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Clean Energy Innovation Research Centre

Oxygen Consumption and CO_2 Generation Test —Principles, Measurement Methods, Constraints and Quality Assessment and Control

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OUTLINE

1. Summary and overview of the testing approach
2. Chemical reaction processes (OxyCon and CO2Gen)
3. Measurement setup and sensor technologies
4. Quality control and validation procedures
5. Practical examples and applications

Overview of Gas-Phase Testing for ML-ARD

Most testing for the assessment and prediction of ML-ARD typically involves:

- static tests including solid-phase elemental and mineralogical contents; and,
- kinetic tests to obtain reaction rates and aqueous concentrations.

Rarely is the full three-phase complexity of ML-ARD, involving interacting minerals, water, and gas, investigated in detail. However, all three phases combined can be important for more reliable understanding and prediction of ML-ARD.

Overview of Gas-Phase Testing for ML-ARD

Gases like O_2, CO_2, and H_2O vapour (relative humidity) can be transferred in and out of the water phase and solid-phase minerals. This results in relative changes in volumes and weights of each phase.

- ✓ O_2 consumption (OxyCon) in air can create a partial vacuum up to 21%. Additional oxygen can then be pulled in, such as through surficial covers, by convection (1) due to partial vacuums and (2) due to thermal gradients from heat generation. This is on top of diffusion.

Dy, E., K. Tufa, E. Fisher, Z-S. Liu, K. Morin, M. O'Kane, T. O'Hearn, C. Huang, and W. Qu. 2021. THE RELATIONSHIPS BETWEEN NEGATIVE PORE-WATER POTENTIAL, WATER CONTENT, RELATIVE HUMIDITY AND SULFIDE OXIDATION IN WASTE ROCK - A CASE STUDY. 14th IMWA Congress 2021, Newport, Wales, United Kingdom, 12-16 July 2021.

Huang, C., L. Ma, Z-S. Liu, E. Dy, K. Tufa, E. Fisher, J. Zhou, M. Goulet, K. Morin, and M. Paradis. 2020. GAS TRANSPORT INSIDE CO-DISPOSAL OF DESULFURIZED TAILINGS AND SULFIDIC WASTE ROCKS. IN: TAILINGS AND MINE WASTE, 2020 Virtual Event, November 15-18, Colorado State University, Colorado, USA., p. 541-550

Overview of Gas-Phase Testing for ML-ARD

- ✓ CO_2 can be released into the air phase by loss from carbonate minerals and/or from aqueous carbonate species. This can lead to an overpressure of CO_2 that can accelerate air movement through minesite components. In the worst case, the release and accumulation of CO_2 from waste rock under a cover can prove fatal to humans as happened at the Sullivan Mine in British Columbia nearly 20 years ago.
- ✓ CO_2 release/accumulation can also affect the pH of water, sometimes at the critical pH range where heavy metals co-precipitation occurs.

Thus, the release or consumption of CO_2 gas is also important for more reliable assessments and predictions of ML-ARD.

Overview of Gas-Phase Testing for ML-ARD

Test procedures for oxygen consumption generation have been available for three decades.[1,2,3,4]

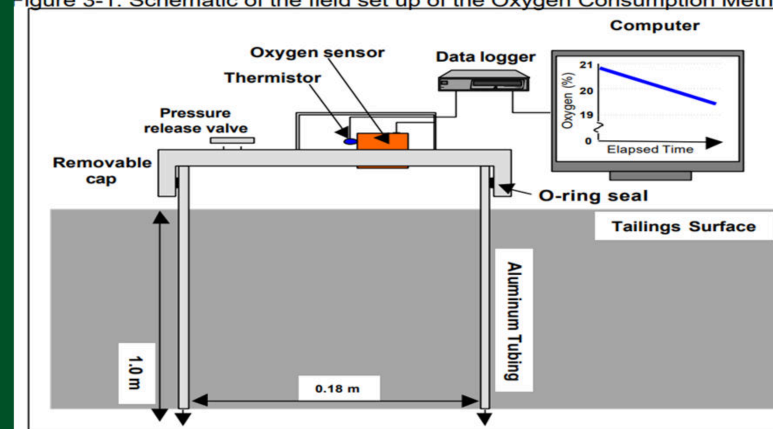
[1]Ronald V. Nicholson, Philip A. Tibble, Gary Williams, SURVEY OF IN SITU OXYGEN CONSUMPTION RATES ON SULPHIDE TAILINGS: INVESTIGATIONS ON EXPOSED AND COVERED TAILINGS, MEND Project 4.6.5ac, November 1997, https://mend-nedem.org/wp-content/uploads/465AC.pdf

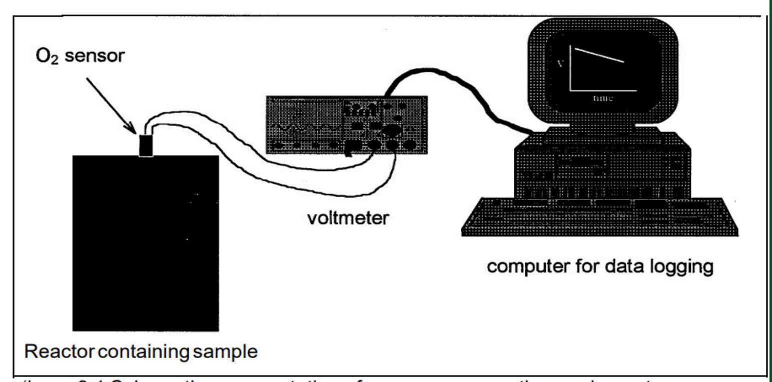
[2]Ronald V. Nicholson, Jeno M. Scharer, and Mark E. Anderson, A RAPID KINETIC TECHNIQUE FOR MEASURING THE REACTIVITY OF SULFIDFE WASTE ROCK: THE OXYGEN CONSUMPTION METHOD, MEND Project 4.6.5b, December 1997, https://mend-nedem.org/wp-content/uploads/465B.pdf

[3]N. Bourgeot, R. Piccinin, and J. Taylor, THE BENEFITS OF KINETIC TESTWORK USING OXYGEN CONSUMPTION TECHNIQUES AND IMPLICATIONS FOR THE MANAGEMENT OF SULFIDIC MATERIALS, Proceedings of the 7th Australian Workshop on Acid and Metalliferous Drainage (Eds. LC Bell and B. Braddock), 117-129, 7th Australian AMD Workshop, 21-24 June 2011.

