

SUPPORTING INFORMATION

**Circular economy approaches to microbially-induced carbonate precipitation for
bioprocessing of geothermal brine for lithium recovery**

Mohammed Rehmanji. ^{*1}, Alastair Skeffington.², Karen A. Hudson-Edwards.¹, and Laura
Newsome.¹,

¹ Camborne School of Mines & Environment and Sustainability Institute, University of Exeter,
Penryn TR109FE, Cornwall, United Kingdom.

² Department of Biological and Environmental Sciences, University of Stirling, Scotland
United Kingdom.

***Corresponding Author and Present Address**

Mohammed Rehmanji, Camborne School of Mines & Environment and Sustainability
Institute, University of Exeter, Penryn TR109FE, Cornwall, United Kingdom.

E-mail: m.rehmanji@exeter.ac.uk; Phone - +447448603289

25 **Table S1.** Chemical composition (mg L⁻¹) of natural brine used in this study. Errors are the
26 standard error of the mean, n = 3.

27

28

29

30

Parameters/Cations/Anions	Natural Brines
T (°C)	28.0 ± 2.3
pH	7.2 ± 0.5
EC (mS)	20.3 ± 1.5
Silica (mg L ⁻¹)	35.0 ± 2.0
Calcium (mg L ⁻¹)	1512.0 ± 2.4
Magnesium (mg L ⁻¹)	27.2 ± 1.3
Potassium (mg L ⁻¹)	204.9 ± 3.3
Sodium (mg L ⁻¹)	2351.0 ± 3.2
Lithium (mg L ⁻¹)	75.2 ± 1.8
Boron (mg L ⁻¹)	12.8 ± 1.3
Copper (mg L ⁻¹)	2.0 ± 0.5
Iron (mg L ⁻¹)	2.5 ± 0.8
Manganese (mg L ⁻¹)	3.0 ± 0.4
Strontium (mg L ⁻¹)	29.0 ± 0.8
Nickel (mg L ⁻¹)	2.5 ± 0.9
Chloride (mg L ⁻¹)	7711.0 ± 4.5
Sulphate (mg L ⁻¹)	270.0 ± 5.5
Phosphate (mg L ⁻¹)	141.9 ± 8.7

31

32

33

34

35

Table S2. Operating conditions of Inductive coupled plasma optical emission spectroscopy (ICP-OES) and wavelengths at which the metals were detected.

Wavelengths and operating conditions used for ICP-OES determination of metals.	
RF power (kW)	1.2
Plasma gas flow (L min ⁻¹)	12
Auxiliary Ar (L min ⁻¹)	1.0
Nebulizer Ar (L min ⁻¹)	0.70
Pump rate (mL min ⁻¹)	1
Readings/replicate	3
Wavelength (nm)	Ca: 422.673; Mg: 285.213; Cu: 327.395; Fe: 238.204; Ni: 230.299; Mn: 294.921; Sr: 421.552; K: 769.897; B: 249.678; Na: 588.995; Sr: 421.552

Table S3. Operating conditions of Ion chromatography (IC) for anion detection in Natural brine.

Operating conditions used for IC determination of anions.	
Eluent KOH (mM)	30
Operation mode	Isocratic
Flow rate (mL min ⁻¹)	0.38
Suppressor (mA)	29
Column temperature (°C)	30
Pressure (psi)	< 4000

Table S4. Operating conditions of scanning electron microscopy (SEM).

Operating conditions used for SEM analysis.		
Operating conditions used for XRD analysis.		
Accelerating voltage (kV)		25
Working distance (mm)	Siemens D5000 diffractometer	20
Electron beam current (pA)	1.5kW, Cu-anode	133
Magnification (X)	40kV, 30mA	$5 - 10^5$
Chamber pressure (Pa)		10
Wavelength	1.5406/1.54439 (Cu K α 1/2)	
Interpretation software	xt microscope control	6.2.7
Detector	Scintillation point detector	
Div. Slit	V6 (variable, 6mm)	
AntiScatter Slit	(same as above)	
Scan Type	θ/θ locked	
Scan Range	2-70 °2 θ	
Step Size	0.02 °2 θ	
Scan time	1 sec/step	
Scan Rotation	Yes	
Interpretation software	EVA v.18.0.0.0.	
PDF Database	JCPDS PDF-2 (2004) database	

Table S5. Operating conditions of X-ray diffraction analysis.

101
102
103
104
105
106
107
108
109
110
111
112
113
114
115
116
117
118
119
120
121
122
123
124
125
126
127
128
129

Table S6. Growth performance of *S. pasteurii* and *B. subtilis* in tryptone soy broth in exponential phase, represented in terms of growth rate (h^{-1}), doubling time (h), maximum optical density (O.D. @ 600 nm) and pH of medium. Errors are the standard error of the mean, $n = 3$.

Parameters/Organisms	<i>Bacillus subtilis</i> in tryptone soy broth	<i>Sporosarcina pasteurii</i> in tryptone soy broth
Growth rate (h^{-1})	0.69 ± 0.05	0.71 ± 0.03
Doubling time (h)	0.99 ± 0.01	0.97 ± 0.02
Maximum OD ₆₀₀	1.15 ± 0.04	1.16 ± 0.05
Maximum pH	7.37 ± 0.06	9.60 ± 0.03

Table S7. Saturation indices calculated for minerals formed via MICP in the natural brine solution.

