Department of Architecture
School of Engineering
The University of Tokyo
Building Material Laboratory

Mechanism of carbonation of cementitious materiaQuantification of CO2 fixed in cementitious materials: Japanese activities

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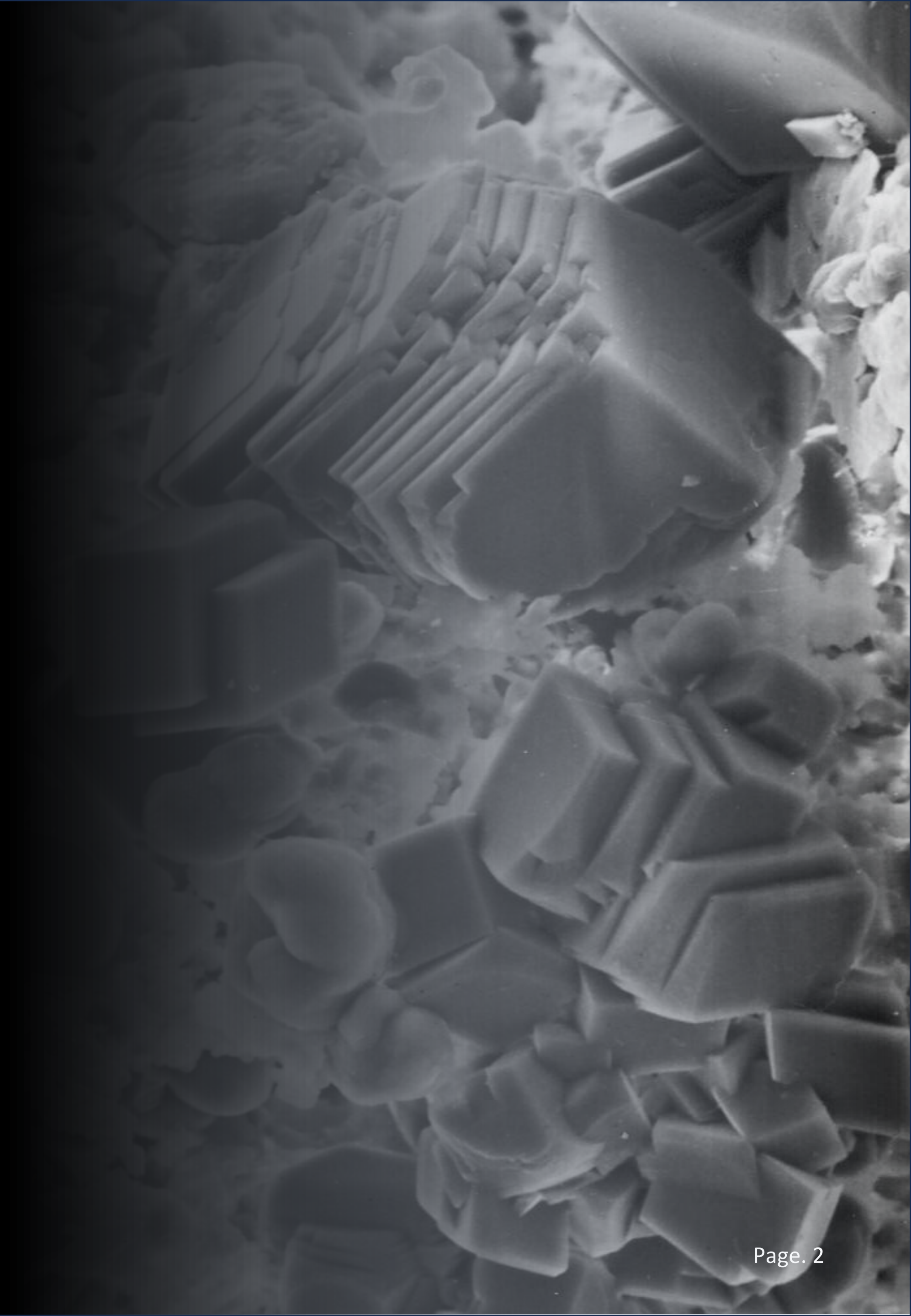
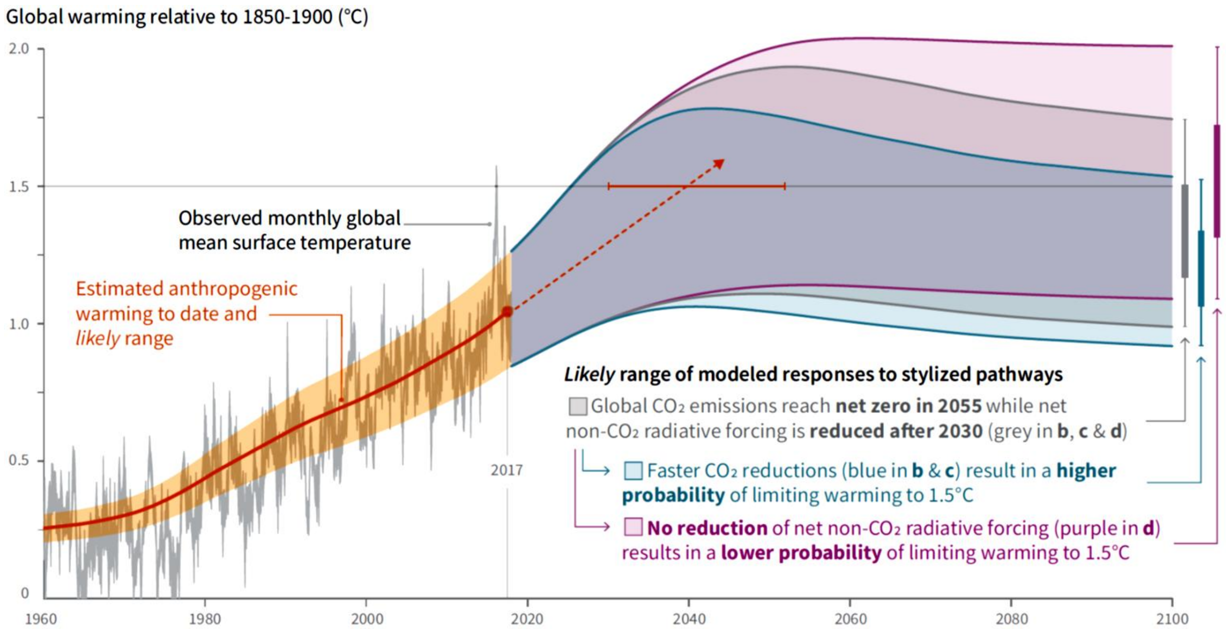
17th July 2025
Morioka, Japan

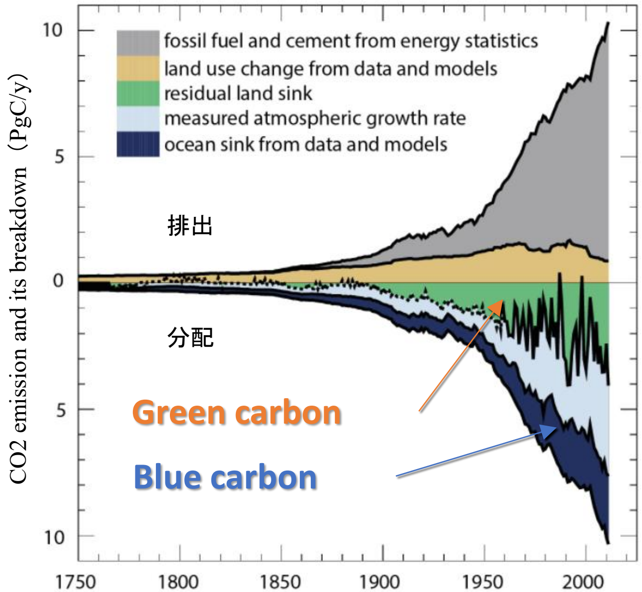
Background



Climate change and CO2 emission



環境省「IPCC『1.5°C特別報告書』の概要」を修正



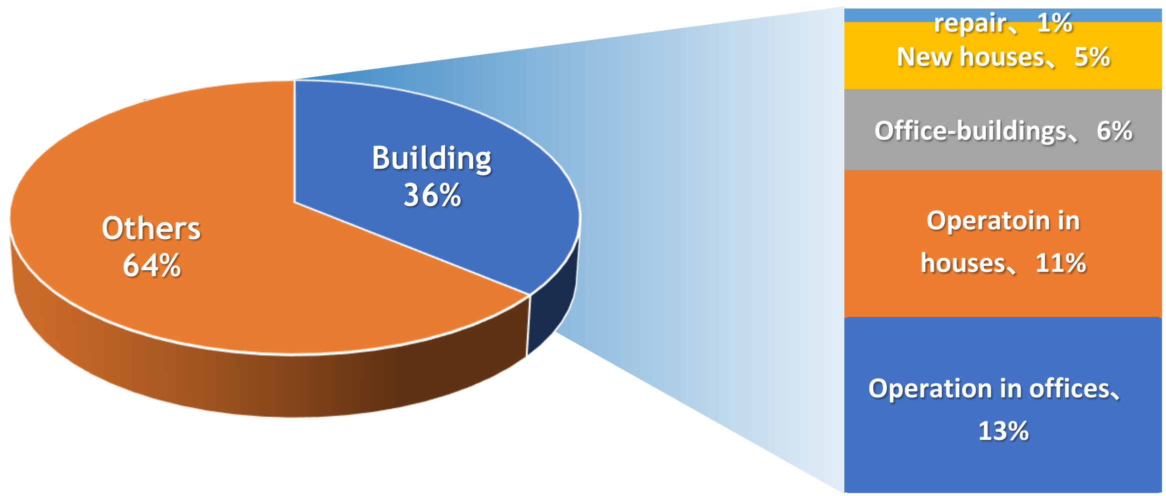
CO_2排出量・吸収量の推移

COP26 （Glasgow、UK）

- The decision is to avoid more than a 1.5-degree increase in the world average climate temperature change.