[4]A. Barnes, S. Pearce. R. Savage, M.T. Roberts. D. Brookshaw, M. Rama, T. Kauppila, S. Muelle, J. Hertrijana, R. Bowell, APPLICATION OF THE WARBURG CONSTANT VOLUME RESPIROMETER METHOD FOR DETERMINATION OF OXYGEN CONSUMPTION RATES OF MINING WASTE, International Conference on Acid Rock Drainage 2022, https://cdn-web-content.srk.com/upload/user/image/RBowell_ApplicationMethodDeterminationOxygenConsumptionRatesMining+Waste_20222023121406482915 1.pdf

'igure 3-1. Schematic of the field set up of the Oxygen Consumption Metho





'igure 3.1 Schematic representation of oxygen consumption equipment

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Chemistry of Acid Generation and Neutralization

Oxygen Consumption (OxyCon) Test is a direct measurement of acid generation rate from the oxidation of sulfide minerals.

$$FeS_2 (s) + 3.75\ O_2 + 3.5\ H_2O \rightarrow Fe(OH)_3(s) + 2SO_4^{=} + 4H^+$$

CO_2 Generation (CO2Gen) Test is a direct measurement of CO_2 generated from neutralization of acid by carbonate minerals.

$$CaCO_3 + 2\ H^+ \rightarrow Ca^{2+} + CO_2(g) + H_2O$$

$$CaMg(CO_3)_2 + 4\ H^+ \rightarrow Ca^{2+} + Mg^{2+} + 2\ CO_2(g) + 2\ H_2O$$

Acid neutralization by silicates (plagioclase, forsterite, etc.) is not measured CO_2 generation.

$$CaAl_2Si_2O_8 + 2H^+ + 2H_2O \rightarrow Ca^{2+} + 2Al^{3+} + 2H_4SiO_4 + 6OH^-$$

E.J. Sherlock, R.W. Lawrence, & R. Poulin, ON THE NEUTRALIZATION OF ACID ROCK DRAINAGE BY CARBONATE AND SILICATE MINERALS. Geo 25, 43–54 (1995). https://doi.org/10.1007/BF01061829

Gretel Parker, Barry Noller and T. Waite, ASSESSMENT OF THE USE OF FAST-WEATHERING SILICATE MINERALS TO BUFFER AMD IN SURFACE WATERS IN TROPICAL AUSTRALIA, Assessment of the use of Fast-Weathering Silicate Minerals to Buffer AMD in Surface Waters in Tropical Australia

What We Know About

OxyCon rates:

- ✓ Bacterial effects may be more pronounced at low pH <4.
- ✓ Reaction of ferric ion can be less significant at higher pH to due low solubility of $Fe(OH)_3$ at higher pH.
- ✓ Rates are typically proportional to surface area.
- ✓ Rates are initially linear with O_2, then changing to nonlinear. This suggests iron oxide decomposition may be the rate limiting step.

Kevin Morin and Nora Hutt, ENVIRONMENTAL GEOCHEMISTRY OF MINESITE DRAINAGE: PRACTICAL THEORY AND CASE STUDIES (1997; ISBN 0-9682039-0-6).

Ronald V. Nicholson, Robert W. Gillham, Eric J. Reardon, PYRITE OXIDATION IN CARBONATE-BUFFERED SOLUTION: 1. EXPERIMENTAL KINETICS, Geochimica et Cosmochimica Acta, Volume 52, Issue 5, 1988, Pages 1077-1085, ISSN 0016-7037, https://doi.org/10.1016/0016-7037(88)90262-1.

V. P. Evangelou, PYRITE OXIDATION AND ITS CONTROL, 1995 CRC Press. https://doi.org/10.1201/9780203741641

What We Know About

Acid neutralization:

- ✓ Carbonates, such as calcite and dolomite, react quickly to neutralize acid.
- ✓ Silicates containing alkali and alkali earth elements, such as forsterite and plagioclase, can also neutralize acid. But their dissolution rate is relatively slower than calcite and dolomite.
- ✓ CO2Gen test does not consider neutralization from fast- and slow-dissolving silicates.

Kevin Morin, TROLIUS GOLD-COPPER MINE SITE, QUEBEC—UPDATED AND CORRECTED ARD-ML PREDICTION REQUIRING MULTI-FACETED AND INTEGRATED STUDIES, BC MEND Workshop, 31st Annual BC MEND Workshop, 2024.
E.J. Sherlock, R.W. Lawrence, & R. Poulin, ON THE NEUTRALIZATION OF ACID ROCK DRAINAGE BY CARBONATE AND SILICATE MINERALS, Geo 25, 43–54 (1995). https://doi.org/10.1007/BF01061829

Measurement Methods and Sensor Technology

"Humidity Cell type"

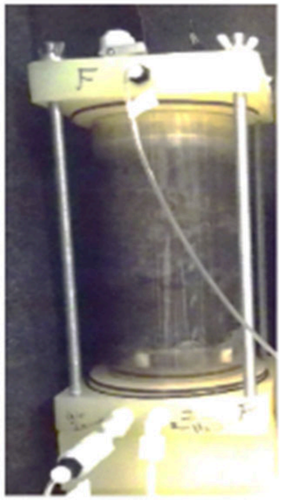


Figure 1 Photograph of the experimental setup, including custom-made columns with connections for water and gas flow.

