Environmental Nuisance or Untapped Resource? Reimagining Potash Mining Tailings and Brines as Valuable Materials Using Zeolites

Brandon W. Stoner, Nicola J. Harris, Wonjae Chang Department of Civil, Geological and Environmental Engineering – University of Saskatchewan, Saskatoon, Saskatchewan, Canada Luverne E.W. Hogg ZMM Canada Minerals Corp., Peachland, British Columbia, Canada



ABSTRACT

We challenge the traditional perception of potash mining byproducts as environmental nuisances which are expensive to monitor and maintain. We propose that potash byproducts can be converted into valuable materials using zeolites. We analyze the mineralogical composition of potash byproducts and assess the major ion content. Results indicate the composition was primarily halite (NaCl) with high elemental Na⁺ and Cl⁻, although significant sylvite (KCl) and K⁺ content remained. Four different types of zeolite adsorbents are assessed as a medium for recovering the residual K⁺ in a cost-effective manner. Batch mixing experiments proved the feasibility of effective K-recovery from diluted potash brines. Following K-recovery the K-enriched (K-form) zeolites are reused as soil amendments for enhancing bioremediation. The benefits provided by the K-form zeolites to indigenous microorganisms are summarized.

RÉSUMÉ

Nous remettons en question la perception traditionnelle que les produits dérivés de l'extraction de la potasse doivent être considérés comme des nuisances environnementales coûteuses à surveiller et à limiter. Nous proposons qu'il est possible de convertir ces sous-produits en matériaux de valeur économique. Nous analysons la composition des sous-produits dans l'eau de production de potasse par diffraction des rayons X et par la teneur en ions majeurs. Les résultats révèlent que la composition est principalement de l'halite (NaCl) avec une teneur élevée en Na⁺ et Cl⁻, bien que de la sylvite (KCl) avec une teneur élevée en K⁺ résiduel. Quatre différents minéraux zéolithiques traités sont proposés comme moyen de récupérer le K⁺ résiduel de manière rentable. Une méthode de mélange par lots a permis une récupération efficace du K⁺ à partir d'eau produite salée de potasse diluée. Après l'adsorption du K⁺, les zéolithes riches en potassium (K) peuvent être réutilisées comme amendements pour sol afin d'améliorer la bioremédiation. Les avantages offerts par les zéolithes de riches en K sont expliqués.

1 POTASH MINING IN CANADA

The term 'potash' refers to any mineral, ore, salt, or processed product that is highly soluble and possesses a high elemental potassium (K) content (Jena 2021; Orris et al. 2014). Potash is primarily used to source K in agricultural fertilizers, although other industrial uses include water treatment, animal feed supplementation, cement additives, and textile manufacturing (Rawashdeh et al. 2016). The mineralogical composition of potash ore bodies includes sylvite (KCl), kainite (KMg(SO₄)Cl·3H₂0), langbeinite (K₂SO₄·2MgSO₄), carnallite (KCl·MgCl₂·6H₂0), and/or polyhalite (K2CaMg(SO4)4.2H20) minerals (Jena 2021). Common gangue materials associated with potash ore include halite (NaCl), insoluble sands, silts, clays, and dolomite (Reid & Getzlaf 2004). The geological occurrence of potash ore is enclosed, subsiding marine basins with arid climates and limited water influx (Luo et al. 2017; Orris et al. 2014). The arid climate results in evaporation rates exceeding the fresh and saltwater influx, resulting in the deposition of the salts which originated in the seawater. The cyclical accumulation of salts from periodic seawater influx-evaporation cycles form extensive potash deposits

(Orris et al. 2014). This is why potash deposits are colloquially referred to as 'evaporites' or 'evaporite deposits'.

Canada is the world's largest potash producer, supplying an estimated 33% of the planet's resource (Paul et al. 2017). Canada's recoverable potash ore reserves are estimated at 4.5 billion metric tons, which translates to 1.1 billion tons of potassium oxide (K2O) equivalent (Jasinski 2023). The largest potash deposit in Canada is the Devonian Elk Point Basin, which spans from southeastern Alberta through southwestern Manitoba, and extends southward into the northern regions of Montana and North Dakota (Luo et al. 2017). Saskatchewan is the heart of the Elk Point Basin, and hence potash mining is a significant component of the province's economy. Saskatchewan's potash sector comprises an 11% of the provincial GDP, or 8.3 billion dollars annually, while directly sustaining at least 6000 jobs in the province (Stroeder, 2022; SMA 2021). Further, the net production of potash mining in Canada is rising steadily, as exports increased from an estimated 9.5 million metric tons of K₂O equivalent in 2010 to 16 million metric tons in 2022 (Orris et al. 2014; Jasinski 2023). Canadian potash production is projected to expand an

additional 3 million tons of K₂O equivalent by 2025, largely driven by bans on Russian and Belarusian exports which have created a worldwide market shortage of the resource (Jasinski 2023).