Current status in construction field in Japan

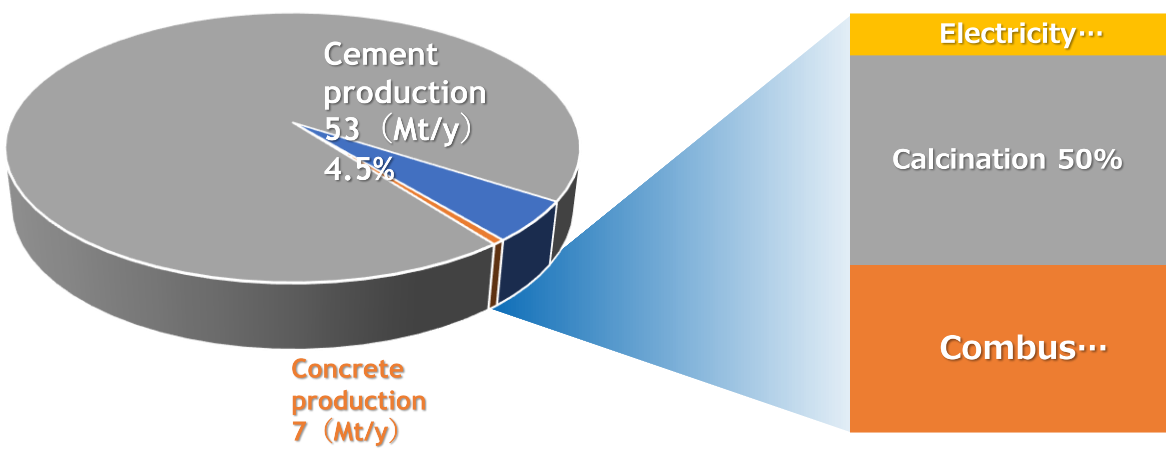
Total CO2 emission : 1,190（Mt/y）・・・2017



World
Buildings : 39%
Operation : 28%
Mat/Const : 11%

Resource: "Bringing Embodied Carbon Upfront" by World Green Building Council

秋山宏、伊香賀俊治、木俣信行「地球環境問題への建築学会の取り組みと展望、建築雑誌、Vol.114、No.1444、1999」を基に作成



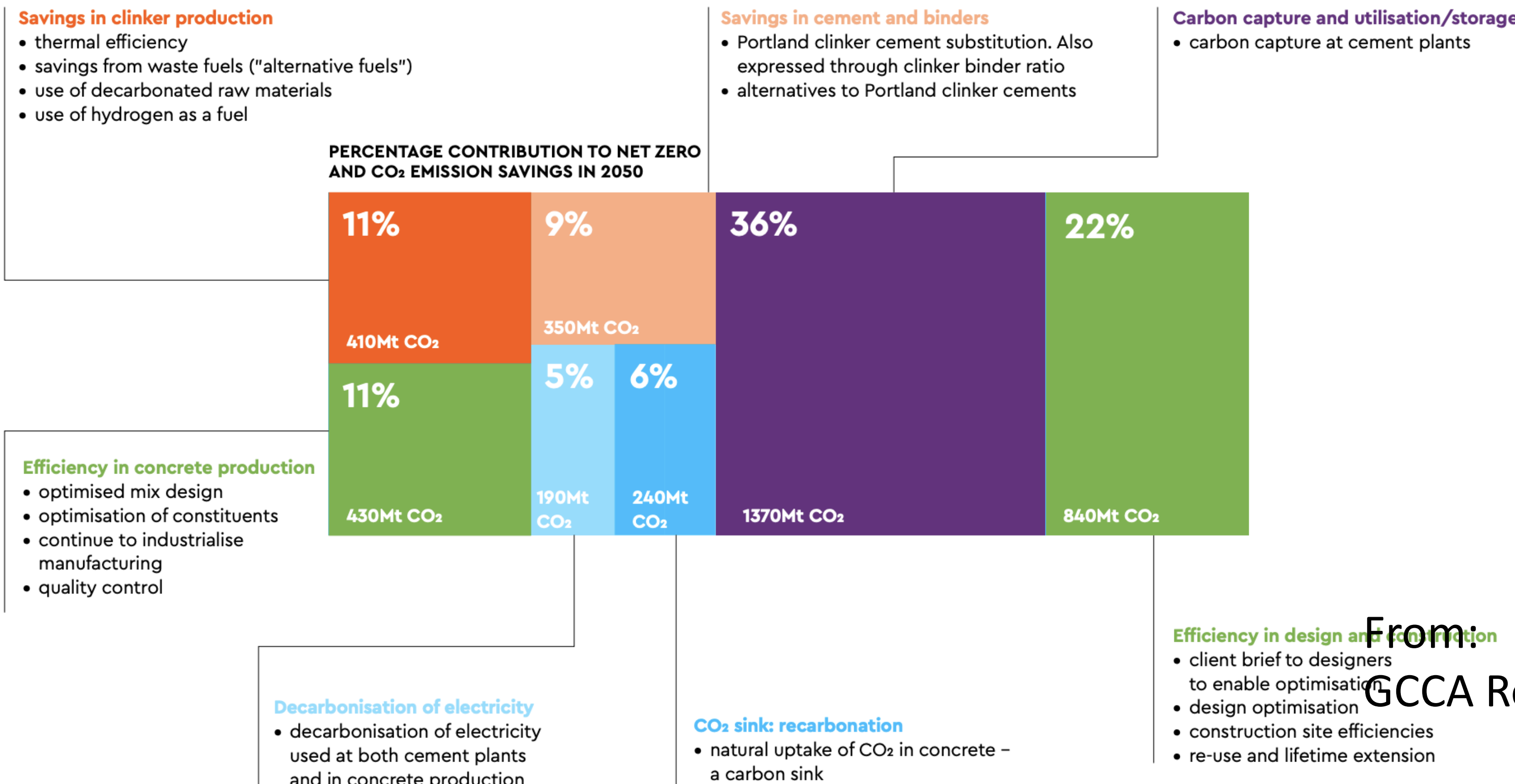
Calcinated-CO_2
26.4（Mt/y）

1996年（peak）
44.2（Mt/y）

国立環境研究所「日本の温室効果ガス排出量データ」、日本コンクリート工学会「コンクリートセクターにおける地球温暖化物質・廃棄物の最小化に関する研究委員会報告書」を基に作成

Cement industry

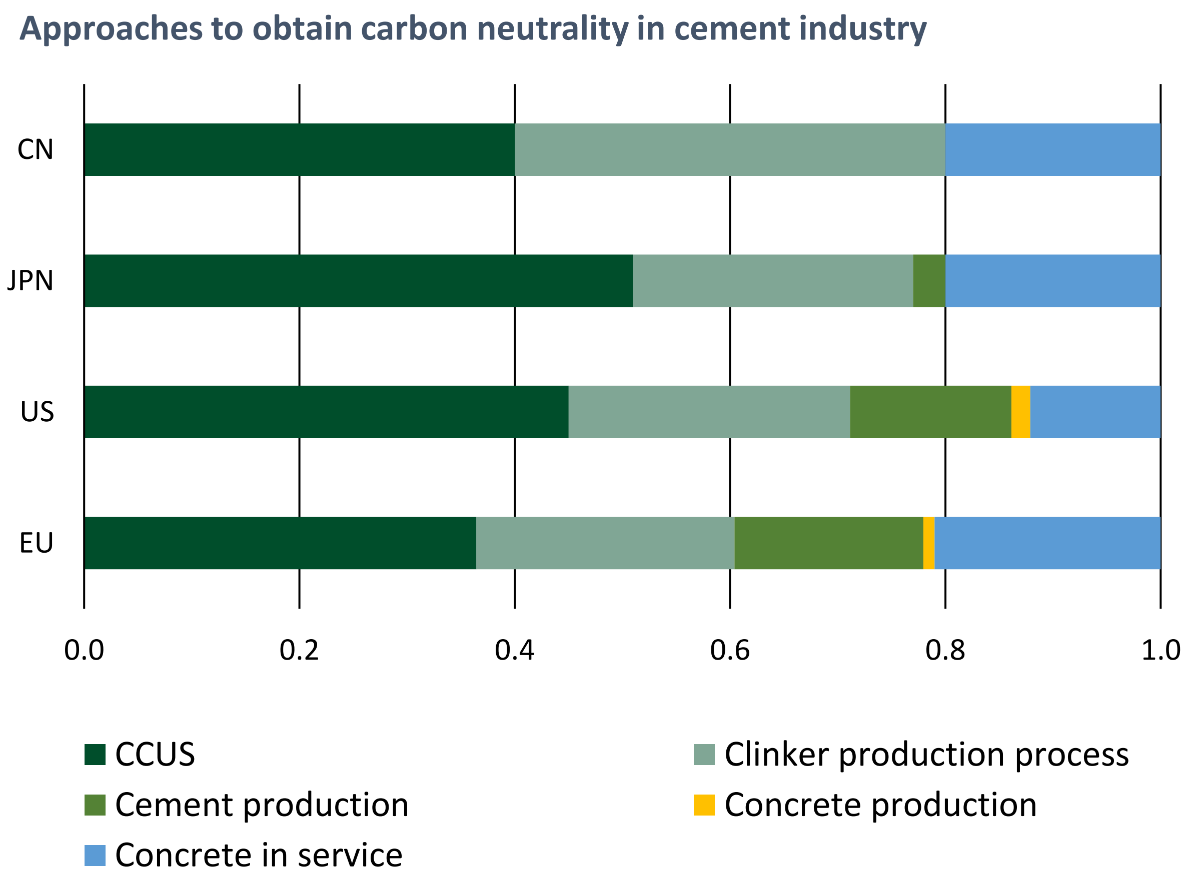
- Carbon neutrality of concrete sector is necessary for our society.
- Several options are undertaken and investigated.



From:
GCCA Roadmap

- CCUS using concrete and concrete component can used as offset. → <u>Quantification of mineralized CO2 is important.</u>

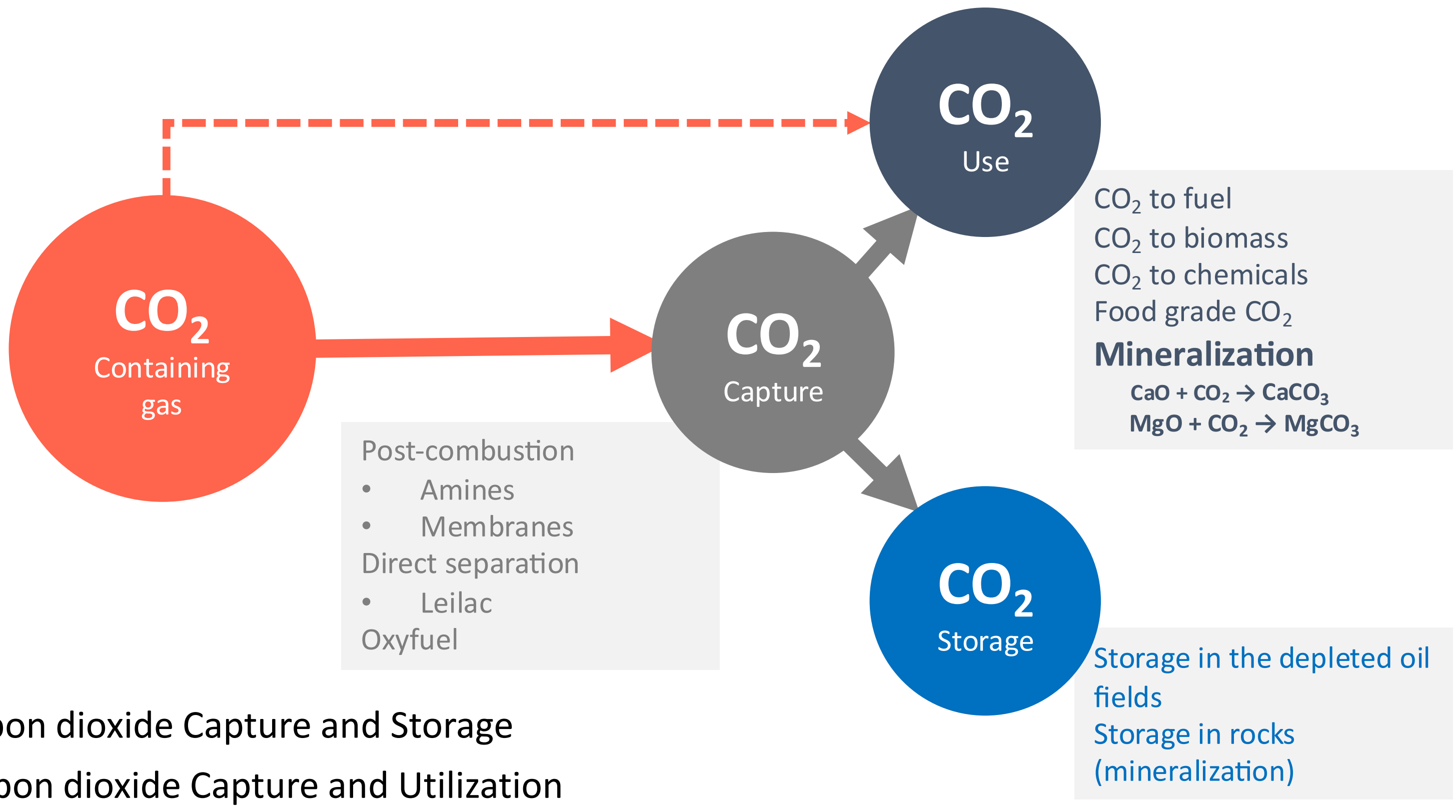
Reduction of the CO_2 emissions



- "CCUS is a key lever in our roadmap, accounting for a total of 36% emissions reductions by 2050.
- Our roadmap sets out the goal of having 10 fully operational plants by 2030. Across our members, we have over 35 projects publicly announced and underway, and up to a hundred more in the pipeline."

