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How DLE Works

Direct Lithium Extraction, DLE, uses a particle or a water immiscible solvent to capture lithium from a brine stream. The more common particle method has historically used intercalated alumina particles. Recently specific ion exchange resins have been developed with a selectivity for lithium. In either case, the particles are almost always arranged in a packed bed column system. Flow sheets have also been developed on the small scale using moving bed systems.

Column systems have a specific operating sequence made up of various steps. These steps include load, displace, strip, wash, regenerate, replace and fill. Column systems are usually three column sets with two set up in series onstream loading and one column offline being stripped and regenerated. The idea is to concentrate the lithium during the load onto the particles, then strip the lithium off the particle using the least amount of stripping fluid possible creating the product cut. Sequences are determined specifically for the column system and brine being extracted using bench scale column experiments.

For a packed bed column system, the particles usually fill about ½ to ¾ of the column volume when loaded. This is to account for the needed expansion space for the particles as the columns go through different steps in the sequence of its operation. In the particle bed, up to 40% of the volume is the interstitial space between the particles. The brine passes through this interstitial space and an equilibrium is established between the particle and the lithium where during certain conditions in the bed the lithium either is loaded onto the particle or is stripped off the particle while letting all the other constituents in the brine pass through the column. The sequence of column operations and the conditions in the column for each step in the sequence is critical to the successful operation of the DLE system.

The fluid flow must minimize back mixing and hydrodynamic disturbances during the transitions between the steps in the columns operating sequence. This is to have the highest driving force available for mass transfer, to enable the use of density differences to change the fluid cuts in the column effectively, and to minimize the grinding of the particles amongst themselves to avoid reducing the size and the uniformity of the particle size distribution in the column.

The particles must have enough surface area to allow contact with the lithium in the brine, however, the particles must also be large enough and uniform enough such that the interstitial space does not become so limiting that the pressure drop in the packed bed column becomes so great that it inhibits flow. The particle size distribution of the particles must be as uniform as possible. The particles themselves must have a resistance to attrition due to the flow dynamics and the particle dynamics that occurs during different operational conditions. In all these systems the particles grind themselves smaller and smaller and it is inevitable that at some point the particles must be replaced. The replacement and regeneration strategy used is one of the drivers of the OpEx maintenance budgets.

Design factors include the scaling of the system based upon the isotherms that were demonstrated by the particular particle with representative brine on the bench and lab scale.

Temperature is important. The traditional intercalated alumina systems require operations near 200F. Ion exchange resins require a lower operating temperature as the resin backbones usually have an upper temperature limit of 140F. The lithium must "see" a site where the mass transfer can occur. The lithium also must have enough time while passing by the site to be captured. The superficial velocity of the liquid through the column is used to characterize this parameter even though the actual fluid dynamics at each individual particle is extremely complex to model. If the superficial velocity is too high, then too much of the lithium will pass through and show up in the bleed concentration of the exiting spent brine. These conditions also affect the capacity of the column to capture lithium. If the superficial velocity is too slow, then the equipment capital cost will become prohibitive.

A performance metric of the particles is the capacity to retain lithium. This is measured as grams of lithium per liter of particles. The particles change density depending upon the conditions present. The volume of the particles is calculated as the initial load volume. This is called a bed volume. A common conservative performance metric is 2 g/L. Many new particles and condition sets have been developed that continually drive to improve this metric.
To give an example. If a 12 foot diameter 30 foot high column is filled to 67% of its actual volume with particles, then the bed volume is (((6*6*3.1415)*30*.67)*7.48*3.875) = 66000 liters. If the particle has a 2 g/L capacity, then the packed bed is fully loaded when 132000g of lithium has been run through and captured by the column. If the feed brine has a concentration of 250 ppm Li (mg/kg), and the bleed concentration is 15 ppm, then 132000g of lithium will have run through the column when or 120,000 gallons of brine has run through the column. A plant producing 15000 MT LCE/yr will require 8000 gpm of feed brine. One column would be fully loaded in 15 minutes. Since all the stripping and regeneration steps must also occur in the column sequence, multiple columns sets in parallel must be used in order to maintain steady state brine flow through the overall system. The sequence timing of each step is critical to the operation.

Columns are arranged in three column sets referred to as daisy chains. Two columns are being loaded with feed brine in series, while the third column is off the main stream, being stripped and regenerated. Many different vendors and operations might use similar words for the different operational steps in the sequence.

Load is the step when feed brine is being fed to the system. The two columns that are in the feed brine flow pathway each are at a different state in their life in the sequence.

