

A Novel Method to Measure CO₂ Uptake: Application to Steel Slags

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Acknowledgements

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- Thien Q. Tran (PhD student) and Alexander Zhao (undergraduate)

- **National Institute of Standards and Technology (NIST)**

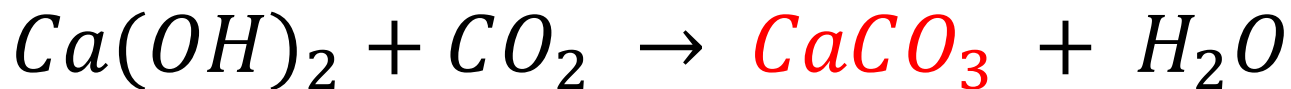
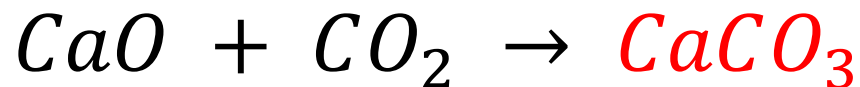
- Dr. Rachael Cook, Paul Stutzman, and Dr. Aron Newman

- **University of Cantabria (Spain)**

- Ali Aghajanian Sabbagh (PhD student) and Dr. Carlos Thomas

Motivation

- How can we quantify how much CO₂ can be captured (mineralized) in infrastructure materials (*e.g.*, concretes, industrial slags)?
- Do we need a new ASTM test method?



Current Option: TGA

- TGA = thermogravimetric analysis
- ASTM C1872 for unhydrated cement

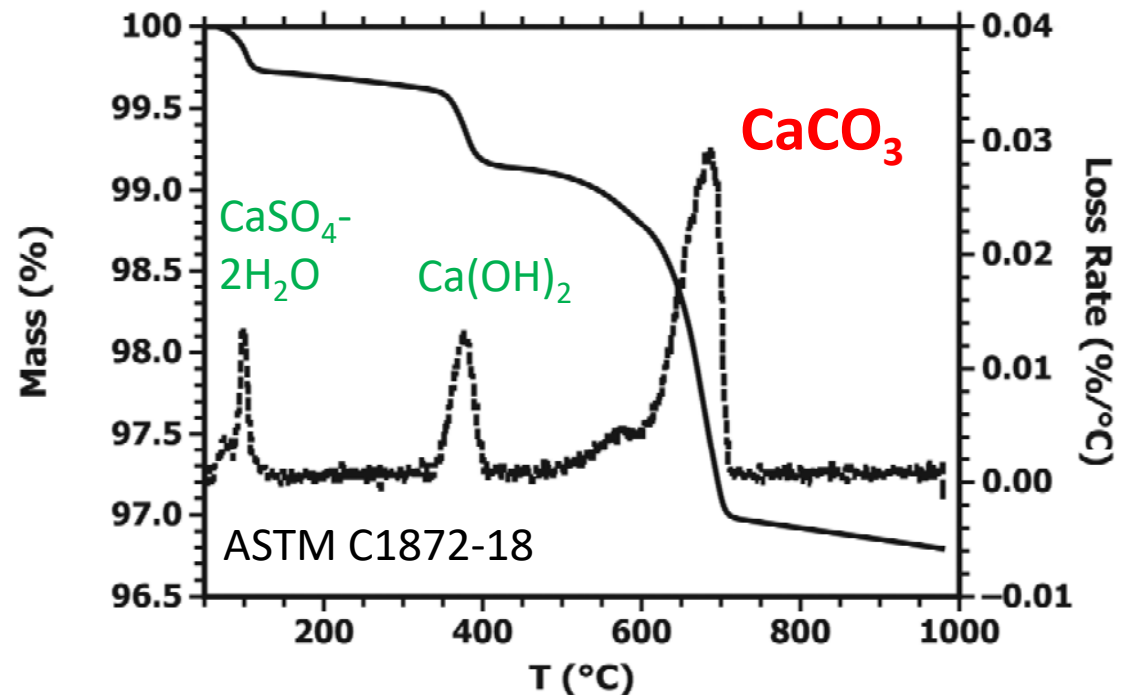
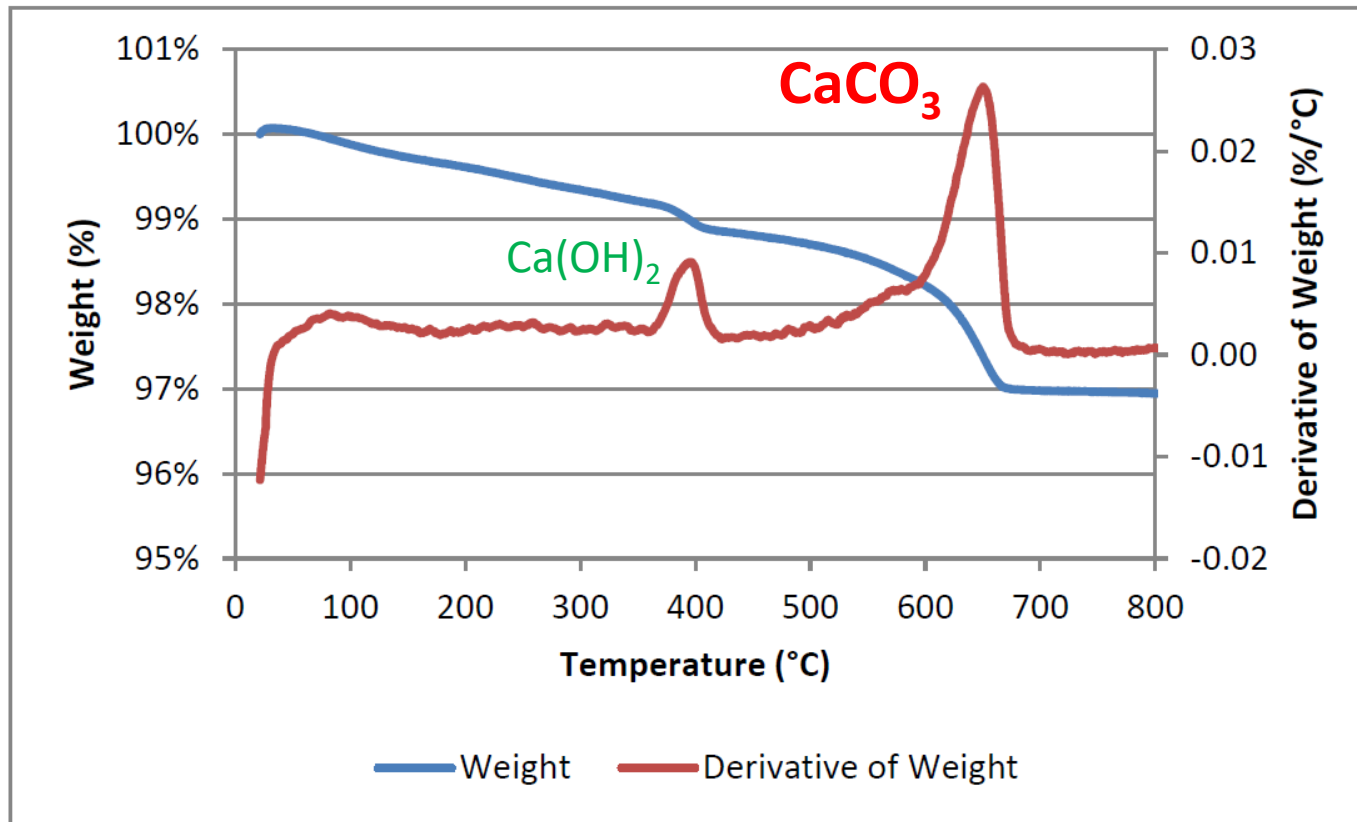


