary	129	180
Agricultural Residues: Secondary	25.5	25.5
Waste Materials: Urban and Mill Wastes	43.4	43.4
Waste Materials: Manure	58.9	58.9
Forest Biomass: Integrated Operations	20.5	40.9
Forest Biomass: Other Removals	0	12.6
Forest Biomass: Pulp	0	3.4
Forest Biomass: Thinnings	0	3.2
Total	**677**	**767**

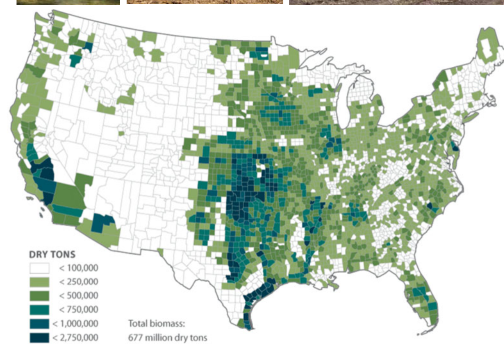

FIGURE 1 Biomass Availability across the Continental United States

Though biomass production is generally widespread, it is most concentrated in the Southern Plains, California, the Corn Belt, and along the Mississippi River. Counties that are not shaded may have biomass available, but in comparatively small amounts.

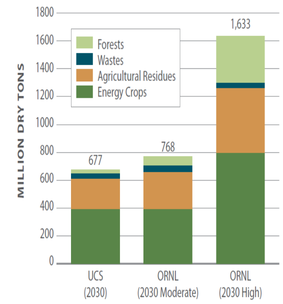

FIGURE 2 Biomass Resource Availability

The ORNL study showed a wide range in biomass resources depending on crop yields and tillage practices. Our results are significantly lower than that study due to stricter sustainability criteria and less optimistic assumptions regarding the adoption of no-till agriculture and increases in crop yields.

Source: *www.ucsusa.org/biomassresources*, Sept 2012

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Typical Biomass Ash Compositions Reported in Literature

ID	Oxide Composition (%)												Ash Content (kg/100 kg)
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	MnO	K_2O	Na_2O	P_2O_5	SO_3	LOI	
Rice Husk Ash (RHA)	68.28	1.28	0.54	0.07	0.37	3.59	0.13	3.14	3.78	0.16	0.61	13.33	20 - 30
Corn Stover Ash (CSA)	49.00	3.27	1.07	0.23	5.12	2.17	-	22.70	0.41	3.74	0.63	9.04	4.80-7.31
Corn Stover Ash (Washed)	64.80	3.21	0.94	0.22	8.86	2.35	-	8.82	0.41	1.79	1.31	4.01	4.80-7.31
Bamboo Leaf Ash (BLA)	78.71	1.01	0.54	0.08	7.82	1.83	-	3.78	0.05	0.99	1.0	3.83	-
Olive-Pine Waste Ash (OPBA)	46.10	12.04	4.78	0.83	19.65	3.71	0.09	4.59	0.78	1.12	0.41	5.58	-
Date Palm Ash (DPA)	35.93	0.65	0.78	-	13.04	6.36	-	7.40	3.60	-	-	8.41	1.14-8.6
Elephant Grass Ash (EGA)	49.90	0.47	0.83	-	10.4	4.22	-	8.60	-	9.91	0.47	14.60	6.9
Banana Leaf Ash (BLA-2)	48.70	2.60	1.40	-	-	-	-	-	0.21	-	-	5.06	20
Wheat Straw Ash (WSA)	86.5	0.28	1.13	-	9.73	0.78	-	1.54	0.1	-	-	1.2	8.6
Sugarcane Bagasse Ash (BGA)	72.12	-	1.54	0.14	6.30	0.166	-	13.81	-	2.75	2.97	2.4	4-6