Sample	Time point	Calcite	Aragonite	Dolomite	Huntite	Magnesite	Vaterite
<i>Bacillus subtilis</i> in Natural brine solution	0	0.51	0.22	-0.48	-5.51	-1.76	-0.09
<i>Bacillus subtilis</i> in Natural brine solution	0.9	0.75	0.46	0.01	-4.52	-1.51	0.15
<i>Bacillus subtilis</i> in Natural brine solution	3	0.88	0.58	0.21	-4.17	-1.44	0.28
<i>Bacillus subtilis</i> in Natural brine solution	7	0.71	0.42	-0.12	-4.84	-1.61	0.31
<i>Bacillus subtilis</i> in Natural brine solution	24	0.91	0.62	0.28	-4.05	-1.41	0.31
<i>Sporosarcina pasteurii</i> in Natural brine solution	0	0.41	0.12	-0.68	-5.91	-1.86	-0.18
<i>Sporosarcina pasteurii</i> in Natural brine solution	0.9	0.92	0.63	1.41	-0.68	-0.29	0.33
<i>Sporosarcina pasteurii</i> in Natural brine solution	3	0.13	-0.16	0.32	-2.34	-0.58	-0.46
<i>Sporosarcina pasteurii</i> in Natural brine solution	7	0.03	-0.26	0.20	-2.51	-0.6	-0.56
<i>Sporosarcina pasteurii</i> in Natural brine solution	24	-0.09	-0.39	0.07	-2.65	-0.61	-0.69

Table S8. Composition of different lithium-rich brines reported from literature.

Deposit Country

Cations/ Anions	Calcium (mg L ⁻¹)	Magne sium (mg L ⁻¹)	Potassium (mg L ⁻¹)	Sodium (mg L ⁻¹)	Lithium (mg L ⁻¹)	Boron (mg L ⁻¹)	Chloride (mg L ⁻¹)	Sulphate (mg L ⁻¹)
Uyuni (Bolivia)	460	7680	7920	98400	320	190	177600	12960
Atacama (Chile)	450	9650	23600	91000	1570	440	189500	15900
Olaroz (Argentina)	1100	2000	5300	111500	570	NA	177500	9800
Hombre Muerto (Argentina)	120	140	9700	103000	900	540	168000	11400
Zabuye Lake (China)	0	0	45960	127900	660	1580	147600	26290
Clayton Valley (USA)	450	230	8000	63700	360	90	100000	6600
Taijinar Salt Lake brine (China)	300	13500	NA	102300	210	310	188100	24000
Southern Tibet geothermal belt (China)	50	20	NA	1700	130	NA	2000	1700
Chott Djerid (Tunisia)	1600	3400	5600	80000	60	NA	144100	6700
Cerro prieto (USA)	30800	3200	23500	60000	250	500	175500	46000
Salton Sea (USA)	25700	110	14500	49200	200	300	142000	100
Rincon (Argentina)	600	3000	6600	97900	300	400	158000	NA
Soultz- sous-Forêts (France)	7200	130	3200	28100	170	40	58600	160
Buhl geothermal well (Germany)	11600	1930	490	64000	40	NA	120300	1600
Landau geothermal well (Germany)	7700	80	4000	28200	180	NA	64200	100

[illegible]

	(France)								
	Buhl geothermal well (Germany)	NA	NA	NA	NA	NA	NA	NA	6
	Landau geothermal well (Germany)	NA	NA	NA	NA	NA	NA	NA	6
	Dieng geothermal power plant (Indonesia)	NA	NA	NA	NA	NA	NA	NA	7
	Coipasa (Bolivia)	NA	NA	NA	NA	NA	NA	NA	8
	Cauchari (Argentina)	NA	NA	NA	NA	NA	NA	NA	8
Current study	Cornwall (United Kingdom)	2	2.5	3	29	2.5	141.9	35	This study

172 *NA represents not assigned

173

174

175

176

177

178

179

180

181

182

183

184

185

186

187

188

189

190

191 **Table S9.** Comparative study reporting different methods to treat saline water samples for
192 metal removal and Li recovery.

Sr No.	Water samples	Method used for Treatment	pH	Time of treatment (Hrs)	Calcium removal efficiency (%)	Magnesium removal efficiency (%)
1	Artificial seawater cementation solution	MICP by <i>Sporosarcina pasteurii</i>	8.5	24	90	NA
2	Hypersaline produced water	MICP by ureolytic bacterial consortium	9	240	96	35
3	Brine from Hombre Muerto, Argentina	Ion Pumping	NA	NA	NA	NA
4	Brine, from north of Argentina	2 step electro membrane process	13.1	500	99.8	97
5	Brine, from Geothermal power plant, Tibet	Ion exchange resin	12	1	5	NA
6	Geothermal water, Tibet	Ion exchange resin	12	12	NA	NA
7	Salt Lake brine from West Taijinar	crystallization-precipitation method	6.7	3	NA	99
8	Dead sea evaporated end brine	Chemical precipitation	6.9	NA	NA	NA
9	Arizaro Salt Lake brine	Electrochemical combined with precipitation	NA	NA	NA	NA
10	This study	MICP by <i>Sporosarcina pasteurii</i>	9.4	0.15	96	46
Sr No.	Water samples	Manganese removal efficiency (%)	Strontium removal efficiency (%)	% Li recovery	References	
1	Artificial seawater	NA	NA	NA	9	

	cementation solution				
2	Hypersaline produced water	92.2	94.2	NA	10
3	Brine from Hombre Muerto, Argentina	NA	NA	4.9	11
4	Brine, from north of Argentina	NA	NA	99.8	12
5	Brine, from Geothermal power plant, Tibet	NA	NA	88.68	13
6	Geothermal water, Tibet	NA	NA	88.42	14
7	Salt Lake brine from West Taijinar	NA	NA	93.2	15
8	Dead sea evaporated end brine	NA	NA	40	16
9	Arizaro Salt Lake brine	NA	NA	74.9	17
10	This study	88	91	96	This study

