

Oxygen Consumption and CO₂ Generation Test —Principles, Measurement Methods, Constraints and Quality Assessment and Control

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OUTLINE

1. Overview
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

- ✓ CO₂ 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 CO₂ that can accelerate air movement through minesite components. In the worst case, the release and accumulation of CO₂ from waste rock under a cover can prove fatal to humans as happened at the Sullivan Mine in British Columbia nearly 20 years ago.
 - ✓ CO₂ 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 CO₂ 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}

¹Ronald 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>

²Ronald 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>

³N. 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.

⁴A. 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_202220231214064829151.pdf

Figure 3-1. Schematic of the field set up of the Oxygen Consumption Method

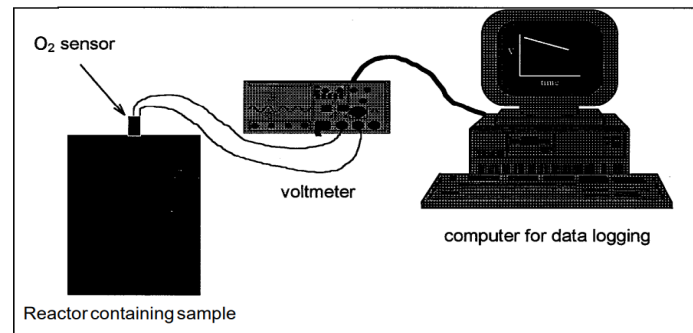
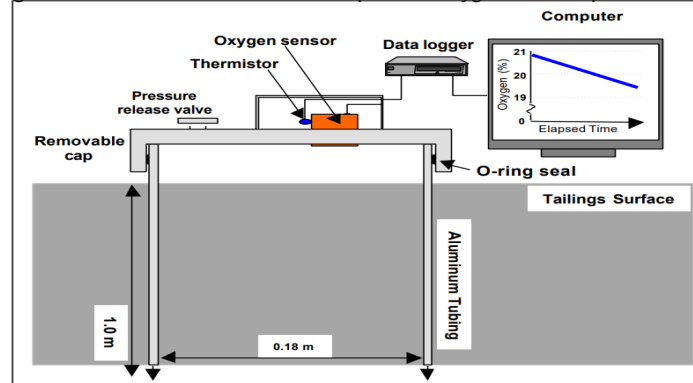


Figure 3.1 Schematic representation of oxygen consumption equipment

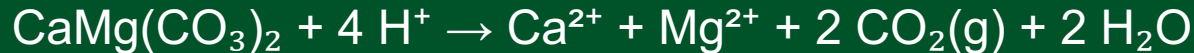
Images reproduced from Refs. 1 and 2 with the permission of the publisher (MEND).

Chemistry of Acid Generation and Neutralization

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



CO₂ Generation (CO2Gen) Test is a direct measurement of CO₂ generated from neutralization of acid by carbonate minerals.



Acid neutralization by silicates (plagioclase, forsterite, etc.) is not measured with CO₂ generation.



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 $\text{Fe}(\text{OH})_3$ 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](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.