There are 11 active potash mines in Saskatchewan, 8 of which are conventional mines and 3 are solution mining operations (Harris et al. 2023; SMA 2021). Briefly, conventional mining involves extracting potash ore from the subsurface and transporting it to the surface for processing. In contrast, solution mining requires drilling a series of injection wells into the subsurface, injecting heated solvents to dissolve the potash minerals into a slurry, and transporting the slurry to the surface for further processing (Jena 2021). Solution mining is considered advantageous over conventional mining as it is more cost effective, has a smaller environmental impact, requires less surface area for mining, and can typically achieve deeper mining depths (Jena 2021). Regardless of what method is employed, potash mining companies strive to continuously improve their resource extraction efficiency and reduce the volume of byproducts produced during the mining and processing processes.

As with any mining operation, potash processing and refinement generates significant volumes of byproducts in the form of granular tailings and liquid brines. These potash byproducts accumulate in the tailings management area throughout the mine's lifespan and have long been perceived as a nuisance that cost mining companies considerable resources to monitor and maintain. With these facts in mind, we pondered a series of research questions with the intent of changing the perception on potash byproducts. How much K remains in the potash byproducts? How can this residual K be recovered in a cost-effective manner? What comes next after K-recovery? Can the byproducts be recycled or transformed into valuable materials? To answer these questions, we begin by closely examining and characterizing the potash mining byproducts.

2 CHARACTERIZING POTASH MINING BYPRODUCTS

2.1 Materials and Methods

Coarse and fine tailings samples were obtained from the mill of a conventional potash mine in Saskatchewan, along with a brine sample from one of the retention ponds. Samples were brought back to the lab and oven dried for one week at 65°C. The weeklong drying process completely dried the granular tailings and evaporated all water content from the brine samples, leaving only salt crystals behind. A mortar and pestle were used to grind the samples into a fine powder, which was subsequently packed into 0.034" polyimide tubing, sealed with Loctite® 454[™] Prism[®] Instant Adhesive, and mounted onto a sample holder. The prepared samples were analyzed via x-ray diffraction (XRD) at a wavelength of 0.6888 Å, with a detector distance of 250.011 mm, using GSAS-II software, as outlined in Toby & Von Dreele (2013). A lanthanum hexaboride standard was used to calibrate the XRD

patterns, which were linearized using a blank polyimide tube to compensate for background interference. Match! 2 software was used to match recorded XRD patterns to reference patterns within the Crystallography Open Database, identifying mineral phases in the samples (Downs & Hall-Wallace 2003; Grazulis et al. 2009; Grazulis et al. 2012).

Small subsamples' of the tailings and brine samples were sent to the Environmental Analytical Laboratory at the Saskatchewan Research Council and analyzed for chemical constituents. Major ions were identified by inductively coupled plasma optical emission spectrometry, and chloride was detected using the ferricyanide method (Harris et al. 2023). For brevity of this paper, pH, total alkalinity, bulk density, carbon, and nutrient content were omitted, but are included in Harris et al.'s manuscript (2023), along with a more comprehensive description of the methodologies.

2.2 Results

The XRD analysis conducted by Harris and co-workers (2017) revealed the mineralogical composition and proportion of each sample type (coarse tailings, fine tailings, and evaporated brine). Figure 1 shows the XRD diffraction spectra for one of the evaporated brine samples (Harris 2017). The results identified halite (NaCl) as the predominant mineral of all three sample types, accounting for 43.56-76.80% of peak area. Sylvite (KCl) was the second most common mineral phase, accounting for 13.74-34.15% of peak area. These two mineral phases accounted for 69% of peak intensity for all three sample types. Fine tailings analysis additionally identified dolomite, anhydrite, and quartz to account for 94.90% of peak intensity.

The results of the major ion analyses are presented in Table 1. The three predominant ions identified were Na⁺, K⁺ and Cl⁻, which is in alignment with the XRD analysis where halite (NaCl) and sylvite (KCl) were identified as the prevailing minerals within each sample type. The relative proportion of each cation remained uniform throughout each sample type. In general, there was a greater proportion of every major ion in the fine tailings, compared to the coarse tailings, except for Na⁺ and Cl⁻. Additionally,

Table 1. Major ion content of potash byproducts

lon	Brine (mg/L)	Coarse Tailings (mg/Kg)	Fine Tailings (mg/Kg)
Na⁺	89500 ± 200	379000 ± 6500	160000 ± 2000
K⁺	58200 ± 300	$\textbf{33200} \pm \textbf{3900}$	132000 ± 8000
Ca ²⁺	2000*	$\textbf{2570} \pm \textbf{90}$	32500 ± 3000
Mg ²⁺	1800*	1330 ± 30	24100 ± 2100
Cl	219000 ± 1000	700000 ± 20000	460000 ± 3200
SO42-	1800*	3900 ± 200	28700 ± 1600

* Standard error is 0. Table modified from Table 1 of Harris et al. (2023).



