Impact of CO_2 Sequestration on the Embodied Impact of Concrete Masonry Products

Craig Walloch
Director of Materials Science
Concrete Masonry and Hardscapes Association (CMHA)

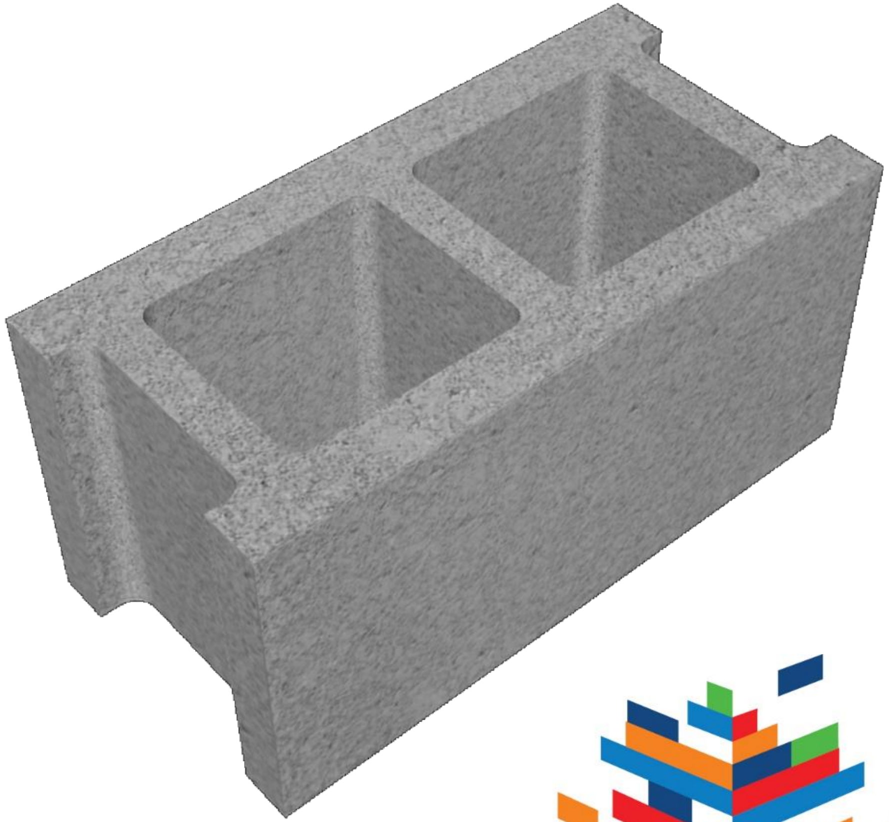
Carbon Sequestration –

Measuring the Rate of Carbonation of CMU

- The Rate of Carbonation of ‘regular’ wet-cast concrete has been widely studied and modeled.
- The rate is generally fairly slow (1 to 5 mm/year) depending on a number of factors including composition, curing, and permeability of the concrete.
- The Rate of Carbonation of dry-cast concrete has not been widely studied
- CMHA (NCMA) undertook research starting in 2020 and presented the results at as 2022 ASTM Masonry Symposium

Dry-Cast Concrete Masonry Units (CMU)

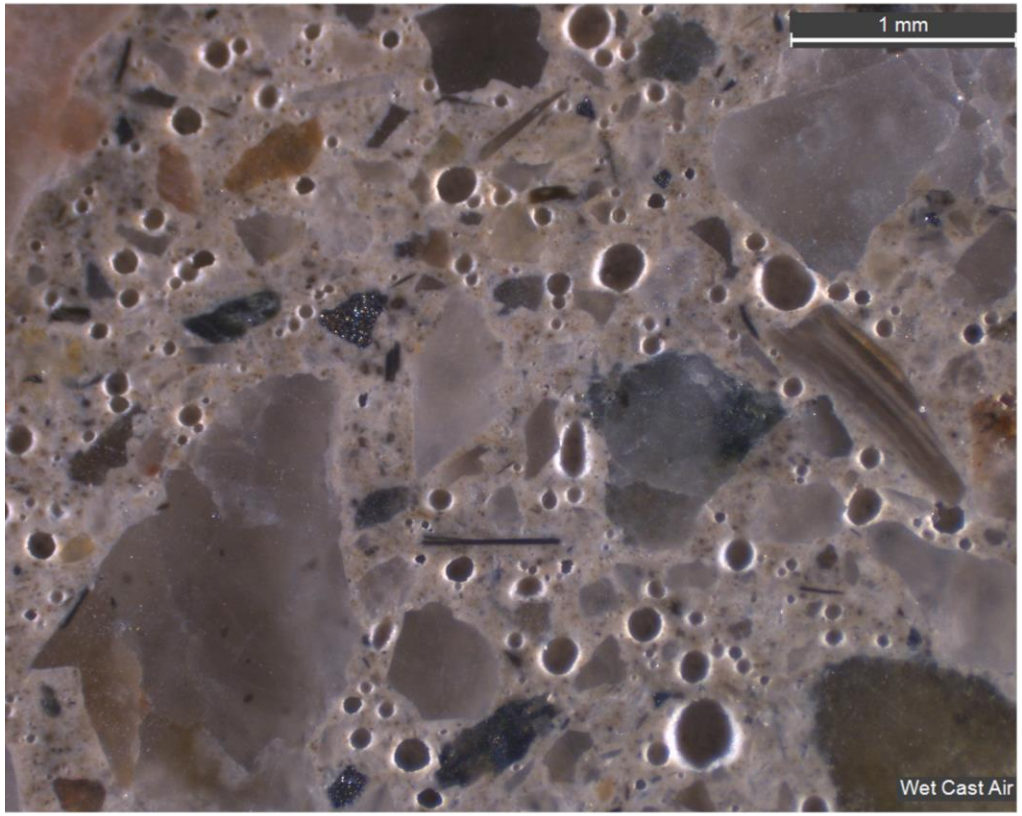
- ***Dry-cast concrete masonry units (CMU)*** are manufactured using vibration to consolidate concrete of stiff (zero-slump) consistency in a mold or form
- CMU are commonly called ***Concrete or Cinder Block***
- The most common shape has nominal dimensions of 8 x 8 x 16 in. (20 x 20 x 40 cm) and are approximately ***50% solid*** with ***webs and face shells*** that are typically ***1 – 1.5 in. (25 – 40 mm)*** in thickness.
- These ***thin elements*** as well as the ***more porous structure*** of the concrete differentiate it from wet-cast concrete and result in ***significantly higher*** natural carbonation ***rates***



CONCRETE STRUCTURE

Wet-Cast Structure

Air-entrained bubbles but no interconnected voids



Dry-Cast Structure

Abundant interconnected voids

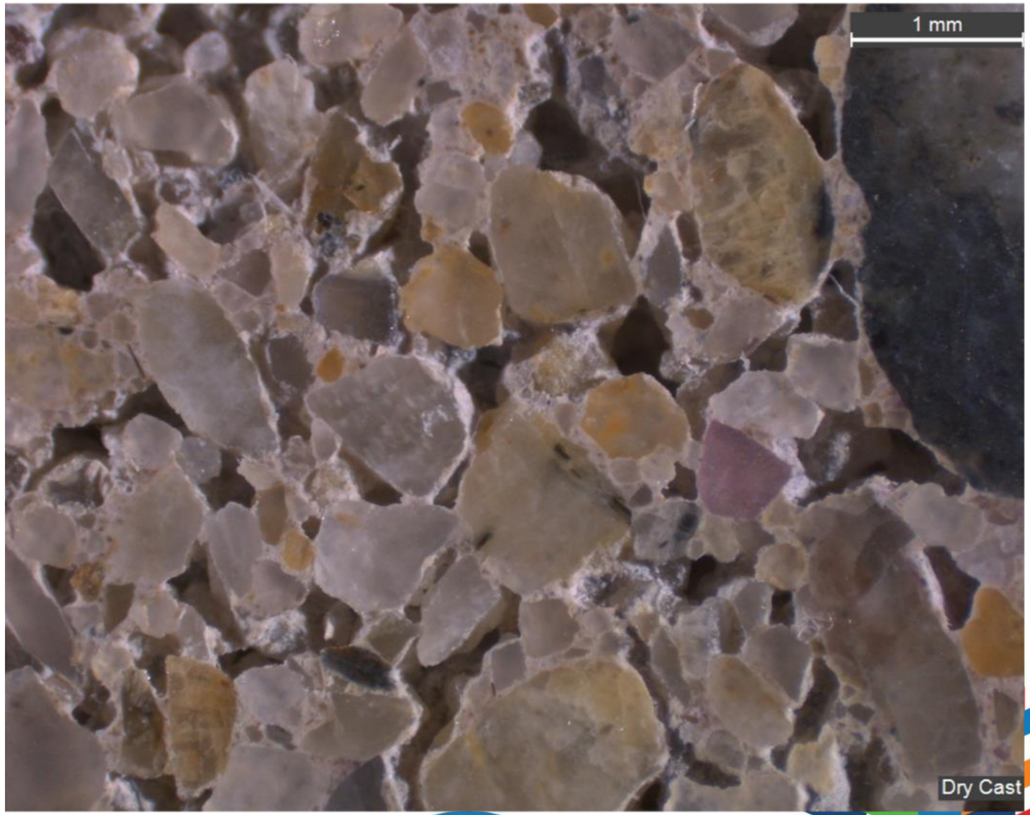
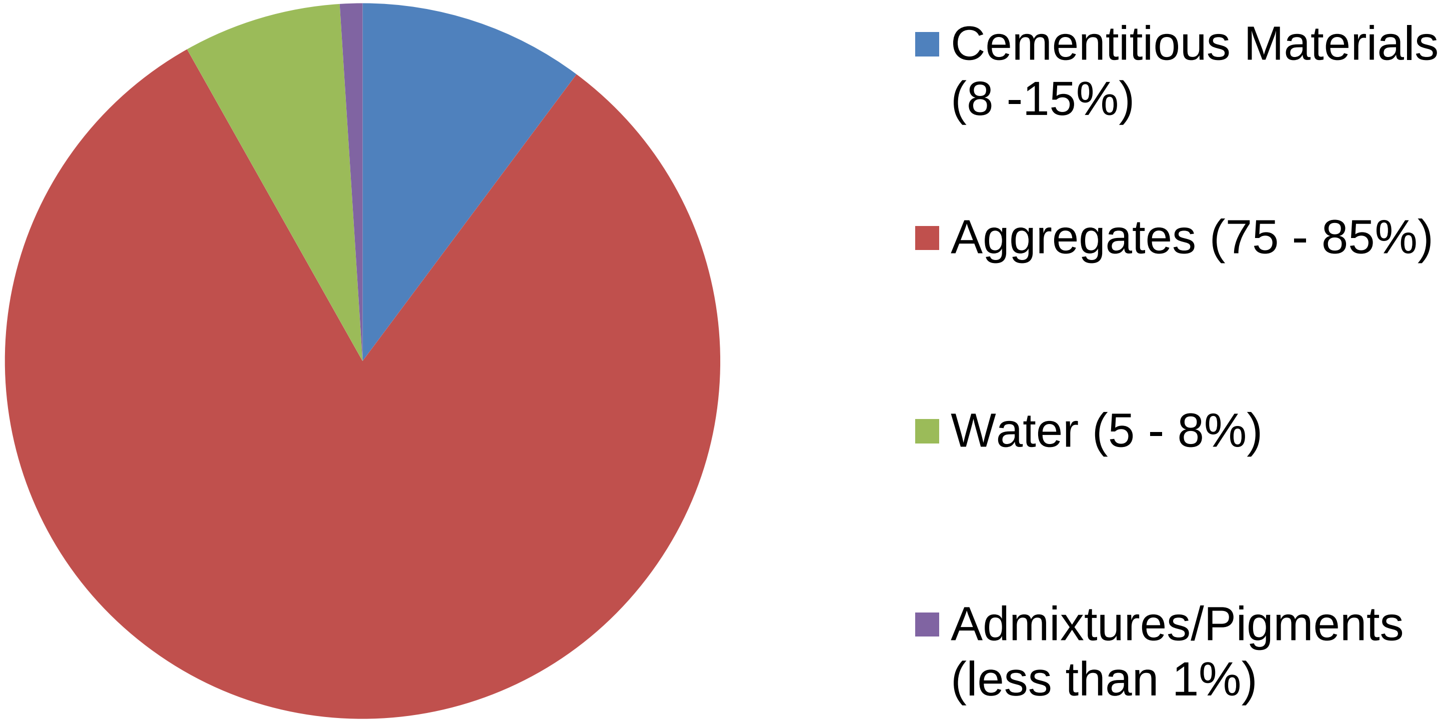
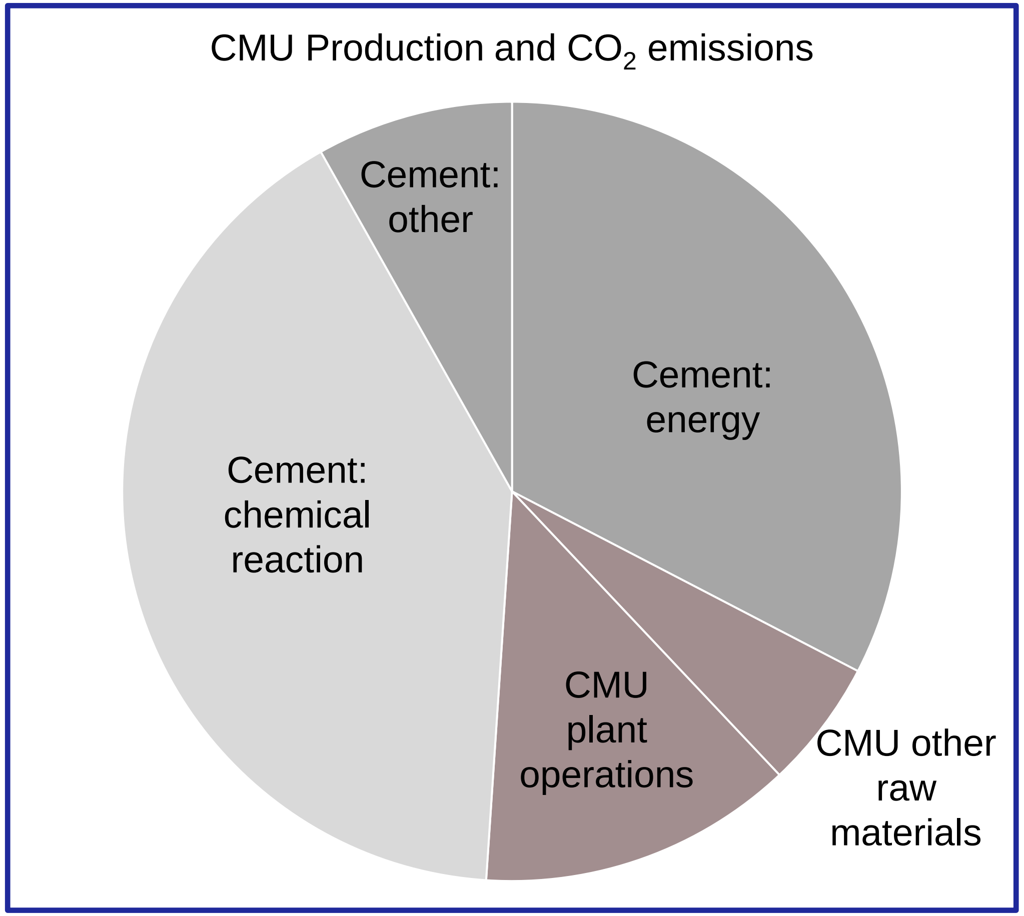