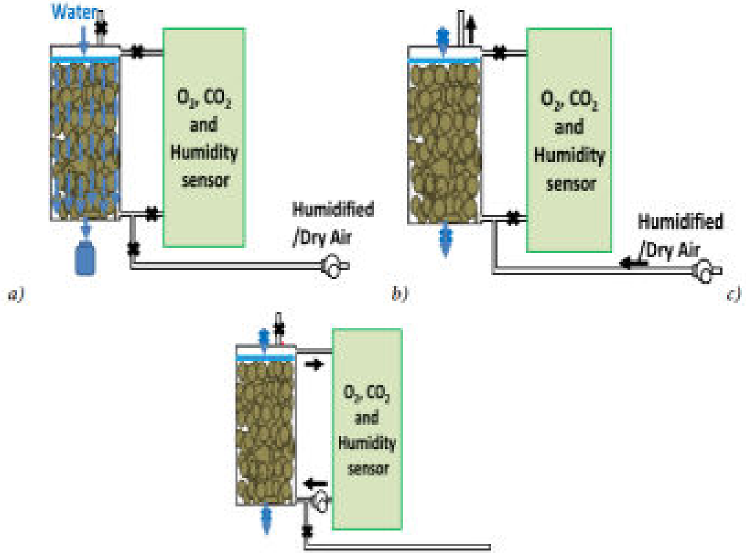
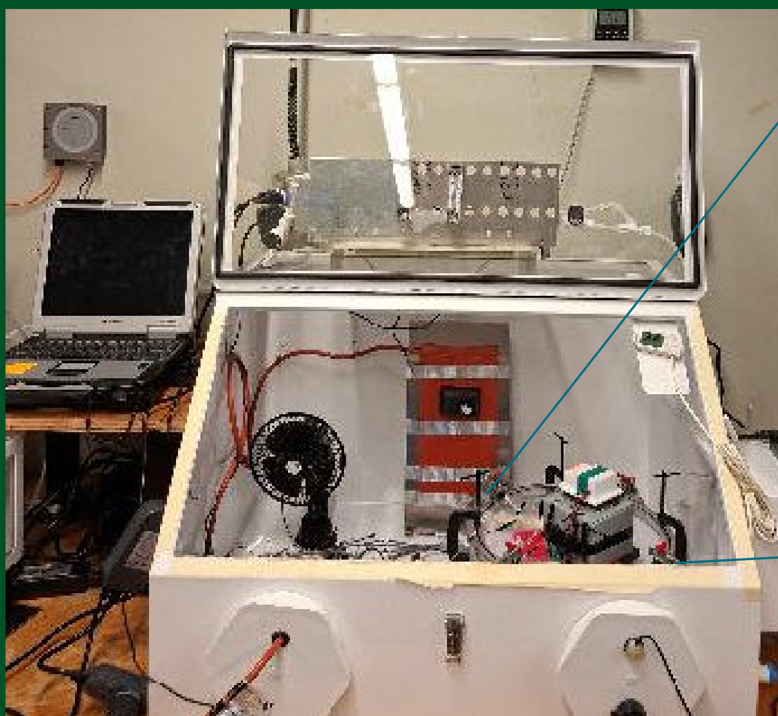


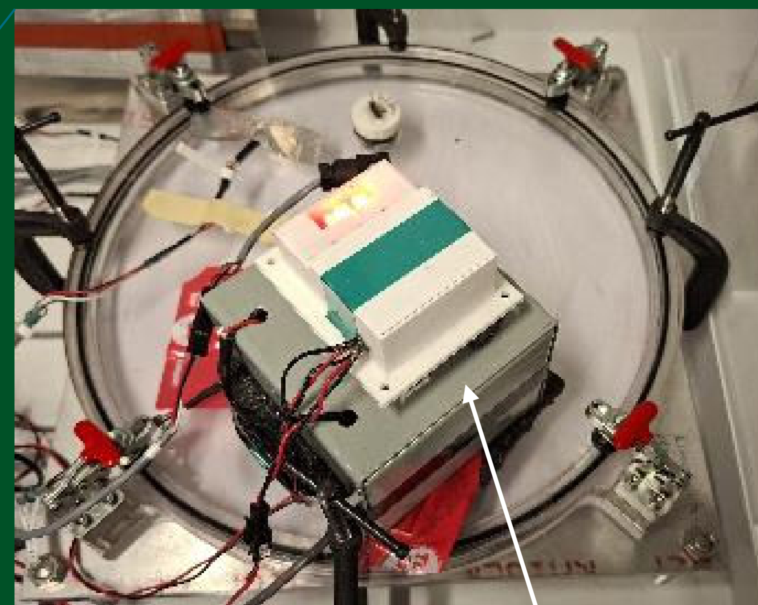
Figure 2 Experimental processes: a) column wetting, b) column drying or humidification and c) oxygen consumption, carbon dioxide generation and humidity monitoring. "X" indicates where valves were closed. Black arrows indicate the direction of air flow while blue arrows indicate the direction of water flow.

Eben Dy, Kidus Tufa, Elizabeth Fisher, Zhong-Sheng (Simon) Liu, Kevin Morin, Michael O'Kane, Tim O'Hearn, Cheng Huang, Wei Qu, THE RELATIONSHIPS BETWEEN NEGATIVE PORE-WATER POTENTIAL, WATER CONTENT, RELATIVE HUMIDITY AND SULFIDE OXIDATION IN WASTE ROCK – A CASE STUDY, 2021 IMWA Proceedings. https://www.imwa.info/docs/imwa_2021/IMWA2021_Dy_139.pdf

Alternative Design

"Flat cell type"





Temperature, O_2, CO_2, RH and pressure sensors

Most Common Types of Sensors

O_2 - electrochemical type[1]

