



# Characterizing cobalt sequestration in manganese-rich coal mine drainage treatment solids

Camille Schaffer<sup>1,2</sup>, Mengling Stuckman<sup>1</sup>, Christina Lopano<sup>1</sup>, Rosemary Capo<sup>2</sup>, Brian Stewart<sup>2</sup>, Bhandari, Gita<sup>3</sup>

<sup>1</sup>US Department of Energy, National Energy Technology Laboratory, Pittsburgh PA;

<sup>2</sup>University of Pittsburgh, Dept. of Geology & Environmental Science

<sup>3</sup>Leidos Research at National Energy Technology Laboratory

## Extended Abstract

Cobalt (Co) is a critical metal essential to the clean energy transition due to its use in rechargeable batteries (Sanoiva et al. 2023). Cobalt demand is concurrently expected to increase; an estimated 31,820 t of Co would be required to electrify 20% of the vehicles in the USA (Rozelle et al 2021), and, as of 2023, apparent consumption of Co in the United States was 6,400 t with a net import reliance of 67% (U.S. Geological Survey 2024). Alternative, domestic sources of Co are being explored because the majority of the global Co supply is extracted using artisanal mining methods that can be destructive to human health (Kara 2023).

Coal mine drainage (CMD) solids, a continuous waste stream from passive treatment systems in Appalachia, USA have been identified as a possible sustainable feedstock for Co. Up to 60 t of Co per year are discharged from CMD in Pennsylvania alone, which could account for over 10% of the 500 t produced by the U.S. in 2023 (U.S. Geological Survey 2024, Rozelle et al 2021). Co is naturally leached from dispersed Co-bearing units by acidic CMD (pH < 5) and during treatment, Co may be efficiently concentrated as a sludge (Hedin et al. 2020). CMD solids are geochemically diverse and consist of iron, aluminum, and manganese (Mn)-rich oxy/hydroxides. Mn-rich phases have been shown to contain high Co concentrations, up to 6,000 mg/kg, and bear comparison to low-grade Co ores (e.g. 2,000–10,000 mg/kg) (Hedin et al. 2020). CMD is sulfate-rich, and during treatment, CMD solids are accumulated in limestone beds as precipitates over a wide pH range, but Co sorption mechanisms have not been studied under these conditions.

Experimental exploration of abiotic Co sorption mechanisms on different birnessite ( $\delta$ -MnO<sub>2</sub>) structure types (hexagonal H-birnessite and triclinic Na-birnessite) that are commonly found in Mn-rich CMD solids (i.e. Tan et al. 2010) offers insights into Co retention mechanisms in CMD treatment systems. This study investigates Co adsorption on synthesized birnessites over a wide pH range and in sulfate-rich solution to simulate CMD treatment conditions. Langmuir and Freundlich adsorption isotherms of Co at pH values of 3.5, 4.5, and 6.5 at 25 °C onto Na- and H-birnessite were generated. Cobalt concentrations in supernatants were determined by inductively coupled plasma-mass spectroscopy (ICP-MS) and chelation ion chromatography developed by Miller et al. (2022). Mineralogy and morphology of pre- and post-adsorption experiment solids characterization by X-ray diffraction and scanning electron microscopy will be presented.

We hypothesized 1) cobalt adsorption would peak with increasing pH (i.e. Tonkin et al. 2004); and 2) the presence of sulfate would enhance adsorption of cobalt onto birnessite, as has been shown with rare earth elements (REEs) and Co on Fe-rich phases (Swedlund et al. 2003, Lozano et al. 2019). Table 1 includes the isotherm model results of the cobalt adsorption experiments at different pH; both isotherms produced similar fits; additional experiments at pH 3.5 for H-birnessite and pH 6.5 for both minerals will be collected due to variation in replicate experiment results and low R<sup>2</sup>. Preliminary results show that Co adsorption peaked at pH 4.5 in both structures, although the maximum adsorption capacity, the maximum quantity of Co adsorbed onto the sorbent surface

**Table 1** Freundlich and Langmuir Isotherm model results of cobalt adsorption experiments onto triclinic Na-birnessite and hexagonal H-birnessite at pH 3.5, 4.5, and 6.5;  $n$  and  $k_F$  are Freundlich adsorption strength and potential constant, respectively, in general,  $0 < n < 1$  demonstrate a thermodynamically favorable adsorption. The  $k_L$  term is a Langmuir constant representing the affinity of binding sites (L/mg),  $q_{max}$  is the maximum adsorption capacity of sorbent (mg/g)

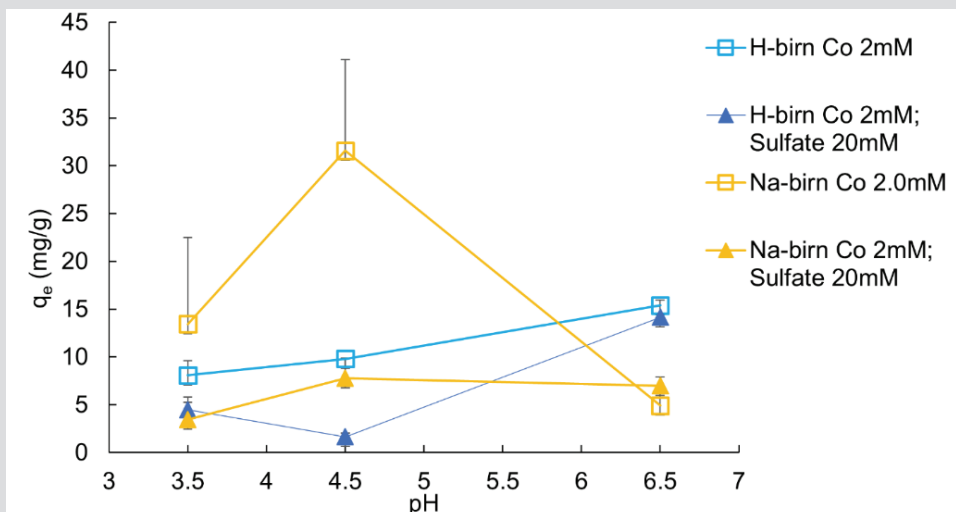
Mineral	pH	Freundlich			Langmuir		
		$k_F$	$n$	$R^2$ (adj.)	$k_L$ (L/mg)	$q_{max}$ mg/g	$R^2$ (adj.)
HBirnessite	3.5	1.99	0.29	0.41			0.47
	4.5	0.58	0.68	0.93	0.002	71.5	0.9
	6.5	8.75	0.1	0.8	0.35	18	0.56
Na'birnessite	3.5	1.7	0.37	0.92	0.04	12.6	0.89
	4.5	1.85	0.65	0.93	0.005	131	0.94
	6.5			-0.05			-0.15