Photo courtesy of ACM Chemistries

CMU Raw Materials



CO_2 EMISSIONS OF CMU PRODUCTION



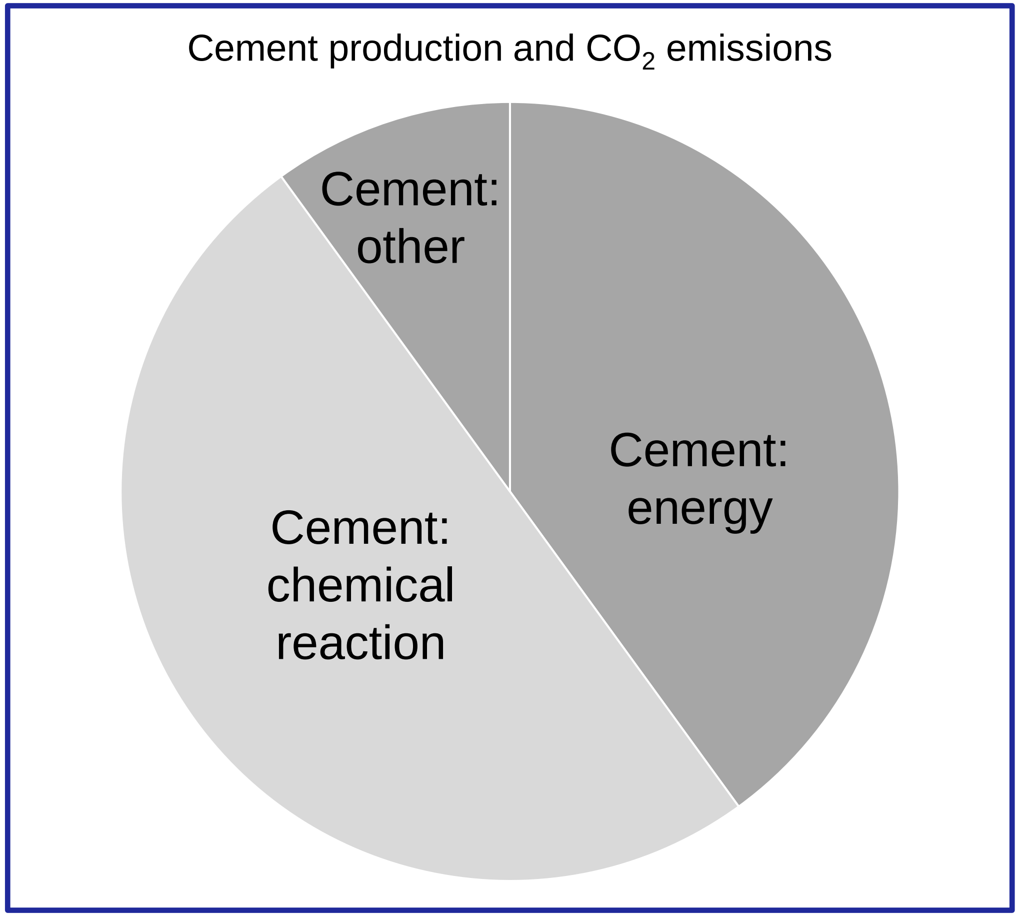
Rough Estimation

≈ 82% due to cement

≈   5% due to other CMU raw materials

≈ 13% due CMU plant operations

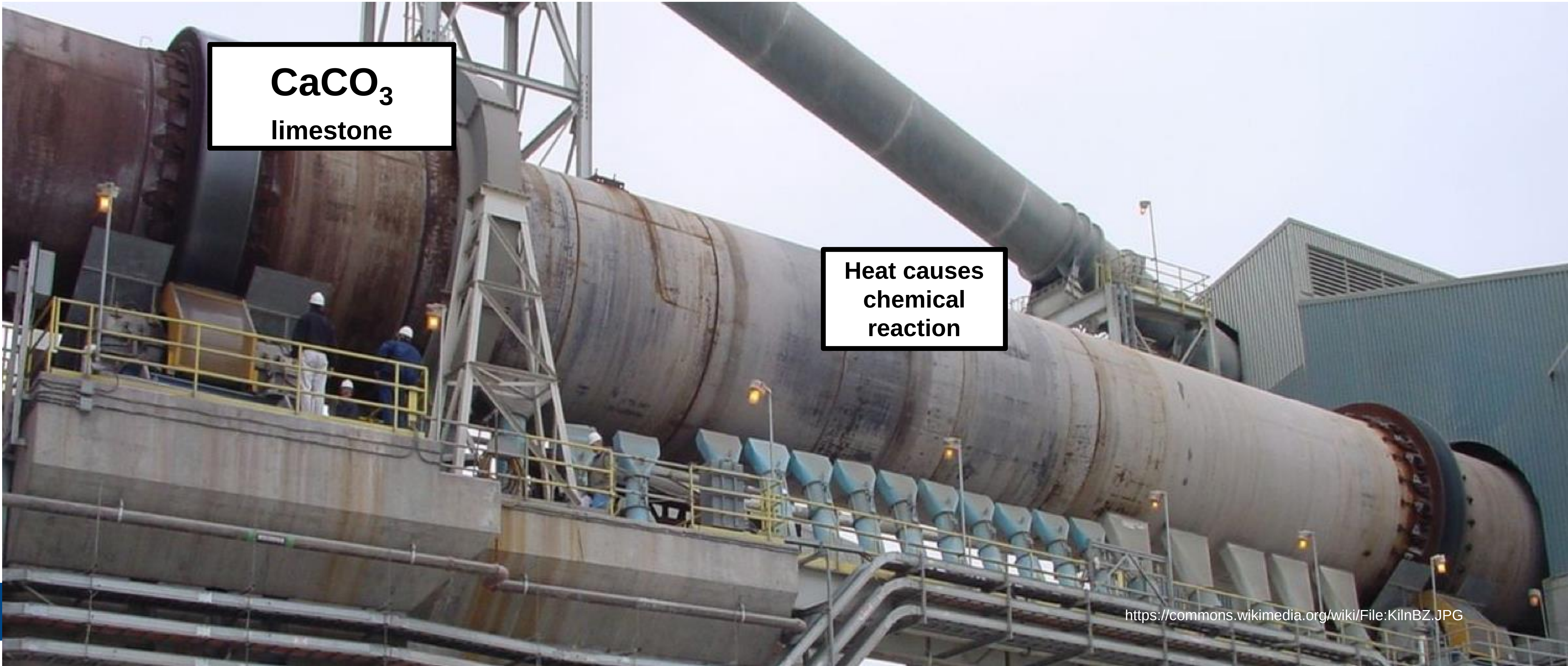
CO_2 EMISSIONS OF CEMENT PRODUCTION



Rough Estimation

≈ 50% due to chemical reaction
≈ 40% due to energy required
≈ 10% other cement plant processes