Works just like an lithium-air battery for hearing aids

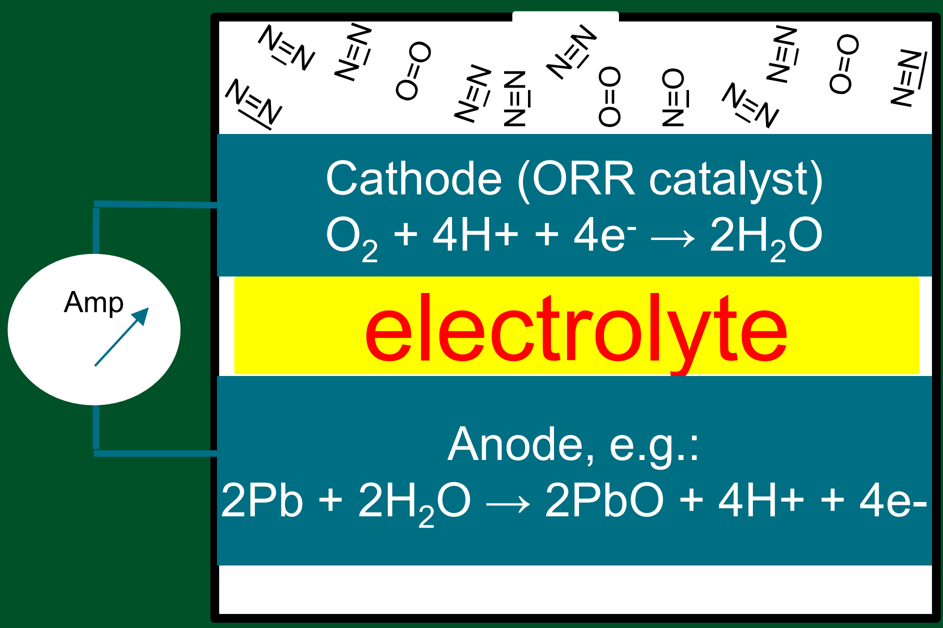
CO_2 - optical type[2]

O_2 and N_2 does not absorb Near-Infrared light

CO_2, H_2O, nitrogen oxides hydrocarbons absorb at different wavelengths (“colors”)

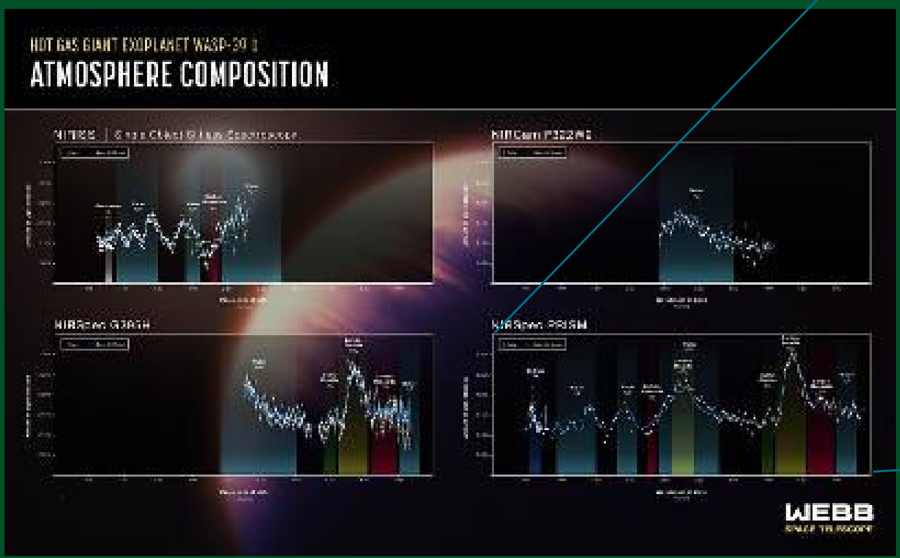
[1] Electrochemical type - Operating principle - Technology - FIGARO Engineering inc
[2] NDIR type - Operating principle - Technology - FIGARO Engineering inc

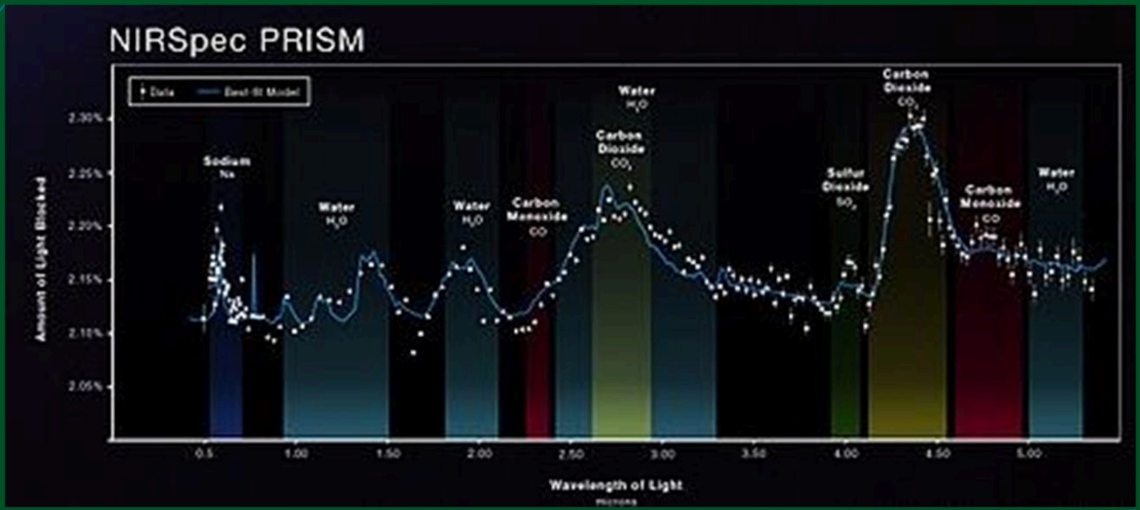
O_2 Electrochemical Sensor



Faraday's Law: Current generated is directly proportional to moles of O_2 reduced