Figure 1. X-ray diffraction (XRD) spectra showing evaporated brine mineralogy. Figure unmodified from its original source (Figure 3-5 of Harris 2017).

the heavy metal contents of potash byproducts are summarized in Table 2 of the Appendix.

2.3 Discussion

The mineralogy identified by XRD analysis was unsurprising, as were the major ions identified within each sample type. The abundance of halite and sylvite in potash byproducts is logical, given the target of the mining operation is the potash deposits of the Elk Point Basin. It is therefore intuitive that Na⁺ is far more abundant than K⁺ in all three types of byproducts, as K⁺ is the target of the mining operations and is mostly recovered during extraction and processing. The key finding of these analyses is that a significant quantity of residual K⁺ remains within all types of potash byproducts, answering our first research question.

3 APPLYING ZEOLITE MINERALS TO RECOVER RESIDUAL POTASSIUM FROM POTASH BYPRODUCTS

3.1 Introduction to Natural Zeolites as Cation Adsorbents

The next research question explored is how the residual K within potash byproducts can be recovered in a cost-effective manner? To begin answering this question, a

medium of recovering K⁺ ions must be contemplated. We propose applying natural zeolite minerals for this purpose. The term 'zeolite' refers to group of over 60 naturally occurring hydrated aluminosilicates (clay minerals) whose crystallographic framework pore space is occupied by exchangeable alkali/alkali-earth cations and water molecules (Delkash et al. 2015; Lin et al. 2013; Zhao et al. 2009). Zeolites possess a porous, three-dimensional crystal framework that is negatively charged due to substitution of Si⁴⁺ for Al³⁺ ions within the tetrahedral layer (Acosta-Herrera et al. 2021; Lin et al. 2013). The innate negative charge of the zeolite framework is balanced by the exchangeable cations within the pore spaces and is what induces the characteristic high cation exchange capacity of these minerals (Eroglu et al. 2017; Santiago et al. 2016). The unique crystallographic structure and resulting physicochemical properties of zeolites enable them to act as chemical adsorbents, and is why the minerals are commonly referred to as 'molecular sieves' (Yukselen-Aksoy 2010).

3.2 Zeolite Minerals' High Affinity for K⁺

Many experiments with zeolites explore the 'selectivity sequences' of individual minerals, where the selective preferences or affinity of a mineral towards a given suite of cations is ranked. Numerous studies report K⁺ at or near the top of their selectivity sequences, indicating that most zeolite minerals possess a naturally high affinity towards K⁺

ions (Pabalan & Bertetti 2001; Regmi & Boyer 2021; Siemens 2018; Tsitsishvili et al. 2017). The high ranking of K⁺ on the reported selectivity sequences, relative to other cations in solution, indicates that zeolites will selectively adsorb K⁺ over ions in solution. Siemens (2018) conducted a series of batch experiments with natural zeolites and diluted potash brines, observing a selectivity sequence of K⁺ > Na⁺ > Ca²⁺ \approx Mg²⁺. Multiple sources corroborate Siemens' work and report similar findings of zeolite minerals possessing a higher affinity for K⁺ than for Na⁺, Ca²⁺ or Mg²⁺ (Gibb et al. 2017; Rahimi et al. 2021; Wang & Peng 2010).

3.3 Application of Different Zeolite Minerals to Recover Residual K⁺ from Potash Byproducts

To investigate our proposed use of natural zeolites to recover residual K⁺, we investigated samples from the newly developed Juniper and TransCanada Zeolite Deposits. Both deposits are geographically located in southern British Columbia, and geologically located at surface, making these minerals low cost to mine and process. The TransCanada Zeolite Deposit is comprised of primarily of analcime (zeolite), along with less abundant mafic and clay minerals. In contrast, the Juniper Zeolite Deposit is a heterogeneous mixture of three zeolite minerals: chabazite, heulandite and phillipsite. The host rock (ore body) is crushed and sieved to a targeted particle size, creating bulk 'TransCanada Ore' (TC Ore) or 'Juniper Ore' (J Ore) which are ~ 50% zeolite purity. From here, the ores can optionally be run through a strong magnetic field, separating the non-magnetic zeolite minerals from the magnetic basaltic minerals. This process converts the 'raw' ore into high purity crystals (HPC), which are up to 98% zeolite crystals.