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Biomass Ash

Renewable Cementitious Material

Rice Fields

Rice Hull
From Rice Mills

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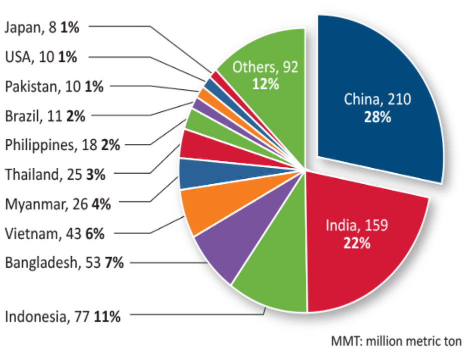
Global Rice Production

- Rice husk ash is a material that i



very year 75
3, USDA 20

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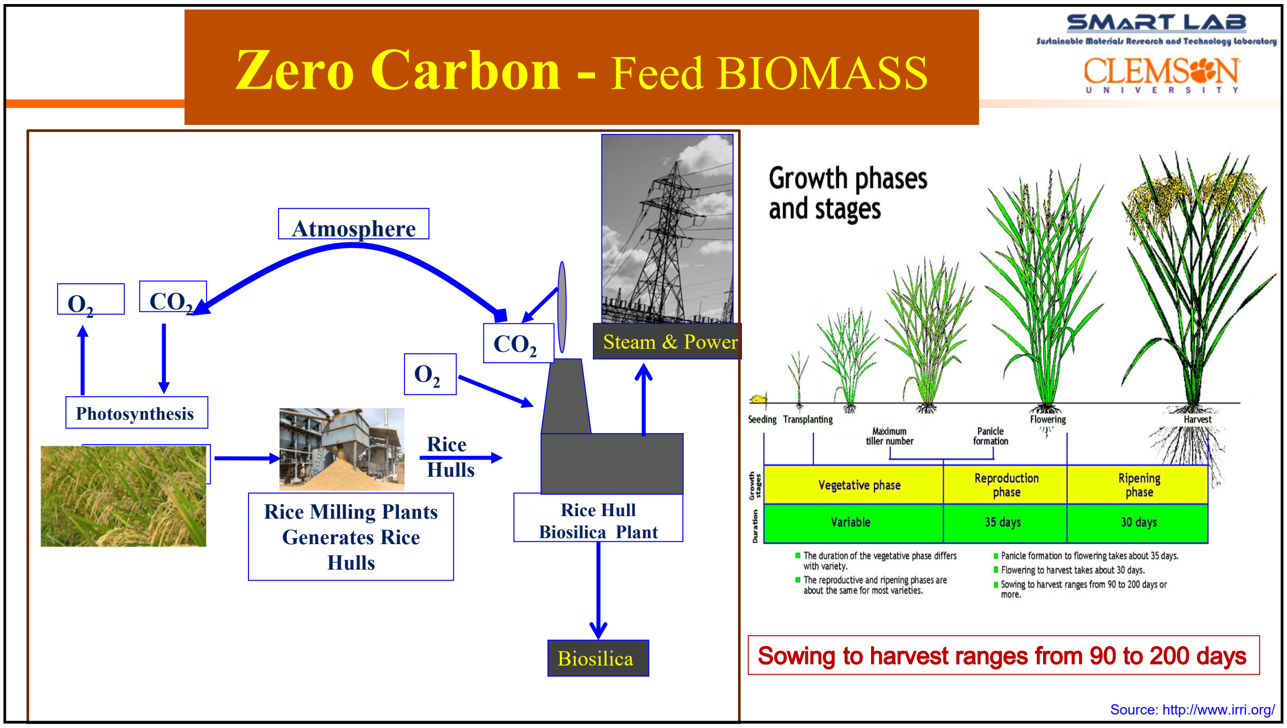
List of Countries by Rice Production