- https://gccassociation.org/2050-net-zero-roadmap-one-year-on/ccus-progress/

Carbon Capture Utilization and Storage



CCS is Carbon dioxide Capture and Storage

CCU is Carbon dioxide Capture and Utilization

Carbon dioxide mineralization is one of the technologies / reactions developed as CCU process

Carbon mineralization in cement and concrete industry allows direct application of the Carbon dioxide containing gas for the mineralization. Carbon dioxide capture (separation cleaning, liquification), is frequently not required.

Ref: Zajac, Maruyama, et al. ICCC 2023, Thailand

Cement and Concrete value Cycle with CO2

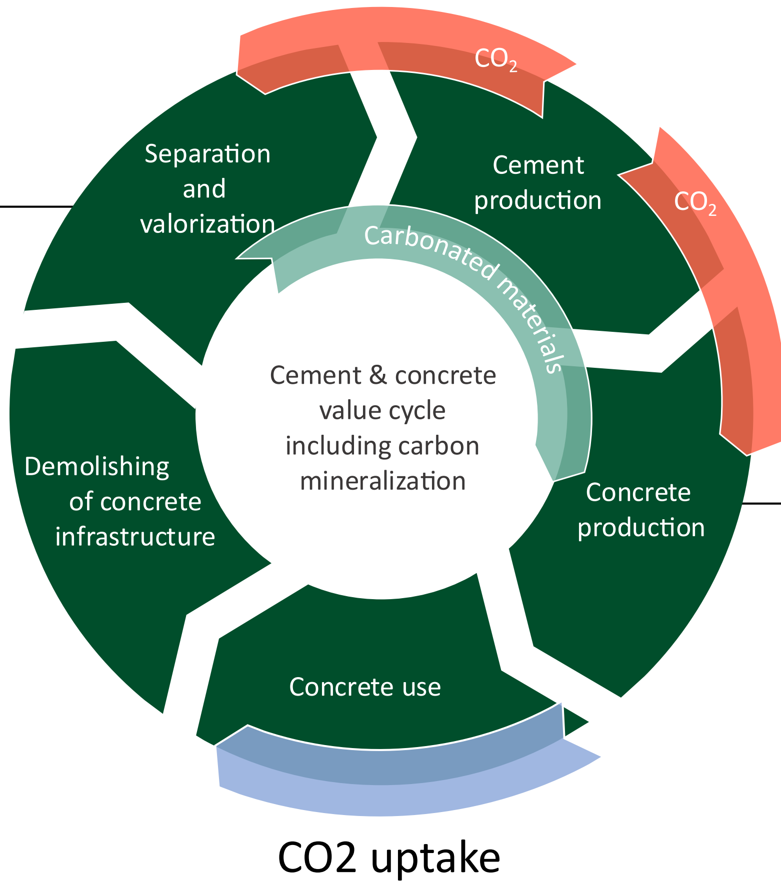
Valorization

Different material streams can be carbonated

- Recycled concrete paste
- Steel slags
- High calcium fly ashes and fly ash containing high content of CaO and MgO
- Other materials containing CaO and MgO

Process allows for

- CO2 sequestration
- Valorization of these materials into SCMs
- Can be conducted at normal temperature and pressure



Carbonation hardening

Carbonation during mixing and carbonation hardening

Carbonation enables application of non hydraulic clinkers and materials

Ref: Zajac, Maruyama, et al. ICCC 2023, Thailand

Carbonation reaction in cement and concrete

- Carbon dioxide (CO_2) mineralization or mineral carbonation is a process where oxides such as CaO or MgO react with carbon dioxide and form minerals of calcium or magnesium carbonate or other metal-oxide carbonate phases.
- Calcium and magnesium carbonates are poorly soluble in water, thermodynamically stable at atmospheric conditions and, thus, they provide a permanent CO2 storage solution

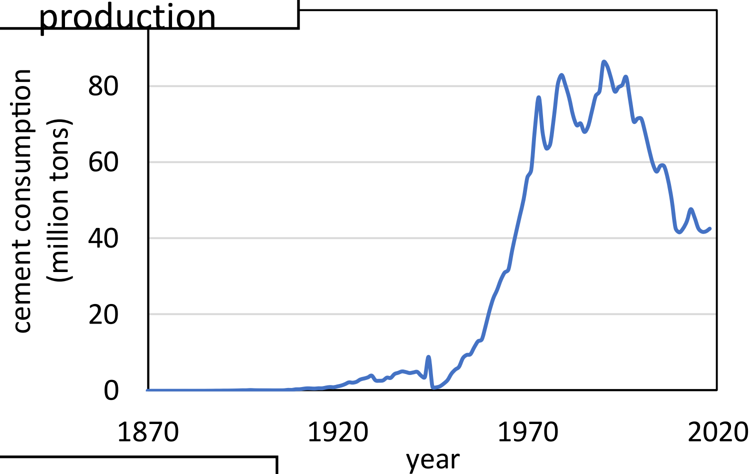
$$CaO + CO_2 \rightarrow CaCO_3$$

$$MgO + CO_2 \rightarrow MgCO_3$$

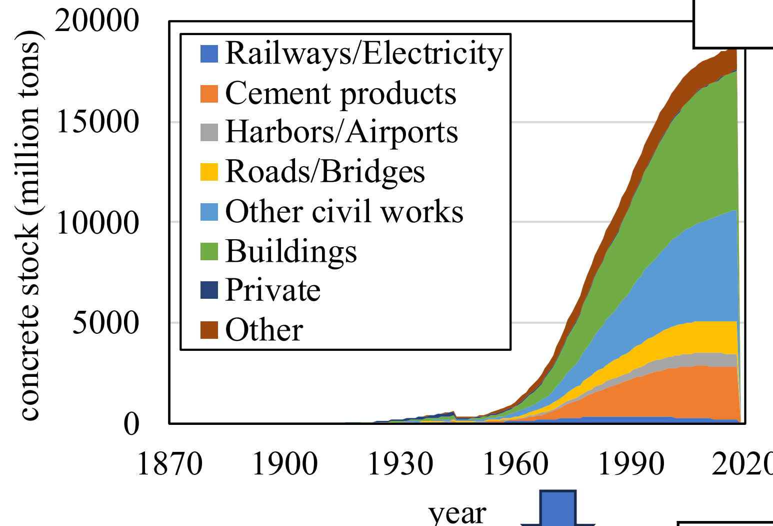
Concrete carbonation

Estimation of CO2 fixation of the existing buildings

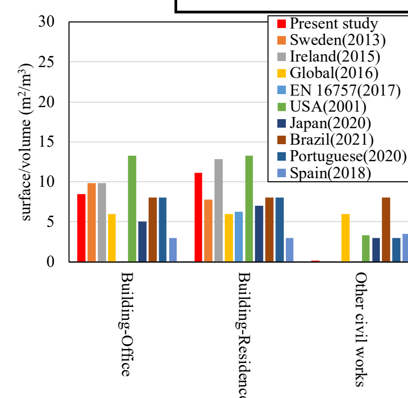
Cement production



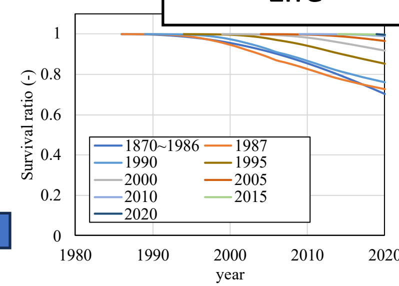
Stocks



Surface/volume



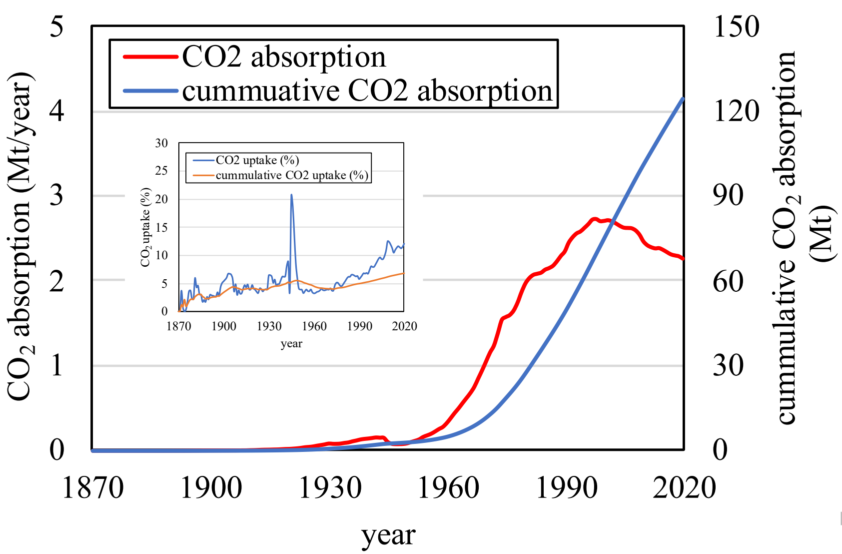
Life



$$U_{SL,t,n} V_{CC,t,n} C_{clinker} f_{CaO} D_c \frac{M_{CaCO_3}}{M_{CaO}} \frac{M_{CO_2}}{M_{CaCO_3}} \quad (1)$$

$$V_{CC,t,n} A_{t,n} \left(\sqrt{t} - n\sqrt{t-n-1}\right) \quad (2)$$

CO2 uptake



D. Sawa, et al.: CO2 uptake estimation in Japan’s cement lifecycle, JCP 2024

Japanese project

Research and Development on Standardization of Evaluation methods for CO_2 Fixation in Concrete

FY2021～FY2030（10 years）

Objective and description

The CO_2 fixation evaluation and quality control methods will be developed based on experimental facts and scientific basis.

Development item 1: Evaluation methods for amount of CO2 fixed by concrete materials and concrete. (EMC-MAT+CON)

Development item 2: Evaluation methods for CO2 fixation amount of concrete in use. (EMC-BUILD)

Development item 3: Quality control method for CO2 fixation process of concrete materials and concrete. (QCM-MATCON)

In order to achieve standardization, work closely with the Preparatory Committee for the Establishment of JIS within the Japan Concrete Institute, and strategically implement other related activities.