produced by Langmuir isotherms, of the triclinic birnessite (131 mg Co/g sorbent) was twice as high as that on the hexagonal structure (71.5 mg Co/g sorbent) (Table 1).

Interestingly, sulfate decreased the  $q_e$ , the amount of Co adsorbed per gram of sorbent (mg/g), on both H-birnessite and Na-birnessite at pH 3.5 and 4.5 but had a modest effect at pH 6.5 (Fig. 1). Sulfate was reported to limit the growth of synthesized birnessites by adsorbing onto edge sites of the octahedral sheet, but also increased the quantity of Mn(III) in the octahedral sheets (i.e. Wang et al. 2016), which oxidizes cobalt upon adsorption before incorporation. Further characterization on how quantities of Mn(III) in the octahedral sheets change in the presence of sulfate and cobalt at different pH ranges could be explored. These experiments suggest that cobalt sulfate complexes and pH of CMD, as well as the Mn-oxide mineral structures present in treatment beds, will affect cobalt

These experimental results can serve as calibration points for equilibrium and kinetic modeling approaches such as PHREEQ-N-AMDTreat+REYs (Cravotta 2021) that are critical for developing effective and implementable remediation processes and to better inform future Co recovery efforts from CMD solids.

**Keywords:** Critical minerals, cobalt, adsorption



**Figure 1** Amount of cobalt adsorbed ( $q_e$ ) at pH 3.5, 4.5, and 6.5 to H-birnessite (H-birn) and Na-birnessite (Na-birn) in solution with 2.0 mM Co (117 mg/L) compared to 2.0 mM Cobalt + 20 mM  $SO_4$  (1921 mg/L). Each point is the average  $q_e$  and error bars represent standard deviation

## References

- Cravotta CA (2021) Interactive PHREEQ-N-AMDTreat water-quality modeling tools to evaluate performance and design of treatment systems for acid mine drainage, *Appl. Geochem.* 126, 104845.
- Hedin BC, Hedin RS, Capo RC, Stewart BW (2020) Critical metal recovery potential of Appalachian acid mine drainage treatment solids. *Int. J. Coal Geol.* 231, 103610. <https://doi.org/10.1016/j.coal.2020.103610>
- Kara S (2023) Cobalt Red: How the Blood of the Congo Powers Our Lives. GRIFFIN, 2023.
- Lozano A, Ayora C, Fernández-Martínez A (2019) Sorption of rare earth elements onto basaluminite: The role of sulfate and pH. *Geochim. Cosmochim. Acta* 258, 50-62. <https://doi.org/10.1016/j.gca.2019.05.016>.
- Miller JD, Stuckman MY, Means N, Lopano C, Hakala JA (2022) Determination of transition metal ions in fossil fuel associated wastewaters using chelation ion chromatography. *J. Chromatogr. A* 1668, 462924. <https://doi.org/10.1016/j.chroma.2022.462924>
- Rozelle P, Mamula N, Arnold B, O'Brien T, Rezaee M, & Pisupati S (2021). Secondary Cobalt and Manganese Resources in Pennsylvania: Quantities, Linkage with Mine Reclamation, and Preliminary Flowsheet Evaluation for the U.S. Domestic Lithium-Ion Battery Supply Chain.
- Savinova E, Evans C, Lèbre, Stringer M, Azadi, & Valenta RK (2023) Will global cobalt supply meet demand? The geological, mineral processing, production and geographic risk profile of cobalt. *Resour. Conserv. Recycl.* 190, 106855. <https://doi.org/10.1016/J.RESCONREC.2022.106855>
- Swedlund PJ, Webster JG, Miskelly GM (2003) The effect of SO<sub>4</sub> on the ferrihydrite adsorption of Co, Pb and Cd: ternary complexes and site heterogeneity. *Appl. Geochem.* 18, 1671-1689. [https://doi.org/10.1016/S0883-2927\(03\)00082-9](https://doi.org/10.1016/S0883-2927(03)00082-9)
- Tan H, Zhang G, Heaney PJ, Webb, SM, & Burgos, WD (2010) Characterization of manganese oxide precipitates from Appalachian coal mine drainage treatment systems. *Appl. Geochem.* 25, 389399. <https://doi.org/10.1016/J.APGEOCHEM.2009.12.006>
- U.S. Geological Survey (2024) Mineral commodity summaries 2024: U.S. Geological Survey, 212 p., <https://doi.org/10.3133/mcs2024>
- Wang, Q., Liao, X., Xu, W., Ren, Y., Livi, K. J., & Zhu, M. (2016) Synthesis of birnessite in the presence of phosphate, silicate, or sulfate. *Inorg Chem.* 55, 10248–10258. <https://doi.org/10.1021/acs.inorgchem.6b01465>