Country	Production (tonnes)
China	211,090,813
India	158,756,871
Indonesia	77,297,509
Bangladesh	52,590,000
Vietnam	43,437,229
Myanmar	25,672,832
Thailand	25,267,523
Philippines	17,627,245
Brazil	10,622,189
Pakistan	10,412,155
United States of America	10,167,050
Cambodia	9,827,001

- When incinerated, ash content of about 20 - 30% by weight of rice husk is produced

Source: USDA, 2018


Zero Carbon - Feed BIOMASS
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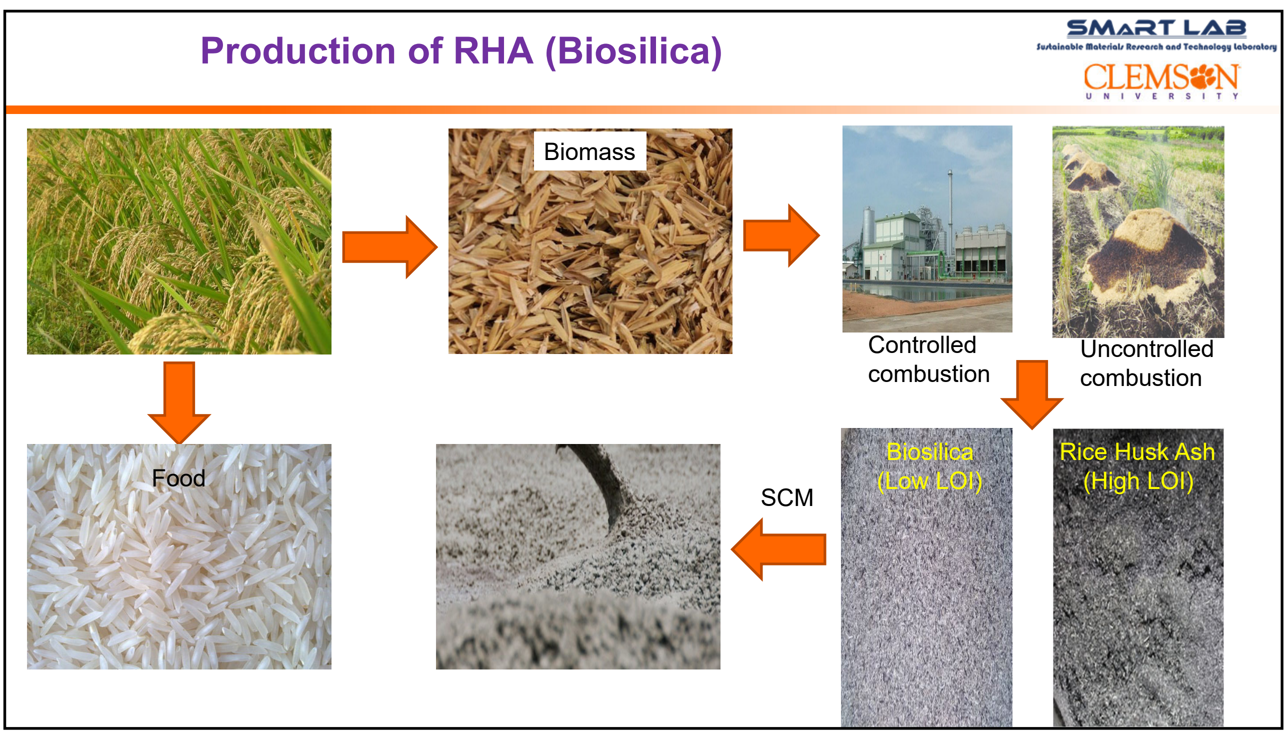
Atmosphere
O2
CO2
CO2
O2
Steam & Power
Photosynthesis
Rice Hulls
Rice Milling Plants Generates Rice Hulls
Rice Hull Biosilica Plant
Biosilica
Growth phases and stages
Seeding
Transplanting
Maximum tiller number
Panicle formation
Flowering
Harvest
Growth stages
Duration
Vegetative phase
Reproduction phase
Ripening phase
Variable
35 days
30 days
The duration of the vegetative phase differs with variety.
The reproductive and ripening phases are about the same for most varieties.
Panicle formation to flowering takes about 35 days.
Flowering to harvest takes about 30 days.
Sowing to harvest ranges from 90 to 200 days or more.
Sowing to harvest ranges from 90 to 200 days
Source: http://www.irri.org/