3.4 Approach

For the initial experiment, synthetic $KCI_{(aq)}$ solution was created by dissolving pure $KCI_{(s)}$ (ACS certified, Fisher Scientific) in ultrapure water. Synthetic $KCI_{(aq)}$ was selected for this experiment to understand how K⁺ ions are adsorbed by zeolite, without competition from other ions. Exactly 25 mL of $KCI_{(aq)}$ was added to a test tube along with 1g of either TC Ore, J Ore, TC HPC, or J HPC. Each experiment was conducted in triplicate. The test tubes were placed on an orbital shaker at 250 RPM for 24 hours. Next, the test tubes were centrifuged (3000 RPM for 10 minutes) allowing easy extraction of the supernatant via pipette. The K⁺ concentration of both the supernatant (C_{final}) and the initial $KCI_{(aq)}$ solution (C_{initial}) were measured using a fully calibrated potassium electrode (OrionTM). Lastly, the K-recovery of each zeolite was calculated using Equation 1.

$$K - Recovery (\%) = \left(1 - \left(\frac{c_{final}}{c_{initial}}\right)\right) \times 100 (\%)$$
^[1]

The next experiment upscaled the test tube-based Krecovery process into a larger, more mass-producible scale. An overhead stirrer (model # 38C830, 5-gallon capacity, 1/15 HP, CAFRAMO) was purchased for batch mixing of the zeolites with potash byproducts. The high ionic strength of undiluted potash brine resulted in the K⁺ concentration exceeding the upper detection limit of the electrode; hence the brine was diluted with deionized water by factor of 1:4, creating a 20% diluted brine. For this experiment, only J HPC samples were used, however several different particle sizes were investigated. Particle sizes reported for this experiment use standard sieve opening designations in millimeters (mm), with a particle size distribution reported. For example, the notation 2.00 - 2.38 indicates that the particles in this sample passed through the sieve with 2.38 mm openings but were retained by the sieve 2.00 mm openings.

A 500 mL beaker was used to mix 30g of J HPC with 60mL of 20% diluted brine. The overhead stirrer was set to 1500 RPM and left to mix for 2 hours. Following mixing, the beaker was left to settle for 12 hours, allowing gravitational settling of the suspended fine particles to the bottom of the beaker. The potassium concentration before and after mixing was measured and the K-recovery of the zeolite samples was calculated, using the methodologies described in the initial experiment.

3.5 Results

The results of the preliminary experiment are displayed in Figure 2. Of the 4 zeolite adsorbents tested, J HPC has the highest affinity for K⁺, exhibiting 82% K-recovery. TC HPC (47%) exhibited moderately better K-recovery than TC Ore (45%) and J Ore (39%), however there was no statistically significant difference between these 3 samples.



Figure 2. K-recovery from synthetic $KCI_{(aq)}$ using different types of refined zeolite adsorbents. This preliminary experiment identified J HPC as the best zeolite adsorbent for recovering K⁺ ions from solution.

The results of the up-scaled K-recovery experiment with varying J HPC particle sizes are shown in Figure 3. Generally, the coarser particles performed better than the finer particles (the x-axis is arranged from the coarsest particles on the left to the finest particles on the right). The optimal particle distribution identified was 0.84 - 2.00 mm with 70% K-recovery, followed by the 2.00 - 2.38 mm (56%) distribution. Nearly identical results were obtained for the 0.84 - 2.38 mm (49%) and 0.50 - 0.84 mm (50%) particle size distributions. A large drop-off in K-recovery was observed with the finer 0.18 - 0.84 mm (13%) and 0.11 mm (11%) distributions.



Figure 3. K-recovery as a function of J HPC particle size distribution. This experiment represents an up-scaled version of the initial experiment, where 20% dilute potash brines were used for mixing instead of synthetic $KCI_{(aq)}$. The x-axis is ordered from coarsest particles on the left to finest particles on the right. Generally, coarser particle distributions exhibited higher K-recovery than finer distributions.