FIG. 1 Sample Thermogravimetric Curve for Unhydrated Portland Cement

TGA Can Work for Steel Slags Too!

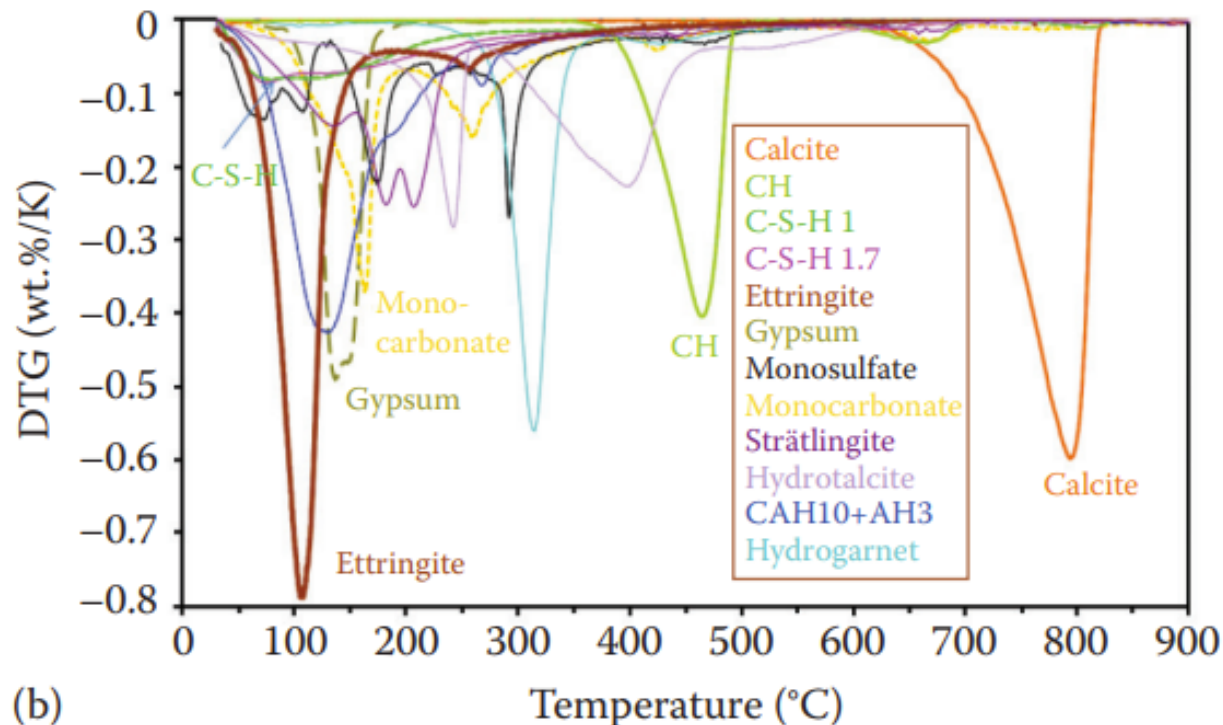


Sample from
a stockpiled
BOF slag

3.0% CaCO_3
1.3% Ca(OH)_2

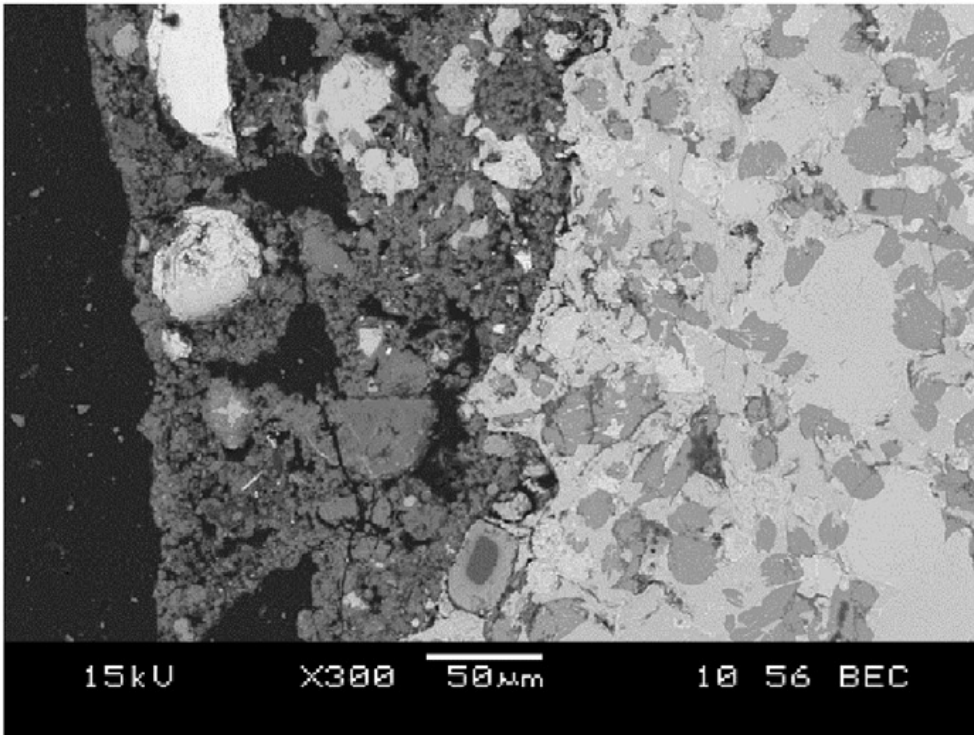
TGA Issue #1

- There can be overlapping peaks, making it difficult to get an accurate estimate of CaCO_3 content



