Supplementary Information for:

Practical and Thermodynamic Constraints on Electromicrobially-Accelerated CO_2 Mineralization

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Lixiviant Compound	**Molecular Weight (Da)**	**Molecular Formula**	**Carbons per Molecule**
Acetic Acid	60.052	CH_3COOH	2
Citric Acid	192.124	$C_6H_8O_7$	6
2,5-Diketo-Gluconic Acid	191.12	$C_6H_8O_7$	6
Gluconic Acid	196.16	$C_6H_{12}O_7$	6
Glucose	180.16	$C_6H_{12}O_6$	6

Table S1. Molecular weights and energy densities for lixiviant molecules considered in this article.

Reaction	Reference
1. Acetic Acid	
Acetyl-CoA + ADP + phosphate → Acetate + ATP + CoA	KEGG R0229
2. Citric Acid	
Pyruvate + CO_2 → Oxaloacetate	KEGG RC00040
Acetyl-CoA + H_2O + Oxaloacetate → Citrate + CoA	KEGG RC00351
3. 2,5-Diketo-Gluconic Acid	
ATP + Pyruvate + HCO_3^- → Orthophosphate + Oxaloacetate	KEGG R00344
ATP + Oxaloacetate → Phosphoenolpyruvate + CO_2	KEGG R00341
Phosphoenolpyruvate + H_2O → 2-Phospho-D-glycerate	KEGG R00658
2-Phospho-D-glycerate → 3-Phospho-D-glycerate	KEGG R01518
ATP + 3-Phospho-D-glycerate → 3-Phospho-D-glyceroyl phosphate	KEGG R01512
3-Phospho-D-glyceroyl phosphate + NADH + H^+ → D-Glyceraldehyde 3-phosphate + Orthophosphate	KEGG R01061
D-Glyceraldehyde 3-phosphate → Glycerone phosphate	KEGG R01015
Glycerone phosphate + D-Glyceraldehyde 3-phosphate → D-Fructose 1,6-bisphosphate	KEGG R01068
D-Fructose 1,6-bisphosphate + H_2O → D-Fructose 6-phosphate + Orthophosphate	KEGG R00762
D-Fructose 6-phosphate → D-Glucose 6-phosphate	KEGG R00771
D-Glucose 6-phosphate + H_2O → D-Glucose + Orthophosphate	KEGG R00303
beta-D-Glucose → D-Glucono-1,5-lactone + NADH+ H^+	KEGG R01521
D-Glucono-1,5-lactone + H_2O → D-Gluconate	KEGG R01519
D-Gluconate → 2-Keto-D-gluconic acid + H^+	KEGG R01739
2-Keto-D-gluconic acid → 2,5-Diketo-D-gluconic acid+ H^+ + NADPH	KEGG R05823
4. Gluconic Acid	
ATP + Pyruvate + HCO_3^- → ADP + Phosphate + Oxaloacetate	KEGG R00344
ATP + Oxaloacetate → ADP + Phosphoenolpyruvate + CO_2	KEGG R00341
Phosphoenolpyruvate + H_2O → 2-phospho-D-glycerate	KEGG R00658
2-phospho-D-glycerate → 3-phospho-D-glycerate	KEGG R01518
ATP + 3-phospho-D-glycerate → ADP + 3-phospho-D-glyceroyl phosphate	KEGG R01512
3-phospho-D-glyceroyl phosphate + NADH + H^+ → D-glyceraldehyde 3-phosphate + Phosphate + NAD^+	KEGG R01061
D-glyceraldehyde 3-phosphate → Glycerone phosphate	KEGG R01015
Glycerone phosphate + D-glyceraldehyde 3-phosphate → D-fructose 1,6-bisphosphate	KEGG R01068
D-fructose 1,6-bisphosphate + H_2O → D-fructose 6-phosphate + Phosphate	KEGG R00762
D-fructose 6-phosphate → D-glucose 6-phosphate	KEGG R00771
D-glucose 6-phosphate + H_2O → D-glucose + Phosphate	KEGG R00303
D-glucose + $NAD(P)^+$ → D-glucono-1,5-lactone + NAD(P)H + H^+	KEGG R01520
D-glucono-1,5-lactone + H_2O → D-gluconate	KEGG R01519