3.6 Discussion

The key finding of the upscaled experiment was that in general, the coarser J HPC particle distributions yielded better K-recovery than the finer distributions. Clay mineral do not behave as discrete particles in water-mixing systems; instead, they form aggregates depending on the particle sizes, surface charges, structure, and the cohesiveness of the clavs. Furthermore, the chemistry of the mixing solution, mixing force, velocity gradient and duration of mixing influences the characteristics of clay aggregates. In our experiment, the smaller, highly reactive colloidal clay particles likely experienced colloid destabilization and coagulation, resulting in dense aggregates which experience a reduction in surface area and porosity in the selected mixing conditions. If large aggregates are 'loosely' formed with coarser particle size mixtures in the selected mixing conditions, there are likely significant voids among aggregated fractions, and hence a

larger effective surface area for ion-exchange and Krecovery. The mixing conditions (force, velocity gradient, and time) should be further optimized to simultaneously maximize K-recovery onto the zeolite particles and increase the efficiency of the process. With this methodology, we have demonstrated that applying natural zeolite adsorbents to recover the residual K from potash brines is feasible and can be completed in a cost-effective manner, answering the second research question.

4 K-FORM ZEOLITE AS A VALUE-ADDED SOIL AMENDMENT

4.1 Recycling K-form Zeolite

In the previous section we discussed recovering residual K from potash byproducts to create potassium-enriched (K-form) zeolites. But what comes next? Can these K-form zeolites be recycled as a valuable material? We propose applying the K-form zeolite as a soil amendment to enhance the bioremediation of petroleum-hydrocarbon (PHC) contaminated soils.

4.2 Bioremediation in Cold Climates

Bioremediation is considered a favourable option for the remediation of PHCs in contaminated soils due to its nondisruptive, in situ, and cost-effective methodologies (Rike et al. 2005; Yang et al. 2009). Despite the effectiveness in warm climates, bioremediation is limited in cold climates such as Canada, where the temperatures fall below 0°C for much of the year and effective remediation ceases (Chang et al. 2011). Low soil moisture, suboptimal pH, poor nutrient availability, frequent and severe temperature variations, and the presence of snow/ice/permafrost are all intrinsic properties of cold climate soils which inhibit effective bioremediation (Chang et al. 2011; Freidman et al. 2016; Yang et al. 2009).

4.3 How K-form Zeolite Benefits Bioremediation

The K-form zeolite will provide several benefits to indigenous microorganisms, improving the quality of contaminated soils in cold climates. Application of zeolite increases both the effective surface area and water retention in contaminated soils, both of which are key to extending the season of effective bioremediation (Kim et al. 2021). The increased water content is critical for partitioning PHCs from the inaccessible non-aqueous phase liquid (NAPL) phase into the bioavailable aqueous phase (De Jonge et al. 1997; Ghoshal et al. 1996). The Kform zeolite also serves as a microbial habitat, sheltering the microorganisms from freezing-related stresses. Additionally, the K-form zeolite provides nutrient stimulation, mainly K, to the microorganisms. The supplemented K is critical for microorganisms to regulate plasma membrane potential, adjust the cellular osmotic conditions, activate enzymes, maintain homeostasis, regulate gene expressions, adjust internal pH, and balance anions within the microbial cell (Ali et al. 2017; Corratgé-Faillie et al. 2010; Epstein 2003; Su et al. 2009). The

supplemented K also increases the salinity of the soil porewater, simultaneously lowering the freezing point depression and mitigating damage to microbial cells caused by growing ice crystals (Kim et al. 2021; Yang et al. 2009). The K-form zeolite soil amendment is not restricted to enhancing bioremediation in cold climates as it will also augment remediation programs in warmer climates; however, K-form zeolite has a set of physicochemical properties that make it uniquely suitable for cold climate applications.

4.4 Implications for the Potash mining Industry: The Circular Economy Concept

The obsolete linear economic model for any conventional mining operation involves mining a resource, processing it, while simultaneously accumulating large volumes of byproducts in the tailings management area. Limited thought was given to the byproducts in this cradle-to-grave approach. Given the rise in socially responsible investing initiatives across the globe (Ng & Zheng 2018) and demands to transparently disclose environment, social and corporate governance (ESG) performances, solutions to improve the sustainability of mining operations are in high demand. We envision our proposed use of zeolite-based K-recovery as a means of transcending the antiquated cradle-to-grave approach and creating a circular economy, as depicted in Figure 4. The approach provides monetary and social incentives by creating a tangible product (soil amendment) from potash byproducts while concurrently mitigating the environmental footprint of the mining operation, thus strengthening ESG performance. The Kform zeolite is recycled and reused as a value-added soil amendment which stimulates the bioremediation of PHCimpacted soils. Throughout this innovative process, additional materials from potash mining byproducts are recovered and reused in a cyclical cradle-to-cradle approach, satisfying a key requirement of a successful circular economy (Lèbre et al. 2017) in the contemporary mining sector.