CEMENT PRODUCTION



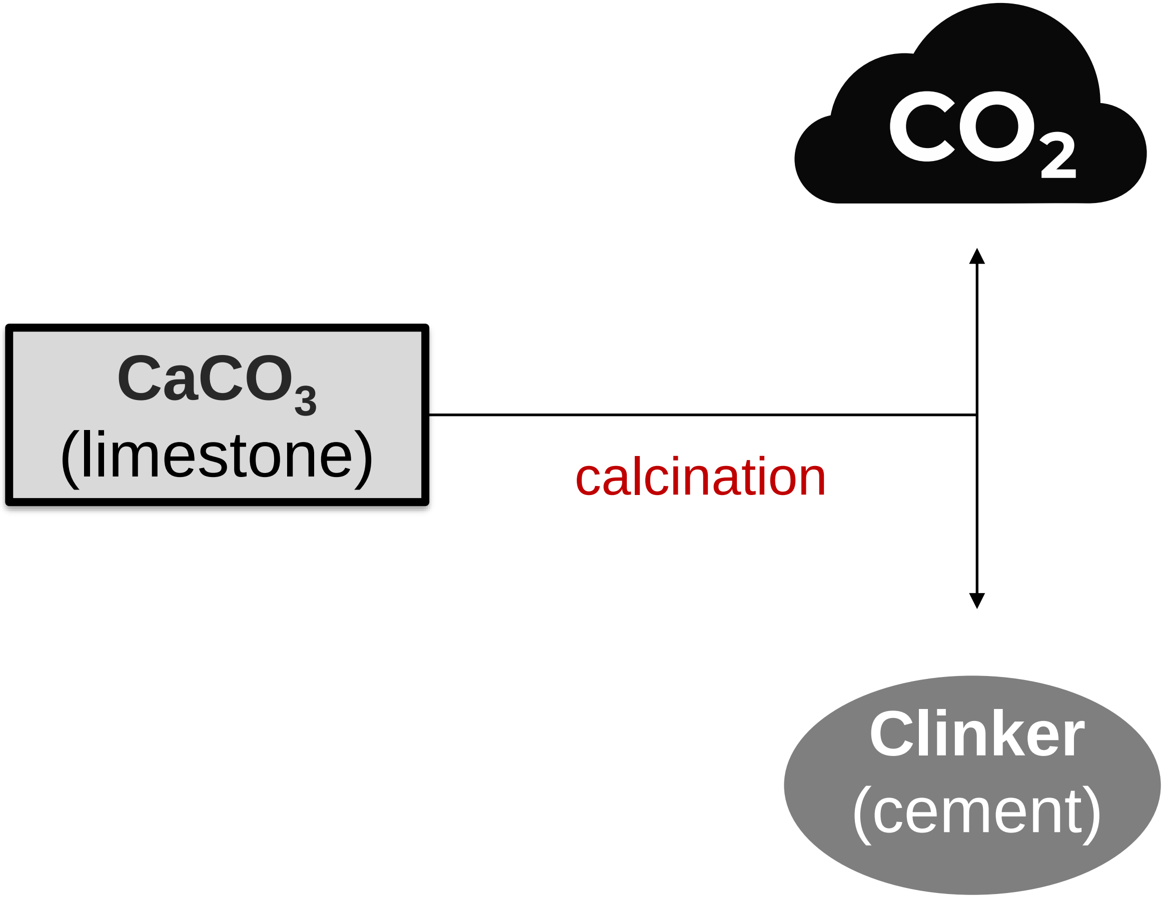
$CaCO_3$

limestone

Heat causes chemical reaction

https://commons.wikimedia.org/wiki/File:KilnBZ.JPG

CEMENT PRODUCTION RELEASES CO_2



CO_2

$CaCO_3$
(limestone)

calcination

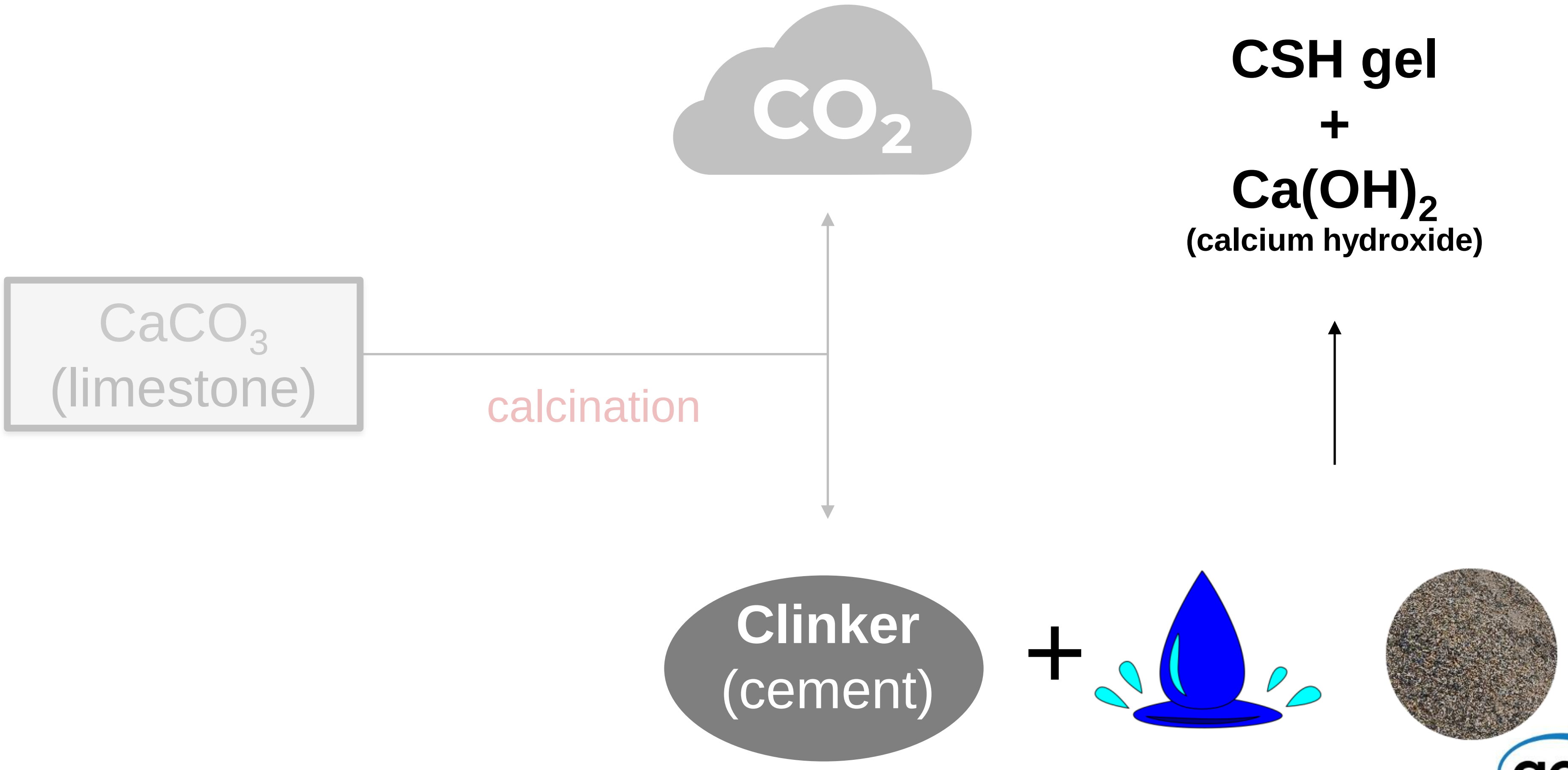
Clinker
(cement)

Clinker image - https://commons.wikimedia.org/wiki/File:كلينكر_سيمان.JPG

Carbon Sequestration Cycle

- Yes, CO_2 is released during cement production…but some of that ***CO_2 is reabsorbed*** by the concrete once placed in service
- This reabsorption of CO_2 is called ***Carbon Sequestration*** or ***Carbon Uptake***
- ***Calcium Hydroxide*** [$Ca(OH)_2$] from the cement hydration process ***carbonates first***
- ***Cement (CSH) Gel also carbonates*** later

CONCRETE HYDRATION ABSORBS CO_2



CO_2

CSH gel

+

$Ca(OH)_2$

(calcium hydroxide)

$CaCO_3$

(limestone)

calcination

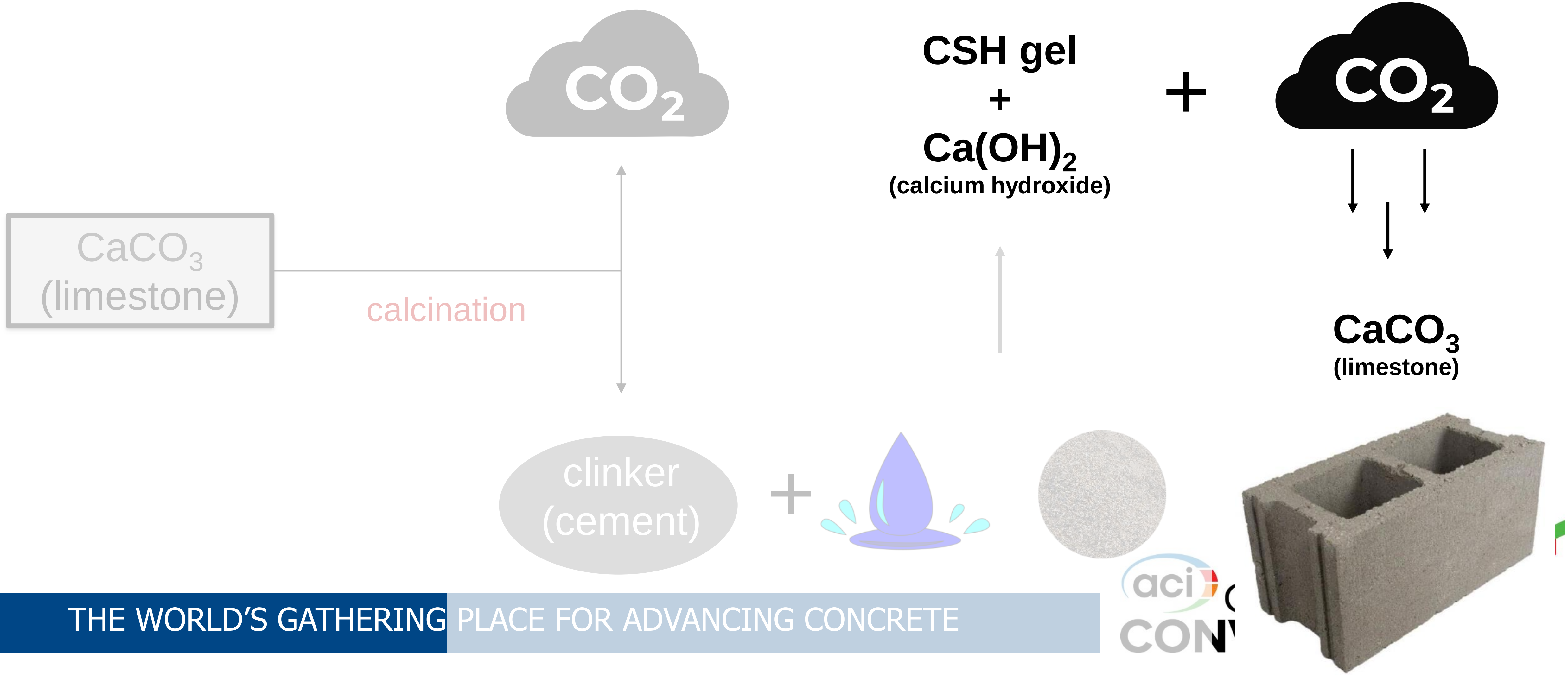
Clinker

(cement)

+

Droplet image - https://commons.wikimedia.org/wiki/File:Water_Droplet.svg
Peter Craven, CC BY 2.0 <https://creativecommons.org/licenses/by/2.0>, via Wikimedia Commons

CONCRETE HYDRATION ABSORBS CO_2



$CaCO_3$ (limestone)

calcination

CO_2

clinker (cement)

+

CSH gel

+

$Ca(OH)_2$

(calcium hydroxide)