Table S2. Reactions for synthesis of lixiviant molecules considered in this article. Reactions for lixiviant synthesis from acetyl-CoA, NAD(P)H, Ferredoxin and ATP were assembled from data from the KEGG database [Kanehisa2000a, Kanehisa2019a, Kanehisa2021a]

Reaction	Reference
1. Calvin Cycle (CBB)	
2 CO_2 + 7 ATP + 4 NADH → 1 Acetyl-CoA	Salimijazi *et al*. [Salimijazi2020b].
3 CO_2 + 7 ATP + 5 NADH → 1 Pyruvate	Salimijazi *et al* [Salimijazi2020b].
2. Wood-Ljungdahl Pathway (WL)	
4 CO_2 + 2 ATP + 8 NADH → 2 Acetyl-CoA	Berg [Berg2011a].
2 Fd_{red} + Acetyl-CoA + CO_2 → Pyruvate	KEGG R01196.
3. Reductive TCA Cycle (RTCA)	
4 CO2 + 4 ATP + 8 NADH → 2 Acetyl-CoA	Alissandratos *et al.* [Alissandratos2015a], Claassens *et al*. [Claassens2016a].
2 Fd_{red} + Acetyl-CoA + CO_2 → Pyruvate	KEGG R01196.
4. 3-hydroxypropionate/4-hydroxybutyrate Cycle (3HP4HB)	
6 HCO_3^- + 10 ATP + 10 NADH → 2 pyruvate	Berg *et al*. [BergI2007a], Claassens *et al*. [Claassens2016a].
2 Pyruvate → 2 Acetyl-CoA + 2 NADH + 2 CO_2	Berg [Berg2002a], Schomburg *et al.* [Schomburg2017a].
5. 3-hydroxypropionate Cycle (3HP)	
6 HCO_3^- + 10 ATP + 12 NADH → 2 Pyruvate	Zarzycki *et al*. [Zarzycki2009a], Herter *et al*. [Herter2002a], Berg [Berg2002a].
2 Pyruvate → 2 Acetyl-CoA + 2 NADH + 2 CO_2	Zarzycki *et al*. [Zarzycki2009a], Herter *et al*. [Herter2002a], Berg [Berg2002a].
6. 4-hydroxybutyrate Cycle (4HB)	
1 CO_2 + 1 HCO_3^- + 3 ATP + 1 NADH + 6 Fd_{red} → 1 Acetyl-CoA	Huber *et al*. [Huber2008a].
2 Pyruvate → 2 Acetyl-CoA + 2 NADH + 2 CO_2	Berg [Berg2002a], Schomburg *et al.* [Schomburg2017a].
7. Formolase Pathway (FORM)	
6 HCO_2^- + 10 ATP + 4 NADH → 2 3-PG	Siegel *et al*. [Siegel2015a], Bar-Even *et al*. [Bar-Even2016a].
2 3-PG → 2 Pyruvate + 2 ATP	Berg [Berg2002a].
2 Pyruvate → 2 Acetyl-CoA + 2 NADH + 2 CO_2	Berg [Berg2002a], Schomburg *et al.* [Schomburg2017a].

Table S3. CO_2-fixation and C_1-assimilation reactions. CO_2-fixation and C_1-assimilation reactions considered in this article were first assembled in Salimijazi *et al*. [Salimijazi2020b] and are restated here for convenience. Overall reactions for production of metabolic intermediates by 6 naturally-occurring CO_2-fixation cycles and the synthetic Formolase formate assimilation pathway, and the FeMoCo nitrogenase N_2-fixation reaction. Reactions can be referenced KEGG database [Kanehisa2000a, Kanehisa2019a, Kanehisa2021a]. Fd_{red}: Reduced Ferredoxin; 3-PG: 3-Phosphoglycerate.