Note

Journal of Advanced Concrete Technology Vol. 21, 789-802, October 2023 / Copyright © 2023 Japan Concrete Institute 789

Technical paper

Error Factors in Quantifying Inorganic Carbonate CO_2 in Concrete Materials

Haruka Takahashi[1*], Ippei Maruyama[2], Takahiro Ohkubo[3], Ryoma Kitagaki[4], Yuya Suda[5], Atsushi Teramoto[6], Kazuko Haga[7] and Takahiro Nagase[8]

Received 4 September 2023, accepted 5 October 2023 doi:10.3151/jact.21.789

Abstract

In this study, CO_2 quantification was performed on various concrete binder and aggregates by back titration, thermogravimetric method, and combustion-infrared absorption method, and their mutual consistency and error factors due to material characteristics were investigated. The back titration measures CO_2 directly and is considered the suitable method for both materials, although the effect of sulfide was a concern. On the other hand, the TGA method was revealed to have the possibility of underestimating or overestimating the CO_2 determination because the oxidation of sulfides in blast furnace slag, combustion of unburned carbon in fly ash, and dehydration of clay minerals in aggregate overlapping with the temperature range of calcination of calcium carbonate. In the combustion-infrared absorption method, elemental or organic carbon encapsulated in aggregate particles may underestimate or overestimate the CO_2 content. In blended cement, sulfur compounds may interfere with the infrared absorption of CO_2 and overestimate the amount of CO_2. Based on these results, back titration was considered the most suitable method for determining CO_2 for concrete materials. It is essential to understand the characteristics of each sample contained and select appropriate methods for CO_2 quantification of concrete materials and concrete.

1. Introduction

In recent years, efforts to carbon neutrality have been promoted worldwide. In the construction sector, the usage of binder with a lower clinker ratio, immobilizing CO_2 in ready-mixed concrete sludge and recycled aggregate for the application of concrete components, technologies to manufacture hardened concrete by using special biner which can immobilize CO_2 by carbonation reaction and hardening chemical reaction, are widely developed.

While the technology to immobilize CO_2 has advanced, there is no standardized method for determining the fixed CO_2 amount in concrete or concrete components in which CO_2 has been immobilized. Therefore, there is an urgent need to standardize these CO_2 quantification methods.

A summary of CO_2 determination methods that have been applied to inorganic materials, including concrete and concrete components, is listed in **Table 1**. Chemical analysis methods that directly measure CO_2 gas produced by acid decomposition of a sample are commonly used as standard methods. In addition, the gasometric method, in which the amount of CO_2 is determined from the pres-

https://doi.org/10.3151/jact.21.789

Background and objective

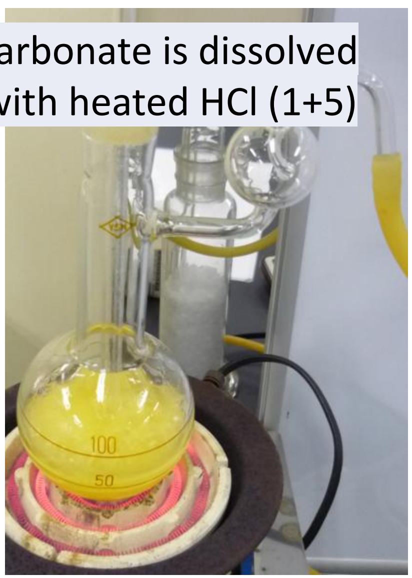
Method	Standards or Ref.	Samples	Principle
Chemical analysis -Volumetric method	EN459-2	Lime	Acid dissolution of samples and measurement of the volume of CO_2 gas generated.
	ISO 1691	Sodium Silicate /Potassium Silicate	
	JIS R 9011	Lime	
Chemical analysis -Gravimetric method	ASTM C 114-18	Cement	Acid dissolution of samples and measurement of the weight of CO_2 gas generated.
	EN 459-2	Lime	
	ISO 29581-1	Cement	
Chemical analysis -Back titration	JCAS I-60-1982	Cement	Dissolve the sample in acid, absorb the generated CO_2 gas in alkaline absorption solution, and titrate the excess alkali with acid.
	JIS R 9011	Lime	
	JIS R 9101	Gypsum	
	Fu, H., et al.	Sediment	
	Koyama, T., et al.	Water	
	Martin, R. L.	Soil	
Gasometric method	Fu. H. et al. 2020	Sediments	Convert the volume of CO_2 released from the reaction between carbonate and HCl into carbonate content using various apparatuses.
	Sano, H., et al.	Steel slag	
Combustion-Infrared Absorption method	ASTM C114-18	Cement	To determine CO_2 generated by combustion of a sample in an oxygen stream by infrared absorption method
	JIS R 9011	Lime	
Coulometric method	Johnson, K.M., et al.	Seawater	The amount of C is determined from the amount of electricity required to absorb the gas generated by HCl treatment into the absorbent solution and to maintain the pH of the absorbent solution constant.
	Yasuda, R., et al.	Cement paste	
	Fu, H., et al.	Sediment	
Thermogravimetric analysis	ASTM C114-18	cement	The weight loss due to the decomposition of $CaCO_3$.

Barium carbonate back titration (JIS R 9101)

$$CO_2\left(mass\,\%\right) = \frac{(v_1 - v_2) \times f \times 0.0044}{s} \times 100,$$

v_1 : the blank HCl titer (mL),
v_2 : the HCl titer of the analyzed sample (mL),
f : the factor of the HCl,
s : the sample weight (g).

Carbonate is dissolved with heated HCl (1+5)



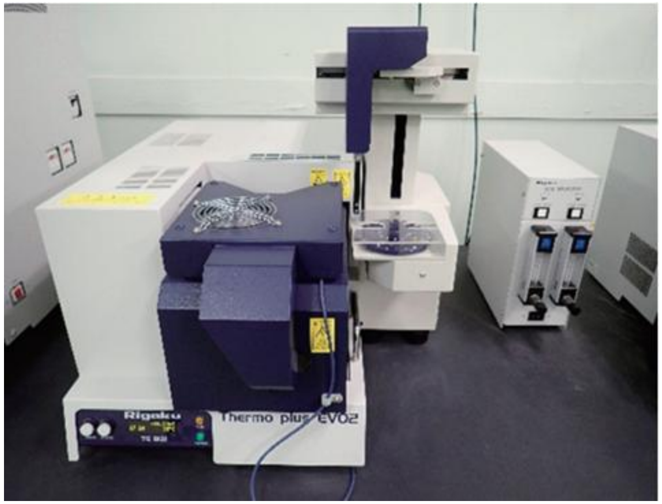
→

Absorbed CO_2 with 0,2M NaOH-$BaCl_2$ solution

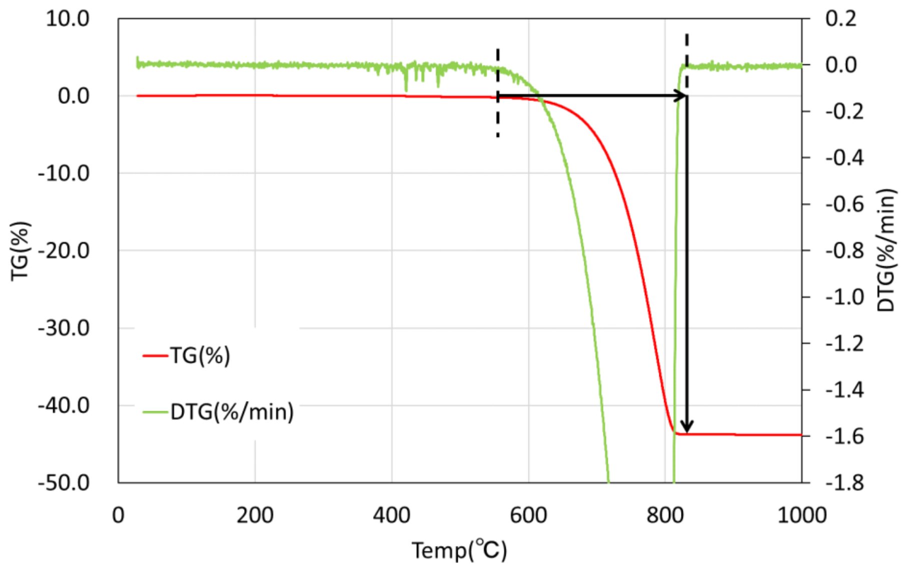
→

Unconsumed 0,2M NaOH is titrated with 0,2M HCl

Thermogravimetric Analysis (TG-DTA)



TG-8121, Thermo plus EVO2, Rigaku



Result of Limestone

- Sample mass of 20 to 25 mg placed in Pt pan
- N_2 purge at a flow rate of 300ml/min
- Heat sample from room temperature to 1000℃ at 10℃/min
- The derived thermogravimetric curve (DTG) was used as a reference to determine the weight loss in the temperature range.

$$CO_2\left(mass\ \%\right) = \frac{(m_1 - m_2)}{s} \times 100,$$

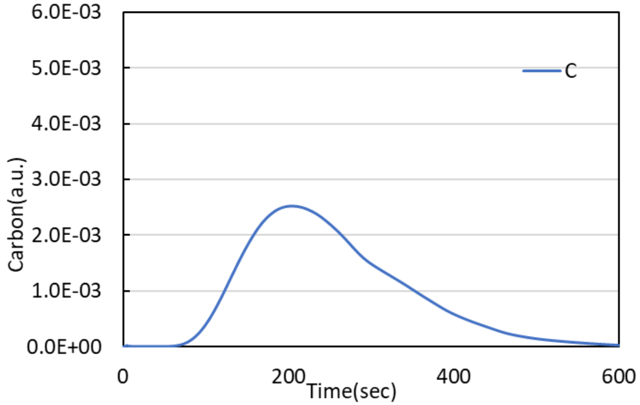
m_1 : weight at the starting point (mg),

m_2 : weight at the endpoint (mg),

s : sample weight (mg).