TGA Issue #1

- C-S-H can be present on weathered steel slags, particularly those with Ca_3SiO_5 and Ca_2SiO_4

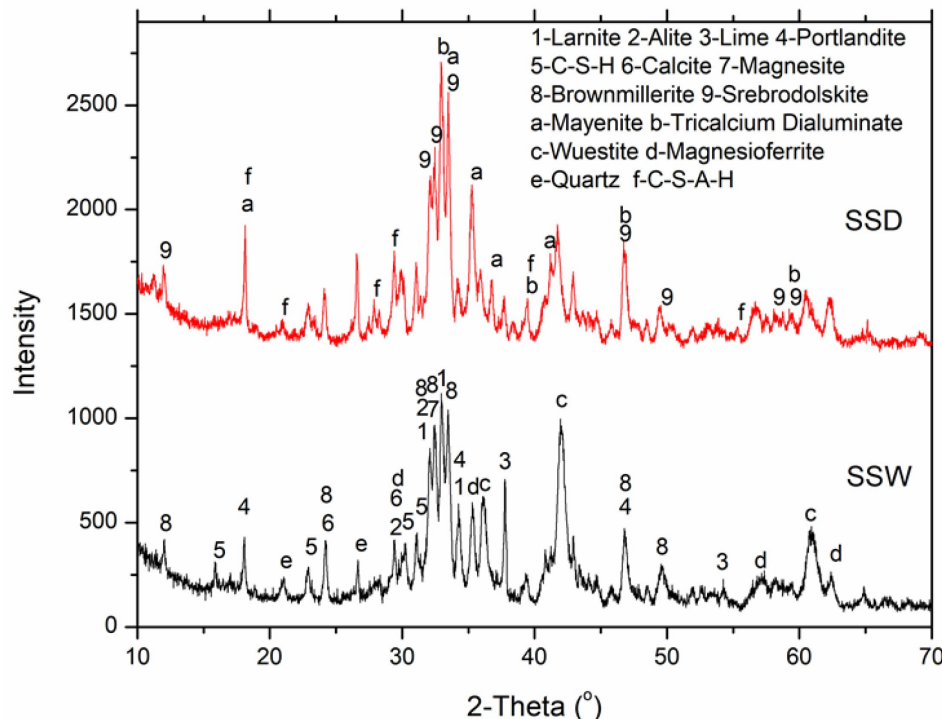


Sample from a stockpiled BOF slag

Slag particle showed some form of a hydrated surface layer, but it was unclear if it was C-S-H