193 *NA represents not assigned

194

195

196

197

198

199

200

201

202

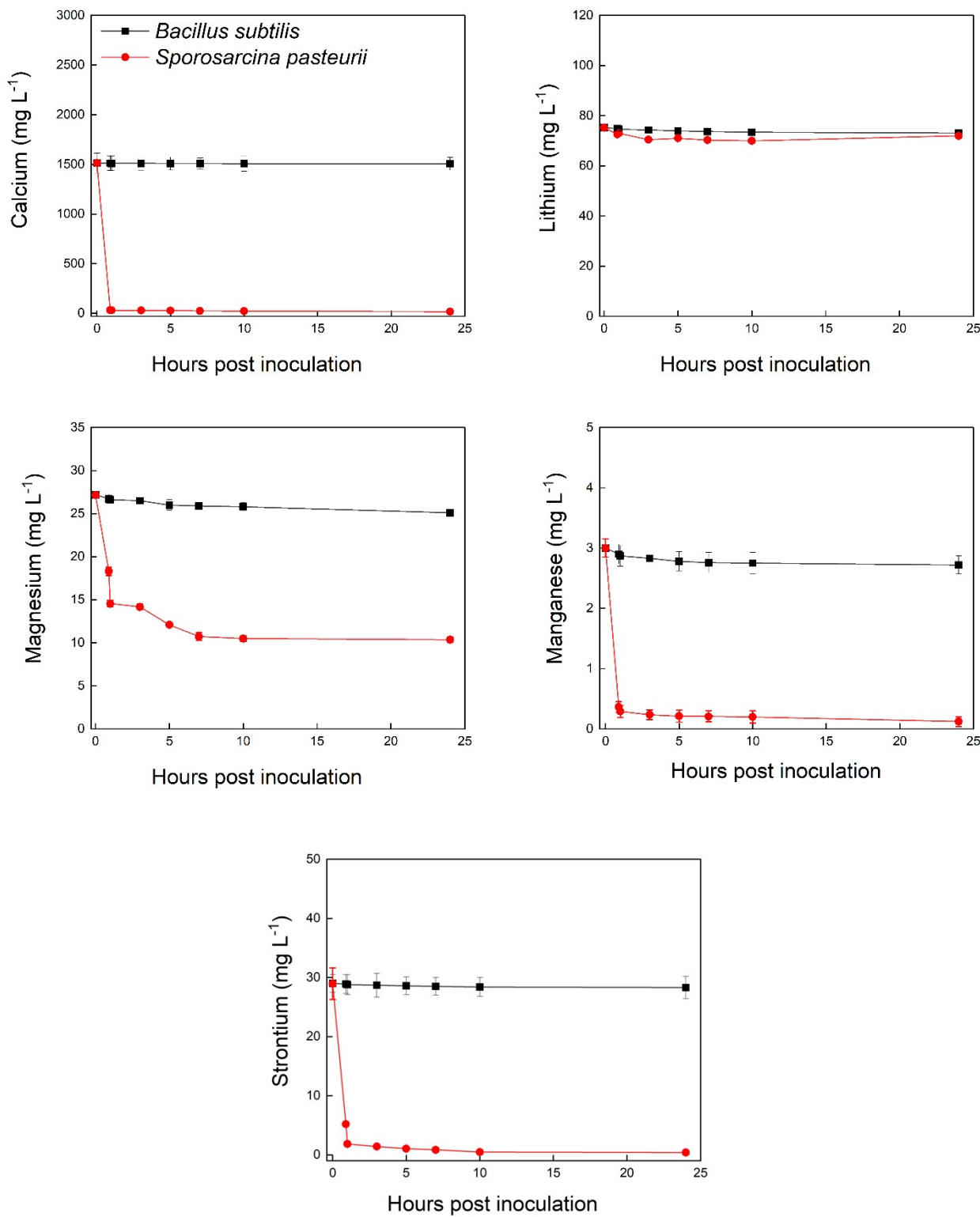
203

204

205

206 **Figure S1.** Microbial induced carbonate precipitation in natural brine inoculated (at O.D. 0.1)
207 with *S. pasteurii* (red circles) and *B. subtilis* (black squares). Plots show concentration of Ca
208 (a), Li (b), Mg (c), Mn (d) and Sr (e) in the solution over time. Error bars are the standard error
209 of the mean, n = 3.