Production of RHA (Biosilica)
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Biomass
Controlled combustion
Uncontrolled combustion
Food
SCM
Biosilica (Low LOI)
Rice Husk Ash (High LOI)

Chemical Composition of RHA / Biosilica

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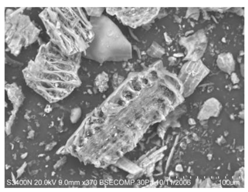
- Average particle size of unground Biosilica is in the range of 25 to 100 microns.
- Specific gravity of Biosilica is 2.2
- Color is off-white, due to its low carbon content.
- High internal porosity and high specific surface area (~30,000 m^2 per kg – BET method)

Microstructure of Biosilica



Oxides	Rice Husk Ash: Zhang et al [1996]	Rice Husk Ash: Nehdi et al [2003]	Biosilica: Vempati [2008]
	%	%	%
CaO	0.55	0.6	-
SiO_2	87.2	89.1	**94.8**
Al_2O_3	0.15	0.1	**0.52**
Fe_2O_3	0.16	0.04	**0.13**
MgO	0.35	0.5	**-**
Na_2O eq	3.54	0.86	**2.92**
Carbon	5.91	5.1	**0.24**
P_2O_5	0.5	0.9	**1.09**

X-Ray Diffractograms of Low Carbon RHA (Biosilica) and Silica Fume

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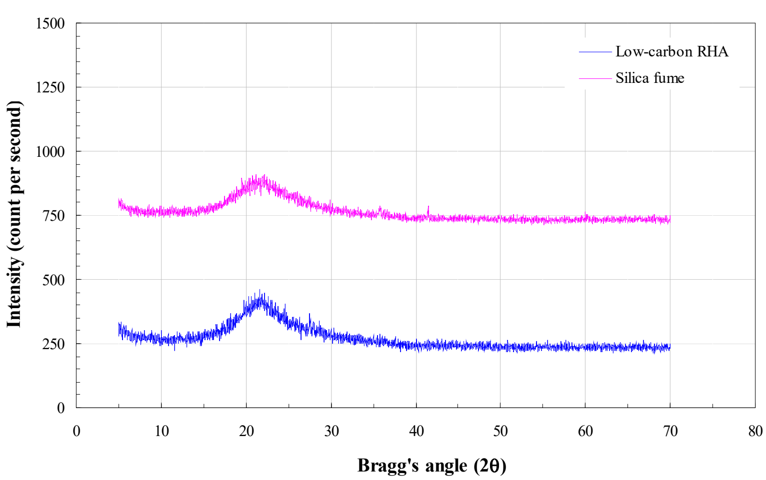

Biosilica (low carbon RHA) is an amorphous material with high silica content and high specific surface area

The composition and some physical properties of biosilica are comparable to that of silica fume.

Pozzolanic Reactivity of Ground and Unground Biosilica / RHA

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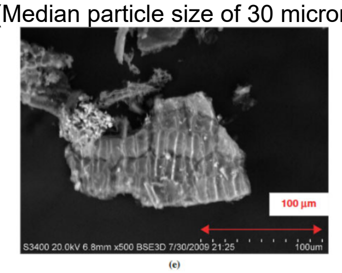
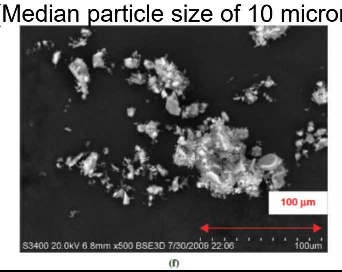
Unground / Raw Biosilica/URHA
(Median particle size of 30 microns)