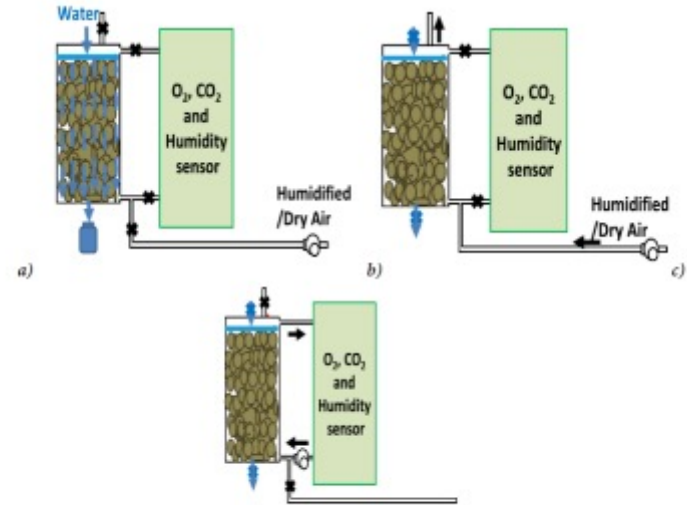
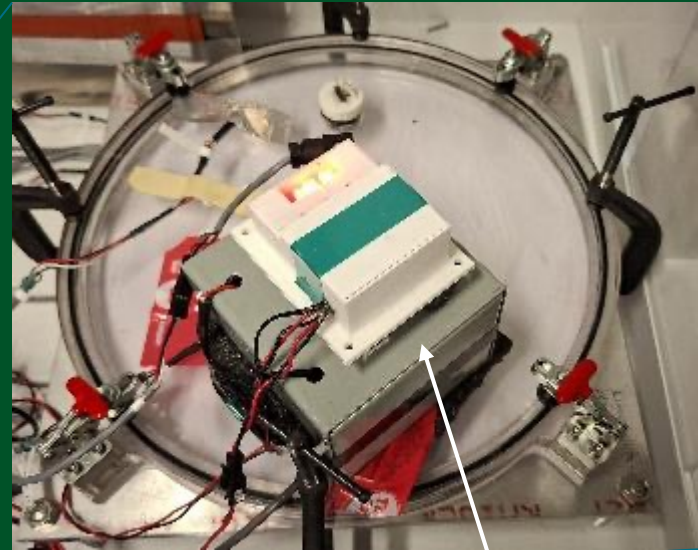
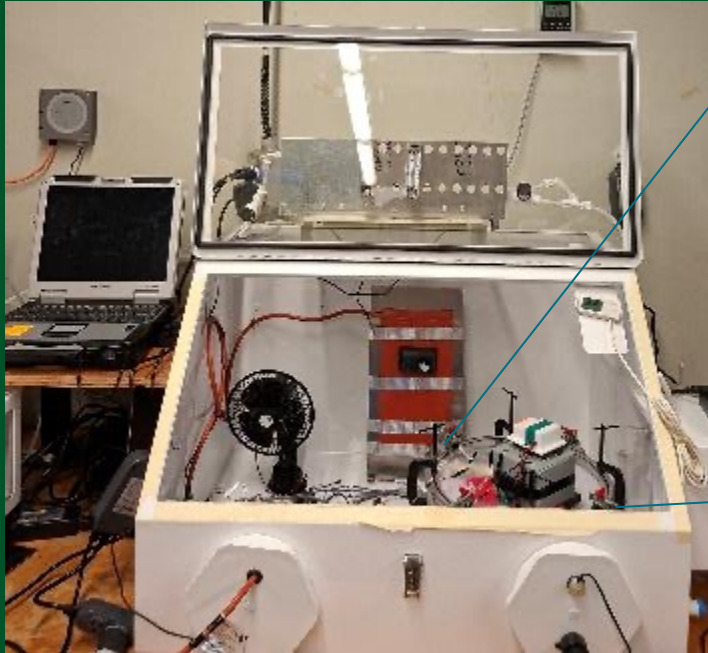


Figure 2 Experimental processes: a) column wetting, b) column drying or humidification and c) oxygen consumption, carbon dioxide generation and humidity monitoring. “X” indicates where valves were closed. Black arrows indicate the direction of air flow while blue arrows indicate the direction of water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

Alternative Design

“Flat cell type”



Temperature, O₂, CO₂, RH and
pressure sensors

Most Common Types of Sensors

O₂ - electrochemical type¹

Works just like an lithium-air battery for hearing aids

CO₂ - optical type²

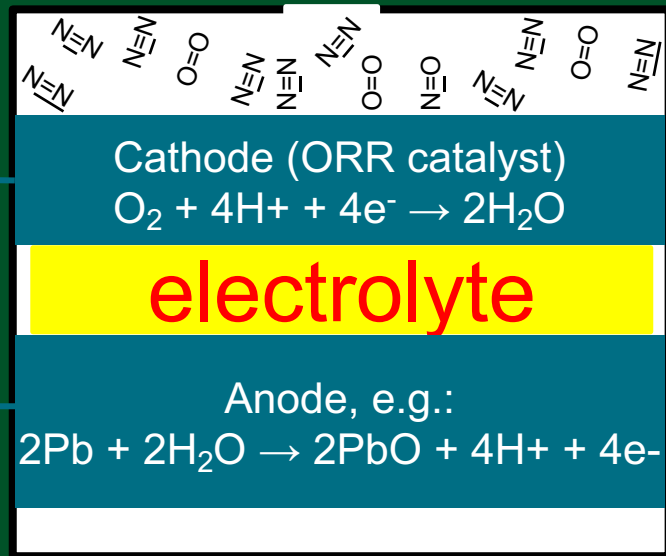
O₂ and N₂ does not absorb Near-Infrared light