TGA Issue #1

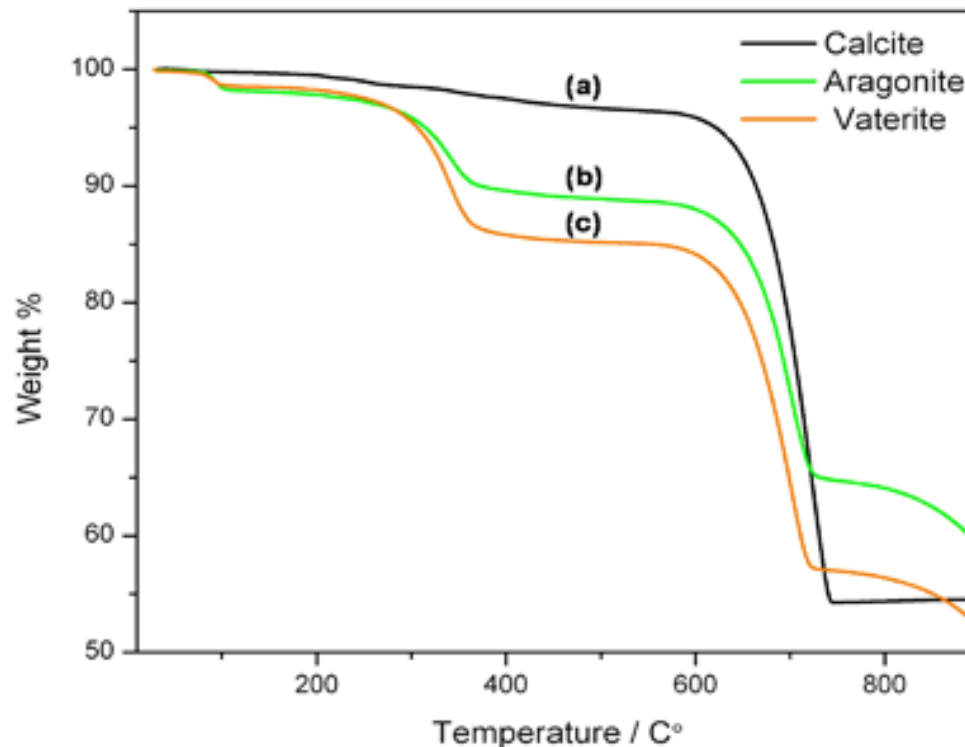
- C-S-H can be present on weathered steel slags, particularly those with Ca_3SiO_5 and Ca_2SiO_4



Evidence of C-S-H in two stockpiled steel slags of unspecified type

TGA Issue #2

- Polymorphs of CaCO_3 (calcite, vaterite, aragonite) do not necessarily have the same behavior in TGA



Siva et al. (2017). "Enhanced Polymer Induced Precipitation of Polymorphous in Calcium Carbonate: Calcite Aragonite Vaterite Phases," *Journal of Inorganic and Organometallic Polymers and Materials*, 27, 770-778.

TGA Issue #3

- Can be costly to buy and maintain
- New TGA may be ~\$15k to \$30k



TA Instruments TGA Q50 Thermogravimetric Analyzer

Manufacturer: TA Instruments

Model: TGA Q50

Condition: Used

[See More Information](#)

Seller Information EquipNet
United States

Phone Number [Login / Register](#)