210



211

212

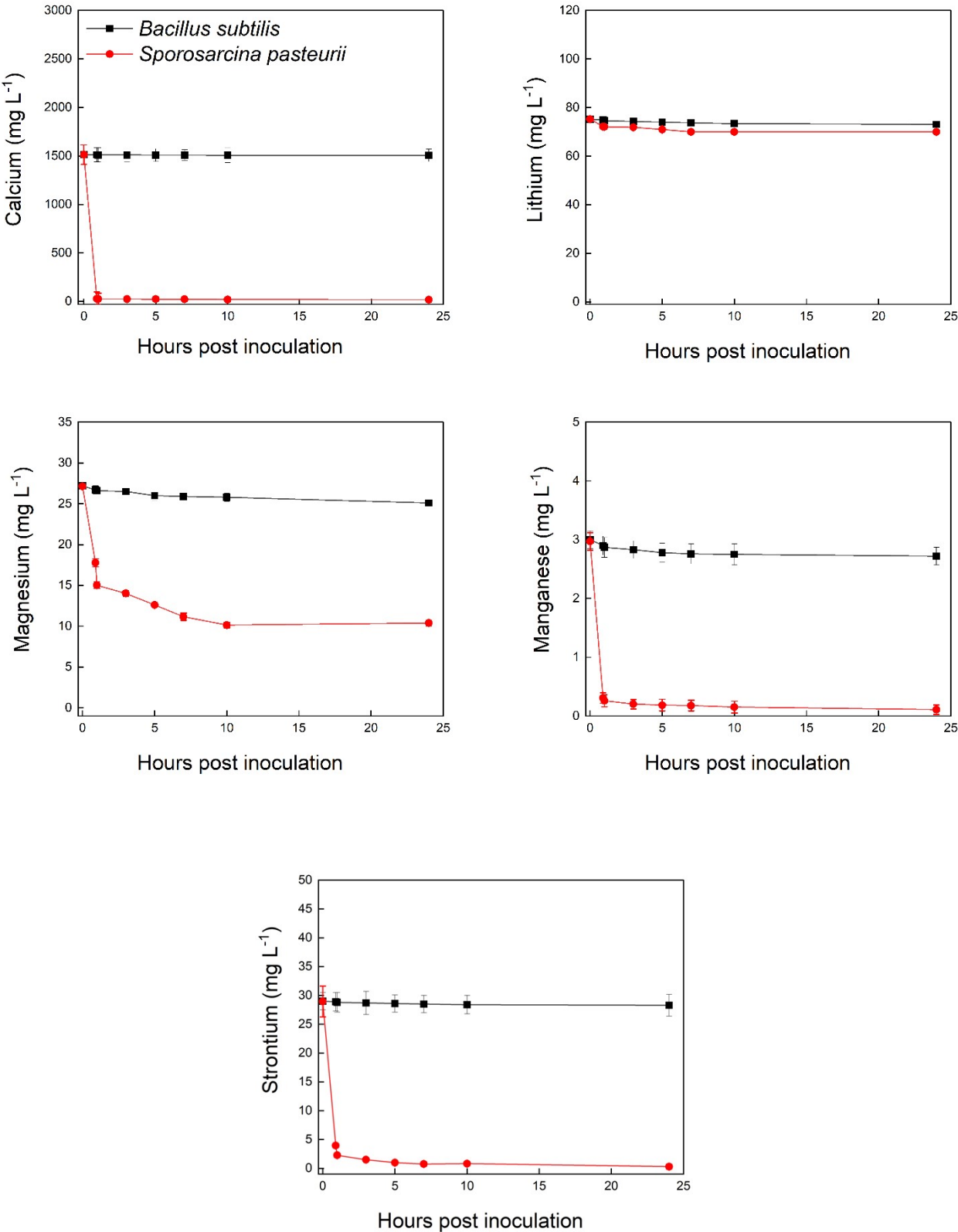
213

214

215

(e)

216 **Figure S2.** Microbial induced carbonate precipitation in natural brine inoculated (at O.D. 0.2)
 217 with *S. pasteurii* (red circles) and *B. subtilis* (black squares). Plots show concentration of Ca
 218 (a), Li (b), Mg (c), Mn (d) and Sr (e) in the solution over time. Error bars are the standard error
 219 of the mean, n = 3.



220

221

222

(e)

223

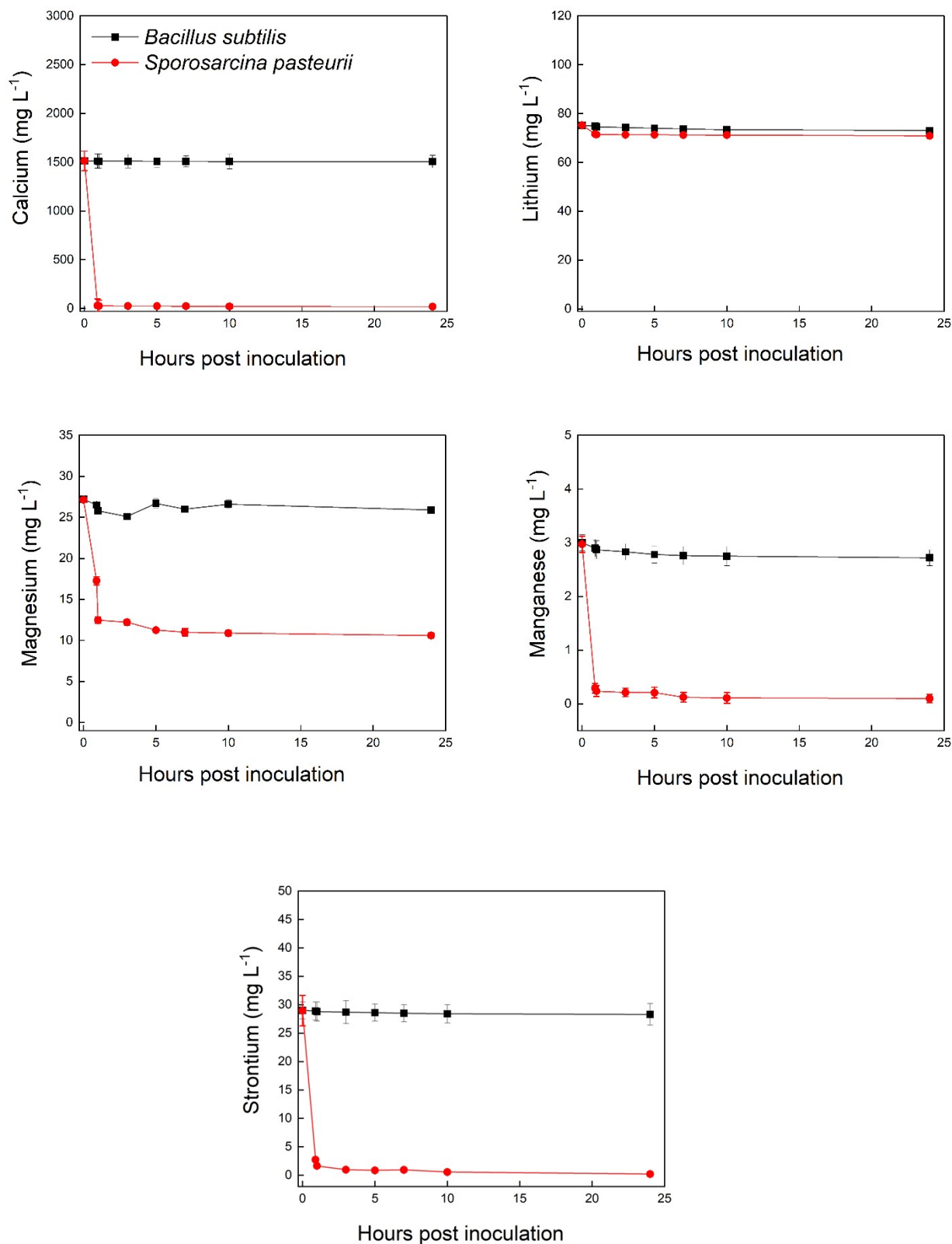
224

225

226

227

228 **Figure S3.** Microbial induced carbonate precipitation in natural brine inoculated (at O.D. 0.3)
 229 with *S. pasteurii* (red circles) and *B. subtilis* (black squares). Plots show concentration of Ca
 230 (a), Li (b), Mg (c), Mn (d) and Sr (e) in the solution over time. Error bars are the standard error
 231 of the mean, n = 3.



