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Treatment of (oilfield) brine via CO_2 mineralization for direct lithium extraction

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Produced water from subsurface oil/gas development, generally termed oilfield brine often contains elevated level of lithium (Li), in addition to high concentrations of Na, K, Ca, Mg and Sr. One such example is the flowback and produced water (FPW) from hydraulic fracturing operations of the Montney tight gas reservoirs in the northeast BC, Canada. On average, ion concentrations (mg/L) for Montney FPW in the Dawson Creek area are 57.7 Li^+, 65,400 Na^+, 17,500 Ca^{2+}, 1,780 Mg^{2+}, 1,280 Sr^{2+}, and 135,400 Cl^-, respectively. The elevated lithium makes this type of oilfield brine an important unconventional source for lithium supply via direct lithium extraction (DLE); however, its extraction faces critical challenges associated with the abundant co-occurrences of other alkali and alkaline elements, causing fouling of and/or competing for the proper function of DLE materials.

This study investigated an integrated CO_2 mineralization procedure using high salinity Li-rich brine to capture CO_2 from flue gas, produce carbonate solids to store CO_2, and generate a Mg/Ca/Sr-depleted brine for DLE operations. A Montney FPW was used for various combination of pH-swing process and CO_2 mineralization treatment using 15% CO_2 flue gas (balanced with N_2). Carbonation of alkaline elements visibly commenced instantly with flue gas streamed in at 1 L/min and brine pH controlled between 8.5-10.5. The amounts of precipitated solids increase with increasing duration of flue gas injection, while the concentrations of Ca, Sr and Mg in the brine decrease over time accordingly but at different kinetics. Although Na and K in the brine were generally not subjected to carbonation during the Mg/Ca/Sr depletion, Li can be co-precipitated with or adsorbed in the precipitated Ca/Sr/$MgCO_3$ solids at later stage, leading to its loss from the residual brine if the pH-swing and carbonation treatments were not carried out properly (Fig. 1). When adequately executed, the proposed procedure can achieve >90% preservation of lithium in the treated brine with Mg, Ca and Sr depleted to <10 mg/L level. Results from DLE using ionic liquid indicate the CO_2-mineralization treated FPW gives rise to >90% extraction of lithium, much higher than that for raw FPW (Table 1).

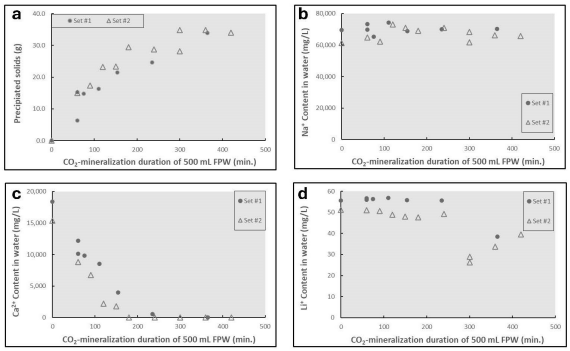

Figure 1. Cross plots showing variation in the amounts of precipitated solids and concentrations of various alkali and alkaline elements in a Montney flowback and produced water (FPW) over the duration of two sets of CO_2 mineralization experiments using 15% (v/v) CO_2 flue gas as carbon source and ammonia for pH control in the 8.5–10.5 pH range.

Table 1. Results of direct lithium extraction (DLE) using ionic liquid method on a raw Montney flowback and produced water (FPW) and its CO_2 mineralization treated derivatives

Brine sample type		pH	Concentrtaion in brine (mg/L)						Li-extraction efficiency (%)
			Na	K	Ca	Mg	Sr	Li	
Raw FPW	pre-DLE	4.59	66,814.5	2,227.8	17,981.1	1,907.5	1,551.2	56.1	
	post-DLE		63,511.7	2,227.8	14,763.6	1,518.8	1,354.0	54.7	2.5
4-hour CO_2 mineralization, NaOH for pH control	pre-DLE	9.14	90,582.0	2,322.0	4,359.0	1.9	1,263.9	54.3	
	post-DLE		86,642.3	2,322.0	3,708.4	0.1	1,202.2	53.1	2.2
6-hour CO_2 mineralization, NaOH for pH control	pre-DLE	9.12	112,843.0	2,371.9	1.6	8.4	0.2	52.6	
	post-DLE		111,631.4	2,371.9	0.2	0.2	0.2	3.7	93.0
	post-DLE		112,361.5	2,371.9	0.3	0.2	0.1	3.0	94.3