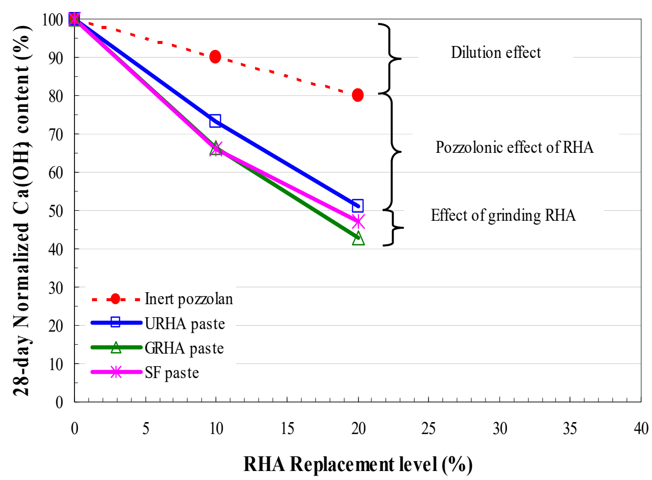
(e)

Ground Biosilica/GRHA
(Median particle size of 10 microns)



(f)

Thermogravimetric Analysis (TGA) Results



Water Demand and Setting Time of Biosilica Ground to Different Fineness

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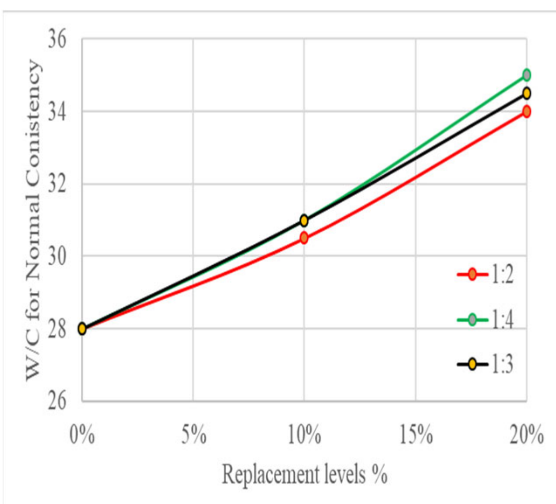

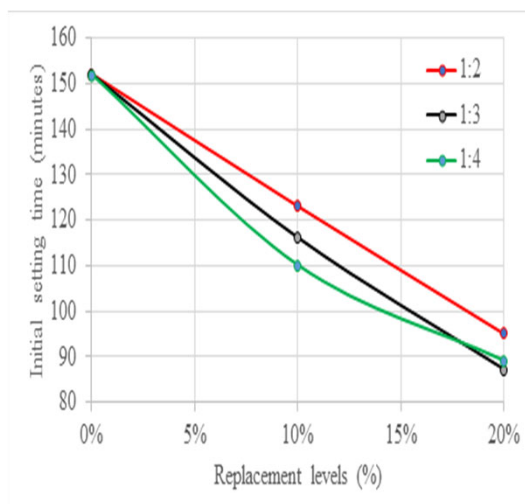

1:4 - (Median Particle Size 10 microns
1:2 - (Median Particle Size 18 microns)