232

233

234

(e)

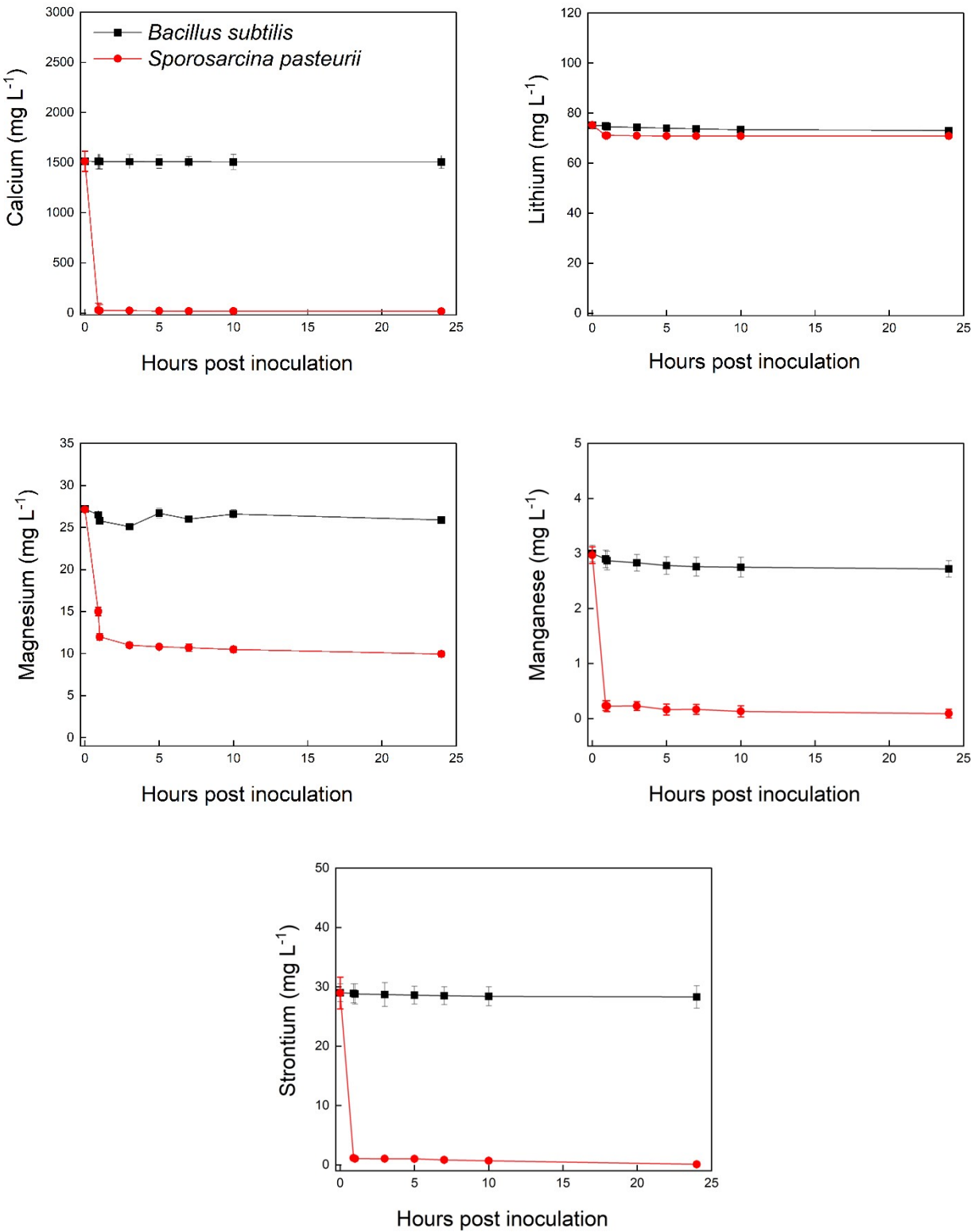
235

236

237

238

239 **Figure S4.** Microbial induced carbonate precipitation in natural brine inoculated (at O.D. 0.4)
 240 with *S. pasteurii* (red circles) and *B. subtilis* (black squares). Plots show concentration of Ca
 241 (a), Li (b), Mg (c), Mn (d) and Sr (e) in the solution over time. Error bars are the standard error
 242 of the mean, n = 3.