CO₂, H₂O, nitrogen oxides and hydrocarbons absorb
at different wavelengths (“colors”)

¹Electrochemical type - Operating principle - Technology - FIGARO Engineering inc

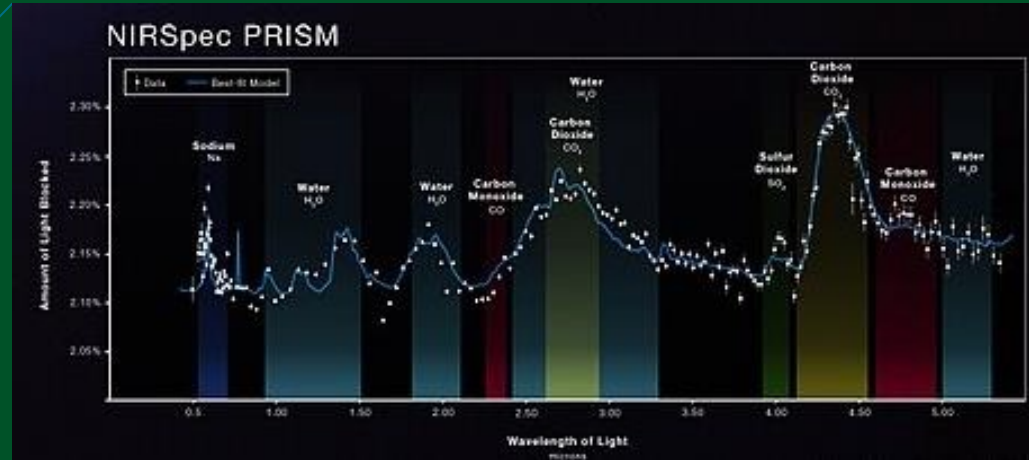
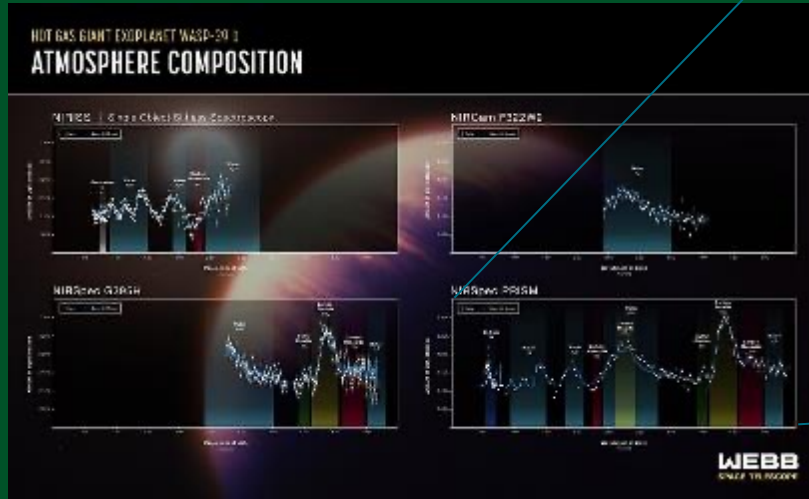
²NDIR type - Operating principle - Technology - FIGARO Engineering inc

O₂ Electrochemical Sensor



Faraday's Law: Current generated is directly proportional to moles of O₂ reduced

CO₂ 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

CO₂ Optical sensor

Beer Lambert's Law:

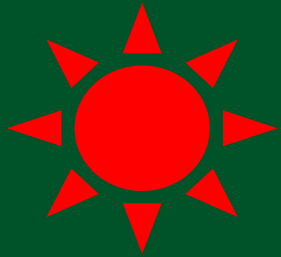
$$A = abc$$

Where A is absorbance,

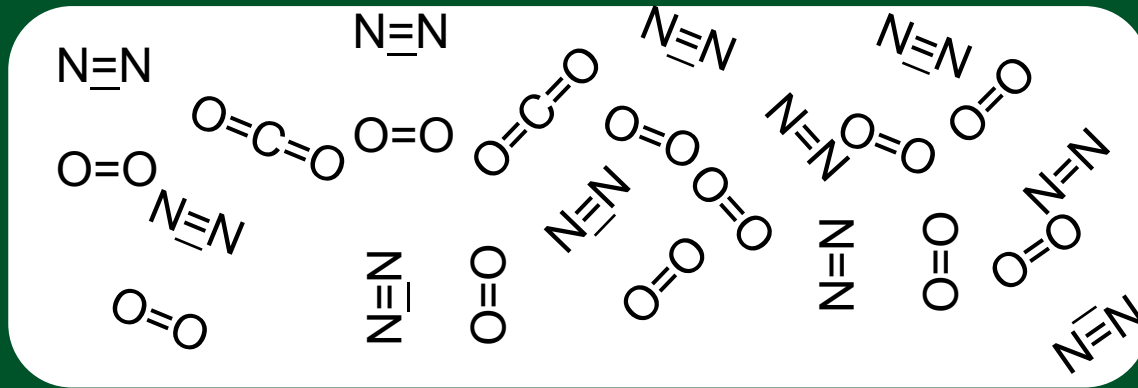
a is absorptivity coefficient,

b is pathlength, and

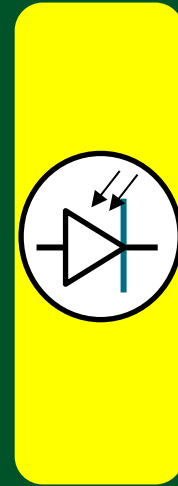
c is concentration



Light Source



Sample Path



Light Detector

Constraints, Calibration and Quality Control

Constraints:	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

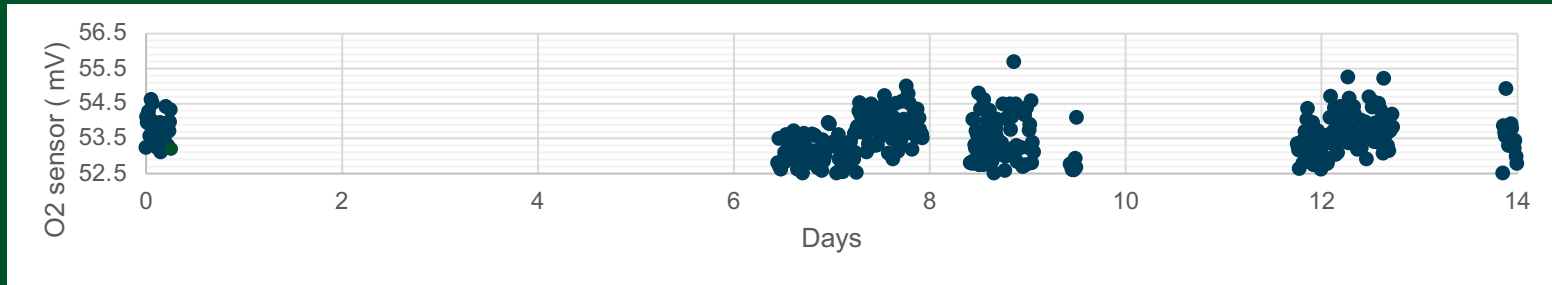
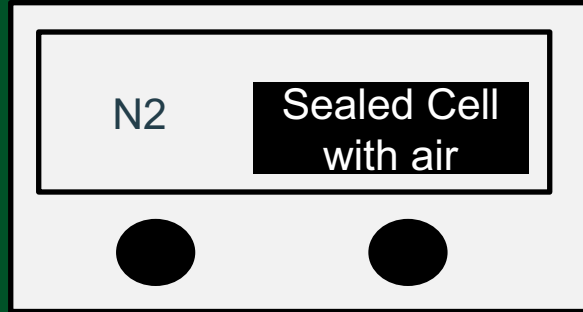


Leaking

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 oxidation rates.
- CO₂ overpressure inside causes outward CO₂ loss, falsely suggesting low CO₂ generation.