+

CO_2

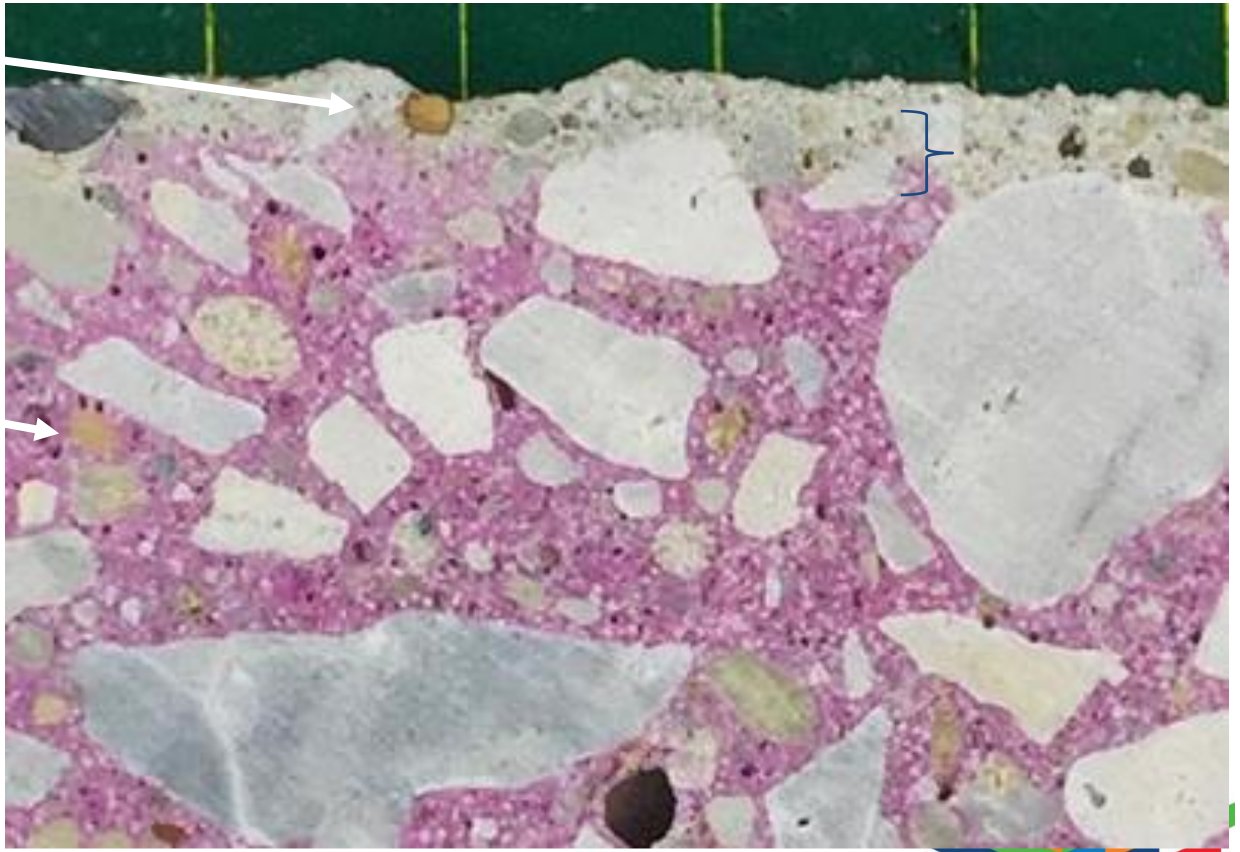
$CaCO_3$

(limestone)

WET-CAST CONCRETE SEQUESTATION

Wet-Cast

- CO2 ***penetrates*** and sequesters ***slowly*** at the outer few mm
- Due to the ***lower permeability*** and lack of interconnected voids



White surface is carbonated

Pink interior is not carbonated

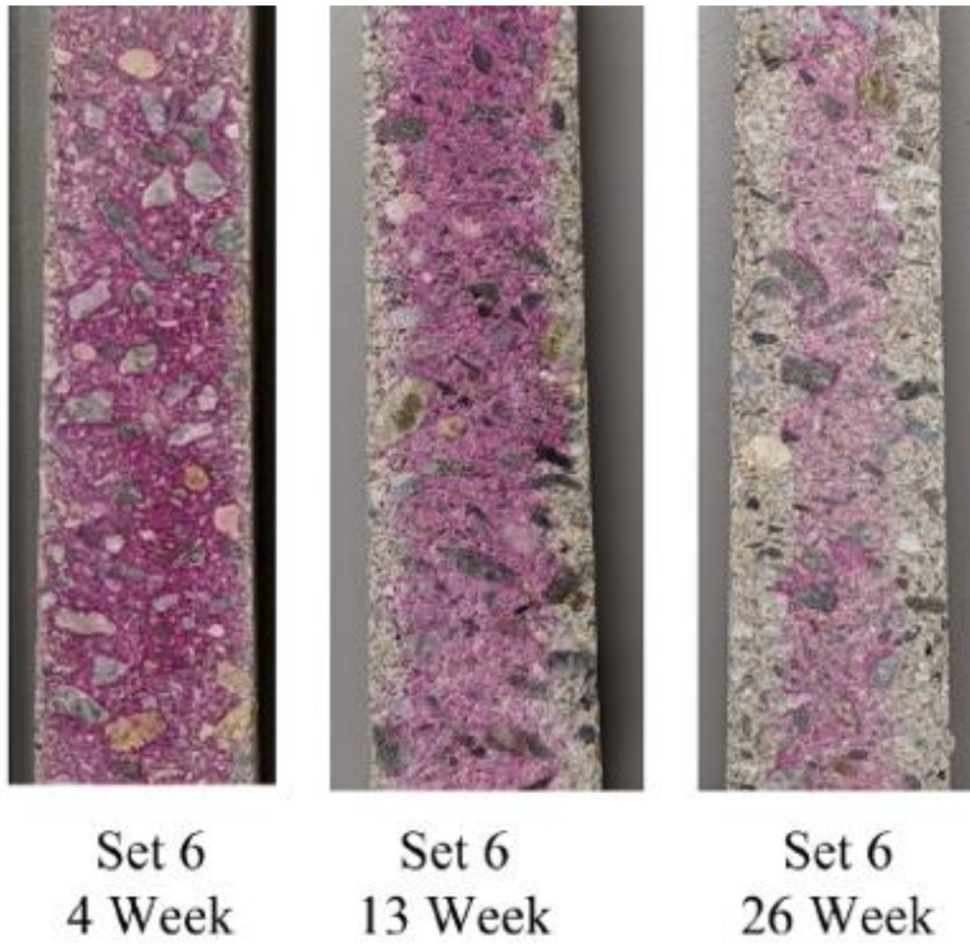
https://precast.org/2015/07/understanding-carbonation/

DRY-CAST CONCRETE SEQUESTRATION

RESEARCH UNDERWAY

Dry-Cast

- CO_2 ***penetrates*** much ***quicker*** and ***deeper***
- Due to the higher permeability and abundance of ***interconnected voids***



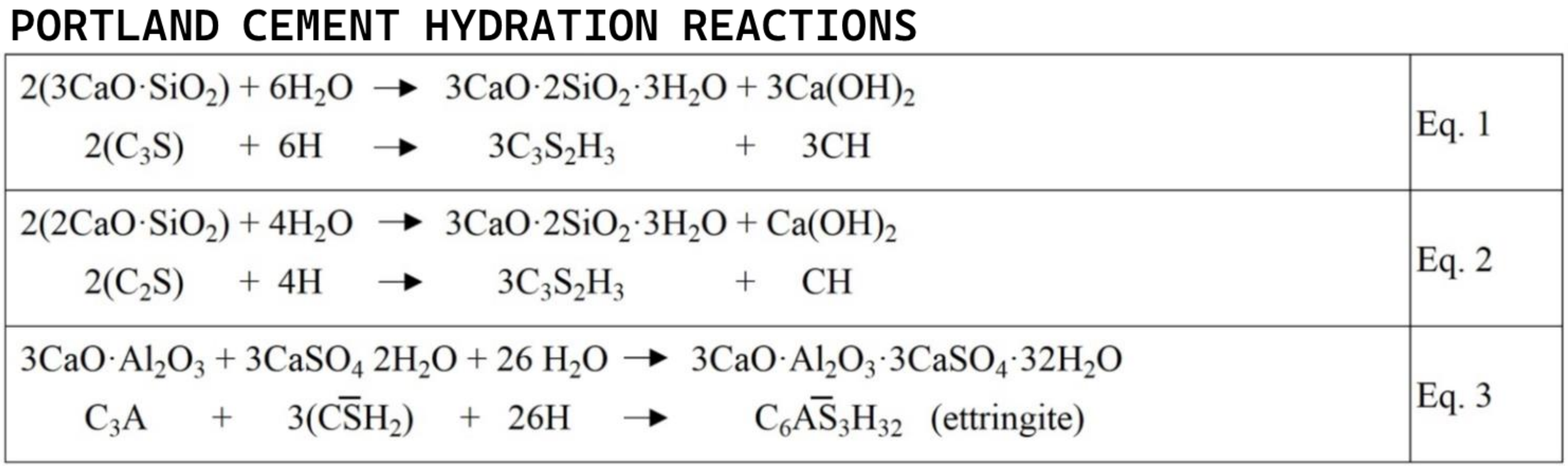
Carbon Sequestration –
Determining the natural carbonation rate of CMU

- There are numerous carbon capture, accelerated carbonation, and related technologies in use and in development today that permanently sequester CO_2
- While it was well known that concrete carbonates, we didn't have a good baseline for ***natural*** dry-cast concrete carbonation
- To generate the baseline, we needed to determine the Carbonation ***Potential*** of the cement and measure the ***Rate of Carbonation*** of CMU over time

Carbon Sequestration –
Calculating the Carbonation Potential of Cement

- The ***Carbonation Potential*** is the total amount of CO_2 that the cement could reabsorb if all of the calcium hydroxide and cement (CSH) gel fully reacted with the CO_2
- This potential will depend on the particular chemistry of the cement but can be theoretically ***calculated for any cement***

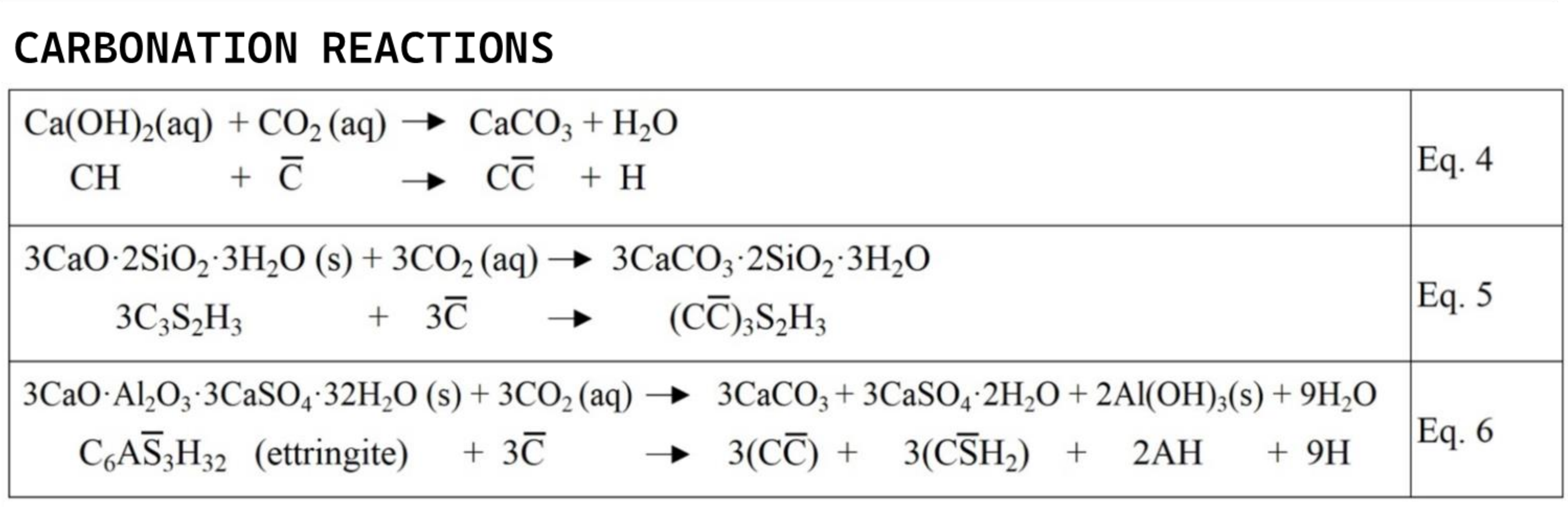
Carbon Sequestration –
Calculating the Carbonation Potential of Cement