243
244

245

246

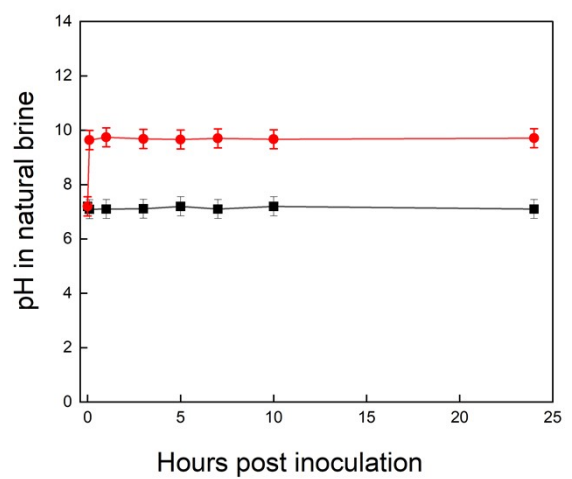
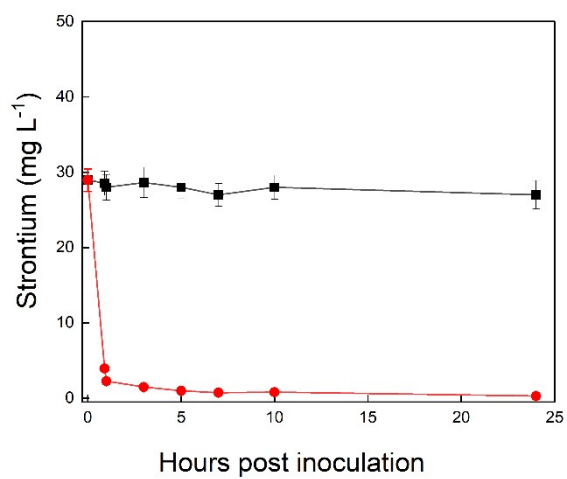
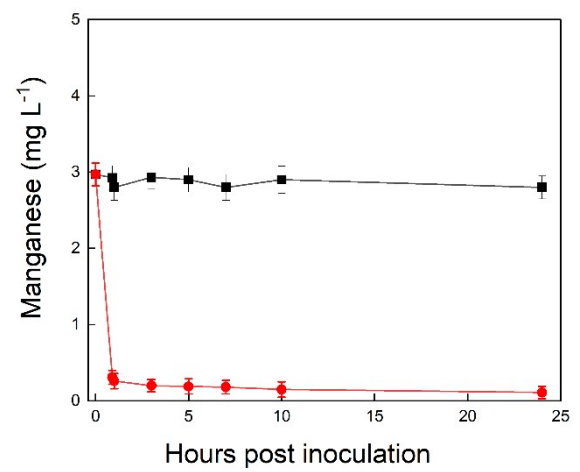
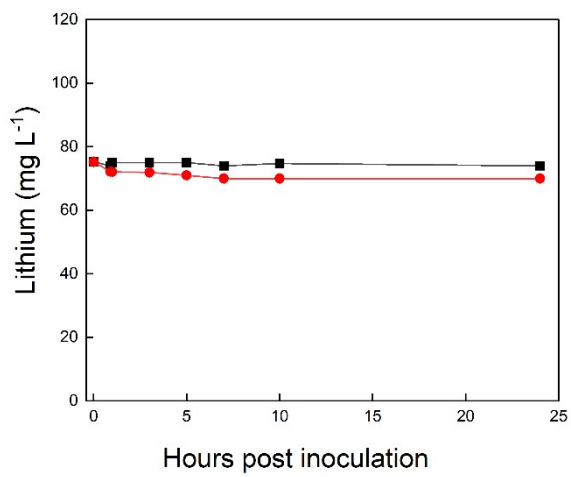
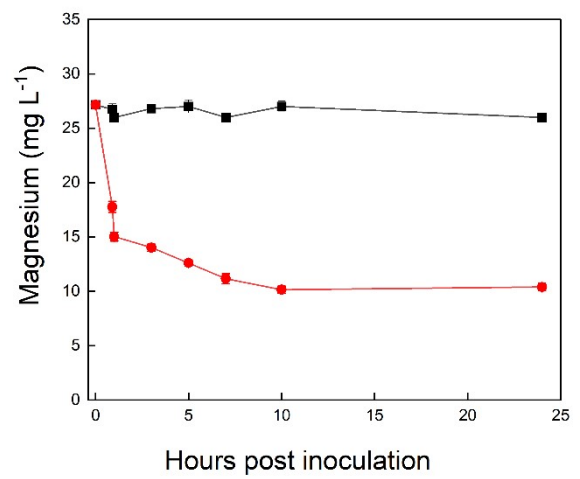
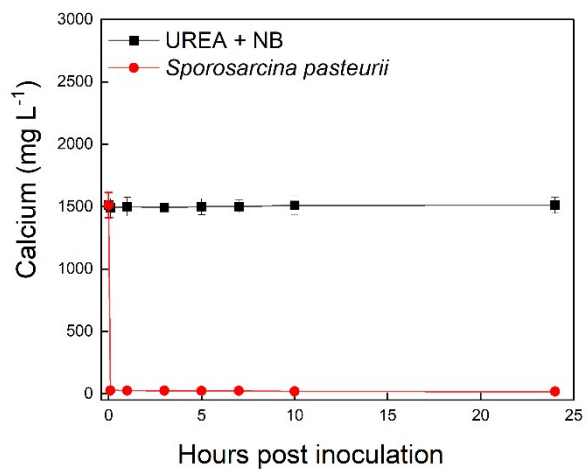
247

248

249

250 **Fig S5** Microbial induced carbonate precipitation in natural brine inoculated with *S. pasteurii*
251 (red circles) and no cell control with only urea added in natural brine (black squares). Plots
252 show concentration of Ca (a), Mg (b), Li (c), Mn (d) Sr (e) and measured pH (f) in the
253 solution over time. Error bars are the standard error of the mean, n = 3.

(e)



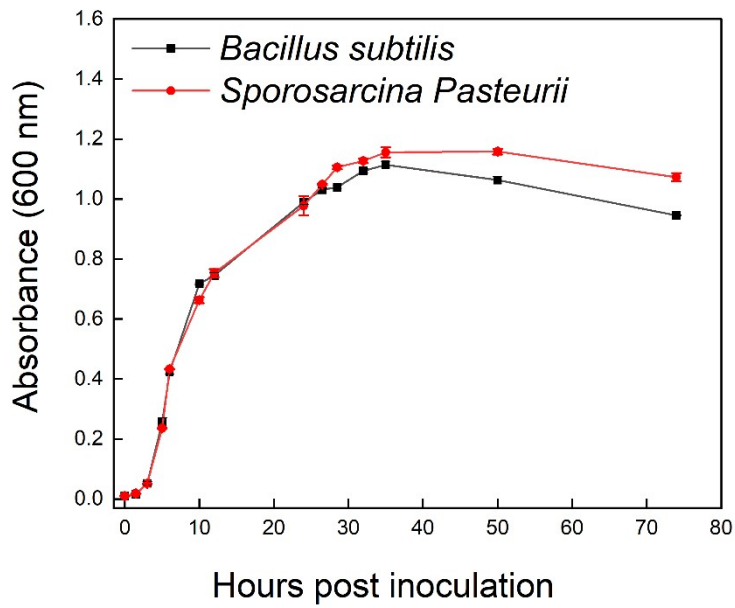
255

256 **Figure S6.** Growth performance of *S. pasteurii* (red circle) and *B. subtilis* (black square) in TSB
257 for MICP treatment. Plot show optical density measured at 600 nm in TSB medium (a), pH of
258 TSB medium (b). Error bars are the standard error of the mean, n = 3.