Figure 4. The zeolite-based circular economy conceptual diagram (black) and its application to the potash mining industry (green). The proposed application of zeolite minerals transcends the antiquated linear economic approach by recovering residual K from potash byproducts. The K-enriched (K-form) zeolites are recycled and converted into a soil amendment that will enhance the

bioremediation of petroleum-hydrocarbon contaminated soils. The approach is an example of a circular economy where materials are recycled in a cyclical manner, eliminating any 'prescribed end' of raw materials.

5 CONCLUSION

We challenged the traditional perception of potash mining byproducts as environmental nuisances. A series of research questions were asked: How much K remains in the potash byproducts? How can this residual K be recovered in a cost-effective manner? What comes next after K-recovery? Can the byproducts be recycled or transformed into valuable materials? We answered these questions by assessing the mineralogical and elemental compositions of potash mining byproducts. Results revealed that potash byproducts were primarily composed of halite (NaCl) and enriched in Na⁺ and Cl⁻, although significant sylvite (KCI) and K⁺ were also present. Natural zeolites were introduced as feasible medium to recover this residual K⁺ in a cost-effective manner. Four different zeolite adsorbents were examined, with J HPCs exhibiting the highest affinity for K-recovery. An up-scaled batch mixing experiment proved the feasibility of effective K-recovery from diluted potash brines. Following K-recovery, we envision recycling the K-enriched (K-form) zeolite as an value-added soil amendment for enhancing the bioremediation of PHC-impacted soils. The benefits provided by the K-form zeolites were explained, along with our vision of this technology being implemented to create a circular economy in the contemporary potash mining industry.

6 REFERENCES

- Acosta-Herrera, A.A. et al. 2021. Competitive adsorption of pollutants from anodizing wastewaters to promote water reuse. *Journal of Environmental Management*, 293: 112877. doi:10.1016/j.jenvman.2021.112877.
- Ali, M.K. et al. 2017. Regulation of Inducible Potassium Transporter KdpFABC by the KdpD/KdpE Two-Component System in Mycobacterium smegmatis. *Frontiers in Microbiology*, 8: 570. doi:10.3389/fmicb.2017.00570.
- Chang, W. et al. 2011. Petroleum Hydrocarbon Biodegradation under Seasonal Freeze-Thaw Soil Temperature Regimes in Contaminated Soils from a Sub-Arctic Site. *Environmental Science & Technology*, 45(3): 1061-1066. doi:10.1021/es1022653.
- Corratgé-Faillie, C. et al. 2010. Potassium and sodium transport in non-animal cells: the Trk/Ktr/HKT transporter family. *Cellular and Molecular Life Sciences*, 67(15): 2511-2532. doi:10.1007/s00018-010-0317-7.
- De Jonge, H. et al. 1997. Relation between Bioavailability and Fuel Oil Hydrocarbon Composition in Contaminated Soils. *Environmental Science & Technology*, 31(3): 771-775.
- Delkash, M. et al. 2015. Using zeolitic adsorbents to cleanup special wastewater streams: A review.

Microporous and Mesoporous Materials, 214: 224-241. doi:10.1016/j.micromeso.2015.04.039.

- Downs, R.T. & Hall-Wallace, M. 2003. The American Mineralogist Crystal Database. American Mineralogist, 88(1): 247-250.
- Epstein, W. 2003. The Roles and Regulation of Potassium in Bacteria. *Progress in nucleic acid research and molecular biology*, 75: 293-320.
- Freidman, B.L. et al. 2016. Effects of Freeze-Thaw Phenomena on Controlled Nutrient Release: Application to Bioremediation. *CLEAN - Soil, Air, Water*, 44(12): 1739-1749. doi:10.1002/clen.201600162.
- Ghoshal, S. et al. 1996. Biodegradation of Napthalene from Coal tar and Heptamethynone in Mixed Batch Systems. *Environmental Science & Technology*, 30: 1282-1291.
- Gibb, N.P. et al. 2017. Synergistic desalination of potash brine-impacted groundwater using a dual adsorbent. *Science of the Total Environment*, 593: 99-108. doi:10.1016/j.scitotenv.2017.03.139.
- Grazulis, S. et al. 2009. Crystallography Open Database an open-access collection of crystal structures. Journal of Applied Crystallography, 42(4): 726-729. doi:10.1107/S0021889809016690.
- Grazulis, S. et al. 2012. Crystallography Open Database (COD): an open-access collection of crystal structures and platform for world-wide collaboration. *Nucleic Acids Research*, 40(Database issue): D420-427. doi:10.1093/nar/gkr900.
- Harris, N.J. 2017. *Hypersaline Potash Mine Tailings and Brine: Microbial Communities and Metal Biosorption Applications.* Master's Thesis, University of Saskatchewan.
- Harris, N.J. et al. 2023. Waste biomass from hypersaline potash mining byproducts: detection and visualization of Cu (II) and Cr (VI) on Croceicoccus sp. FTI14 biosorbent. *Waste Management Bulletin*, 1(3): 45-57
- Jasinski, S.M. 2023. Potash in *United States Geological Survey Mineral Commodity Summaries 2023.* U.S. Government Publishing Office, St. Louis, Missouri, United States. ISBN 978-1-4113-4504-1,136-137 doi:https://doi.org/10.3133/mcs2023.
- Jena, S.K. 2021. A Review on Potash Recovery from Different Rock and Mineral Sources. *Mining, Metallurgy* & *Exploration*, 38(1): 47-68. doi:10.1007/s42461-020-00286-7.
- Kim, J. et al. 2021. Manipulation of Unfrozen Water Retention for Enhancing Petroleum Hydrocarbon Biodegradation in Seasonally Freezing and Frozen Soil. *Environmental Science & Technology*, 55(13): 9172-9180. doi:10.1021/acs.est.0c07502.
- Lèbre, É. et al. 2017. The Role of the Mining Industry in a Circular Economy: A Framework for Resource Management at the Mine Site Level. *Journal of Industrial Ecology*, 21(3): 662-672. doi:10.1111/jiec.12596.
- Lin, L. et al. 2013. Adsorption mechanisms of high-levels of ammonium onto natural and NaCI-modified zeolites. *Separation and Purification Technology*, 103: 15-20. doi:10.1016/j.seppur.2012.10.005.
- Luo, X. et al. 2017. Geological Structure and Subsurface Stratigraphy of the Middle Devonian-age