Addition of Biosilica results in Increased Compressive Strength

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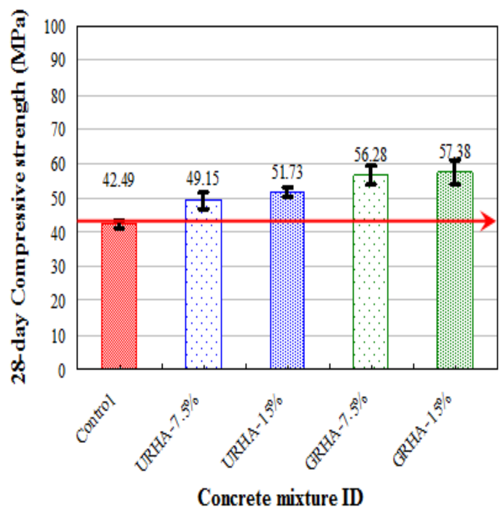
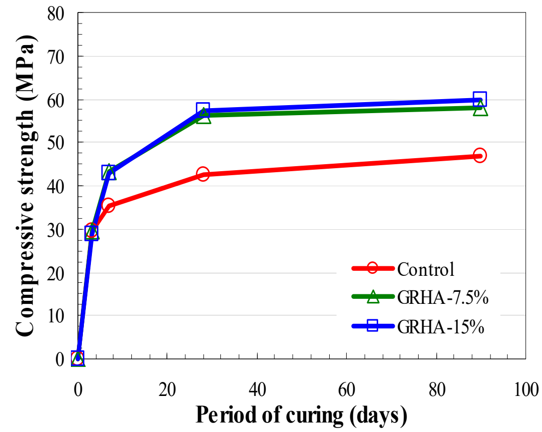
35% increase in comp strength with 15% GRHA over Control





Biosilica Substantially Reduces Chloride Permeability (ASTM C1202)

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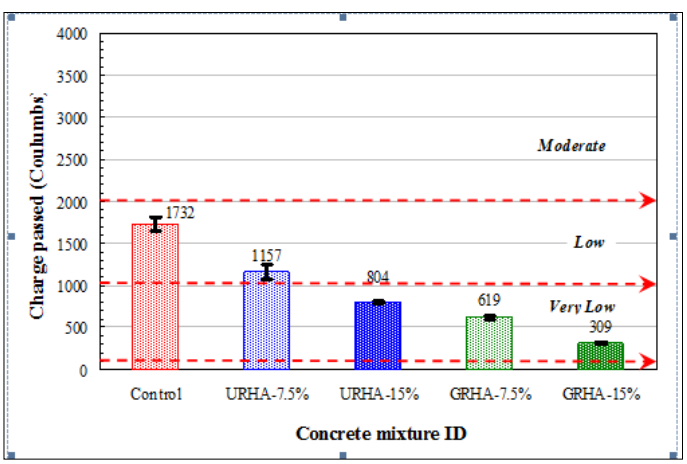

Figure – Comparison of Chloride Permeability Values of Biosilica Concretes after 56-Day Curing

82% decrease in chloride permeability with 15% GRHA compared to Control

Resistance of Biosilica (RHA) Mixtures to Sulfate Attack (ASTM C1012)

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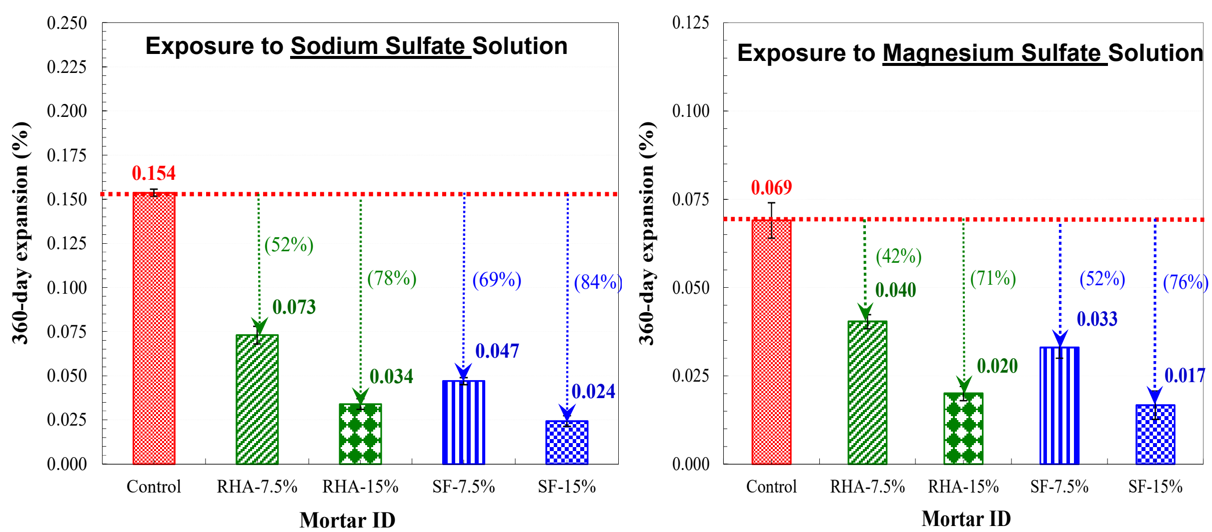