259

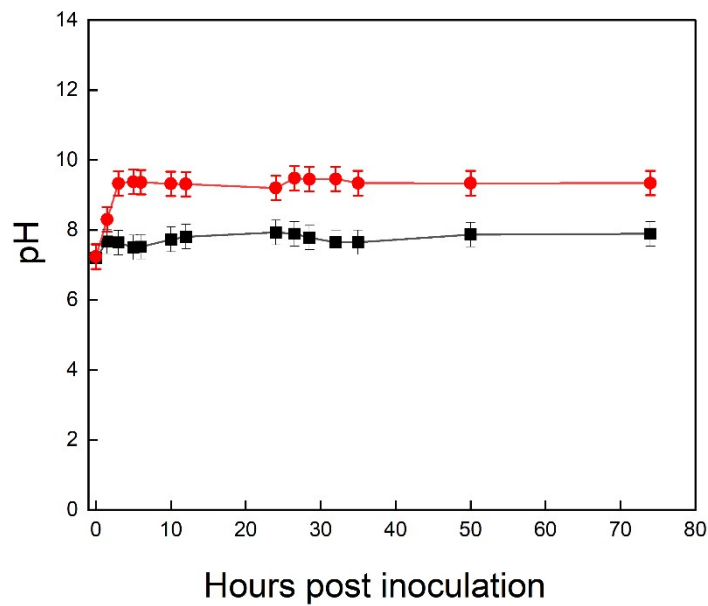
260

261



270

271



281

282

283

284

Figure S7. XRD analysis of powdered precipitates with *S. pasteurii* cells in the natural brine solution.

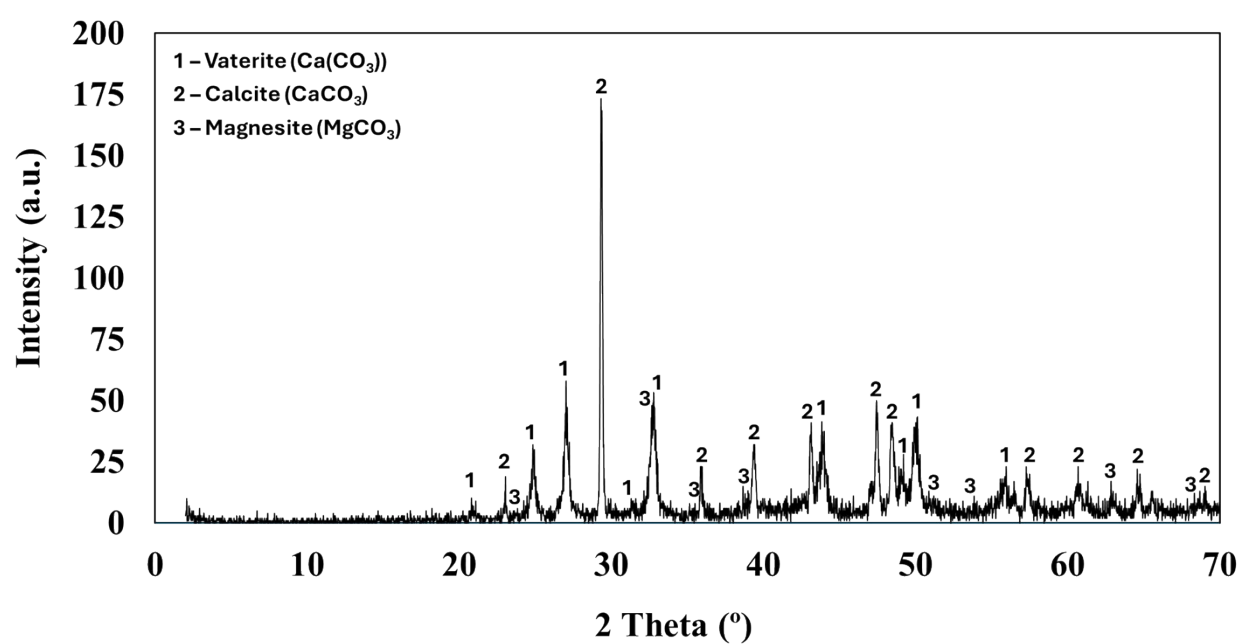
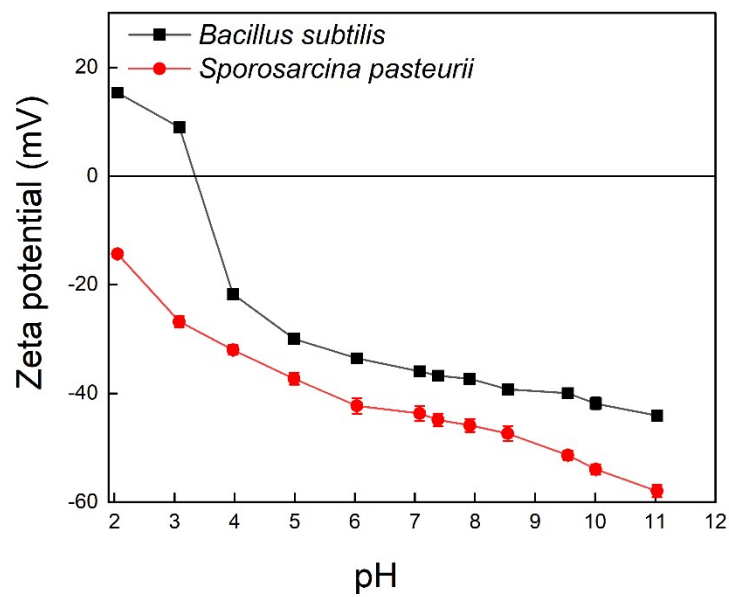


Figure S8. Surface charge on *S. pasteurii* (red circle) and *B. subtilis* (black square). Plot shows zeta potential (mV) in TSB medium at different pH values (2-11). Error bars are the standard error of the mean, n = 3.