Scenario	ATP	NAD(P)H	Fd_{red}	CO_2	HCO_3^-	HCO_2^-	Total C	Target Molecule	Target Formula	Target
Acetic_3HP	4	5	0	-1	3	0	2	Acetate	CH_3COOH	1.0
Acetic_3HP4HB	4	4	0	-1	3	0	2	Acetate	CH_3COOH	1.0
Acetic_4HB	2	1	6	1	1	0	2	Acetate	CH_3COOH	1.0
Acetic_CBB	6	4	0	2	0	0	2	Acetate	CH_3COOH	1.0
Acetic_FORM	3	1	0	-1	0	3	2	Acetate	CH_3COOH	1.0
Acetic_RTCA	1	4	-0	2	0	0	2	Acetate	CH_3COOH	1.0
Acetic_WL	-0	4	-0	2	0	0	2	Acetate	CH_3COOH	1.0
Citric_3HP	10	11	0	0	6	0	6	Citrate	$C_6H_8O_7$	1.0
Citric_3HP4HB	10	9	0	0	6	0	6	Citrate	$C_6H_8O_7$	1.0
Citric_4HB	6	3	12	4	2	0	6	Citrate	$C_6H_8O_7$	1.0
Citric_CBB	14	9	0	6	0	0	6	Citrate	$C_6H_8O_7$	1.0
Citric_FORM	8	3	0	0	0	6	6	Citrate	$C_6H_8O_7$	1.0
Citric_RTCA	4	8	2	6	0	0	6	Citrate	$C_6H_8O_7$	1.0
Citric_WL	2	8	2	6	0	0	6	Citrate	$C_6H_8O_7$	1.0
DKG_3HP	16	12	0	-2	8	0	6	2 5-DKG	$C_6H_8O_7$	1.0
DKG_3HP4HB	16	10	0	-2	8	0	6	2 5-DKG	$C_6H_8O_7$	1.0
DKG_4HB	12	2	16	2	4	0	6	2 5-DKG	$C_6H_8O_7$	1.0
DKG_CBB	20	10	0	4	2	0	6	2 5-DKG	$C_6H_8O_7$	1.0
DKG_FORM	14	4	0	-2	2	6	6	2 5-DKG	$C_6H_8O_7$	1.0
DKG_RTCA	10	8	4	4	2	0	6	2 5-DKG	$C_6H_8O_7$	1.0
DKG_WL	8	8	4	4	2	0	6	2 5-DKG	$C_6H_8O_7$	1.0
Gluconate_3HP	16	13	0	-2	8	0	6	D-Gluconate	$C_6H_{12}O_7$	1.0
Gluconate_3HP4HB	16	11	0	-2	8	0	6	D-Gluconate	$C_6H_{12}O_7$	1.0
Gluconate_4HB	12	5	12	2	4	0	6	D-Gluconate	$C_6H_{12}O_7$	1.0
Gluconate_CBB	20	11	0	4	2	0	6	D-Gluconate	$C_6H_{12}O_7$	1.0
Gluconate_FORM	12	5	0	0	0	6	6	D-Gluconate	$C_6H_{12}O_7$	1.0
Gluconate_RTCA	10	9	4	4	2	0	6	D-Gluconate	$C_6H_{12}O_7$	1.0
Gluconate_WL	8	9	4	4	2	0	6	D-Gluconate	$C_6H_{12}O_7$	1.0

Table S4. Net molecular input requirements for lixiviant synthesis by 6 naturally-occurring CO_2-fixation cycles and the synthetic Formolase formate assimilation pathway. Fd_{red}: Reduced Ferredoxin. 3HP: 3-hydroxypropionate cycle [Zarzycki2009a]; 3HP4HB: 3-hydroxypropionate/4-hydroxybutyrate pathway [BergI2007a, Claassens2016a]; 4HB: Dicarboxylate/4-hydroxybutyrate cycle [Huber2008a]; Calvin-Benson-Bassham cycle [Berg2002a]; FORM: Formolase formate assimilation pathway [Siegel2015a]; RTCA: Reductive Tricarboxylic Acid cycle [Alissandratos2015a, Claassens2016a]; WL: Wood-Ljungdahl (WL) Pathway [Berg2002a]. Results can be reproduced running the BALANCE.PY code in the ELECTROCO2 repository [Barstow2021b].