CO_2 Optical Sensor

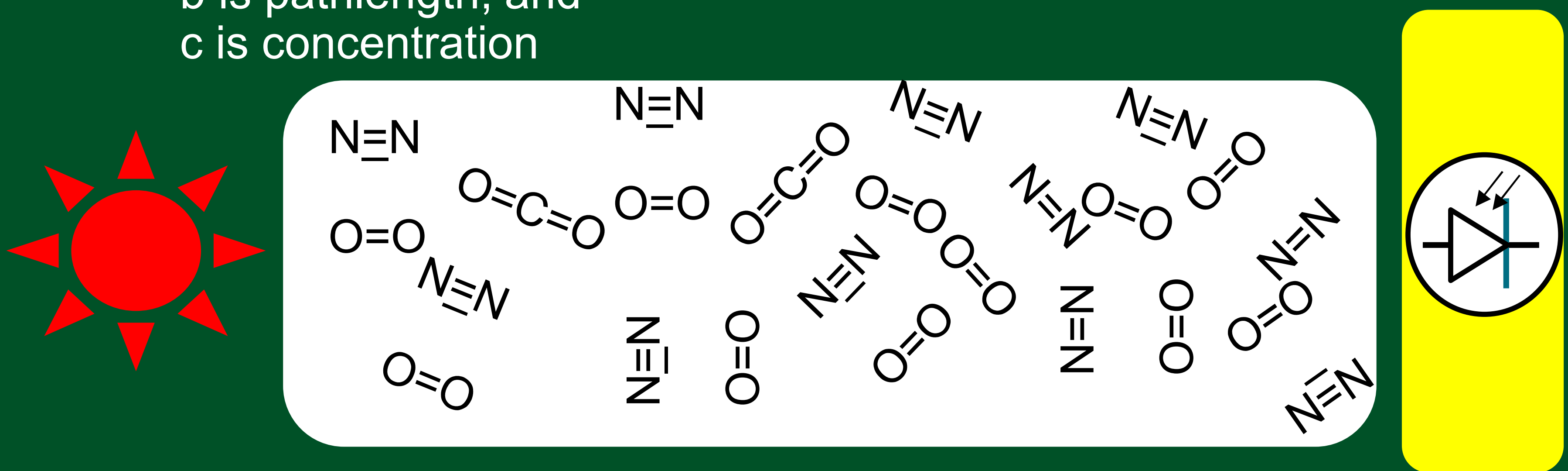




Date 22 November 2022 (upload date)
Source WASP-39 b Atmospheric Composition (NIRSpec, NIRCam and NIRISS)
Author NASA, ESA, CSA, J. Olmsted (STScI)
https://upload.wikimedia.org/wikipedia/commons/4/49/WASP-39_b_Atmospheric_Composition_%28NIRSpec%2C_NIRCam_and_NIRISS%29_%28weic2221b%29.jpeg

CO_2 Optical sensor

Beer Lambert's Law:
A = abc
Where A is absorbance,
a is absorptivity coefficient,
b is pathlength, and
c is concentration



Constraints, Calibration and Quality Control

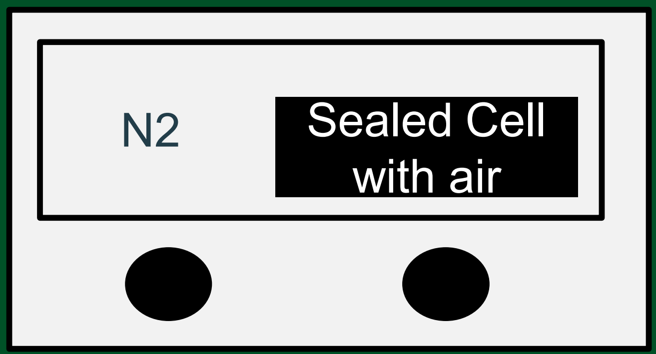
Contraints:	Solution
Sensor drift and aging	Calibration and Quality Control
Signal to noise limitation (harder to monitor slower reaction)	Cell design and sensor range selection
Leaking	Leak testing

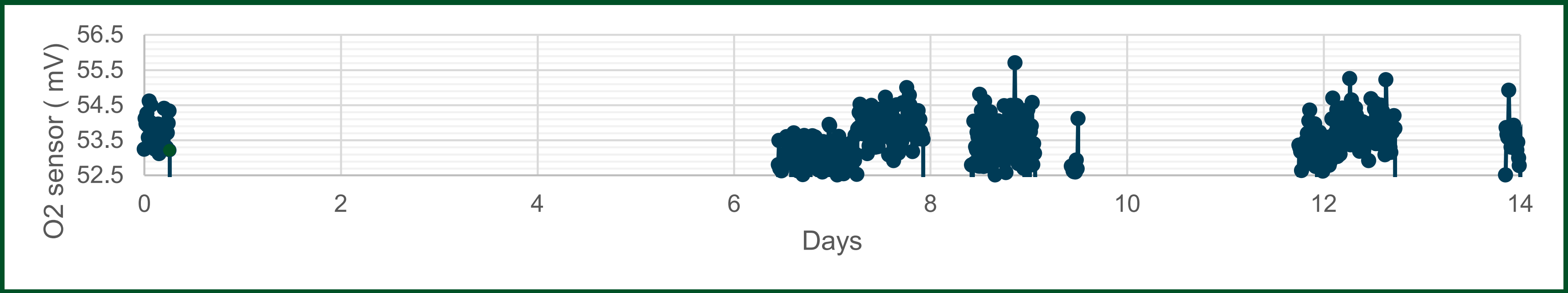
Leaking

It is impossible to create a perfect seal with these chambers since there are doors, joints, sensor holes, and gas valves.

- Diffusion can be minimized through proper sealing until effects are negligible.
- But Oxygen consumption creates a partial vacuum, drawing air/oxygen inward and falsely suggesting low oxygen rates.
- CO_2 overpressure inside causes outward CO_2 loss, falsely suggesting low CO_2 generation.