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Sugarcane Bagasse Ash (BGA)	72.12	-	1.54	0.14	6.30	0.166	-	13.81	-	2.75	2.97	2.4	4-6

Acid Treated (AT) vs Non-Acid Treated (NAT) Biosilica

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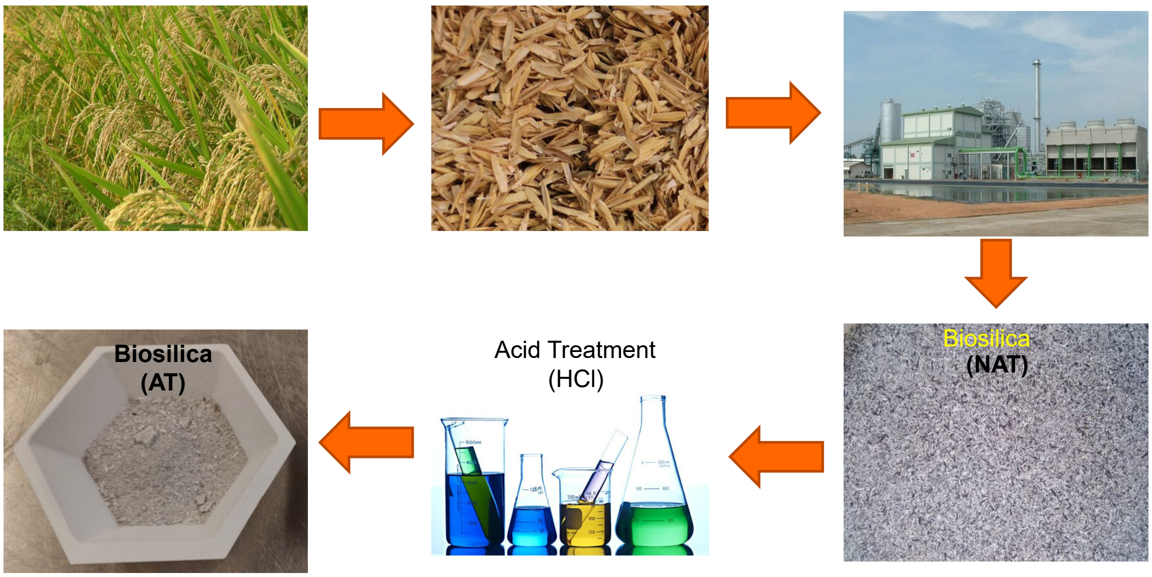

Chemical composition of Rice husk ash (AT and NAT), Silica Fume (SF) and Ground Glass Fiber (GGF)

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Oxide	Non- Acid Treated RHA (NAT)
SiO_2	93.29
CaO	0.66
Fe_2O_3	0.26
Al_2O_3	0.08
MgO	0.39
MnO	0.204
P_2O_5	0.808
TiO_2	0.013
Na_2O	0.14
K_2O	1.838
$Na_2O_{eq.}$	1.489

Expansion due to Alkali-Silica Reaction (AASHTO T380 – MCPT)