PORTLAND CEMENT HYDRATION REACTIONS

$2(3CaO\cdot SiO_2) + 6H_2O \rightarrow 3CaO\cdot 2SiO_2\cdot 3H_2O + 3Ca(OH)_2$ $2(C_3S) + 6H \rightarrow 3C_3S_2H_3 + 3CH$	Eq. 1
$2(2CaO\cdot SiO_2) + 4H_2O \rightarrow 3CaO\cdot 2SiO_2\cdot 3H_2O + Ca(OH)_2$ $2(C_2S) + 4H \rightarrow 3C_3S_2H_3 + CH$	Eq. 2
$3CaO\cdot Al_2O_3 + 3CaSO_4\ 2H_2O + 26\ H_2O \rightarrow 3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 32H_2O$ $C_3A + 3(C\overline{S}H_2) + 26H \rightarrow C_6A\overline{S}_3H_{32}$ (ettringite)	Eq. 3

Carbon Sequestration –
Calculating the Carbonation Potential of Cement



CARBONATION REACTIONS

$Ca(OH)_2(aq) + CO_2\,(aq) \rightarrow CaCO_3 + H_2O$ $CH + \bar{C} \rightarrow C\bar{C} + H$	Eq. 4
$3CaO\cdot 2SiO_2\cdot 3H_2O\,(s) + 3CO_2\,(aq) \rightarrow 3CaCO_3\cdot 2SiO_2\cdot 3H_2O$ $3C_3S_2H_3 + 3\bar{C} \rightarrow (C\bar{C})_3S_2H_3$	Eq. 5
$3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 32H_2O\,(s) + 3CO_2\,(aq) \rightarrow 3CaCO_3 + 3CaSO_4\cdot 2H_2O + 2Al(OH)_3(s) + 9H_2O$ $C_6A\bar{S}_3H_{32}$ (ettringite) $+ 3\bar{C} \rightarrow 3(C\bar{C}) + 3(C\bar{S}H_2) + 2AH + 9H$	Eq. 6

Carbon Sequestration –
Calculating the Carbonation Potential of Cement

Cement Compositon with Molecular Weight Values

CCN	Oxide	MW
C	CaO	56
S	SiO_2	64
H	H_2O	18
A	Al_2O_3	102

Carbon Sequestration Reactions with Molecular Weight Values

$2C_3S$	+	6H	=	Total	=>	$C_3S_2H_3$	+	3CH	=	Total
464		108		572		350		222		572
% of Original C_3S Weight						75.4%		47.8%		123.3%
% of Total Reaction Products						61.2%		38.8%		100.0%

% of Phase in Cement		Ca(OH)$_2$ [CH]			CO2 Uptake
		from Phase		in Cement	
49.2%	x	47.8%	=	23.5%	14.0%

Carbon Sequestration –
Calculating the Carbonation Potential of Cement

Carbon Sequestration Reactions with Molecular Weight Values

											% of Phase in Cement		Ca(OH)$_2$ [CH]			CO2 Uptake
													from Phase		in Cement	
2C_3S	+	6H	=	Total	=>	$C_3S_2H_3$	+	3CH	=	Total						
464		108		572		350		222		572						
% of Original C_3S Weight						75.4%		47.8%		123.3%	49.2%	x	47.8%	=	23.5%	14.0%
% of Total Reaction Products						61.2%		38.8%		100.0%						
2C_2S	+	4H	=	Total	=>	$C_3S_2H_3$	+	CH	=	Total						
352		72		424		350		74		424						
% of Original C_2S Weight						99.4%		21.0%		120.5%	20.2%	x	21.0%	=	4.3%	2.5%
% of Total Reaction Products						82.5%		17.5%		100.0%						
											Stotal				**27.8%**	**16.5%**

$C_3S_2H_3$ Content		Reaction Product $C_3S_2H_3$		% of C_3S or C_2S in Cement		**% of Cem $C_3S_2H_3$**	From $C_3S_2H_3$	21.6%
C_3S	=	75.4%	x	49%	=	37.1%		

Carbon Sequestration Reactions with Molecular Weight Values

											% of Phase in Cement (from Fig 3)		$Ca(OH)_2$ [CH] from Phase		$Ca(OH)_2$ [CH] in Cement	CO_2 Uptake
$2C_3S$	+	6H	=	Total	=>	$C_3S_2H_3$	+	3CH	=	Total						
464		108		572		350		222		572						
% of Original C_3S Weight						75.4%		47.8%		123.3%	49.2%	x	47.8%	=	23.5%	14.0%
% of Total Reaction Products						61.2%		38.8%		100.0%						
$2C_2S$	+	4H	=	Total	=>	$C_3S_2H_3$	+	CH	=	Total						
352		72		424		350		74		424						
% of Original C_2S Weight						99.4%		21.0%		120.5%	20.2%	x	21.0%	=	4.3%	2.5%
% of Total Reaction Products						82.5%		17.5%		100.0%						
											Stotal				**27.8%**	**16.5%**

$C_3S_2H_3$ Content		Reaction Product $C_3S_2H_3$		% of C_3S or C_2S in Cement		**% of Cem $C_3S_2H_3$**
C_3S	=	75.4%	x	49%	=	37.1%
C_2S	=	99.4%	x	20%	=	20.1%
				Total $C_3S_2H_3$		**57.2%**

From $C_3S_2H_3$ 21.6%

Stotal **38.1%**

Molecular Weight

$C_3S_2H_3$	$3(CO_2)$
350	132
	37.7%

37.7% x 57.2% **= 21.6%**

C_3A	=>	$3(CO_2)$					
270		132	9.8%	x	48.9%	= From C_3A	4.8%
		48.9%					

Carbonation Potential of the Cement Phases (CPCP) **Total** **42.9%**

Carbon Sequestration Research

Measuring the Rate of Carbonation of CMU

- NCMA (CMHA) undertook research starting in 2020 and presented the results at as ***2022 ASTM Masonry Symposium***
- ***CMU*** were collected from producers ***across North America*** along with the ***raw materials (cement and aggregate)*** and the mix designs used in the CMU
- An analytical method call ***Thermogravimetric Analysis (TGA)*** was used to determine the amount of ***CO_2*** that was ***bound in the concrete***
- After correcting for the CO_2 that was initially bound in the raw materials – this yielded that amount of ***CO_2 that was reabsorbed*** by the cement hydration products due to ***carbon sequestration***

Carbon Sequestration Research
CMU Sample Preparation

- ***CMU*** stored in the exterior yard at ***NCMA lab***
- ***Nine sets*** were included in the study
- ***Face Shell Coupons*** were harvested at ***various ages*** (4, 13, 26 weeks plus 1 & 2 years [after paper was written])
- Coupons were ***vacuum-sealed*** to stop further carbonation

Carbon Sequestration Research
CMU Sample Preparation

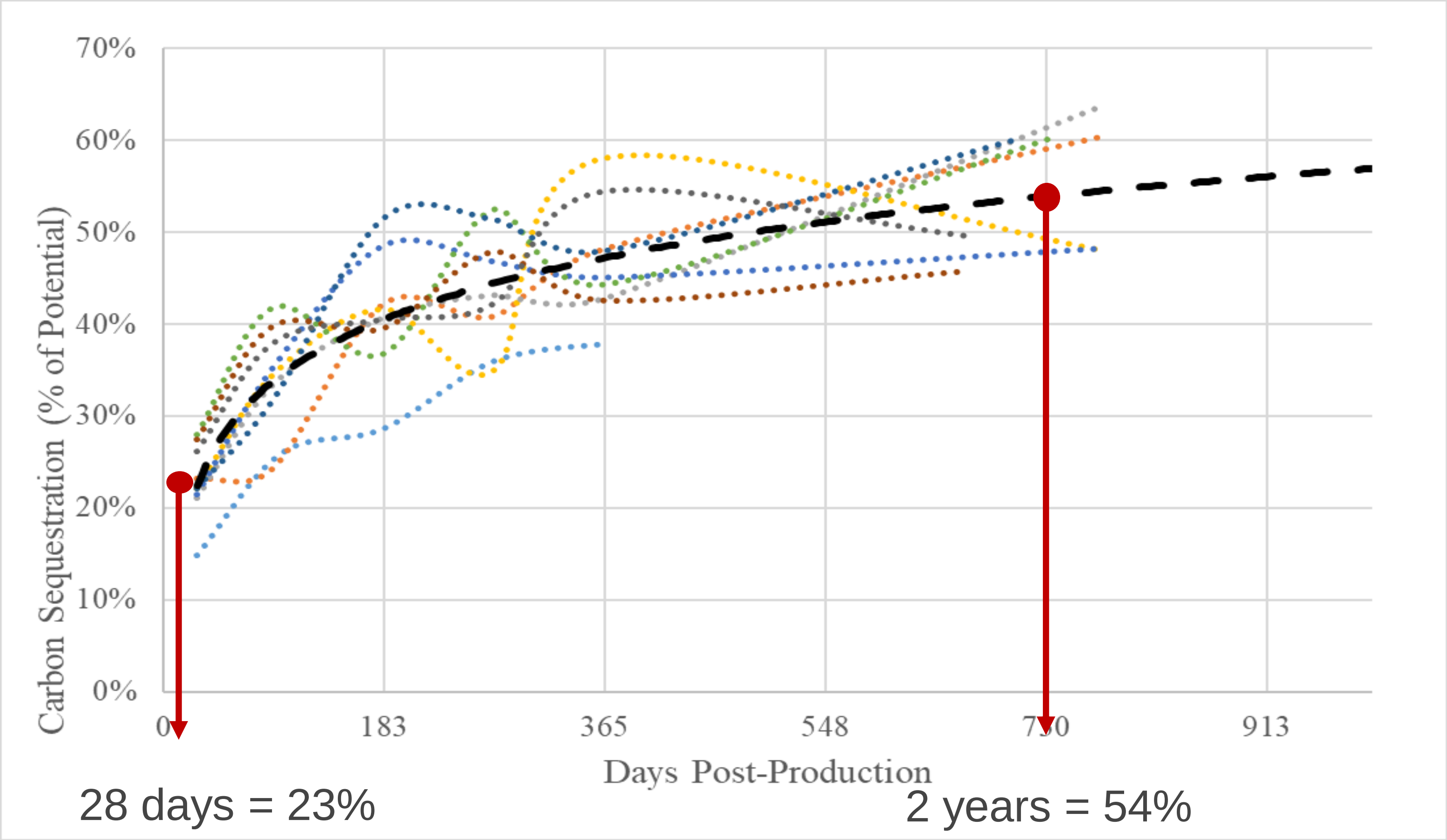
- A ***3 to 6-mm slice*** was cut from the center of each coupon, dried, ground and ***analyzed by TGA***

Preliminary Summary of Test Results (% of potential sequestration)

• 28 days	~ 23% of potential
• 6 mo.	~ 41% of potential
• 1 year	~ 47% of potential
• 2 years	~ 43% of potential