Saskatchewan Basin. *Procedia Engineering*, 174: 1148-1160. doi:10.1016/j.proeng.2017.01.268.

- Ng, A. & Zheng, D. 2018. Let's agree to disagree! On payoffs and green tastes in green energy investments. *Energy Economics*, 69: 155-169. doi:10.1016/j.eneco.2017.10.023.
- Orris, G.J. et al. 2014. Potash—A global overview of evaporite-related potash resources, including spatial databases of deposits, occurrences, and permissive tracts. Scientific Investigations Report: 76. Available from

https://pubs.er.usgs.gov/publication/sir20105090S

- Pabalan, R.T. & Bertetti, F.P. 2001. Cation-Exchange Properties of Natural Zeolites. *Reviews in Mineralogy and Geochemistry*, 45(1): 453-518. doi:10.2138/rmg.2001.45.14.
- Rahimi, E. et al. 2021. Potassium-enriched clinoptilolite zeolite mitigates the adverse impacts of salinity stress in perennial ryegrass (Lolium perenne L.) by increasing silicon absorption and improving the K/Na ratio. *Journal of Environmental Management*, 285(112142): 1-11. doi:10.1016/j.jenvman.2021.112142.
- Paul, B., Dynes, J. J., & Chang, W. 2017. Modified zeolite adsorbents for the remediation of potash brineimpacted groundwater: Built-in dual functions for desalination and pH neutralization. *Desalination*, 419: 141-151. doi:10.1016/j.desal.2017.06.009
- Rawashdeh, R.A. et al. 2016. The potash market and its future prospects. *Resources Policy*, 47: 154-163. doi:10.1016/j.resourpol.2016.01.011.
- Regmi, U. & Boyer, T.H. 2021. Ammonium and potassium removal from undiluted and diluted hydrolyzed urine using natural zeolites. *Chemosphere*, 268: 128849. doi:10.1016/j.chemosphere.2020.128849.
- Reid, K.W., & Getzlaf, M. N. 2004. Decomissioning Planning For Saskatchewan's Potash Mines. 28th Annual BC Mine Reclamation Symposium, Cranbrook, British Columbia, Canada. doi:10.14288/1.0042463.
- Rike, A.G. et al. 2005. In situ biodegradation of hydrocarbons in arctic soil at sub-zero temperatures field monitoring and theoretical simulation of the microbial activation temperature at a Spitsbergen contaminated site. *Cold Regions Science and Technology*, 41(3): 189-209. doi:10.1016/j.coldregions.2004.10.005.
- Santiago, O. et al. 2016. Novel pre-treatment of zeolite materials for the removal of sodium ions: potential materials for coal seam gas co-produced wastewater. *Springerplus*, 5: 571. doi:10.1186/s40064-016-2174-9.
- Saskatchewan Mining Association (SMA). 2021. Saskatchewan Potash: Nourishing the earth. Saskatchewan Mining Association. Available from http://saskmining.ca/ckfinder/userfiles/files/SMA-Potash-Infographic-2021-DIGITAL.pdf [Accessed May 11, 2023]
- Siemens, A.M. 2018. Environmentally Sustainable Mining: Reusable Zeolite for Sodium Mitigation from Potash brine Impacted Groundwater. Master's Thesis, University of Saskatchewan.
- Stroeder, J. 2022. Saskatchewan Potash Producers Ramp Up Production. Government of Saskatchewan. Available from

https://www.saskatchewan.ca/government/news-andmedia/2022/june/22/saskatchewan-potash-producersramp-up-

production#:~:text=Saskatchewan%20is%20the%20la rgest%20potash,for%20new%20mines%20and%20ex pansions. [Accessed May 9, 2023]

