Geochemical characterization of lithium deposition in fossil energy wastes

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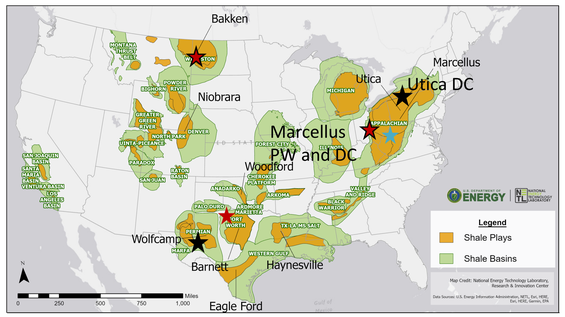
Background and Study Goal

Lithium is a critical mineral used in rechargeable batteries for electric vehicles (EVs) and future modernization of electric grids with sensitive supply chains that are subject to volatility[1]. Therefore, methods to recover lithium from domestic unconventional sources are actively being pursued in the United States. Herein, we report on the lithium recovery potential from four fossil energy waste feedstocks: oil and gas produced waters (PW in red star, n > 200) from Marcellus, Bakken and Permian basins ; oil and gas drill cuttings (DC in black star, sample number n = 16 as); coal byproducts (n>20), such as acid mine drainage (AMD) and passive AMD treatment solids (AMD solids) from Appalachian coal basin in blue star.



Produced waters from Oil and Gas production fields

Solids from Shale Gas production and Coal Mine Drainage

Solid wastes from fossil energy development
- Shale Gas development (hydraulic fracturing)
- Acid Mine Drainage (AMD)

Bulk solid Characterization
- 17 drill cuttings and core
- About 20 AMD solids
- Elemental composition: ICP-MS, TOC content
-Mineralogy: XRD

Elemental Distribution and Mobility
- Sequential extraction
- Utilize Different Extractants to targe solid fractions that are water soluble, exchangeable (bond to clay), carbonates, Fe/Mn oxides, sulfides and organics and non-extractable residuals.

Future Projects
- Green-roof soil amendment potential
- Explore targeted extraction of lithium

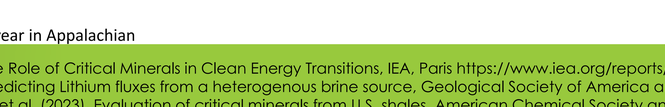
Coal | AMD | AMD treatment | AMD solids

18,000 tons/year in Appalachian

Characterization and Estimates of Lithium in U.S. Oil and Gas Produced Water (PW)[2]

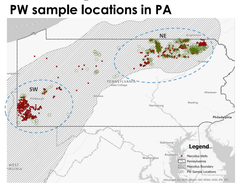
Lithium geochemistry in U.S. PW (n>200)

- **Up to 300mg/L Li was found in Marcellus shale produced waters, comparable to the dominant source of Li mining, the brine ponds in Chile (1000mg/L)**
- **At the same total dissolve solid (TDS) level, Marcellus Shale waters contain more Li compared to Bakken Shale and Permian Basin waters**
- **Marcellus shale brine contain high percentages of Ca and Mg, whereas Permian basin brine contain up to 89% Na.**



Pennsylvania PW Lithium Mass estimates

PW sample locations in PA



Exponential decline curve equation to estimate PW volume

$$PW = \int_0^{10} (Qi * e^{-Dt} + L)\, dt$$

Q_i is the initial production rate

D is the rate of decline

t is the time after the well SPUD date

L is the lift factor.

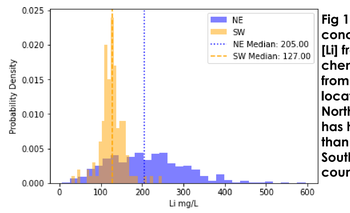


Fig 1. Li concentration [Li] from 654 chemical reports from 553 well locations Northeastern PA has higher [Li] than Southwestern counter part.

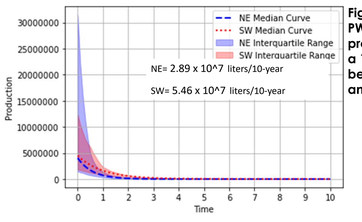


Fig 2. Rage of PW volumes produced over a 10-yr span between NE and SW PA

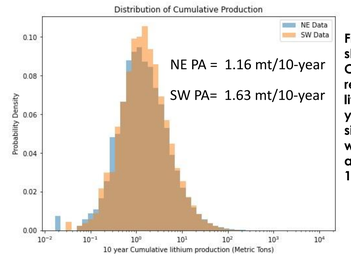


Fig 3. Histogram showing Monte Carlo simulation results of total lithium mass yields from a single Marcellus well in either NE and SW PA over a 10-yr time frame

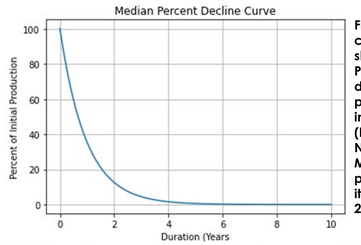


Fig 4. Decline curve plot showing median PW production decline as a percent of the initial production (IP) volume (t = 0). Note, the median Marcellus well produces ~20% of its IP within the first 2 years.