Price

In Stock

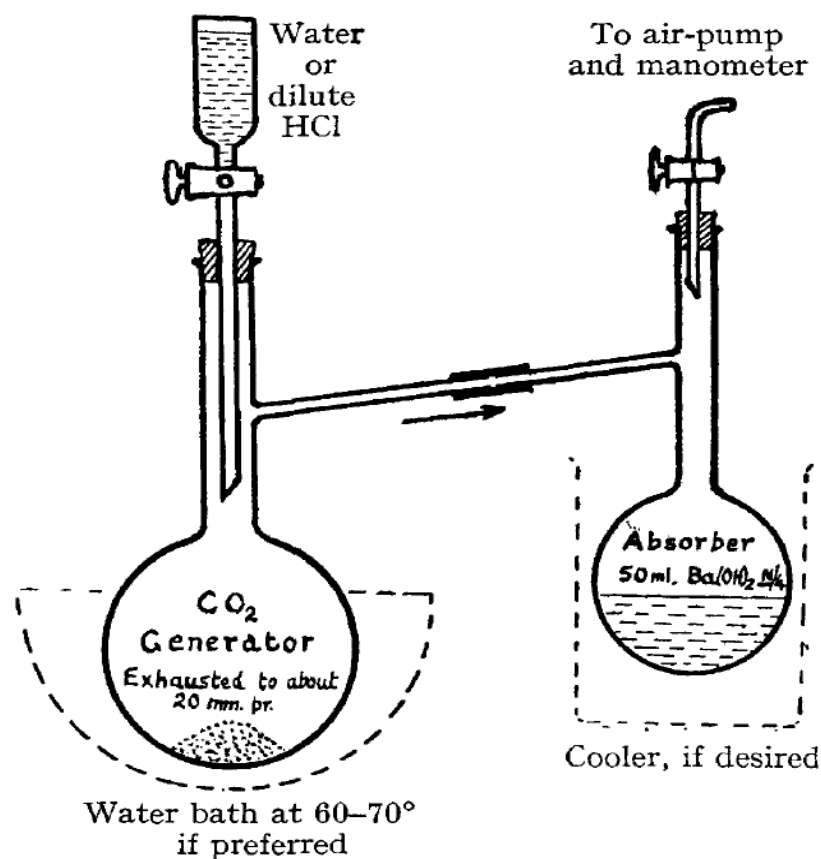
\$12,000.00^{USD}

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A New (Old) Test Method

- Earliest publication appears to be Van Slyke in 1918
- Method appears to be largely forgotten after the 1940s

Cornell's Setup in 1936



Van Slyke DD. The determination of carbon dioxide in carbonates. J Biol Chem. 1918;36(2):351-354.

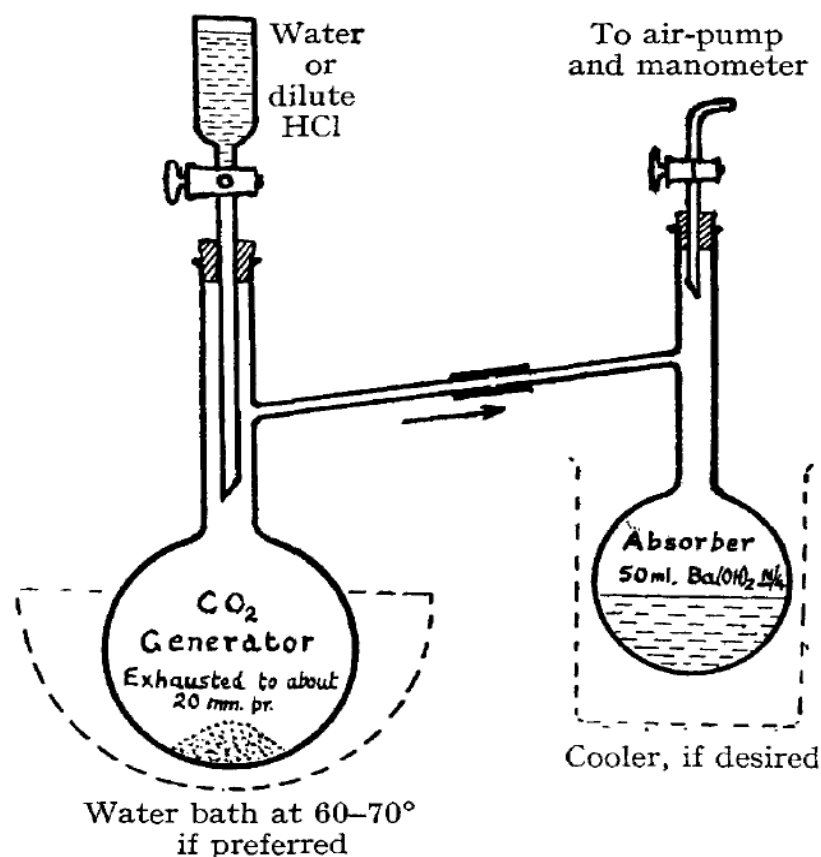
Cornell GW. Determination of carbon dioxide. Analyst. 1936;61(728):756-757.

CO₂-Baryta Titration Test

General procedure:

1. Seal system under vacuum.
2. Introduce HCl acid to sample. CaCO₃ will decompose and release CO₂.
3. CO₂ gets absorbed by Ba(OH)₂ solution.
4. Titrate Ba(OH)₂ solution to determine how much CO₂ was absorbed.

Cornell's Setup in 1936



Cornell GW. Determination of carbon dioxide. Analyst. 1936;61(728):756-757.