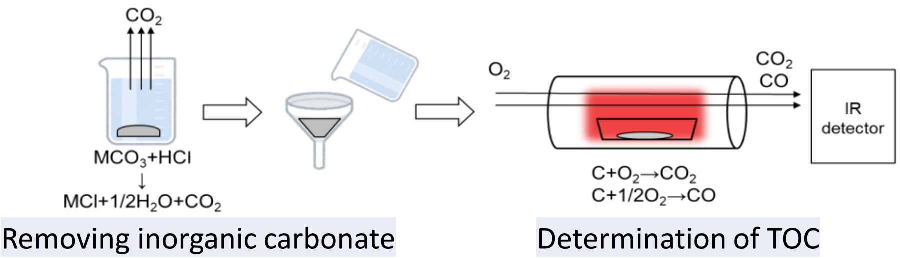
Combustion-Infrared absorption method: Total carbon/sulfur analyzer (T-C)

EMIA-Step, HORIBA



Measurement example ($CaCO_3$)

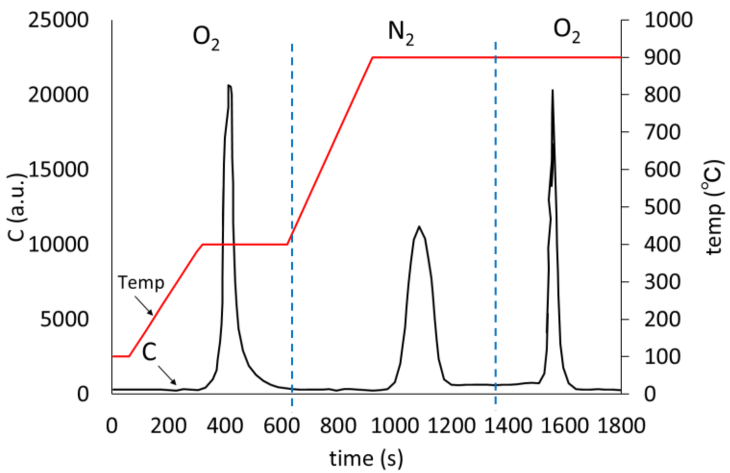
- Reference to ISO 10694
- Total carbon(TC) is determined by heating at 900℃ in oxygen flow
- Organic carbon(TOC) is determined in the same manner as TC for removing the carbonate sample with HCl or heating at 600℃ in oxygen flow
- TIC ＝TC - TOC



Schematic diagram of TOC

Combustion-Infrared absorption method: TOC analyzer (Solid-TOC)

Soli TOC® Cube, Elementar



Classification of carbons and temperature program. (DIN 19539, Appendix B)

・Reference to DIN 19539

Parameter	Starting Temperature (°C)	Heating Rate (°C/min)	Final Temperature (°C)	Holding Time (s)	Carrier Gas
TOC_{400}	150	70	400	120	O_2
TIC_{900}	400	70	900	250	N_2
ROC	900	-	900	100	O_2

Large sample

Journal of Advanced Concrete Technology Vol. 22, 383-390, June 2024 / Copyright © 2024 Japan Concrete Institute 383

Technical report

Development of a Large-scale Thermogravimetry and Gas Analyzer for Determining Carbon in Concrete

Ippei Maruyama[1*], Koichiro Noritake[2], Yoshinobu Hosoi[3] and Haruka Takahashi[4]

Received 3 May 2024, accepted 3 June 2024 doi:10.3151/jact.22.383

Abstract

One carbon neutralization measure applied in the concrete sector is the use of artificial carbonate in concrete for immobilization. This CO_2 reduction technology corresponds to the CO_2 emitted during concrete production. When considering the marketability of these technologies, especially for newly developed products in the carbon market, it is essential to quantify the amount of CO_2 fixed as inorganic carbonate. Additionally, as a representative test specimen for concrete containing aggregate, a φ100 × 200 mm cylinder specimen is conventionally used for physical property evaluation. To evaluate the amount of CO_2 fixed in one batch of concrete, a mass far from that of the conventional chemical analysis sample may need to be analyzed. Therefore, in this study, we investigated a pulverization process for concrete analytical materials. We also propose a new analytical apparatus that can be used to measure large cylinder specimens. Experimental results showed that the newly developed analyzer, equipped with a mass balance and CO_2 and H_2O gas analyzer for large cylinders, exhibited excellent analytical variability and measurement speed performance. It was also inferred that the homogenization process is necessary to grind the entire cylindrical concrete specimen into a fine powder and homogenize it to improve the representativeness of the concrete.

1. Introduction

The concrete sector is prioritizing the achievement of carbon neutrality (Japan Cement Association 2022; IEA 2009; Portland Cement Association 2024; Scrivener *et al.* 2018; CEMBUREAU 2020). One reason for this is that in conventional concrete, the decomposition of calcium carbonate during the production of Portland cement and high-temperature calcination results in high (Takahashi *et al.* 2023; Torrenti *et al.* 2022). Conventional methods exist, such as the decomposition of calcium carbonate through high temperatures using mass change (ASTM 2018), a mass spectrometer, or an IR sensor (ASTM 2017; JSA 2006) dissolving the sample in acid and absorbing the generated CO_2 gas in alkaline solution, then titrating the excess alkali with acid (JSA 2006, 2018); or dissolving the sample in acid and measuring the mass or volume of generated CO_2 gas

http://dx.doi.org/https://doi:10.3151/jact.22.383

Measuring Concrete sample

Sampling

Drying

Splitting + crushing

Crushing

- Under 10mm

Sample reduction

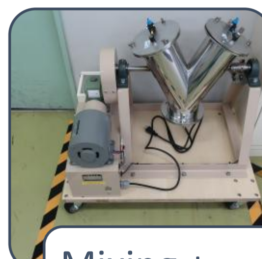
- 1/8(～450g)

Fine crushing

- Under 5mm
- 1/16 (~230g)

Grounding

- Under 150μm
- 30～50g/time×5

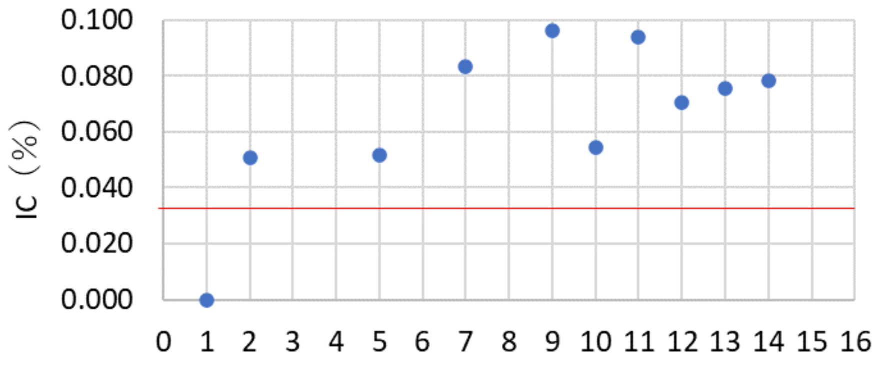


Mixing + reduction

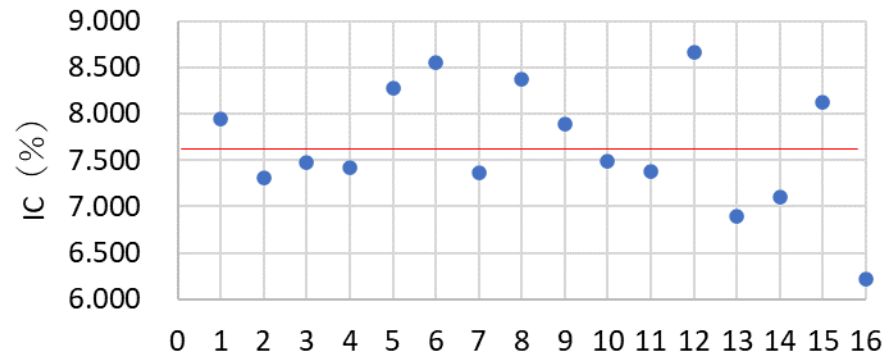
- 30~180 min.

OPC-Concrete：W/C=0.5、28d **sealed curing**

- Specimen A（Coarse agg= Granite）
- Specimen B（Coarse agg = Granite 70% + Limestone 30%) (CO_2 =7.3 mass%)
- T-C measurement results:



Sample number, Specimen A

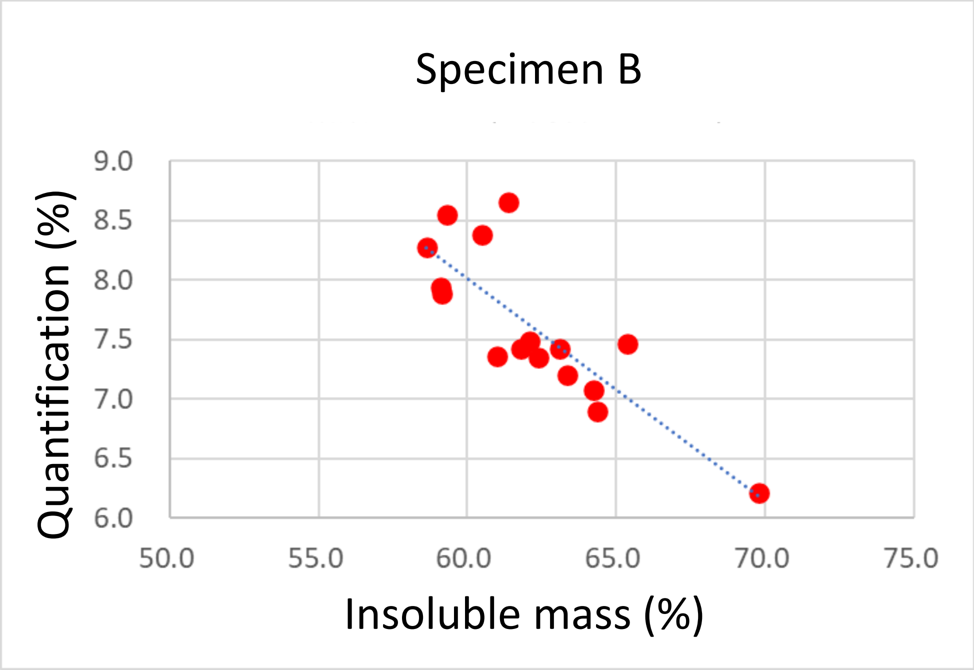


Sample number, Specimen B

Large scattering!

I. Maruyama, K. Noritake, Y. Hosoi, H. Takahashi, Development of a large-scale thermogravimetry and gas analyzer for determining carbon in concrete, J. Adv. Concr. Technol. 22 (2024) 383–390. https://doi.org/10.3151/jact.22.383.

CO2 quantification and aggregate content



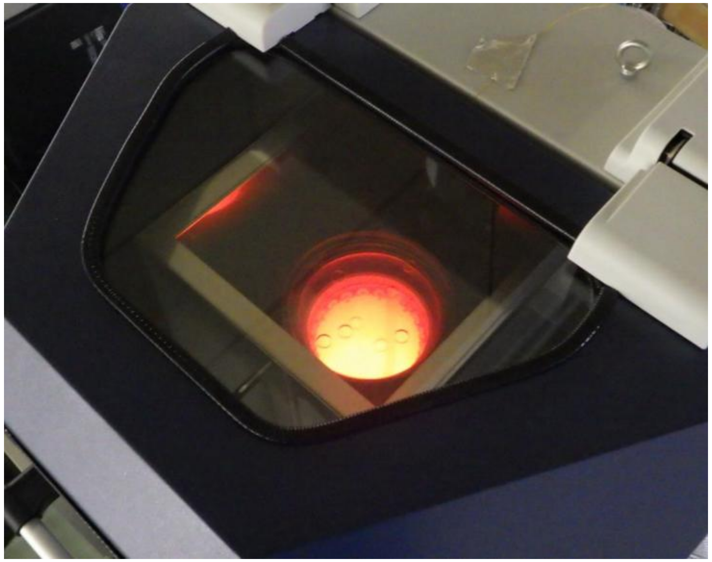
- Insol. test was conducted, and inhomogeneity of aggregate ratio in sample was confirmed.

I. Maruyama, K. Noritake, Y. Hosoi, H. Takahashi, Development of a large-scale thermogravimetry and gas analyzer for determining carbon in concrete, J. Adv. Concr. Technol. 22 (2024) 383–390. https://doi.org/10.3151/jact.22.383.

Another solution

- ✓ Large size TG-Gas analyzer is developed. Mass difference and CO2 and H2O is analyzed as a function of time/temperature.
- ✓ Prototype machine is developed with RIGAKU and under calibration in Utokyo.