Leak Test



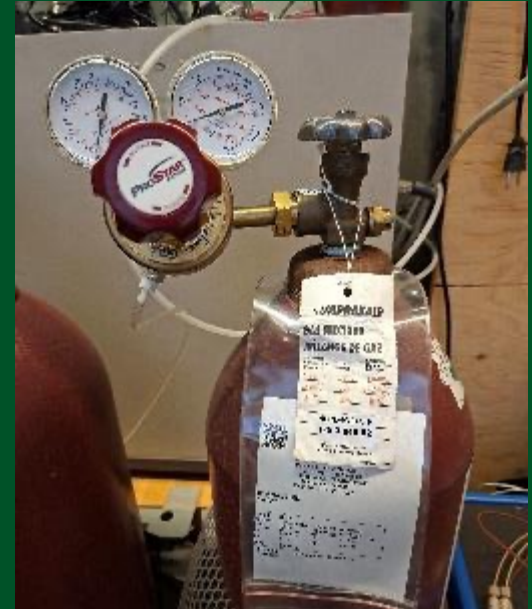
Calibration



Blank (99.999% N₂ gas)



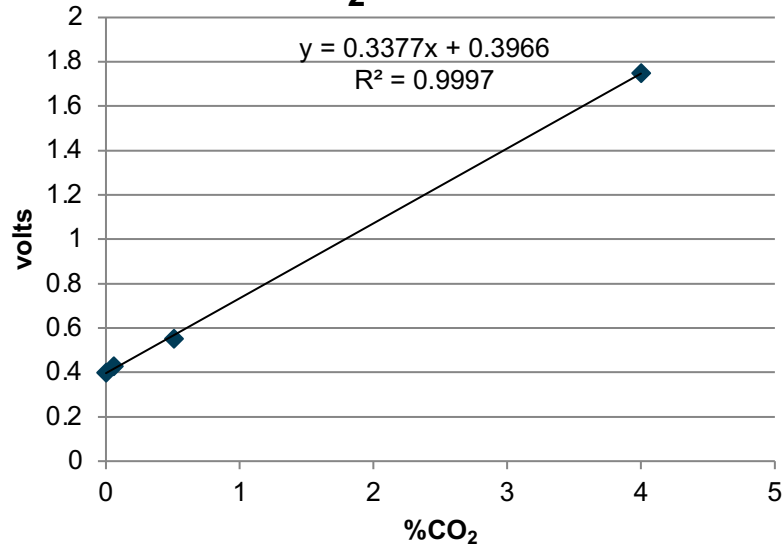
Standard 1 (0.5% CO₂,
1% O₂ in N₂)



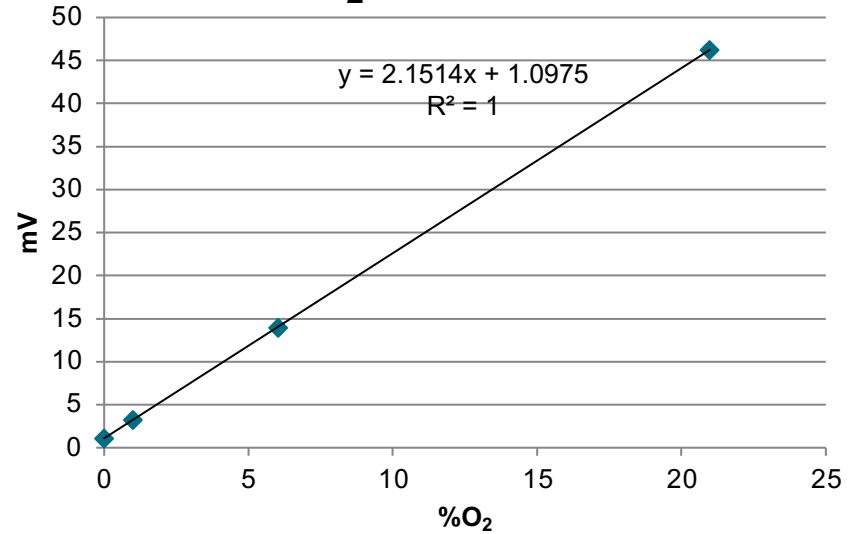
Standard 2 (4% CO₂,
6% O₂ in N₂)