CO₂-Baryta Titration Test

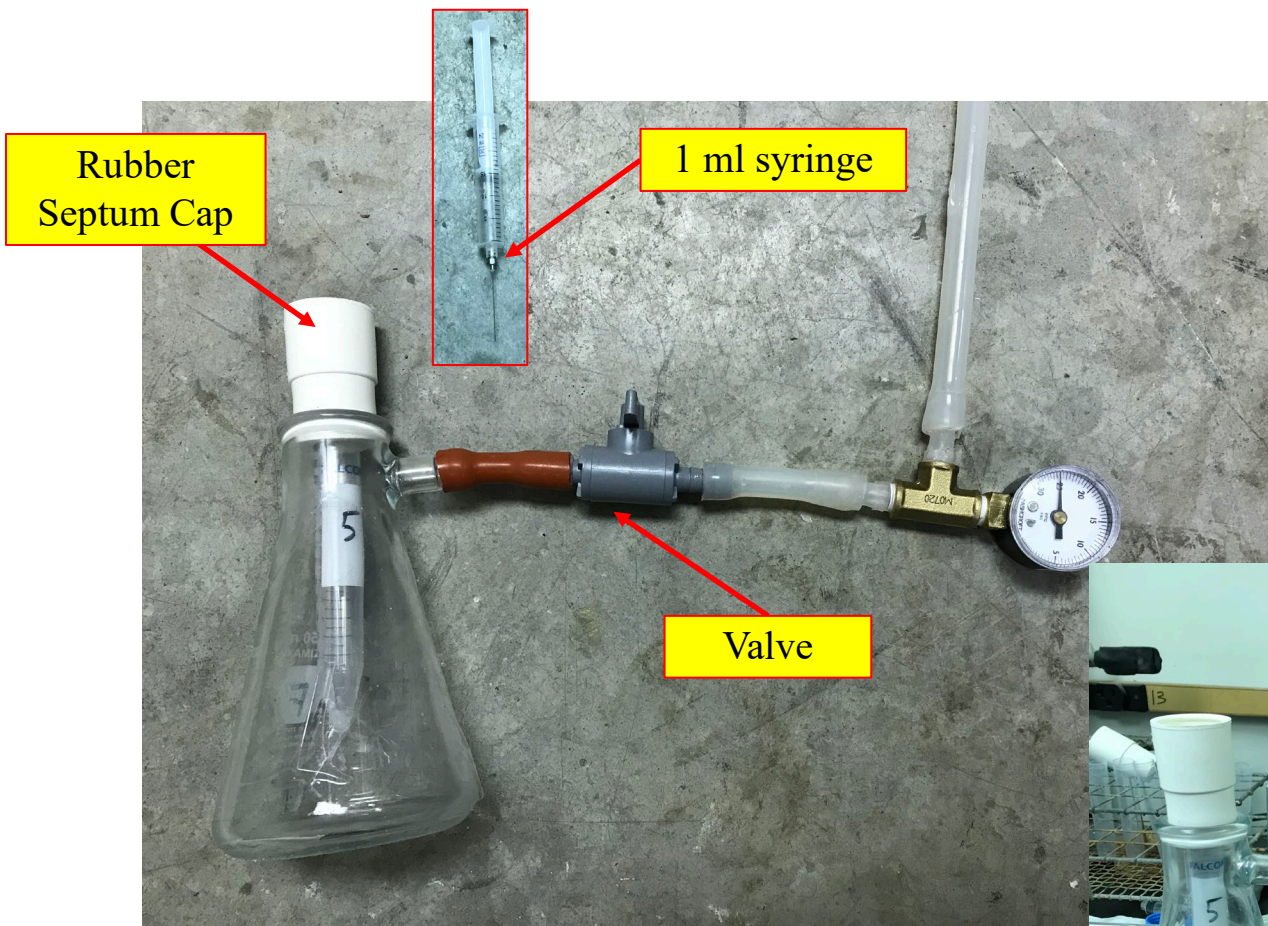


Mass of CO₂
captured by the
baryta solution = 0.022(b – b₀)

