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Responses to Docket #23-ERDD-01

Additional submitted attachment is included below.

Responses to Docket # 23-ERDD-01

Lithium Recovery from Geothermal Brine

4. What are the greatest technical barriers to the commercialization of lithium recovery from geothermal brine? What technologies provide the greatest opportunities to facilitate the commercialization of lithium recovery from geothermal brine? What would be the most effective use of R&D funding to advance commercialization of lithium recovery from geothermal brine? What specific technologies or approaches are presenting a particular challenge, and what are some alternatives?

1) The greatest technical barrier is the lack of cost-effective, high efficiency lithium selective materials that both can withstand the complex brine environment (high TDS, high interfering competing cations) and be produced at large scale.

Currently, adsorption, ion exchange, solvent extraction, and membrane processes, have been explored for direct lithium extraction (DLE) and demonstrated greatly improved lithium recovery compared to the conventional evaporation method.[5] However, DLE technologies face several major barriers that lead to the overall high operational cost. A key challenge is the underperformed lithium selective materials/processes due to complex brine environment.[1,2] Current lithium selective sorbents/ion exchange resins experienced largely reduced adsorption capacity, kinetics, and lithium selectivity due to the charge screening by the extreme high TDS (>300g/L). Therefore, a large quantity of adsorbents is needed, and huge chemical and water consumption are required during the lithium stripping and sorbent regeneration process. Moreover, Common membrane processes (e.g., Nanofiltration(NF), and electrodialysis(ED)) have limited lithium selectivity, and also require high energy consumption when dealing with such brines due to the high osmotic pressure or reduced charge efficiency.

Additionally, the interference from divalent cations such as Ca^{2+} and Mg^{2+} severely limited the lithium extraction. Though ion sieves such as Li-Mn-O and Li-Ti-O have been reported in literature demonstrating high lithium selectivity over competing cations. However, significant concentrations of divalent cations such as Ca^{2+} and Mg^{2+} remain in the product brine, resulting in low purity of the final Li_2CO_3 or LiOH products.[3] Higher selectivity may be achieved under basic condition (pH>9).[4] Therefore, addition of soda ash and lime is necessary to adjust pH and precipitate out the divalent cations, leading to high chemical consumption, chemical sludge production, and hence cost.[3] Additionally, such materials still face challenges of mass production and are not commercialized yet. DLE technologies with highly effective separation of divalent cations and feasible for high TDS application are greatly needed.

2) Electro-based technology such as electrodialysis would be the most promising DLE technology for commercialization. ED uses an electrical field to separately remove positively and negatively charged species through ion exchange membranes (IEMs),

which selectively transport the counter-ions (e.g., cations as to cation exchange membranes) and reject the co-ions via Coulomb force. Therefore, it operates at ambient temperature and pressure, is more tolerant to fouling and scaling, and demands less chemical and energy consumption than pressurized membrane systems. With the development and application of lithium selective IEMs, it can achieve the selective transport and concentration of lithium driven by electricity, with largely enhanced energy efficiency. Additionally, unlike adsorption or solvent extraction, no harsh chemicals or processes are needed for lithium stripping or material regeneration, and thus requires minimal chemical and water consumption. Moreover, the electro-based DLE has little environmental impact and carbon footprint as it can be driven by 100% renewable energy.

3) Easy access to the real geothermal brine and testing sites would be of great benefit to test the actual performance of DLE technologies. Geothermal brine is a complex and unstable stream of high temperature containing a large quantity of scaling and fouling species (e.g. Silica, Ca^{2+}, Mg^{2+}). Whereas the synthetic geothermal brine prepared in the lab would never be similar to that of the real geothermal brine.

4) The electro-based DLE technologies such as ED is promising to commercialize, however, current IEMs used have no selectivity between same-charge, same-valence ions (i.e., Li^+ and Ca^{2+} or Na^+), and thus wouldn't be energy-efficient when applied for lithium extraction. IEMs with high Lithium selectivity and permeability can be developed to enhance the overall energy efficiency.

5. What brine pretreatment issues have been especially challenging to overcome? What technologies or techniques have been successfully tested at a TRL of 3, 4, or 5?

Silica scaling is a key challenge when dealing with geothermal brine, as the silica is increasingly oversaturated (silica >400 mg/L in Salton Sea area)[5] when the brine temperature decreases overtime. Silica scaling not only leads to the pipeline blockage and equipment failure, but also adversely affects the lithium extraction process due to the scaling on lithium selective materials (adsorbents or membranes).[6] Currently, several silica control strategies have been developed. pH adjustment by the addition of soda ash/lime is a common practice for both silica and divalent ion removal which is at TRL5,[7] however requires large chemical consumption. Additionally, micro-template (seeds) assisted silica removal have been reported in literature to be effective to removal silica down to undersaturation. This technology is at TRL4.[8,9]

6. What technologies or processes can reduce waste products from the lithium recovery process (such as by decreasing mass or by recovering additional co-products in the lithium recovery process)? What TRL are these technologies?

Electro-based DLE technologies such as lithium selective ED can reduce the waste. As a membrane separation process driven by electricity, the material and chemical consumption are minimal, compared to the adsorption, ion exchange or solvent extraction technologies, which need large quantity of materials for lithium extraction. Consequently, no material regeneration is needed in the lithium selective ED process. More importantly, the lithium selective ED can achieve a high Li/divalent ion selectivity, and thus largely reduce the chemical (i.e. soda ash) addition and waste generation for Ca/Mg removal, which is critical for lithium extraction. Currently this technology is at TRL4-5.

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