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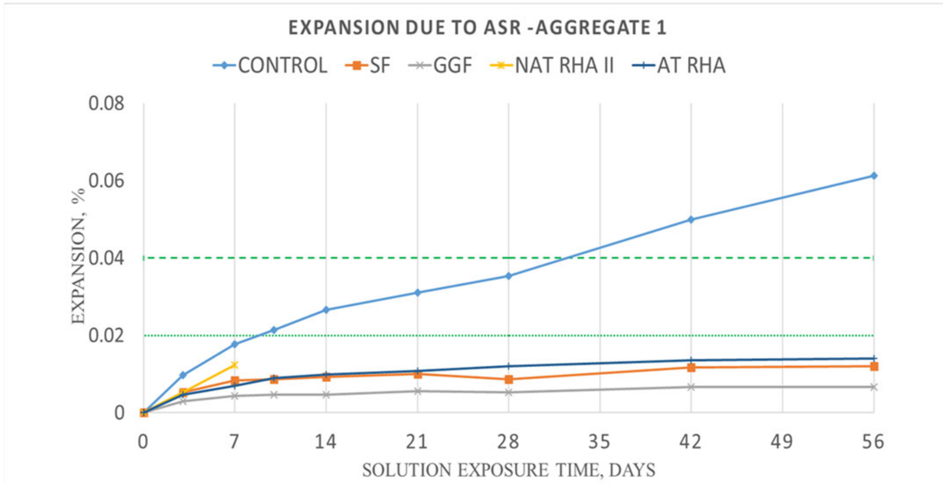

Replacement levels of the SCMs were 20% by the weight of cement
ASTM C1293 expansion of Aggregate 1 = 0.065% at 1 year

Biosilica as an SCM

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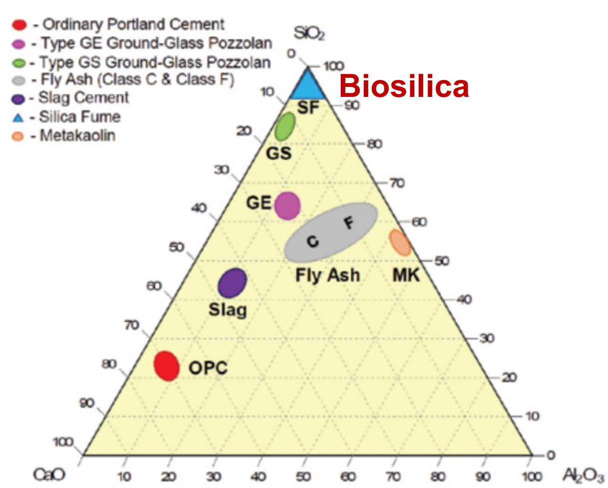

Fig. 1: Ternary plot contextualizing GGPs versus OPC and other SCMs (Note: For ternary plots, values are in wt.%, and they are normalized to the sum of SiO_2, Al_2O_3, and CaO)[4-8]
(figure courtesy of Marija Krstic)

Conclusions

- **Biosilica** from rice husk is a highly siliceous and an amorphous material and as a result is an **effective low-carbon SCM**.
- **Grinding of biosilica to a finer particle size** significantly **improves the performance** by increasing the pozzolanic reactivity, improving the compressive strength and durability of concrete **(Resistance to Chloride Ingress, Sulfate Attack)**
- Due to its high internal porosity, **biosilica results in higher water demand** for achieving normal consistency, although this can be **addressed with use of water reducers** and grinding it finer.
- **Acid washing of biosilica helps reduce its alkali content** and significantly improves the mitigation of ASR distress in concrete.
- **Mineral residues from combustion of biomass** can yield potentially valuable low-carbon **SCMs**, without affecting food supplies or other needs.
- **Nature and composition of the biomass ash and therefore its effectiveness as an SCM** is dependent on the specific source and processing methods.

Thank you!

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