336

337

338

339

340 **Figure S9.** Urea uptake by *S. pasteurii* cultivated using commercial urea (black square) and
341 cow urine-based urea (red circle) in CaCl_2 solution. Plot shows urea concentration in CaCl_2
342 solution over time. Error bars are the standard error of the mean, $n = 3$.

343

344

345

346

347

348

349

350

351

352

353

354

355

356

357

358

359

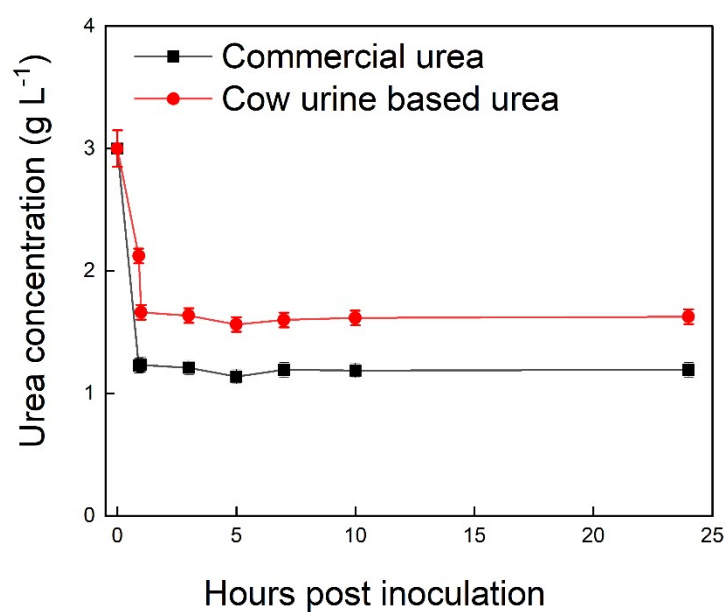
360

361

362

363

364



365

366

367

368

369 **Supplementary References**

370 **THIS REFERENCE NUMBERS ARE NOT THE SAME AS IN THE MAIN MANUSCRIPT**

- 371 1 D. E. Garrett, *Handbook of Lithium and Natural Calcium Chloride*, 2004, 1–476.
- 372 2 M. G. Franco, Y. J. Peralta Arnold, C. D. Santamans, R. L. López Steinmetz, F. Tassi, S.
- 373 Venturi, C. B. Jofré, P. J. Caffé and F. E. Córdoba, *Journal of South American Earth*
- 374 *Sciences*, 2020, **103**, 102742.
- 375 3 S. Xu, J. Song, Q. Bi, Q. Chen, W.-M. Zhang, Z. Qian, L. Zhang, S. Xu, N. Tang and T. He,
- 376 *Journal of Membrane Science*, 2021, **635**, 119441.
- 377 4 A. Somrani, A. H. Hamzaoui and M. Pontie, *Desalination*, 2013, **317**, 184–192.
- 378 5 W. T. Stringfellow and P. F. Dobson, *Energies*, DOI:10.3390/en14206805.
- 379 6 B. Sanjuan, R. Millot, Ch. Innocent, Ch. Dezayes, J. Scheiber and M. Brach, *Chemical*
- 380 *Geology*, 2016, **428**, 27–47.
- 381 7 F. A. Setiawan, E. Rahayuningsih, H. T. B. M. Petrus, M. I. Nurpratama and I. Perdana,
- 382 *Geothermal Energy*, 2019, **7**, 22.
- 383 8 C. F. Baspineiro, J. Franco and V. Flexer, *Science of The Total Environment*, 2020, **720**,
- 384 137523.
- 385 9 J. Yang and Y. Wang, *Efficiency and Characteristics of MICP in Environments with Elevated*
- 386 *Salinity, Diminished Oxygen, and Lowered Temperature: A Microfluidics Investigation*,
- 387 2024.
- 388 10 L. Hu, H. Wang, P. Xu and Y. Zhang, *Water Research*, 2021, **190**, 116753.
- 389 11 V. C. E. Romero, K. Llano and E. J. Calvo, *Electrochemistry Communications*, 2021, **125**,
- 390 106980.
- 391 12 C. H. Díaz Nieto, N. A. Palacios, K. Verbeeck, A. PrévotEAU, K. Rabaey and V. Flexer, *Water*
- 392 *Research*, 2019, **154**, 117–124.
- 393 13 K. Zhao, B. Tong, X. Yu, Y. Guo, Y. Xie and T. Deng, *Chemical Engineering Journal*, 2022,
- 394 **430**, 131423.
- 395 14 W. Ding, J. Zhang, Y. Liu, Y. Guo, T. Deng and X. Yu, *Chemical Engineering Journal*, 2021,
- 396 **426**, 131689.
- 397 15 X. Lai, P. Xiong and H. Zhong, *Hydrometallurgy*, 2020, **192**, 105252.
- 398 16 A. Alsabbagh, S. Aljarrah and M. Almahasneh, *Minerals Engineering*, 2021, **170**, 107038.
- 399 17 D. Liu, Z. Zhao, W. Xu, J. Xiong and L. He, *Desalination*, 2021, **519**, 115302.

400

401

402

403