Calibration

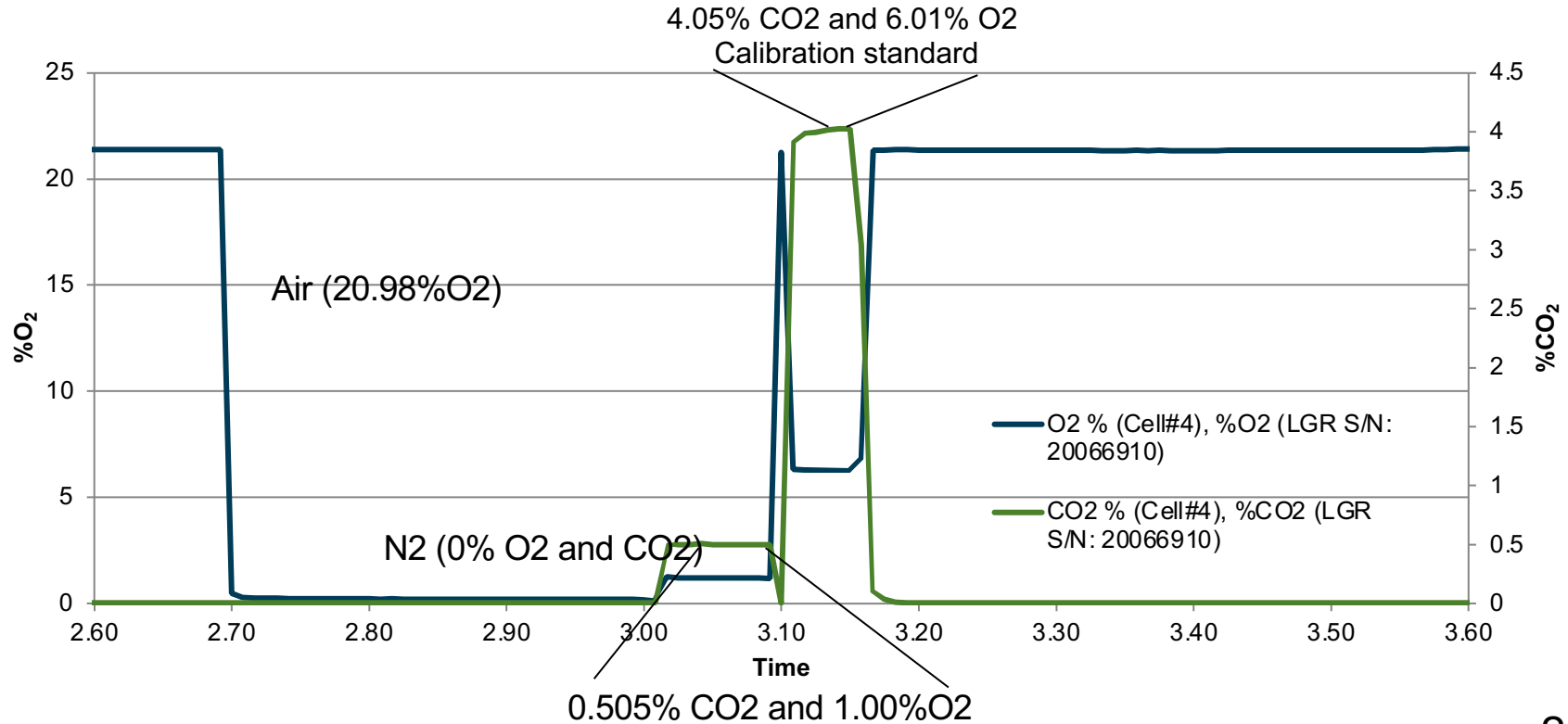
CO₂ Sensor



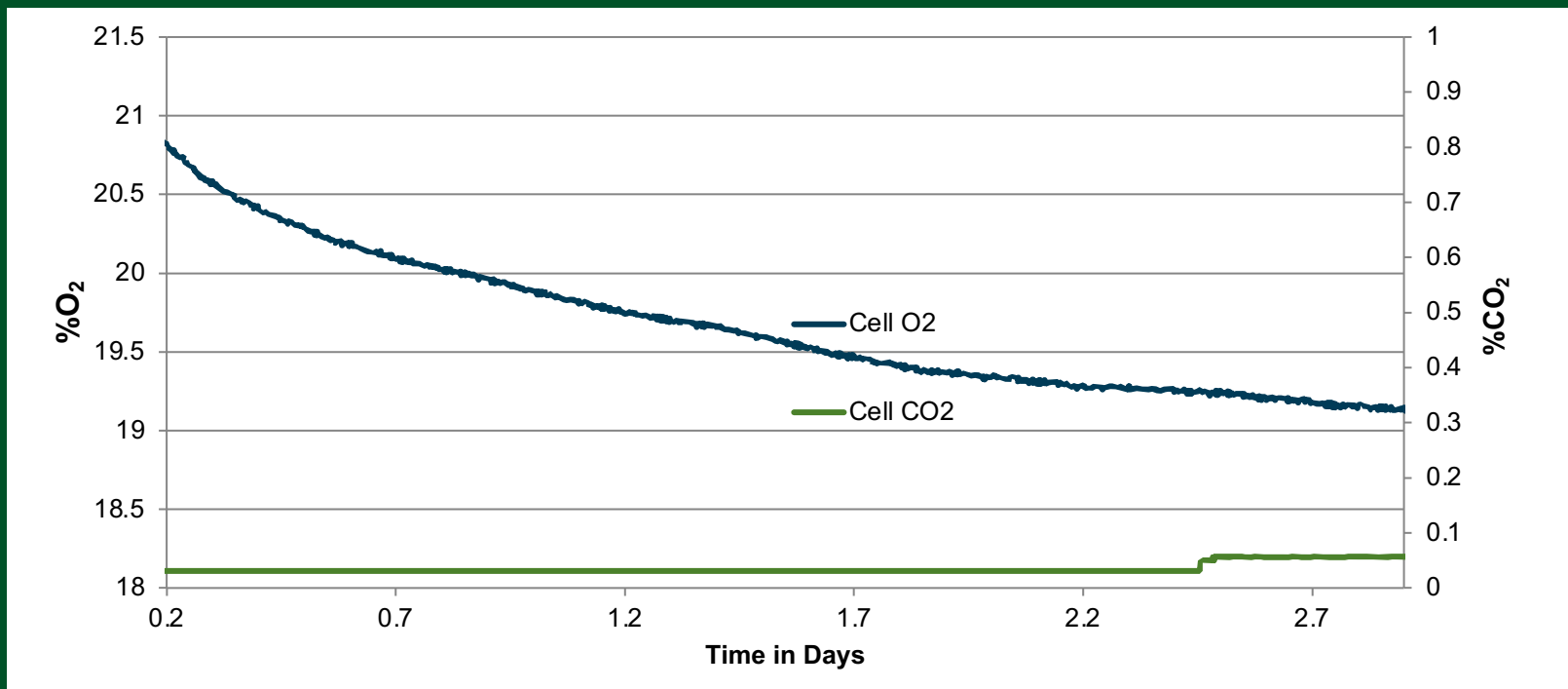
O₂ Sensor



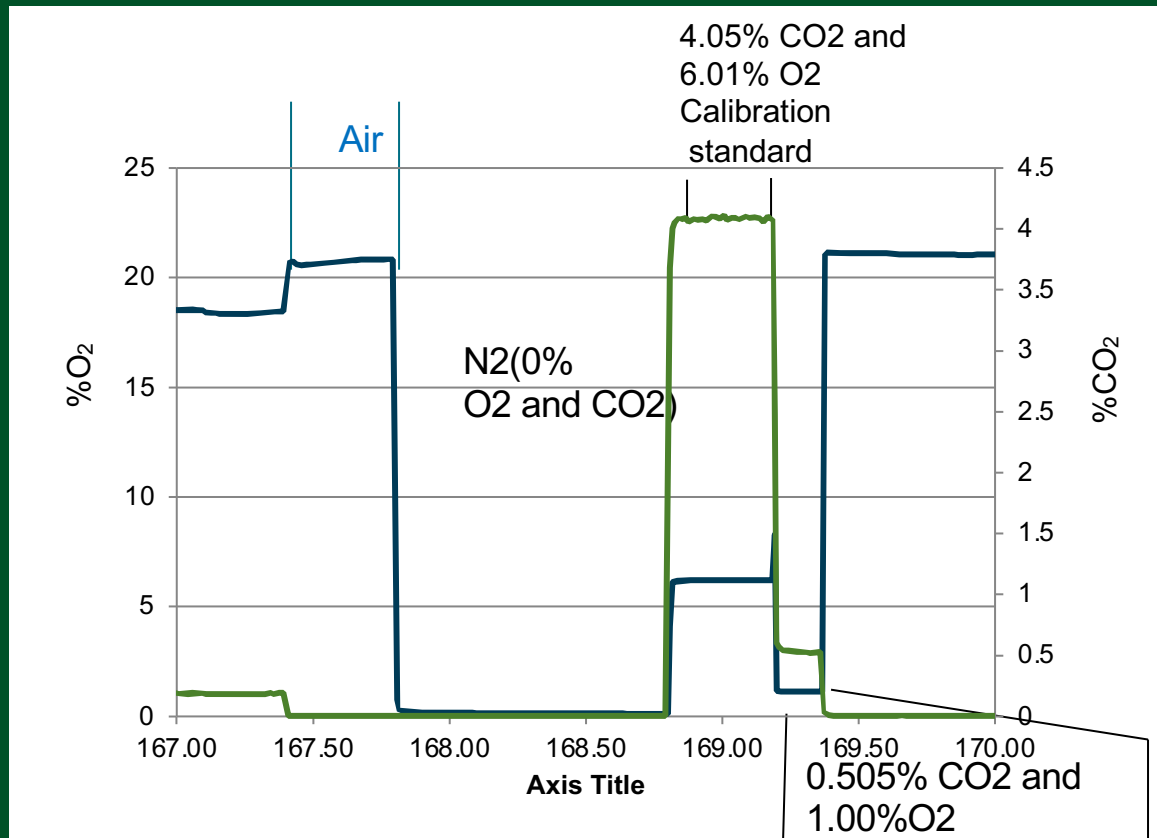