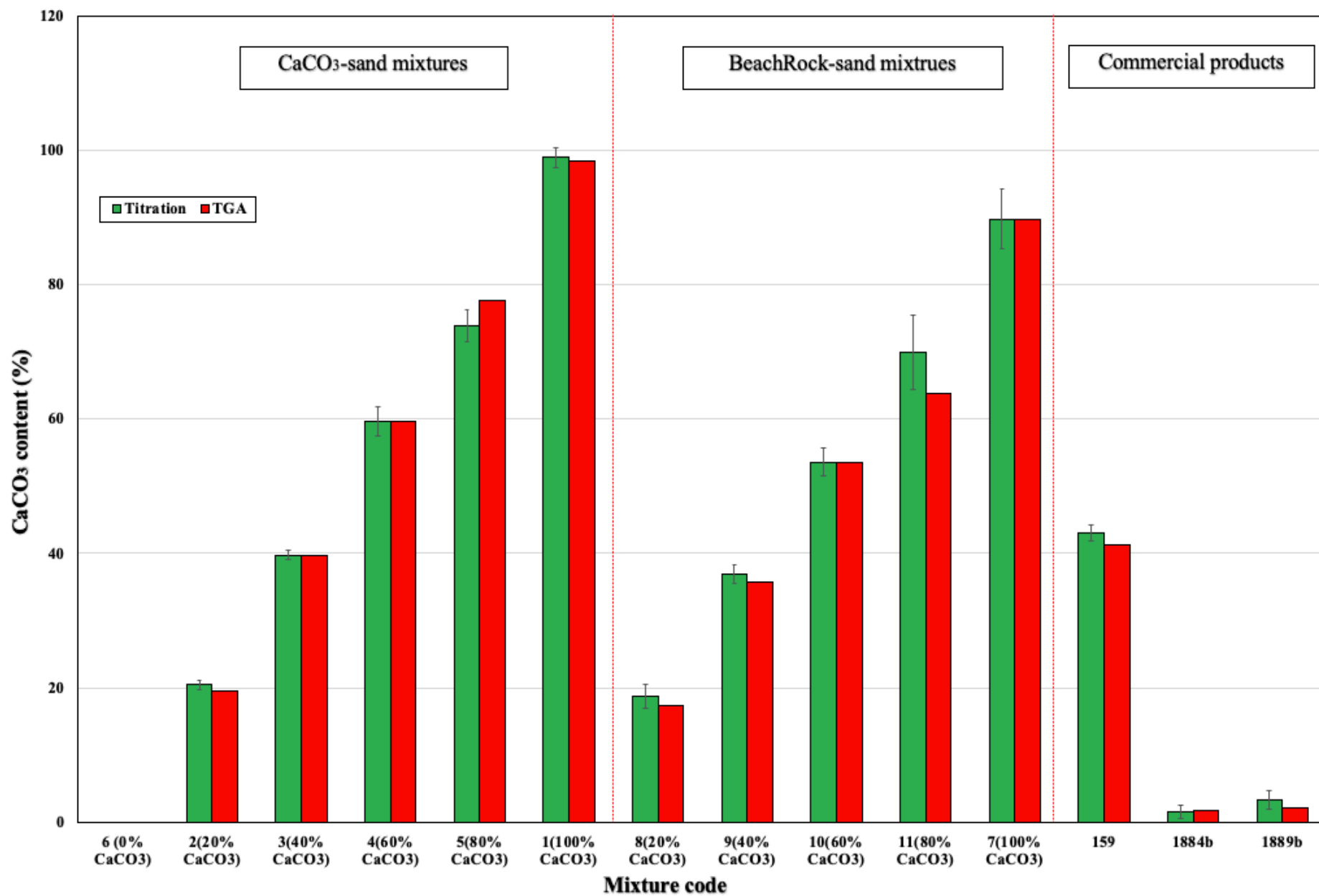
b = mL of 0.1N HCl titrated

b₀ = mL titrated in blank sample

Setup at Virginia Tech



CaCO₃ content determined by TGA vs. titration method

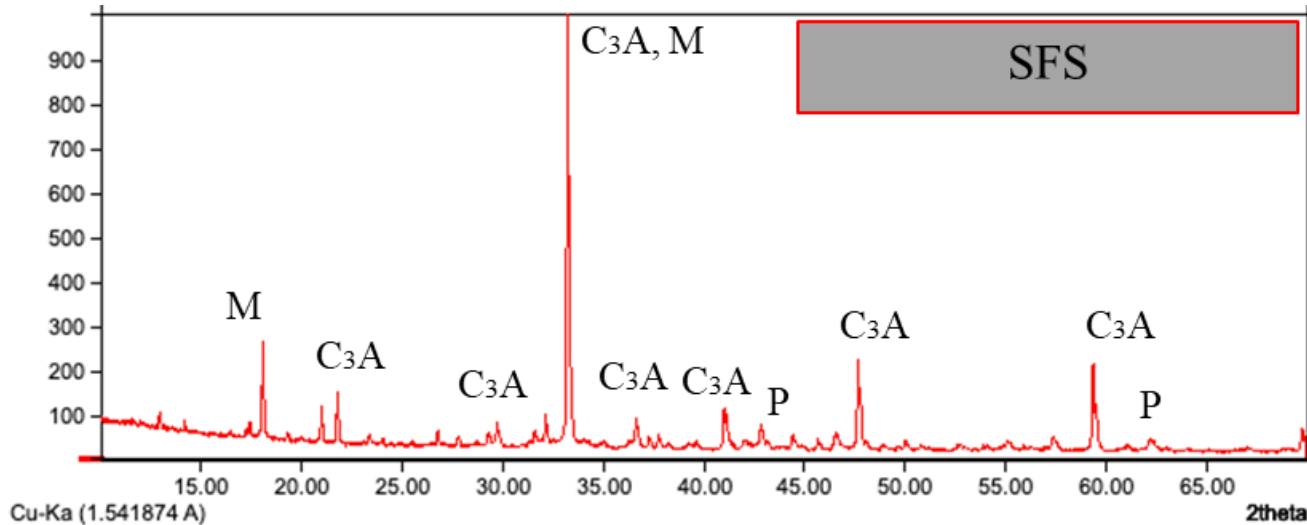


Accelerated Carbonation Tests

- Compacted powdered steel slag (LMF and EAF slags)
- Exposed to alkaline water (pH 10) and 58 psi CO₂ pressure for 24 hours



LMF Slag before Carbonation



C_3A = tricalcium aluminate ($Ca_3Al_2O_6$)

M = mayenite ($Ca_{12}Al_{14}O_{33}$)

P = periclase (MgO)

