

saturated or undersaturated in association with higher PCO₂ and lower pH. Therefore, we recalculated the pH for equilibrium with calcite and the corresponding PCO₂ assuming that Ca and alkalinity were conservative.

The partial pressure of carbon dioxide in the leaching columns and humidity cells was calculated through geochemical modeling using a spreadsheet developed by Dr. Charles A. Cravotta of USGS. The equilibrium computations were performed utilizing thermodynamic data from Ball and Nordstrom (1991) to estimate the PCO₂ and pH of solutions within the columns and cells, prior to equilibration with the atmosphere. The following chemical parameters were determined every other week: pH, alkalinity, acidity, iron, manganese, calcium, magnesium, and specific conductance. Additionally temperature was known. The spreadsheet estimates ionic strength from conductance using relationships explained in Hem (1985) and Langmuir (1997) and was well suited for limited chemical analyses resulting from the study. The activity coefficients were determined using the Debye-Huckel equation (see Hem, 1985). Temperature correction was by the van't Hoff equation (Hem, 1985) and the equilibrium pH was computed simply by subtracting the calcite saturation index from the reported pH of the leachate. Then, the PCO₂ at equilibrium with calcite was recalculated considering this equilibrium pH and the reported alkalinity.

Table 2.3. Partial pressure CO₂ as determined from geochemical modeling. “Calculated” values were determined for water that was saturated or oversaturated by assuming the saturation index for calcite was 0.0 (i.e., at saturation). Q1 and Q3 are the 25th and 75th percentiles respectively.

Description	N	Median %PCO ₂ Unadjusted	Q1 %PCO ₂ Unadjusted	Q3 %PCO ₂ Unadjusted	Median %PCO ₂ Calculated	Q1 %PCO ₂ Calculated	Q3 %PCO ₂ Calculated	Median Saturation Index Calcite
Shale Air Column Lab 1	22	0.12	0.10	0.21	0.25	0.18	0.55	+0.290
Sandstone Air Column Lab 1	22	0.08	0.05	0.11				-0.236
Shale 10% CO ₂ Column Lab 1	22	0.28	0.17	0.41	2.50	1.08	6.54	+0.963
Sandstone 10% CO ₂ Column Lab 1	22	0.19	0.07	0.40	1.48	0.07	0.24	+0.494
Shale Air Humidity Cell Lab 1	22	1.48	0.07	0.12				-0.972
Sandstone Air Humidity Cell Lab 1	22	0.12	0.03	0.08				-1.044
Shale 10% CO ₂ Humidity Cell Lab 1	22	0.90	0.10	1.06				-0.431
Sandstone 10% CO ₂ Hum. Cell Lab 1	22	0.75	0.06	0.82				-0.822
Limestone 10% CO ₂ Lab 2	12	10.45	9.09	11.36	14.97	12.25	16.79	+0.147
Sandstone 10% CO ₂ Lab 2	13	10.05	9.07	11.31	9.71	6.61	13.18	-0.030
Shale 10% CO ₂ Lab 2	14	12.55	9.27	16.19	30.19	21.27	32.79	+0.383