Quality Control: Beginning of OxyCon Test



Experiment



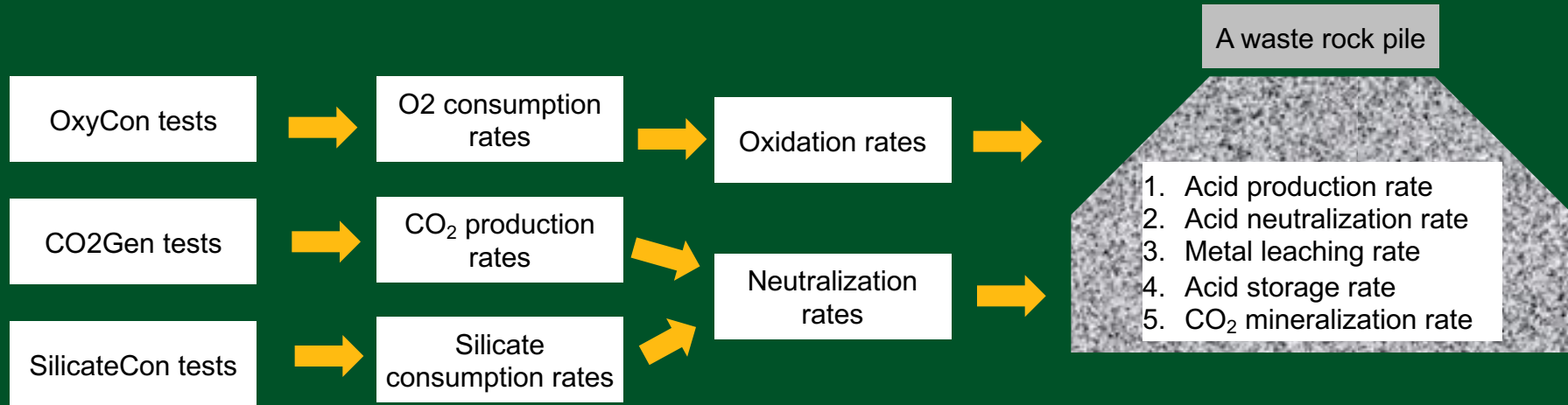
Quality Control: End of OxyCon Test



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 CO₂ mineralization.

Thank you

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