Free CaO = 3.0%

$Ca(OH)_2$ = 2.1%

$CaCO_3$ = 2.3%

Using the
ethylene
glycol test
and TGA

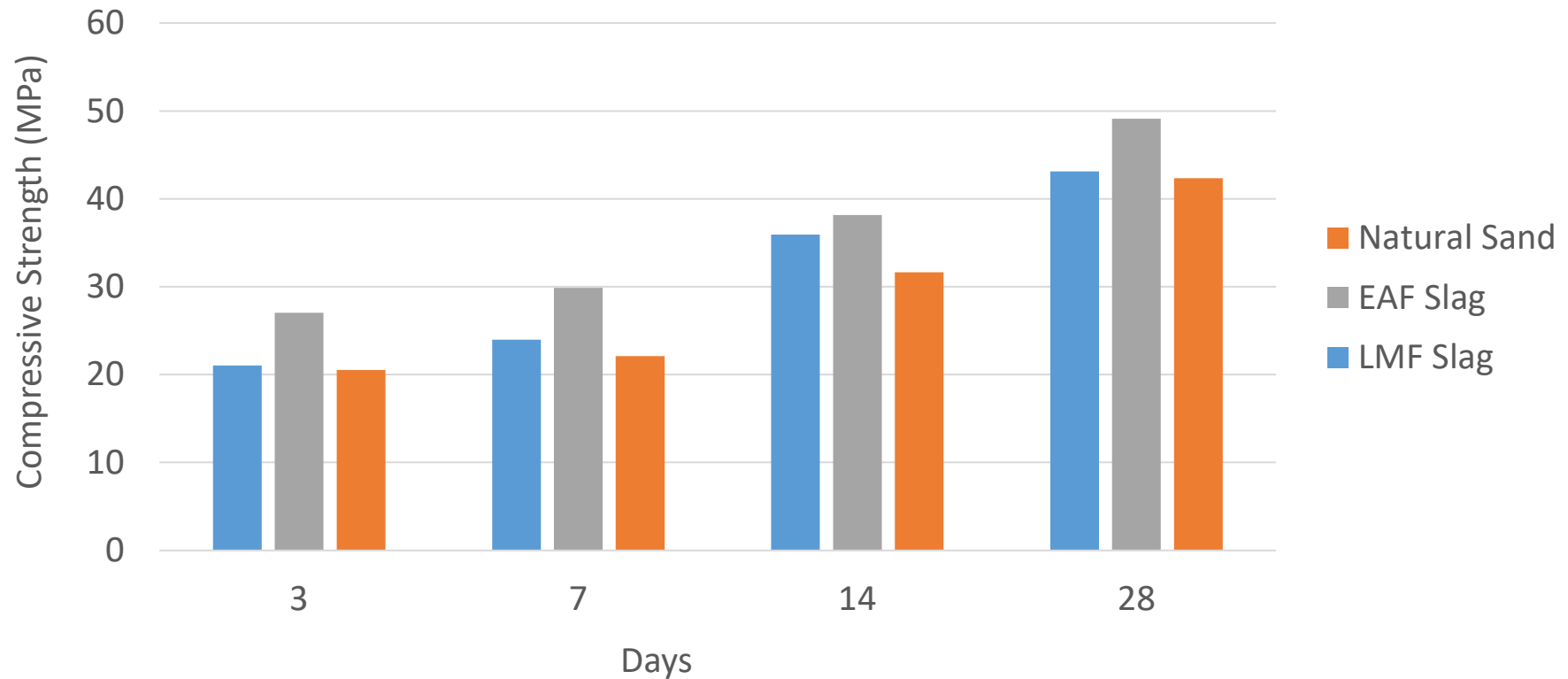
$CaCO_3$ = 3.3%

CO_2 -baryta
titration
test

LMF Slag after Carbonation

- After accelerated carbonation, **$\text{CaCO}_3 = 11.4\%$** by the CO_2 -baryta titration test
 - This is 5.0% CO_2 captured by initial sample mass
- From the initial composition (free $\text{CaO} = 3.0\%$, $\text{Ca(OH)}_2 = 2.1\%$, $\text{CaCO}_3 = 2.3\%$), the potential for total CaCO_3 is **10.5%** by stoichiometry
- *Why is there a discrepancy in these numbers?*

Mortar Strength: Carbonated Slag



Conclusions

- Titration method produces the same results as TGA for control samples
 - Steel slag and concrete samples are still being tested and benchmarked
- TGA instruments cost ~\$15k-30k while the titration method setup will be ~\$250
- Accelerated methods can be used to carbonate steel slags
- Carbonated steel slag may increase mortar strength

Future Work: CO₂-Baryta Titration

- Compare auto-titrator to manual titration to improve reproducibility
- Expand range of testing samples to include more concretes and steel slags
 - Consider accelerated carbonation samples
 - Consider stockpiled/aged/weathered samples
- Validation if CO₂ is extracted from other phases (*e.g.*, MgCO₃) during the titration method
- Pursue titration method as an ASTM standard

Future Work: Slag Carbonation

- Technologies to mineralize CO₂ in fresh steel slags
- Technologies to mineralize CO₂ in stockpiled or weathered steel slags
- Mineralogical and morphological changes to the steel slag due to carbonation
- Confirmation that accelerated carbonation mitigates any expansion potential of the slag
 - Applications in concrete, asphalt, fill, base, *etc.*
- Sensitivity analysis of accelerated carbonation (*e.g.*, time, temperature, pressure, particle size)

Thank you for your attention!

Any Questions or Comments?