Leak Test


N2
Sealed Cell with air


O2 sensor (mV)
56.5
55.5
54.5
53.5
52.5
0
2
4
6
8
10
12
14
Days

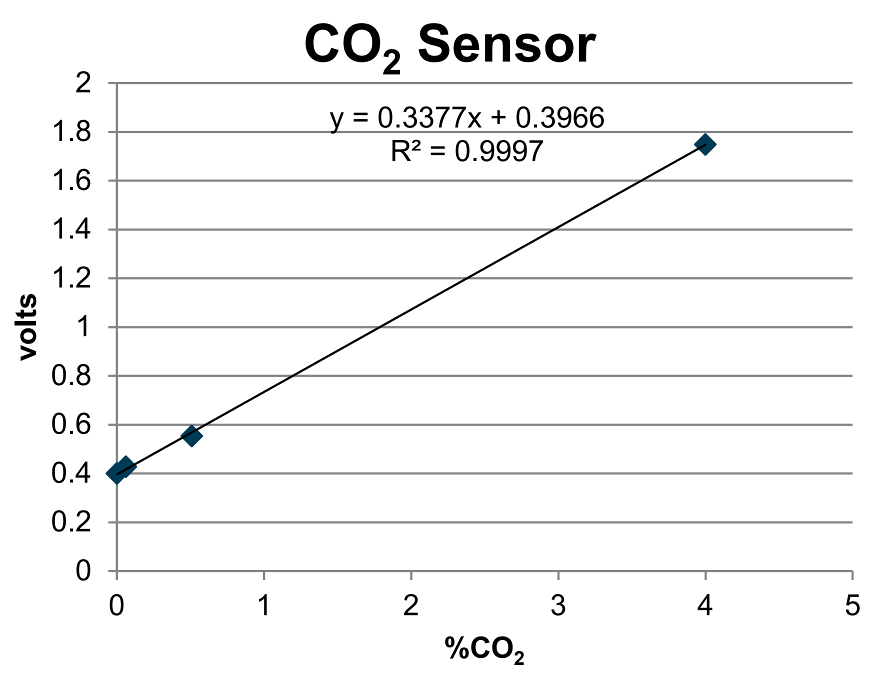
Calibration

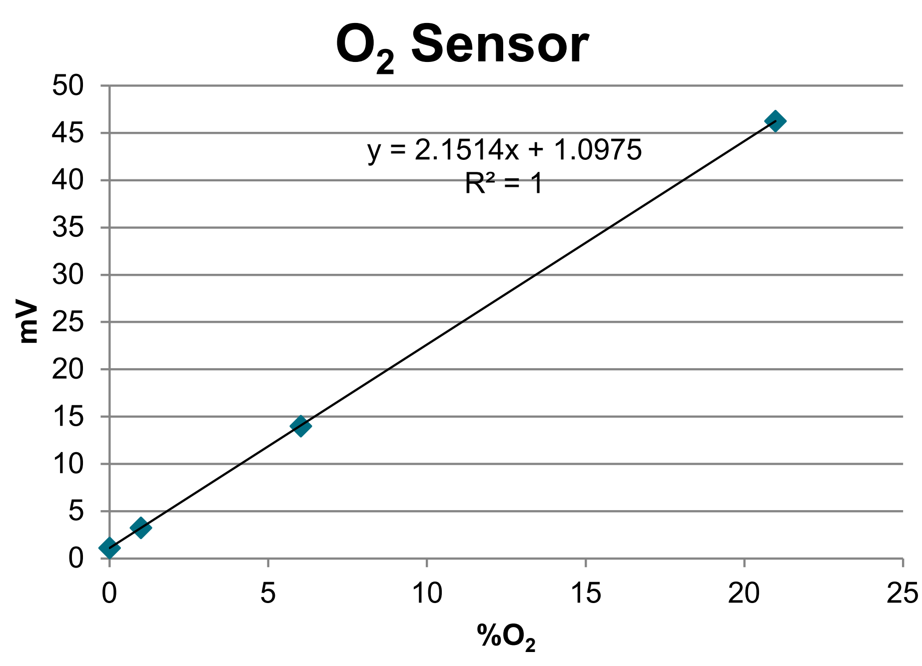
Blank (99.999% N_2 gas)

Standard 1 (0.5% CO_2, 1% O_2 in N_2)

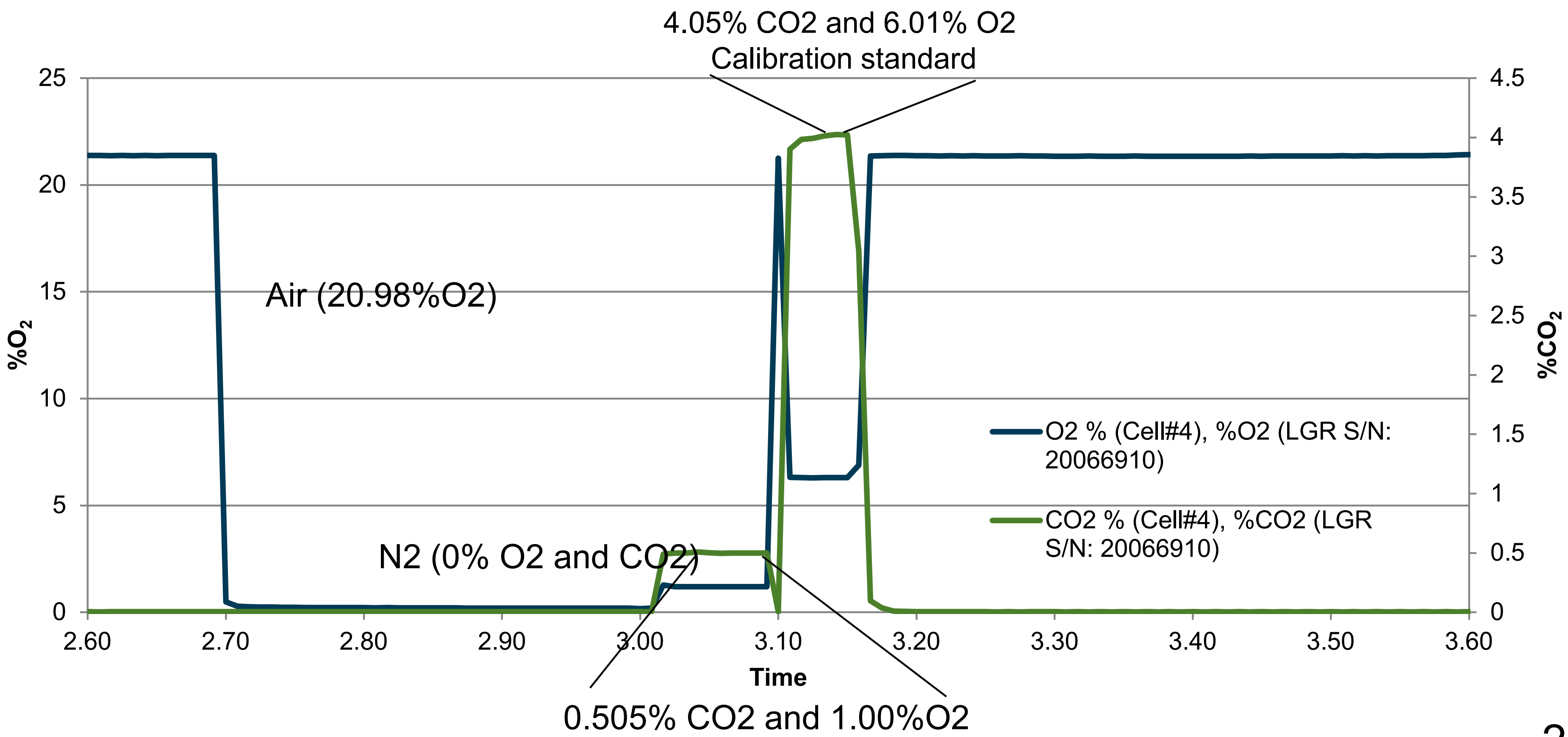
Standard 2 (4% CO_2, 6% O_2 in N_2)