Setting of the concrete
Specimen ϕ10x20 cm



Heating process

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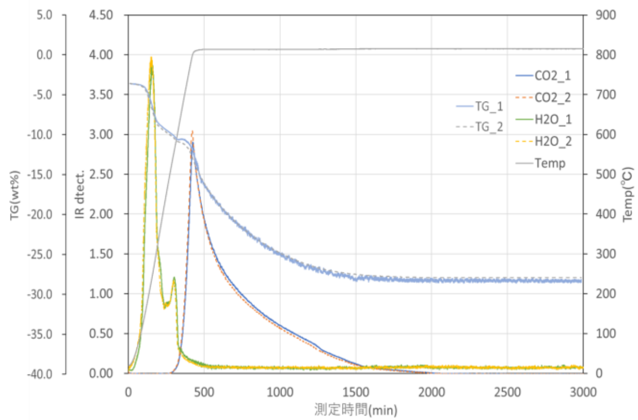
Example of the results



- Obtained data are sound.
- The data acquisition peri
hou

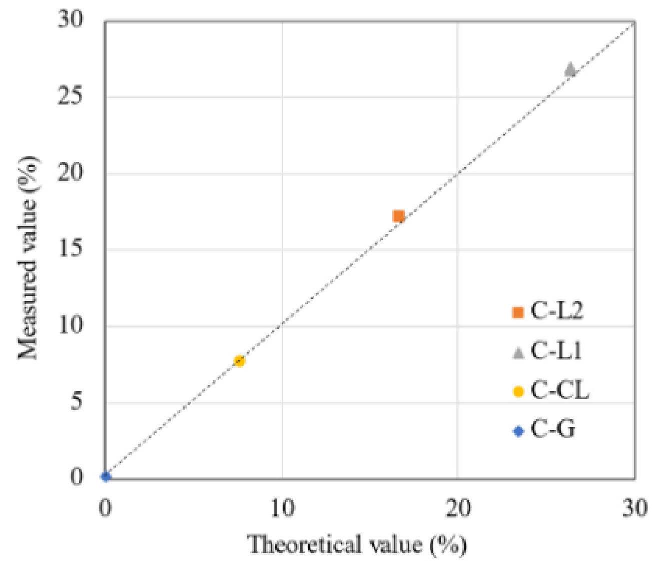


Fig. 4 Comparison between the theoretical values of CO_2 content calculated by the mixture proportions and CO_2 content of each component and measurement results by back-titration method.

試料	CO_2(%)				
	Design value	No.1		No.2	
		IR	TG※	IR	TG※
Specimen A	26.5	26.1	26.9	26.5	26.3
Specimen B	16.5	16.3	16.5	16.2	16.5

I. Maruyama, K. Noritake, Y. Hosoi, H. Takahashi, Development of a large-scale thermogravimetry and gas analyzer for determining carbon in concrete, J. Adv. Concr. Technol. 22 (2024) 383–390. https://doi.org/10.3151/jact.22.383.

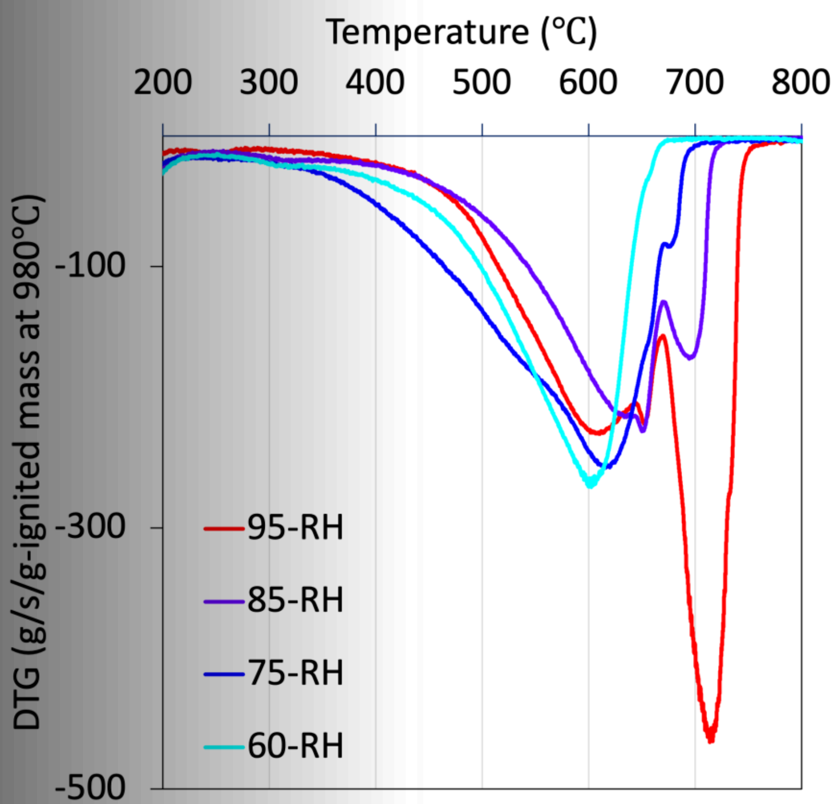
Summary

- Data acquisition need appropriate understanding of sample.
- Particle size, Disturbing substances, encapsulation of target materials (CaCO3) or related materials (Elemental carbon, organic carbon) may influence the results.
- Sample powder reduction is very difficult for concrete sample. Further development is needed.
- Concrete TG-Gas analyzer is newly developed.

Acknowledgement

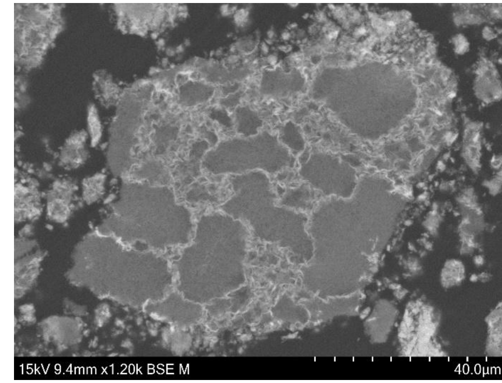
The results of this report were commissioned (JPNP21023) by the New Energy and Industrial Technology Development Organization (NEDO).

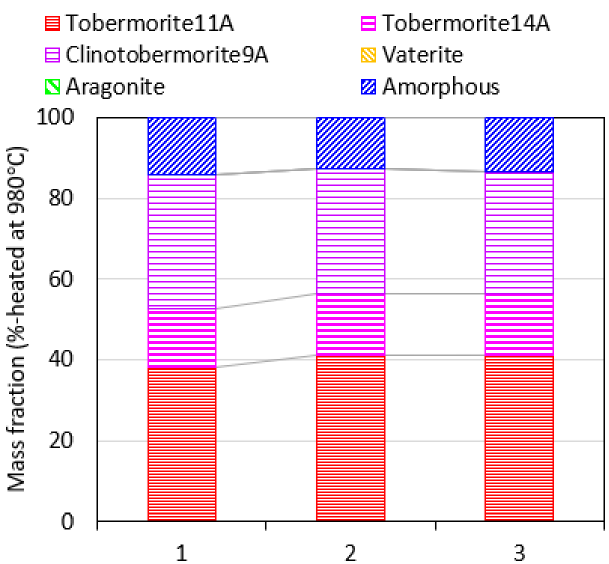
What is the reason of the low-temperature decomposition during TG?



Synthesize Tobermorite, CSH with Ca/Si 0.84

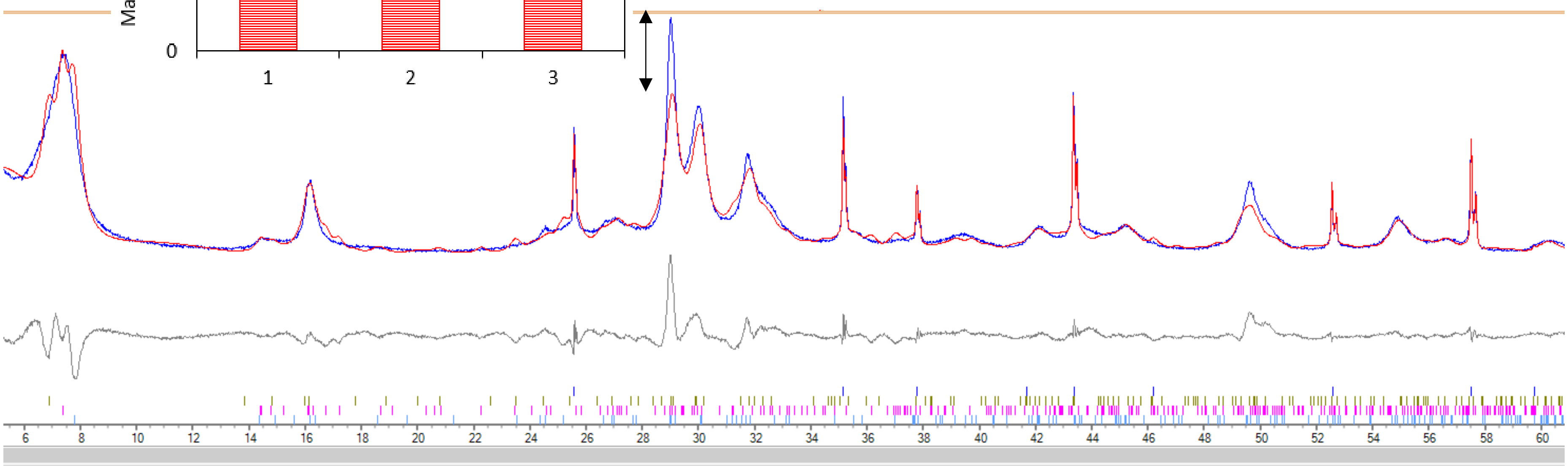
Fitting on TOPAS 6.0 with uncarbonated CSH0.84





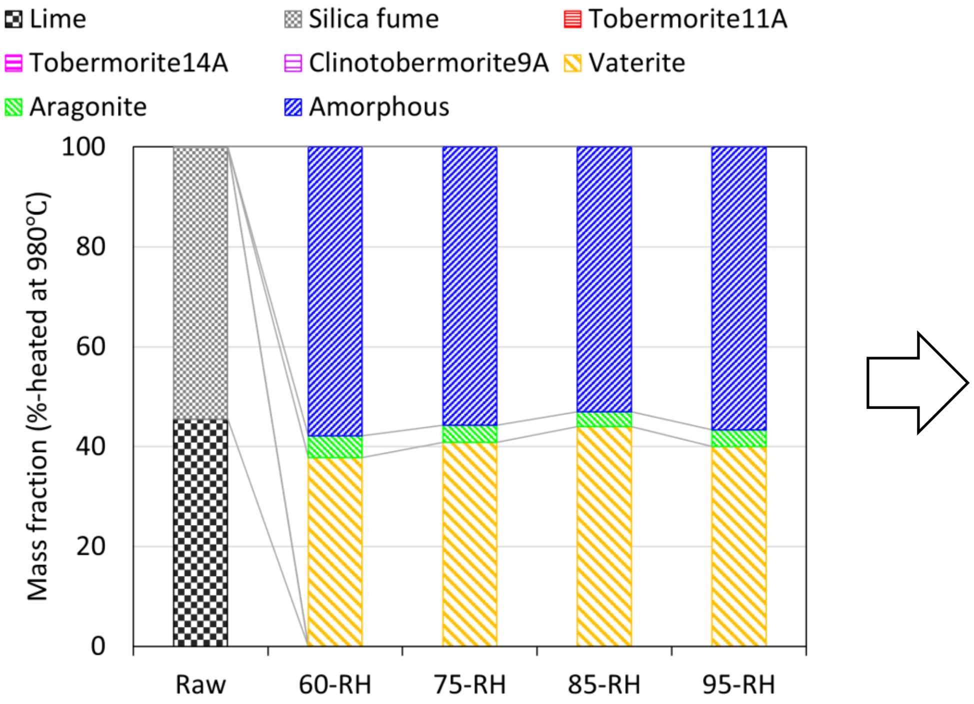
Corundum	
Plombierite(MERLINO,9013974)	12.01 %
Clinotobermorite(MERLINO,9002244)	23.08 %
11ATobermorite(MERLINO,9005500)	38.25 %
Int Amor	16.67 %