Projected results

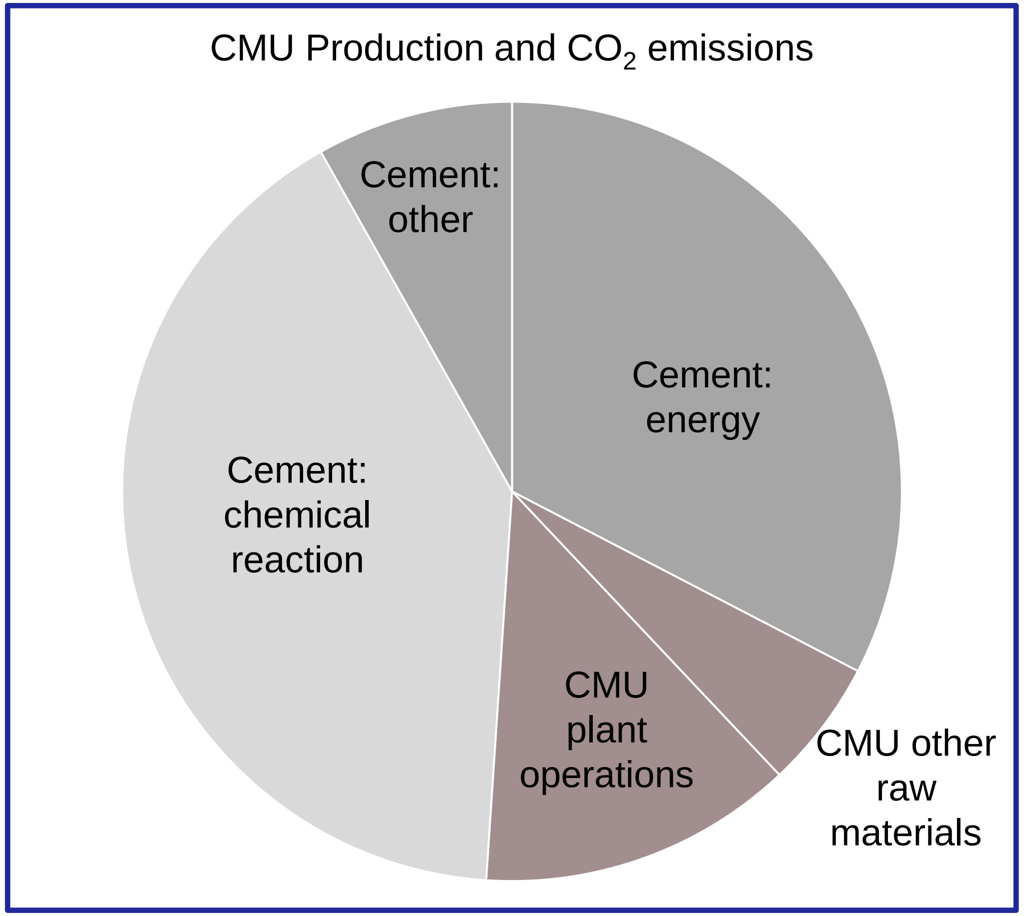
• 5 years	~ 60% of potential
• 20-25 years	~ 75% of potential



28 days = 23%

2 years = 54%

CO$_2$ EMISSIONS OF CMU PRODUCTION



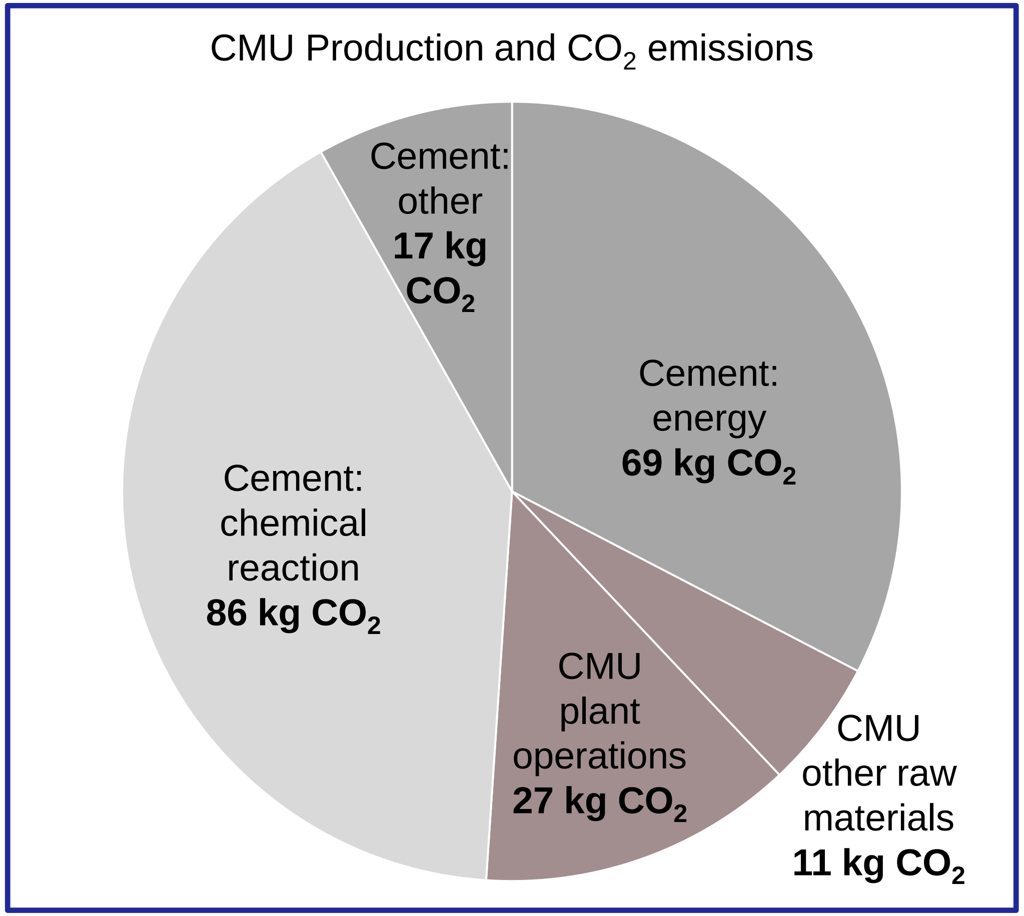
Rough Estimation

≈ 82% due to cement

≈ 5% due to other CMU raw materials

≈ 13% due CMU plant operations

CO_2 EMISSIONS OF CMU PRODUCTION (PER M^3)



In this scenario, 1 m^3 of CMU (≈140 8x8x16) emits 210 kg CO_2e

≈ 86 kg CO_2 due to chemical reaction

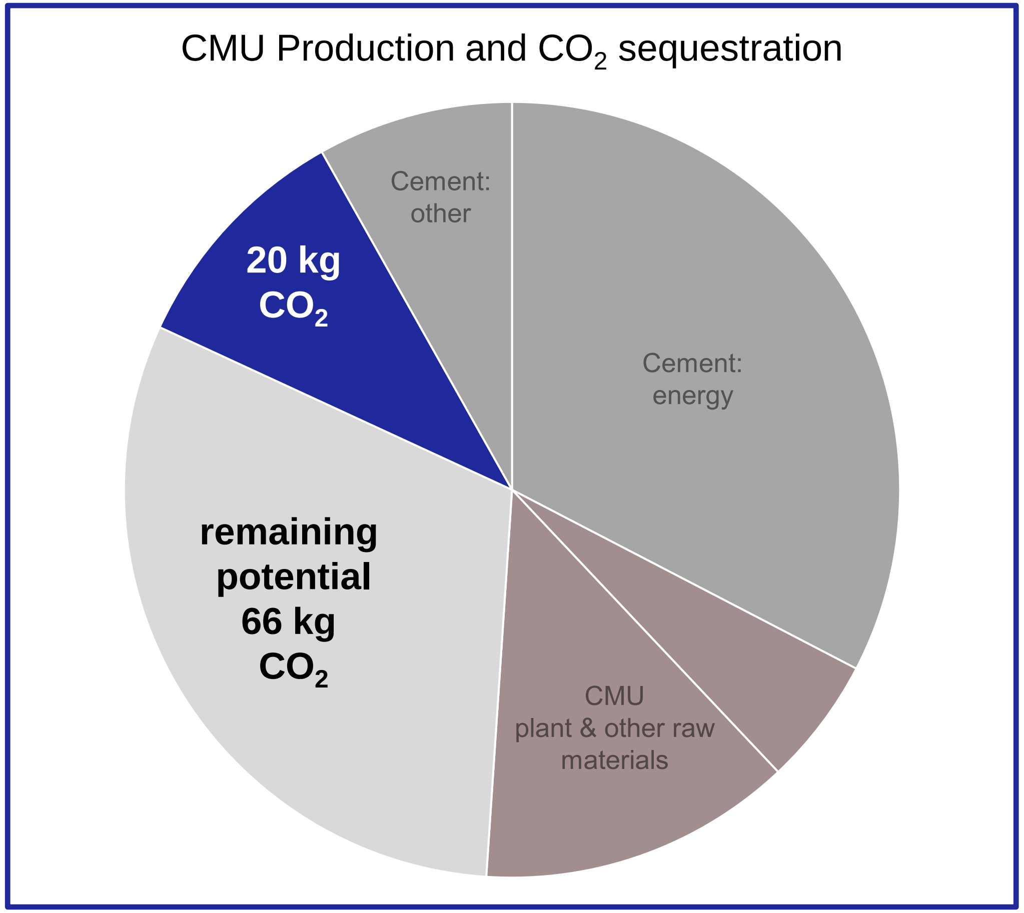
≈ 17 kg CO_2 due cement plant operations

≈ 69 kg CO_2 due to energy use

≈ 11 kg CO_2 due to other CMU raw materials

≈ 27 kg CO_2 due CMU plant operations

Dry-Cast CO_2 Sequestration of CMU (PER M^3)



28 days

23% of potential

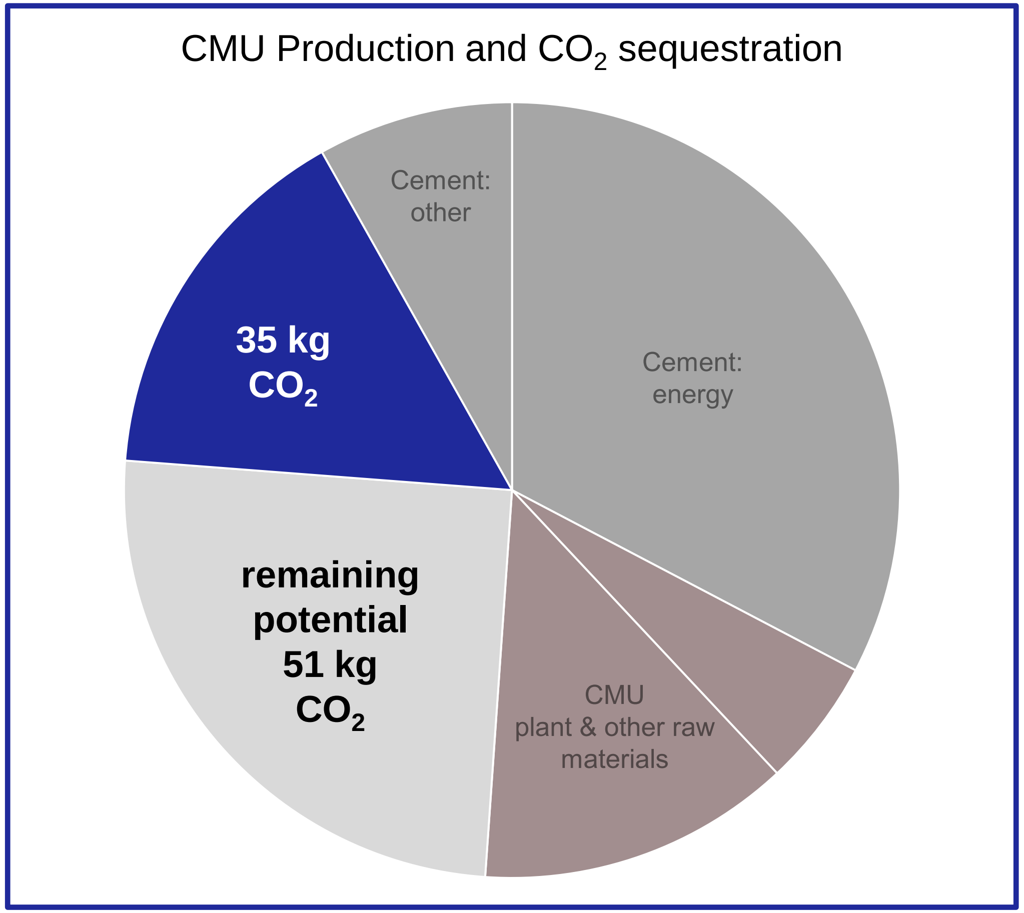
  – emissions associated with chemical reaction only

10% of total associated emissions

  – emissions associated with the whole process of CMU manufacturing

- Total sequestration ≈ 20 kg CO_2

Dry-Cast CO_2 Sequestration of CMU (PER M^3)