- Su, J. et al. 2009. The Potassium Transporter Trk and External Potassium Modulate. Salmonella enterica Protein Secretion and Virulence. *Infection and Immunity*, 77(2): 667-675. doi:10.1128/iai.01027-08.
- Toby, B. H., & Von Dreele, R. B. 2013. GSAS-II: the genesis of a modern open-source all purpose crystallography software package. *Journal of Applied Crystallography*, 46(2): 544-549. doi:10.1107/s0021889813003531
- Tsitsishvili, V. et al. 2017. Ion Exchange Properties of Georgian Natural Zeolites. *Chemistry Journal of Moldova*, 12(1): 95-101. doi:10.19261/cjm.2017.413.
- Wang, S. & Peng, Y. 2010. Natural zeolites as effective adsorbents in water and wastewater treatment. *Chemical Engineering Journal*, 156(1): 11-24. doi:10.1016/j.cej.2009.10.029.
- Yang, S.-Z. et al. 2009. Bioremediation of Oil Spills in Cold Environments: A Review. *Pedosphere*, 19(3): 371-381. doi:10.1016/s1002-0160(09)60128-4.
- Yukselen-Aksoy, Y. 2010. Characterization of two natural zeolites for geotechnical and geoenvironmental applications. *Applied Clay Science*, 50(1): 130-136. doi:10.1016/j.clay.2010.07.015.
- Zhao, H. et al. 2009. Integrated treatment process using a natural Wyoming clinoptilolite for remediating produced waters from coalbed natural gas operations. *Applied Clay Science*, 42(3-4): 379-385. doi:10.1016/j.clay.2008.03.007.

7 APPENDIX

In addition to the XRD and ICP-OES analyses, the 'subsamples' of potash brines, coarse tailings and fine tailings were analyzed for heavy metal content via Inductively coupled plasma mass spectrometry (ICP-MS), as summarized in Table 2. The samples were analyzed at the Saskatchewan Research Council's Environmental Analytical Laboratory. Standard sample preparation and analytical methods were used for the ICP-MS analysis (Rice et al. 2012).

Table 2. Heavy metal content of potash byproducts

Heavy Metal	Brine (mg/L)	Coarse Tailings	Fine Tailings
Aluminum	0.76 ± 0.01	640 + 20	12200 + 700
Arsenic	0.01*	0.23 ± 0.03	1.2 ± 0.1
Antimonv**	ND		ND
Barium	0.82 ± 0.01	2.73 + 0.13	41 + 3
Beryllium	ND	ND	0.4*
Boron	ND	ND	24 ± 1
Cadmium**	ND	ND	ND
Chromium	0.17*	0.70*	17 ± 2
Cobalt	ND	ND	2.6 ± 0.3
Copper	0.75*	ND	2.3 ± 0.5
Iron	$\textbf{0.80} \pm \textbf{0.01}$	340 ± 10	6000 ± 300
Lead	ND	0.1*	0.5*
Manganese	3.0*	$\textbf{7.5}\pm\textbf{0.2}$	83 ± 7
Molybdenum	0.04*	ND	0.1*
Nickel	0.12*	0.6*	11.5 ± 1.0
Selenium	$\textbf{0.13} \pm \textbf{0.01}$	ND	0.2*
Silver	≤ 0.009	ND	ND
Strontium	36*	14*	98 ± 8
Thallium**	ND	ND	ND
Tin	ND	ND	0.3*
Titanium	ND	19 ± 1	90 ± 7
Uranium	ND	ND	0.3*
Vanadium	0.01*	0.8*	18 ± 1
Zinc	0.25 ± 0.01	ND	11 ± 1

ND indicates no data available.

* Standard error is 0.

** Metal tested for but not detected in any sample type. Table modified from its original source (Table 3-4 of Harris 2017).

Reference

Rice, E. W., Bridgewater, L., & American Public Health Association (Eds.). 2012. *Standard methods for the examination of water and wastewater*, vol. 10, American Public health Association, Washington, DC, USA.