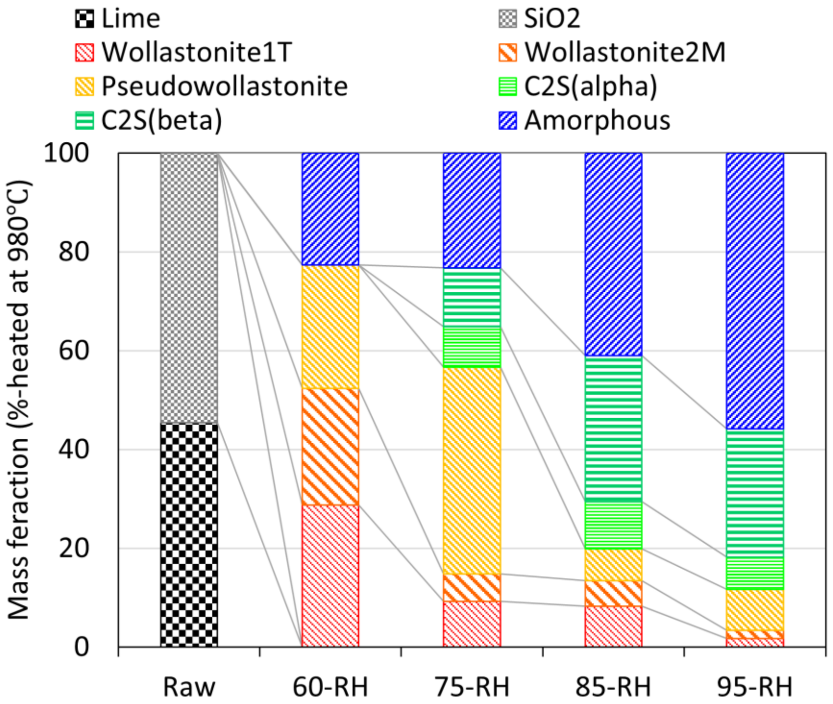
Double chain (Clinotobermorite, 11ATobermorite)



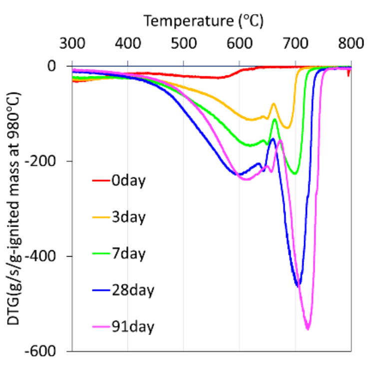
Carbonation of CSH Ca/Si 0.84

Mass fraction of carbonated samples after heating at 800℃

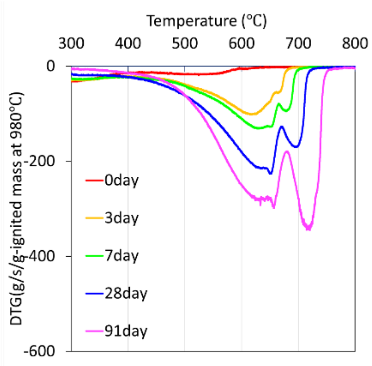




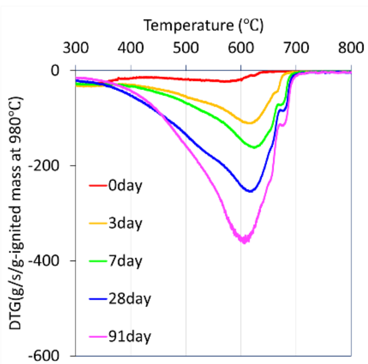
Although mineral compositions after carbonation were almost same,
heating products were different.



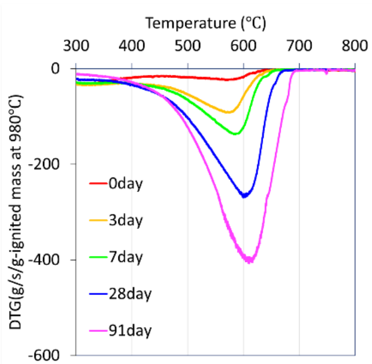
(a) 95-RH



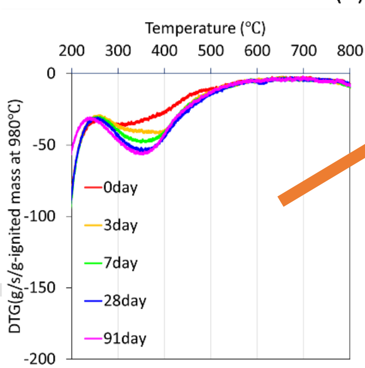
(b) 85-RH

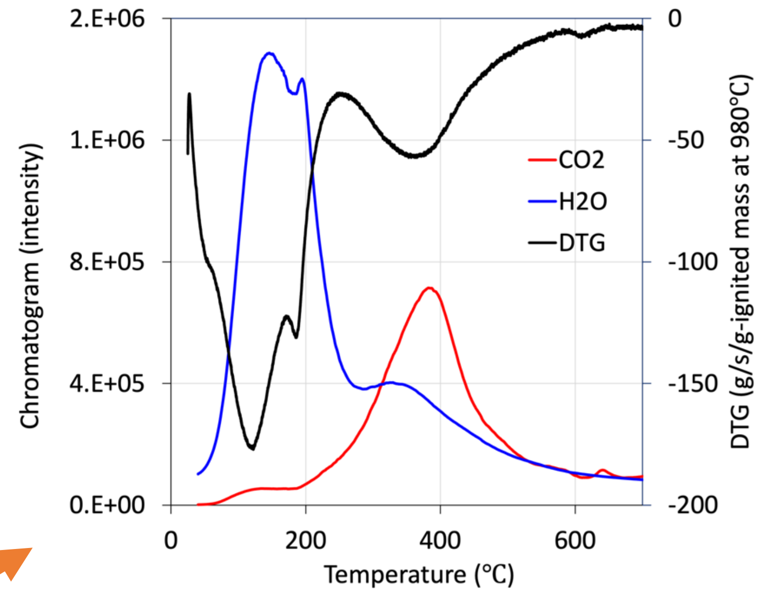


(c) 75-RH



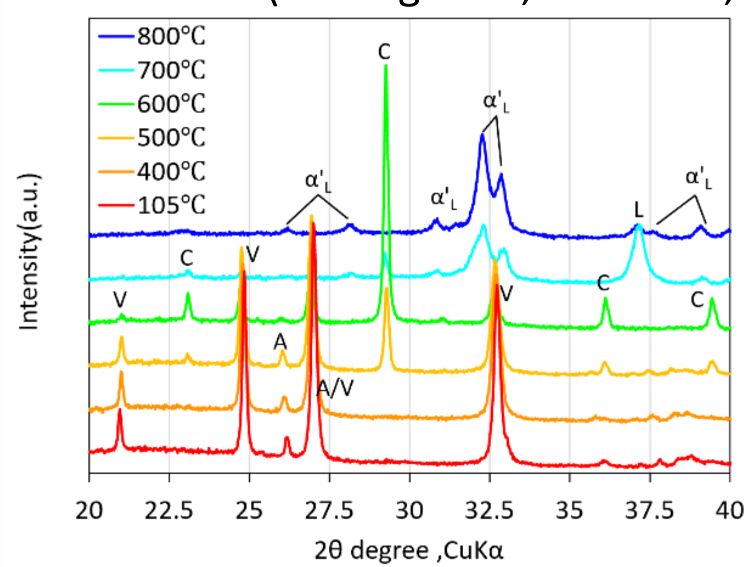
(d) 60-RH



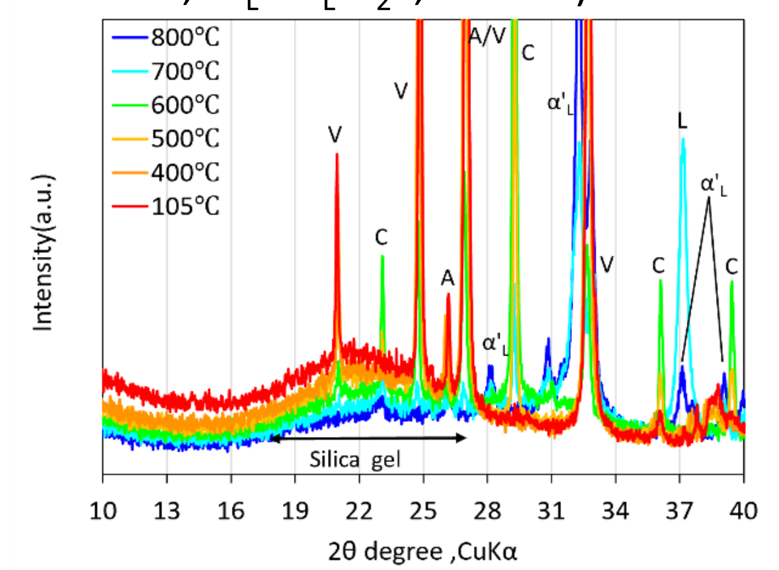


In-situ Heating XRD 95% RH

(A: Aragonite, C: Calcite, V: Vaterite, α'$_L$: α'$_L$-C_2S, L: Lime)

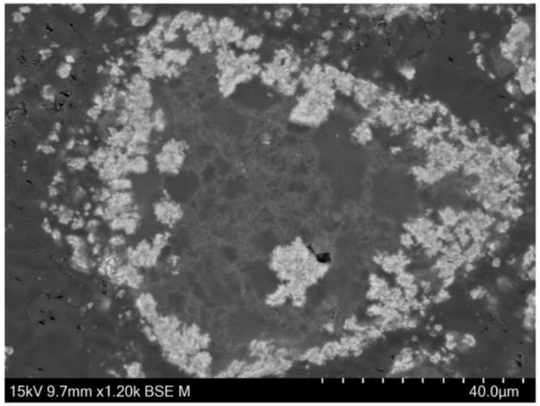


(a) 2θ=20-40° (offset)



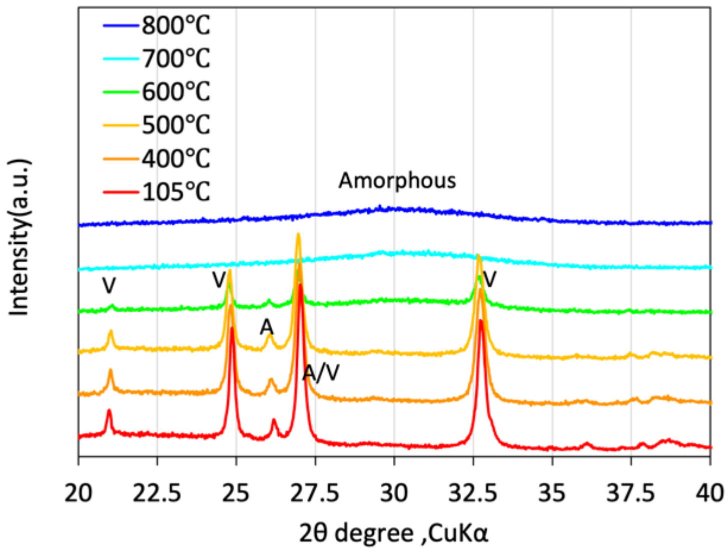
(b) 2θ=10-40°

- Phase change of CC is confirmed.
- Silica-gel is consumed during heating.
- Some of the belite phases are produced.