6 months

41% of potential

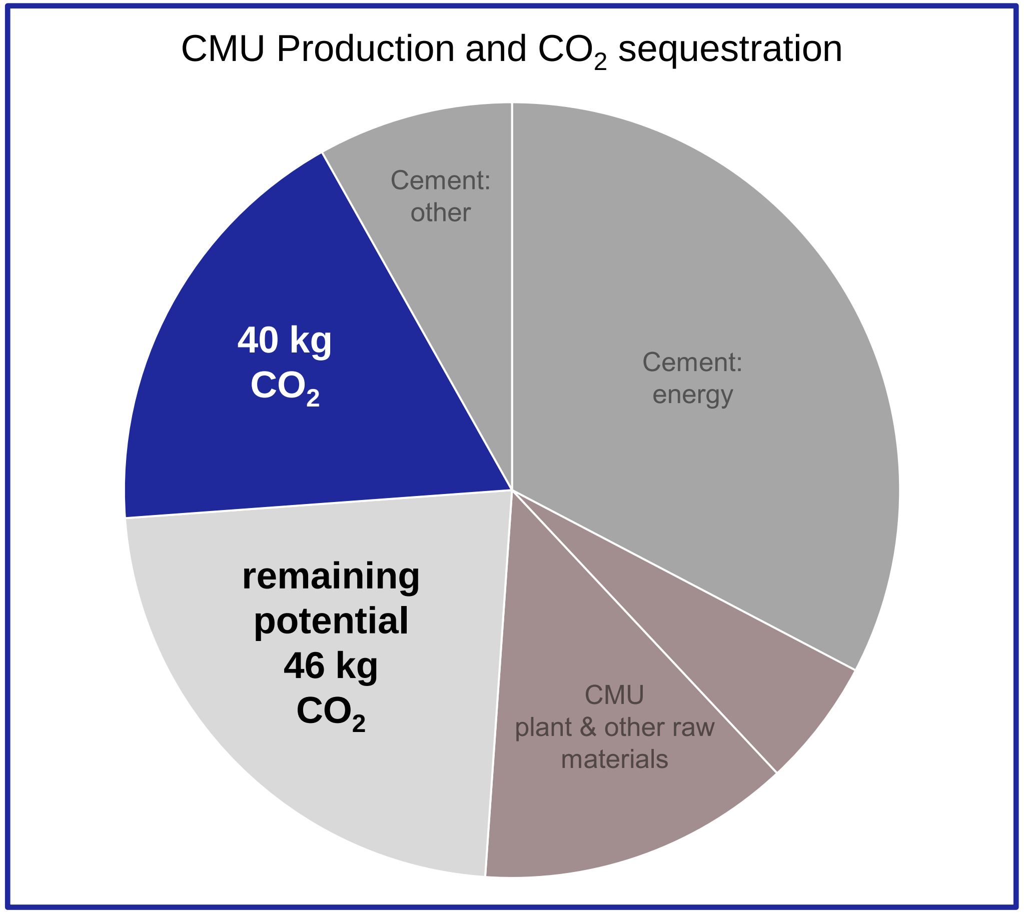
  – emissions associated with chemical reaction only

17% of total associated emissions

  – emissions associated with the whole process of CMU manufacturing

- Total sequestration ≈ 35 kg CO_2

Dry-Cast CO_2 Sequestration of CMU (PER M^3)



1 year

47% of potential

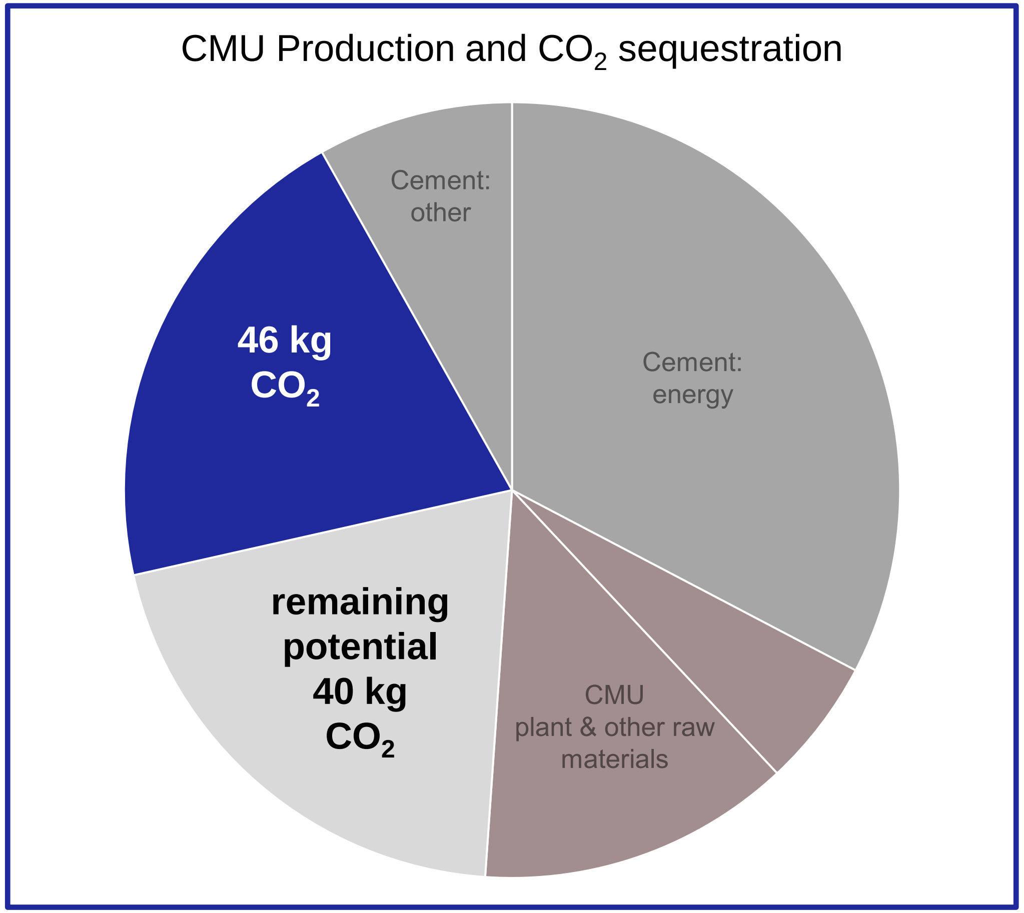
- emissions associated with chemical reaction only

19% of total associated emissions

- emissions associated with the whole process of CMU manufacturing

- Total sequestration ≈ 40 kg CO_2

Dry-Cast CO_2 Sequestration of CMU (PER M^3)



2 years

54% of potential

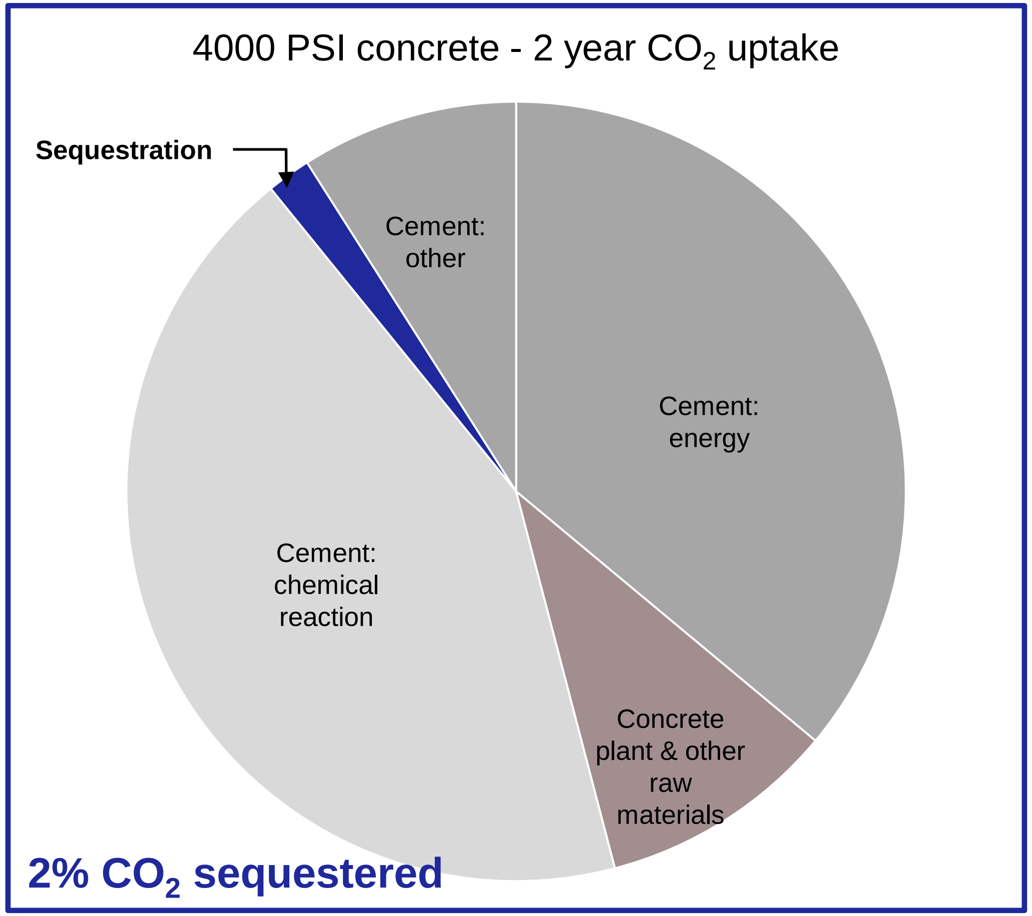
- emissions associated with chemical reaction only

22% of total associated emissions

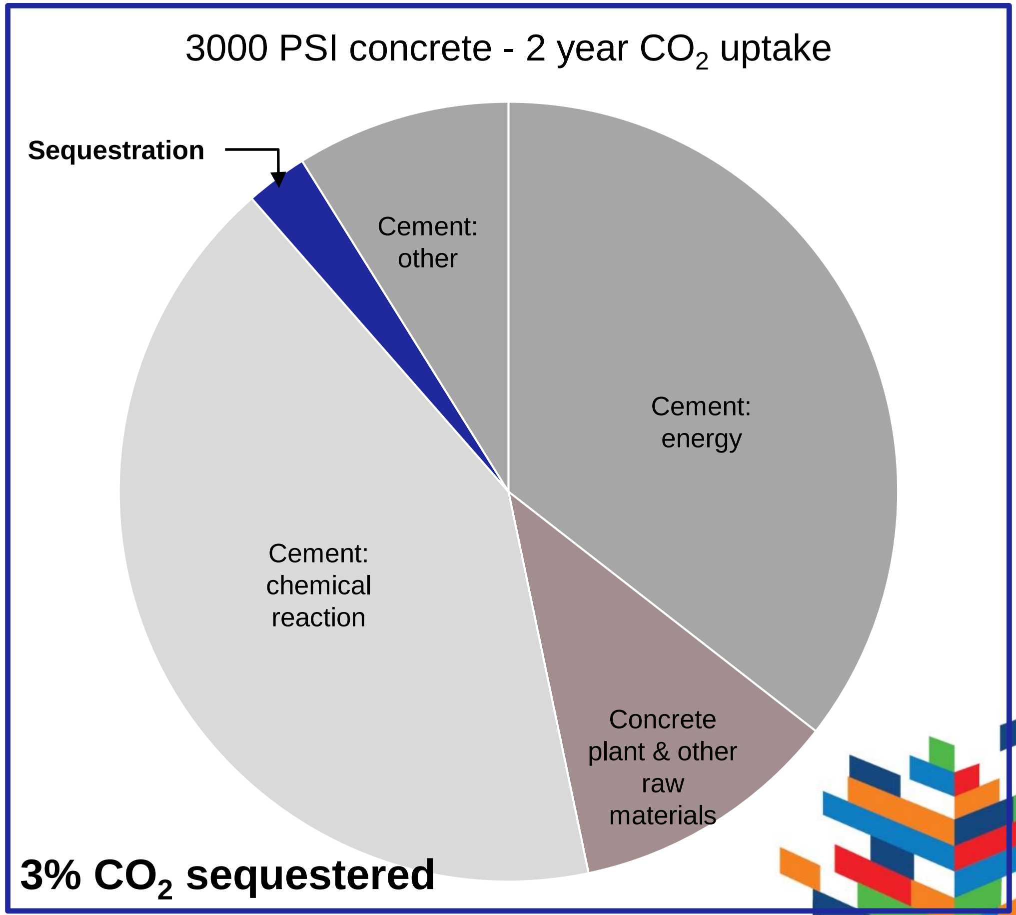
- emissions associated with the whole process of CMU manufacturing