Calibration

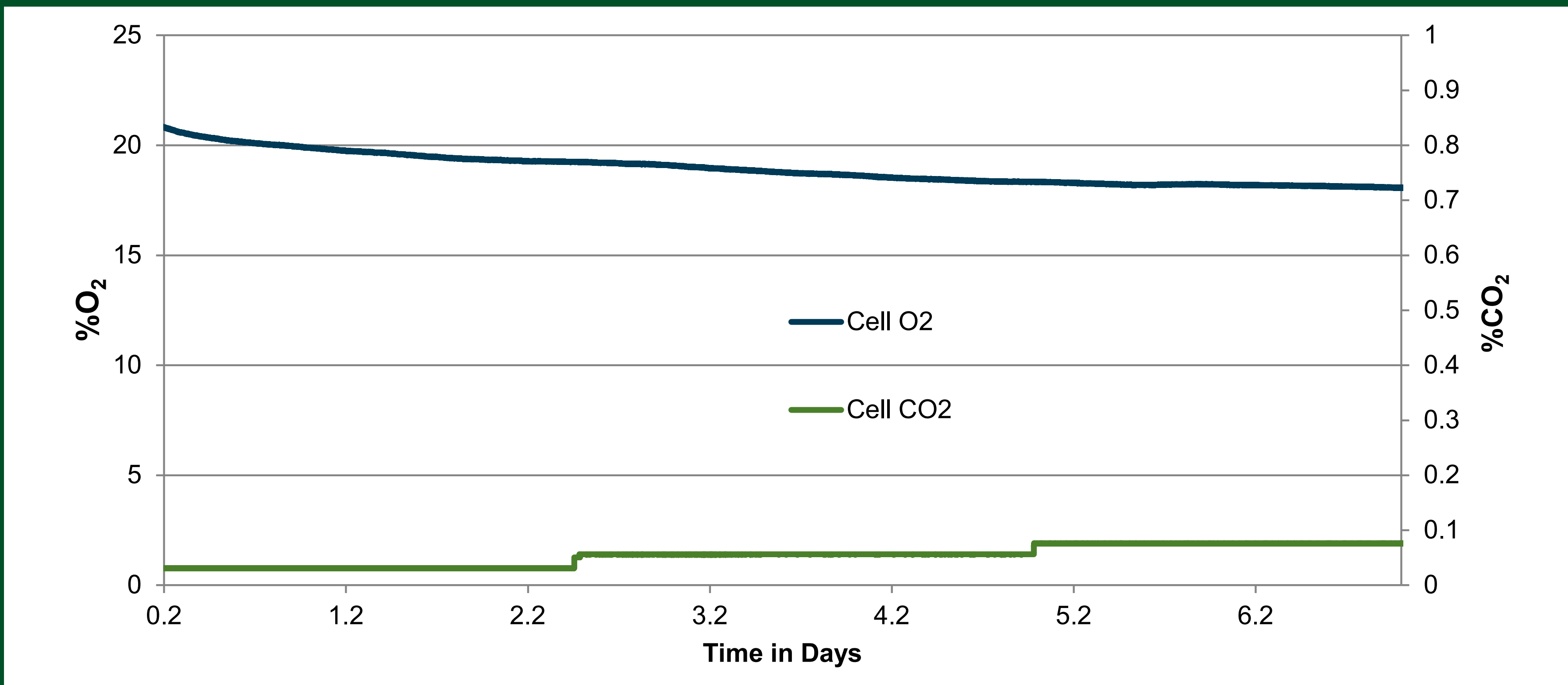




Quality Control: Beginning of OxyCon Test

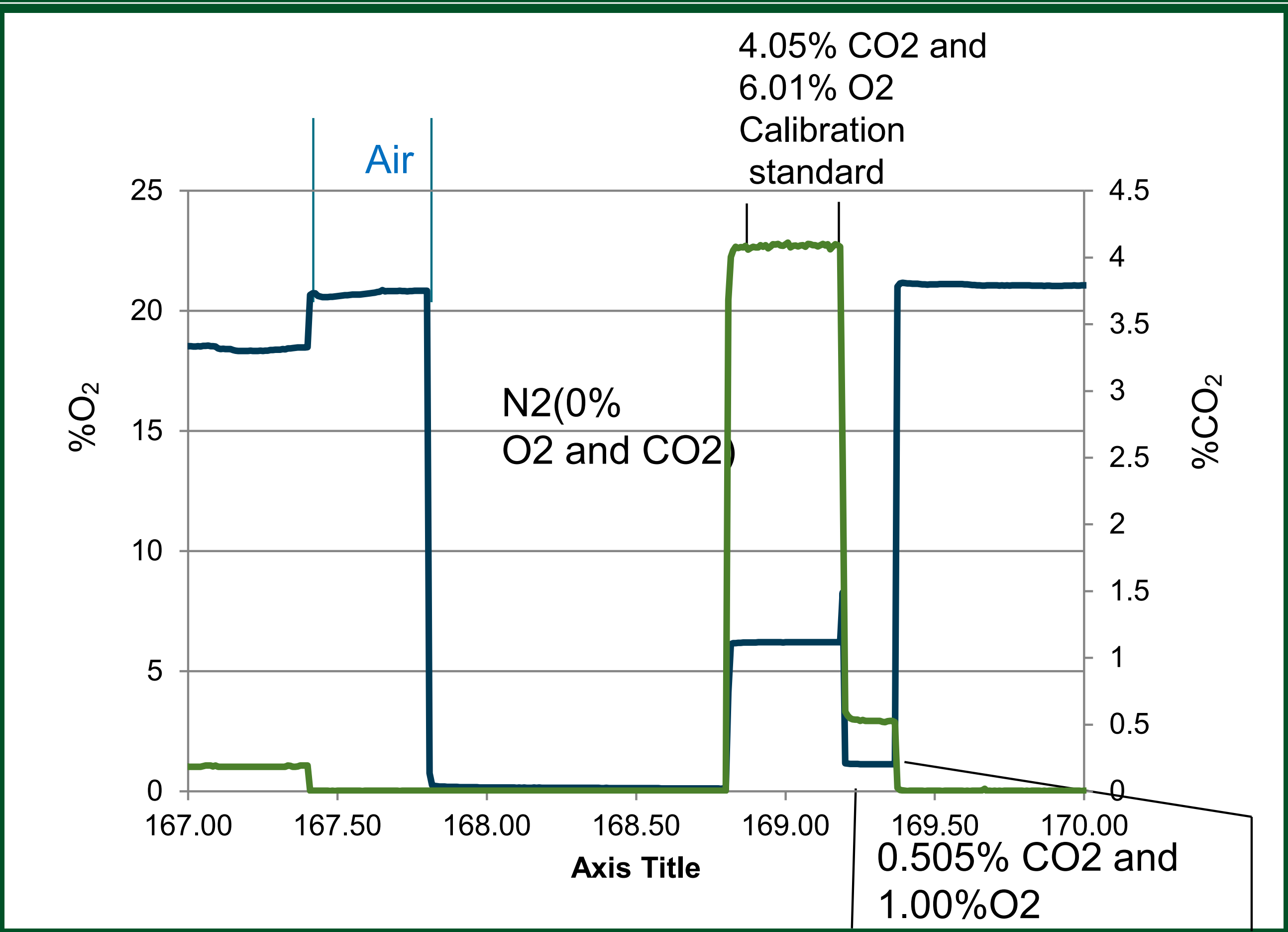


Experiment



25
20
15
10
5
0
%O2
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
%CO2
Cell O2
Cell CO2
0.2
1.2
2.2
3.2
4.2
5.2
6.2
Time in Days

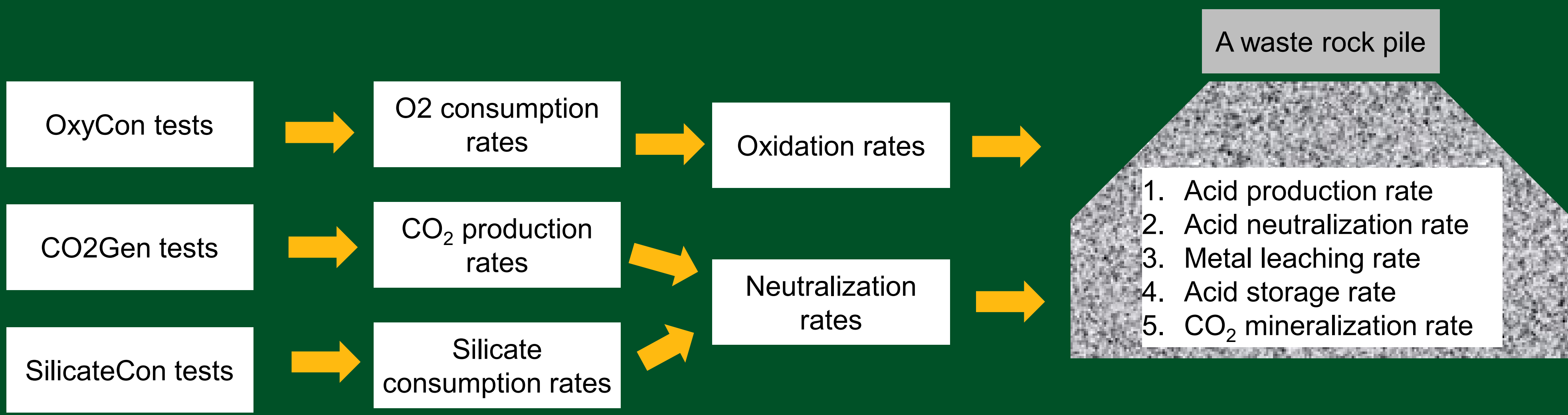
Quality Control: End of OxyCon Test



Sample applications

- ✓ Determination of reaction rate, e.g. PAG versus NAG, for waste disposal design.
- ✓ Parametric Study considering effects of moisture content, temperature, etc.
- ✓ Understanding neutralization mechanism, CO_3 versus soluble silicates.
- ✓ Parameterization for pile-scale multi-phase reactive transport modeling and simulation.

Pile-scale modeling and simulation



OxyCon and CO2Gen tests provide essential geochemical properties of mine components for pile-scale modeling and simulation to predict acid rock drainage, metal leaching, and CO_2 mineralization.

Thank you

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