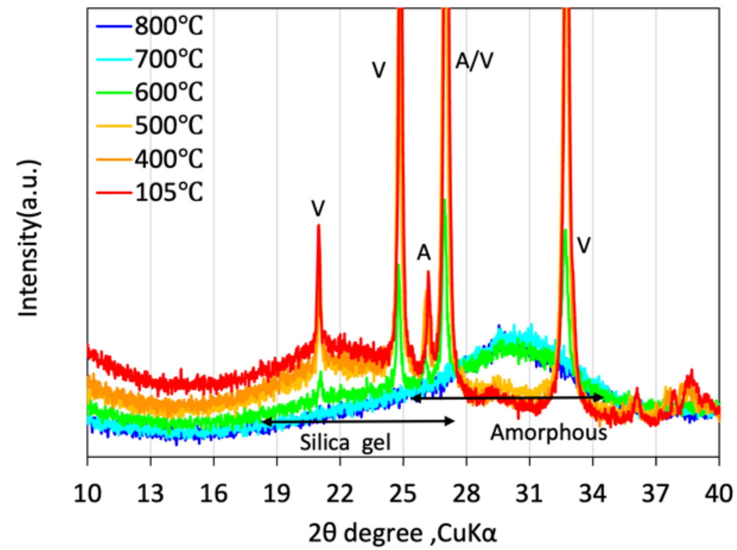


(a) 95-RH

In-situ heating XRD 60% RH

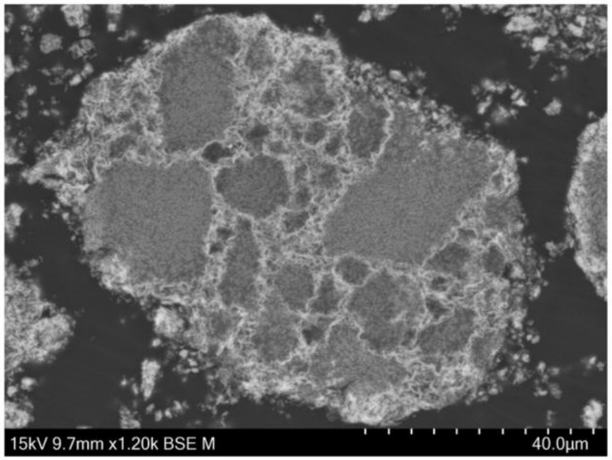


(a) 2θ=20-40° (offset)



(b) 2θ=10-40°

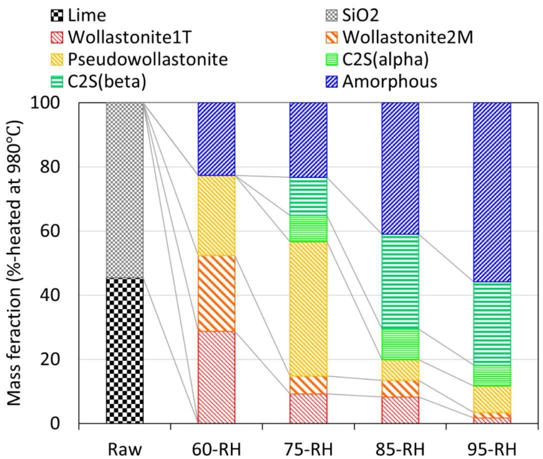
- No, belite is formed.
- No phase change of CC is confirmed.
- New amorphous (pre-cursor of clinker) is formed.

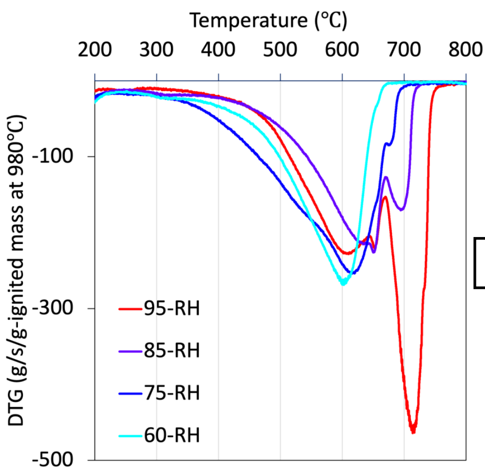


(d) 60-RH

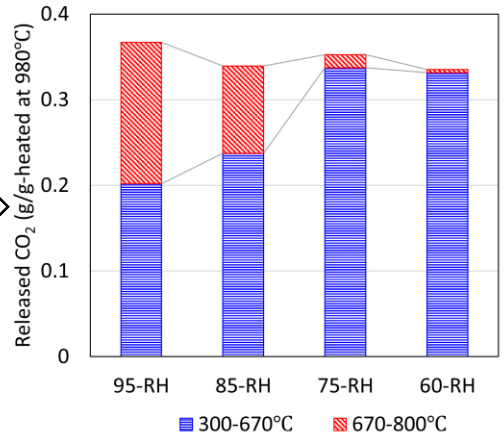
Carbonation of CSH Ca/Si 0.84

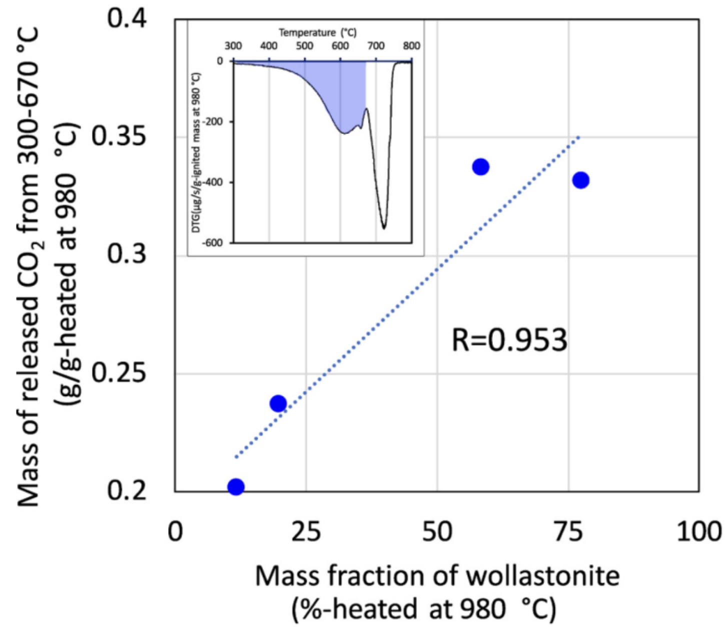
Released CO2 at low temperature vs Mass fraction of wollastonite





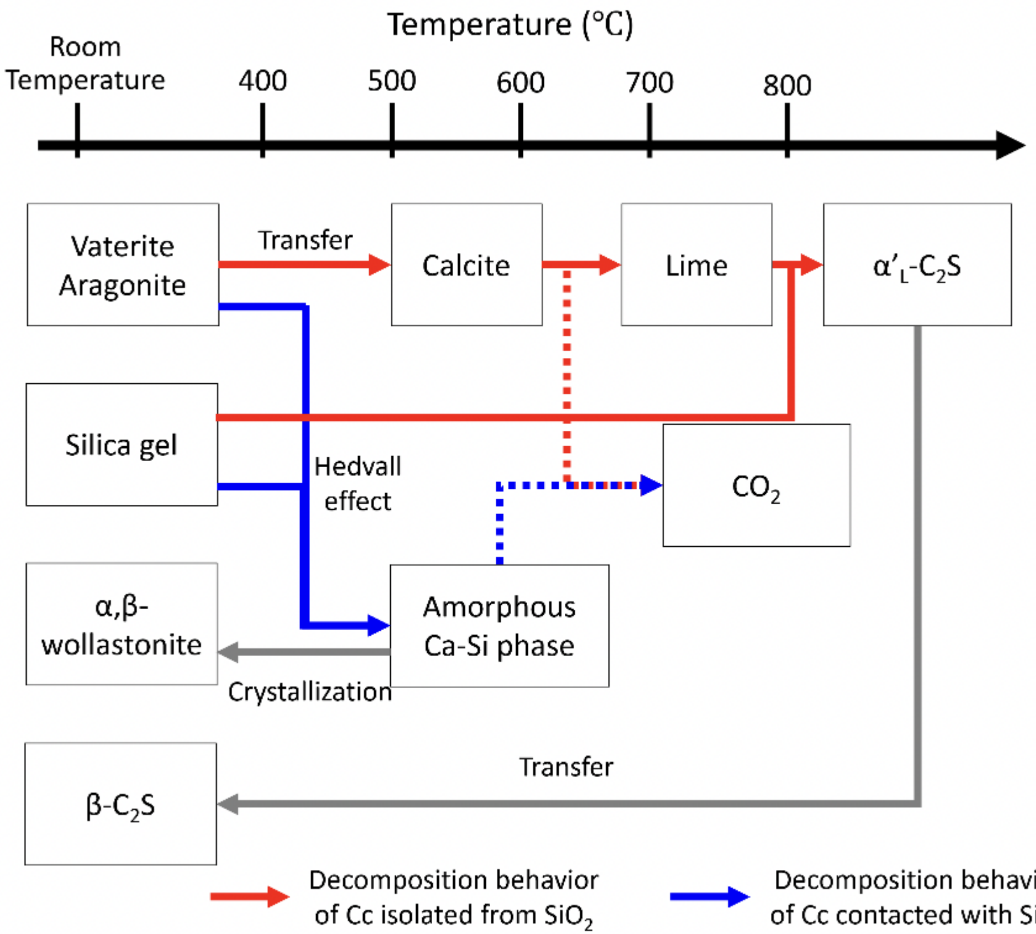
Released CO_2

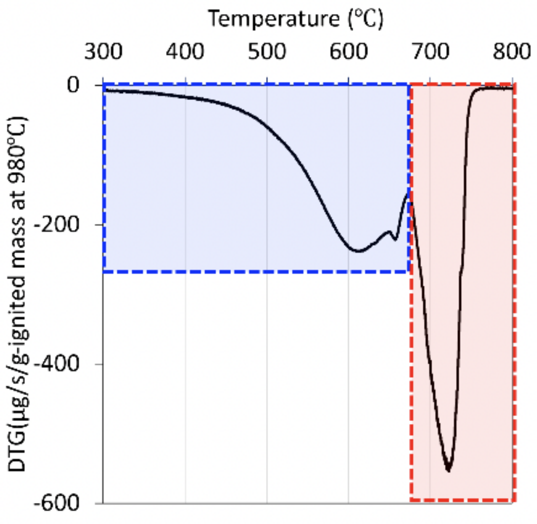




Although mineral compositions after carbonation were almost same,
heating products were different.

Pathways of decomposition





What we learned:

- The existing techniques have a limit. We need to understand both the material and the methods.
- The decomposition method (heating or acid) may sometimes influence the data.
- Variation of concrete samples is also an important feature.
- Currently, we can not select a single method that fits all kinds of cementitious materials.
- Further research and collaborations are necessary.

Thank you for your listening

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