- Total sequestration ≈ 46 kg CO_2

Wet-Cast CO_2 Sequestration of 10” Thick Wall (PER M^3)

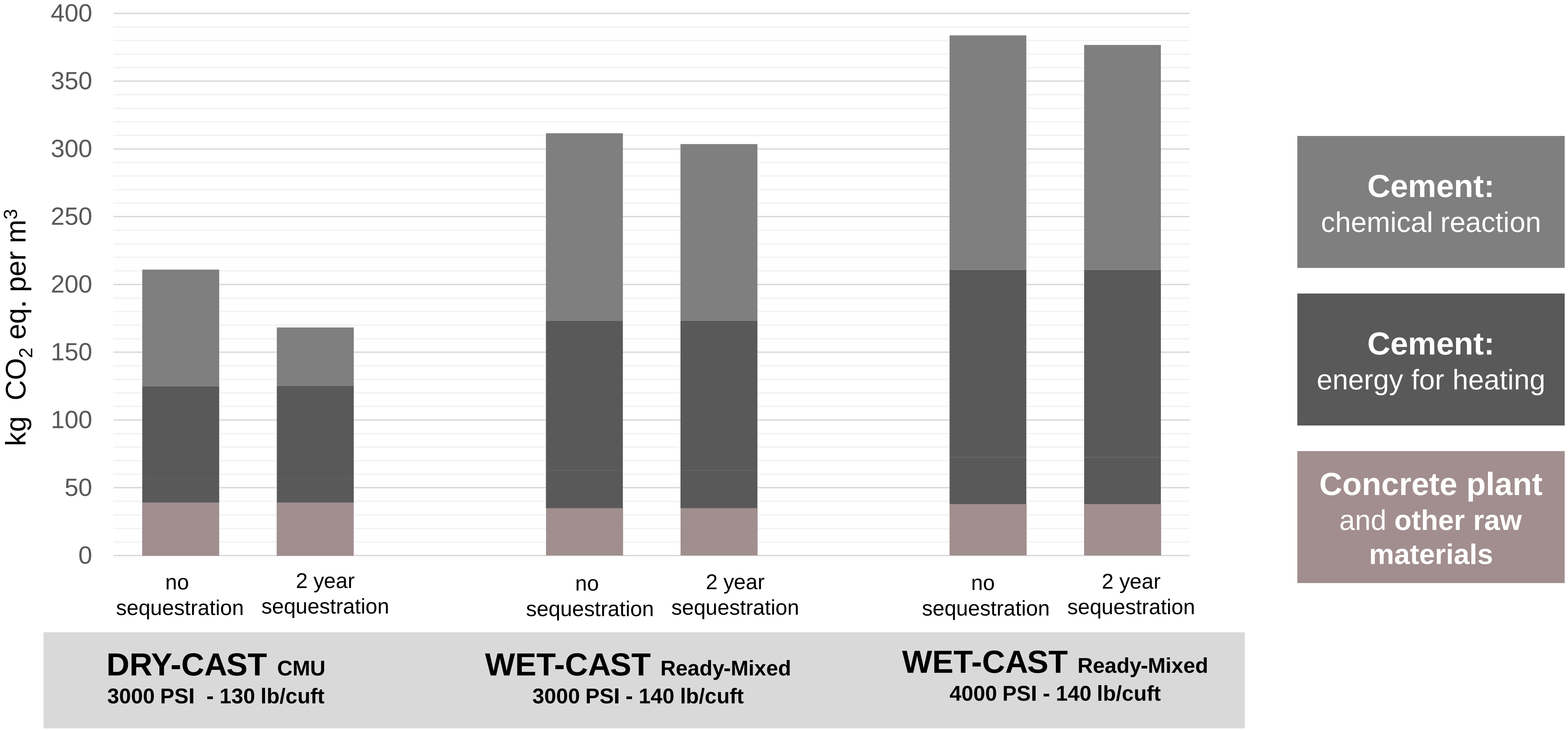


2% CO_2 sequestered



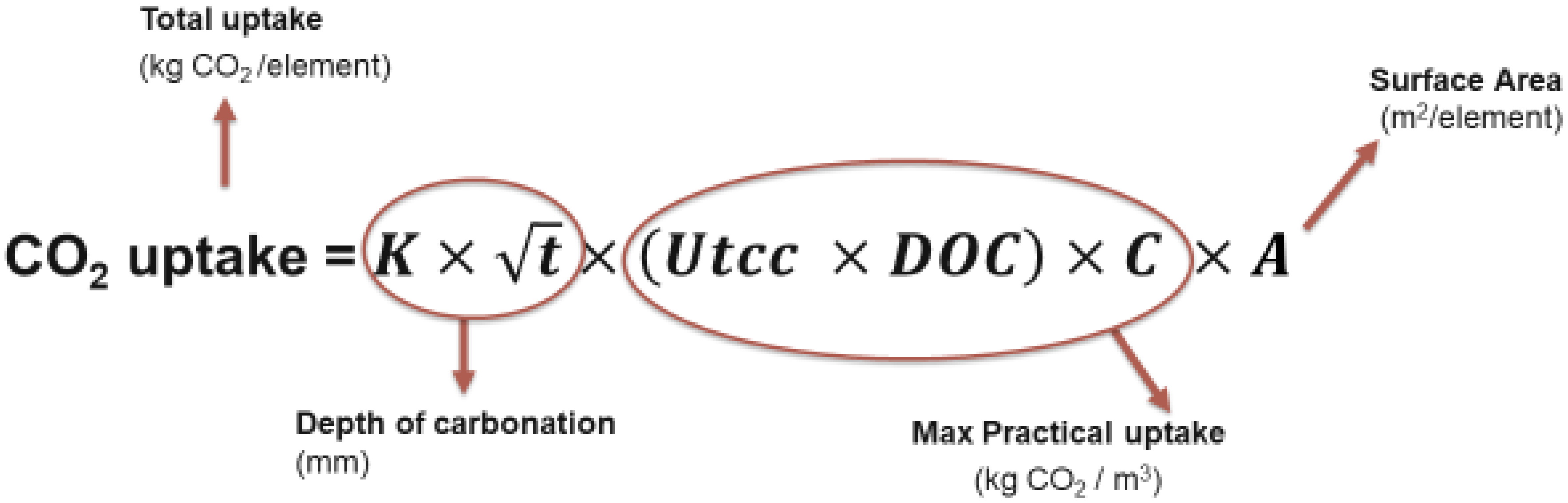
3% CO_2 sequestered

Relative Comparison - Total Embodied Carbon per m^3



Future Work - MODELING

- CMHA is partnering with the ***MIT Concrete Sustainability Hub (CSHub)*** to model the ***natural carbon uptake of CMU*** and masonry systems
- Modeling will build off of the EN16757 model of wet-cast concrete



Total uptake
(kg CO_2 /element)

Surface Area
(m^2/element)

$$CO_2 \text{ uptake} = K \times \sqrt{t} \times (Utcc \times DOC) \times C \times A$$

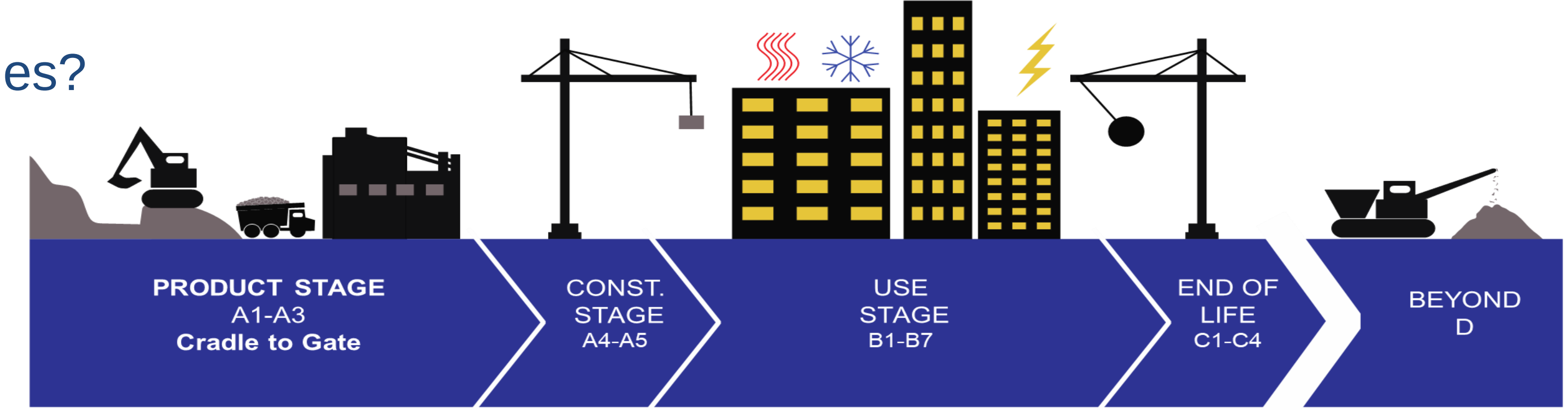
Depth of carbonation
(mm)

Max Practical uptake
(kg CO_2 / m^3)

EN 16757. Sustainability of Construction Works - Product Category Rules for Concrete and Concrete Elements, Annex BB (2017)

Future Work - MODELING

- While the modeling will ***build off of the classic wet-cast model*** there are some ***unique issues*** that may need to be addressed
- First – the classic model addresses carbonation only during the Use Stage (B1–B7)
  - CMU also have significant carbon uptake in the ***Cradle-to-Gate Stage (A1-A3)*** due to the combination of (a) ***high porosity*** (interconnected voids), (b***) thin elements*** and (c) ***hollow structure*** which causes a ‘chimney effect’ when they are stored in the yard.
  - During this early-age carbonation the cement is in a very active hydration state and is continuously ***producing more calcium hydroxide*** as the C3S phase hydrates so it is ***not in a steady-state*** that the classic model is built on
  - How might these effect K values?



PRODUCT STAGE
A1-A3
Cradle to Gate

CONST.
STAGE
A4-A5

USE
STAGE
B1-B7

END OF
LIFE
C1-C4

BEYOND
D

Future Work - MODELING

- Other issues to ponder:
- Wet-cast concrete has a fairly homogenous micro-pore structure of the cement paste/mortar (except possibly for the finished surface) while ***CMU has another level of porosity*** – the ‘***macro’ interconnected voids***. How might this affect the K values?
- Because dry-cast concrete is lacking water, it is harder to disperse all of the cement during mixing. CMU are typically estimated to have ***20 – 30% of the cement that is agglomerated*** and ‘not hydratable’. How does this impact DOC values?

Future Work - MODELING

- To help address these issues additional testing is in progress
  - ***Early age tests*** (1 to 28-day)
  - ***Profile testing*** of face shells – (a) Outer crust (0-6 mm), (b) intermediate layer (6-12 mm), and (c) center core (12-18 mm)
- ***Concrete pavers*** will also be studied using profile testing
- Once fundamental baseline modeling is completed further work will look at:
  - ***Effect of exposure conditions*** (e.g. painted, stucco or render, etc.) on the DOC values of masonry systems
- Working towards building reliable models for masonry and other dry-cast manufactured concrete products

Impact of CO_2 Sequestration on the Embodied Impact of Concrete Masonry Products

Questions?

Thank you!