- **Regional variations in median Lithium concentrations(Fig 1.) and PW volume (Fig 2.) between NE and SW PA.**
- **MLE Lithium mass yield of SW PA is marginally higher than NE PA (1.63 mt/10-year and 1.16 mt/10-yr respectively; Fig 3.)**
- **The majority of lithium mass yield from a Marcellus well is produced in the first 2 years (Fig. 4)**

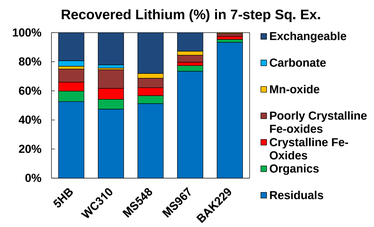
Characterization Lithium in U.S. Shale Drill Cuttings[3]

- **Sample Heterogeneity from different shale basins with Li up to 72mg/kg.**
- **Bak-229 with high Li is a high TOC and high pyrite content samples.**

Table 1. Select critical mineral contents for drill cuttings from different US basins (mg/kg).

Sample	Ba	V	Cr	Ni	Cu	Zn	Li	REE	Rb	Sr	TOC
MS-5HA	30167	150	84	70	36	79	24	168	131	766	2
MS-5HB	51723	917	80	363	229	1691	4	204	89	**1227**	10
MS-5HC	48515	250	44	97	66	99	BDL	160	74	1125	3
MS-5HD	47938	824	85	228	139	561	BDL	159	116	1077	7
MS-476	1302	382	104	216	177	357	18	235	**225**	157	4.2
MS-505	1010	465	74	249	180	116	BDL	**239**	135	134	7.8
MS-548	790	1165	104	517	282	1671	8	232	94	122	13
MS-967	488	1112	97	518	**294**	62	6	153	92	152	12
BAK-229	188	**1575**	131	**654**	125	284	**72**	169	119	52	**19**
BAK-254	207	65	73	BDL	BDL	BDL	23	146	65	79	4
BAK-300	110	392	56	249	65	**2567**	5	87	61	39	8
WC-310	2385	132	201	103	41	452	BDL	184	126	279	5.6
WC-400	947	148	188	99	34	222	BDL	130	75	515	4
WC-460a	9561	123	185	101	41	197	BDL	183	127	330	5.5
WC-460b	2836	113	178	102	38	285	BDL	179	103	288	5.4
WC-480	1592	138	**206**	105	46	189	BDL	217	142	402	4.9
Utica	**76271**	53	45	33	67	106	BDL	123	52	915	11.1

- **Highest recovered Li in exchangeable fraction (e.g., clay phases)**
- **Up to 53% recovery in low Li concentration shale (WC310)**
- **7% recovery in high Li concentration shale (Bak229)**



Lithium in Acid Mine Drainage Treatment solids[4]

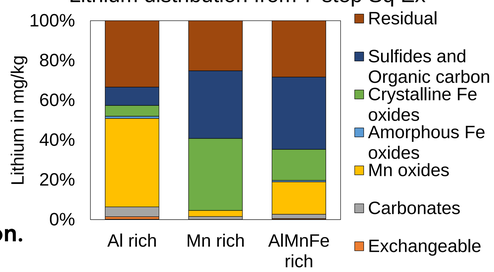
- **Lithium content in AMD solids is reasonably high (up to 440 mg/kg), comparable to Australian lithium mining ore (~400mg/kg)**
- **AMD solids also contain high contents of REE, Co, Ni and Zn for potential co-extraction**

Table 2. Select elemental contents for AMD solids

	C	S	Al	Si	Fe	Mn	Ca	REY	Li	Co	Ni	Cu	Zn
Al rich solid	2%	2%	**18.0%**	19.3%	2.1%	0.1%	1.2%	1113	**38**	22	50	106	315
MnCa rich solid	4%	ND	3.5%	6.1%	0.5%	**18.1%**	16.8%	1590	**108**	6026	8889	89	13585
AlMnFe rich solid	1%	1%	**15.4%**	9.7%	**5.2%**	**8.5%**	2.8%	1900	**440**	2059	3002	518	5812

Unit: wt% for major elements and mg/kg for trace elements

Al-rich solid | MnCa-rich solid | AlMnFe-rich solid



- **67%-75% lithium recoverable Li from AMD solids**
- **Li recovered from steps primarily targeting Mn oxides, crystalline Fe oxides, and sulfides and organic carbon.**

Feedstock	Li content	Li extractability	Estimated Li reserve
Produced waters	Up to 300 mg/L	Complete	0.16 mt/yr in regional PA
Drill cuttings	Up to 72 mg/kg	Low	Unknown
AMD solids	Up to 440 mg/kg	High	0.2-4513 kg/yr in Pennsylvania

References: 1: IEA (2021), The Role of Critical Minerals in Clean Energy Transitions, IEA, Paris https://www.iea.org/reports/the-role-of-critical-minerals-in-clean-energy-transitions, License: CC BY 4.0
2: J. Mackey et al. (2023), Predicting Lithium fluxes from a heterogenous brine source, Geological Society of America annual meeting, Oct 2023, Pittsburgh, PA
3. M. Barczok, M. Stuckman, et al. (2023), Evaluation of critical minerals from U.S. shales. American Chemical Society annual meeting 2023, San Francisco, CA, Aug 13-17, 2023.
4. Mengling Stuckman, "Chemically Informed critical mineral recovery from acid mine drainage treatment solids", DOE Resource Sustainability review meeting, Pittsburgh, PA Oct 25-27, 2022

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