#	Inverse CO_2 Mineralization Economy, ζ (Mol g^{-1})	Lixiviant Concentration, c_{lix} (Moles per m^3 or mM)	Extraction Efficiency, η_{ex}	Precipitation Efficiency, η_{precip}	Pulp Density, ρ_{pulp} (grams per m^3)	Note
ζ_1	2.00×10^{-4}	100.0	1.00	1.00	5.00×10^5	Our most optimistic estimate of inverse CO_2 mineralization economy, ζ.
ζ_2	2.23×10^{-4}	100.0	1.00	0.90	5.00×10^5	Value of ζ corresponding to use of entire US biomass production.
		111.5	1.00	1.00	5.00×10^5	
		100.0	0.90	1.00	5.00×10^5	
		102.8	0.97	0.97	4.87×10^5	
ζ_3	1.06×10^{-3}	100.0	1.00	0.19	5.00×10^5	Value of ζ corresponding to first global agricultural transition identified by Slade *et al*. [Slade2014a].
		100.0	0.19	1.00	5.00×10^5	
		530.0	1.00	1.00	5.00×10^5	
		100.0	1.00	1.00	9.40×10^4	
		100.0	0.44	0.44	5.00×10^5	
		229.9	1.00	1.00	2.18×10^5	
		151.7	0.66	0.66	3.30×10^5	
ζ_4	3.18×10^{-3}	100.0	0.25	0.25	5.00×10^5	Value of ζ corresponding to second global agricultural transition identified by Slade *et al*. [Slade2014a].
		398.9	1.00	1.00	1.25×10^5	
		199.8	0.50	0.50	2.50×10^5	
ζ_5	6.36×10^{-3}	237.5	0.42	0.42	2.10×10^5	Value of ζ corresponding to third global agricultural transition identified by Slade *et al*. [Slade2014a].
		316.8	0.32	0.32	5.00×10^5	
		316.8	1.00	0.32	1.58×10^5	
ζ_6	1.27×10^{-2}	282.5	0.35	0.35	1.77×10^5	Value of ζ corresponding to use of entire global net primary production [Slade2014a].

Table S5. Possible combinations factors that produce significant values of inverse CO_2 mineralization economy, ζ. We calculated possible combinations of values of c_{lix}, η_{ex}, η_{precip}, and ρ_{pulp} that produce each of the values of ζ highlighted in **Figure 2**.

Supplementary Note 1: Calculation of Lixiviant pH

What is the pH of a weak organic acid, with a given pK_a, at a particular analytical concentration? We have adapted this answer from [Helmenstine2019a].

The association constant, K_a,

$$Ka = [H+][B-]/[HB] \tag{S1}$$

where $[H^+]$ is concentration of H^+ ions, $[B^-]$ is concentration of conjugate base ions, and [HB] is the concentration of undissociated acid molecules. We assume that the acid releases one H^+ ion for every B^- ion, so

$$[H^+] = [B^-]. \tag{S2}$$

To simplify the algebra, we denote $[H^+]$ as x. Thus,

$$[HB] = C - x,$$

where C is the analytical concentration of the acid. Thus, using **Equation S1**,

$$\mathrm{K_a} = \frac{x \times x}{C - x}, \tag{S3}$$

$$x^2 = \mathrm{K_a}\,(C - x), \tag{S4}$$

$$x^2 + \mathrm{K_a}x - C\,\mathrm{K_a} = 0. \tag{S5}$$

The proton concentration, x, can be found using the positive root of the quadratic equation,

$$x = -\frac{b}{2a} \pm \frac{1}{2a}\sqrt{b^2 - 4ac}, \tag{S6}$$

$$x = -\frac{\mathrm{K_a}}{2} \pm \frac{1}{2}\sqrt{\mathrm{K_a^2} + 4C\,\mathrm{K_a}}. \tag{S7}$$

Thus,

$$\mathrm{pH} = -\log_{10}\left(-\frac{\mathrm{K_a}}{2} + \frac{1}{2}\sqrt{\mathrm{K_a^2} + 4C\,\mathrm{K_a}}\right). \tag{S8}$$

For acetic acid (pKa = 4.75), citric acid (pKa = 3.13), and gluconic acid (pKa = 3.72) at 100 mM,

$$\mathrm{pH_{acetic}} = 2.9, \tag{S9}$$

$$\mathrm{pH_{gluconic}} = 2.4, \tag{S10}$$

$$\mathrm{pH_{citric}} = 2.1. \tag{S11}$$

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