A fresh column is one that has just come into service after having been stripped and regenerated. A column at breakthrough is when the discharge or spent brine lithium concentration begins to rise above the bleed concentration. A column is at saturation when the spent brine concentration matches the feed brine concentration.

The spent brine analytical determines the operational state of the column. It is critical to have rigorous sample taking, sample preparation and analytical methods to support the columns. Most times, these are samples that must be drawn from the stream, taken to an analytical lab and run on an ICP (ICP = inductively coupled plasma). This is a topic for another article. The turn around time on the sample data is usually longer than the ability to effect changes if there is a problem. When the columns are first started up, and in conjunction with using the laboratory runs data, a time based switching criteria is set up for the operations of the columns and the actual run samples from the commercial columns is used to ensure performance is maintained against that pre-established time sequence.

The two columns in series accepting the feed brine flow are in what is called a lead/lag series arrangement. The feed brine is fed to the lead column. The discharge brine from the lead column is fed to the lag column. The lag column discharge is the spent brine.

A freshly regenerated column is placed into the lag position in the daisy chain. When the lag position discharge brine hits breakthrough, the lag column is switched to the lead position. When that lead column's discharge hits saturation, that column is taken offline to be stripped and regenerated.

The column sequence must also consider the transitions between each step. When the column is taken offline when it is fully saturated, it will be full of brine that still has impurities in it along with the lithium captured by the particles. The particles must always remain in a liquid solution as draining the column would only occur during heavy maintenance on the column. A displacement step is required. This displacement step discharge will be recirculated back to the brine feed tank. The displacement solution is a brine with a slight density difference that would help to avoid back mixing at the interface with the saturated brine in the column. Usually, the displacement solution is a clean lithium chloride brine or an acid solution. This displacement solution pH and temperature are important as well. Hydrochloric acid and/or sodium hydroxide is usually used to adjust the pH if needed. This moves all the impurities left in the saturated brine in the column to the brine feed tank. Systems have also used lithium hydroxide as opposed to sodium hydroxide in order to keep the sodium concentrations low, however, since most systems use and evaporator at some point down stream, the addition of sodium at this point may not be a significant concern. It all depends upon the way the overall system is put together.

Once displacement step is completed, then the column is stripped. The stripping solution is a lower concentration lithium chloride solution which will encourage the lithium to be released from the particle. The pH and temperature of the stripping solution is critical to performance of the column. The trick is to use the least amount of stripping solution while stripping out all of the lithium captured in the particles. The volume of stripping solution determines the load on the reverse osmosis and evaporation systems downstream. In many cases use of a reverse osmosis system downstream creates a trade off between the amount of stripping solution used in the stripping step versus the amount of lithium that is left in the column. Ideally, all the lithium would be stripped out of the particles with the least amount of stripping solution, but that is never the case. If extra stripping solution is used to drive off the last bit of lithium, and RO system can make up for this additional water load avoiding throwing the energy balance off at the downstream evaporator. These interacting factors are best analyzed using scenarios from the working mass and energy balance model for the overall system.

Once the column is stripped, another displacement step is required since there will still be clean concentrated lithium product brine left in the column. After this second displacement step, the column is regenerated with a pH adjusting solution.   All of the various strip and displacement solutions are captured and recycled into the system. The strip solutions run slower than the load solutions. Overall timing must fit such that all the offline steps can occur while the online column capacity can handle the load of feed brine. Usually, a flow rate of 1000 gpm is used as a limit for the column sizes in the scenario in this example. That would require eight sets of columns to cover the feed capacity. Since 30% of the volume of the system is recycle, that would require and addition three sets of columns. Add to that the need for an offline locked out maintenance option, this adds at least one more set. The minimum for the 8000 gpm raw brine feed rate would be 12 sets of columns, or a total of 36 columns. Each column is running 1000 gpm, and there are at least 7 valves on each column. There are then rather large storage tanks for holding the various cuts and solutions, and the system becomes quite complex very quickly.

The other detail in this sequence of steps is the flow direction. Load, displacement and strip is usually downflow. Downflow meaning flowing from the top of the packed bed to the bottom. Up flow is used to disturb the bed at some point to try and release the smaller particles that are continually being created due to the expansion and contraction of the particles or the interparticle grinding that is occurring in the column during the various operations. Up flow could be used during the regeneration step, or during one of the later displacement steps. The ability to keep the up flow discharge clear of particle build up and problems with small particle layers being created on top of the bed is a needed detail discussion of the distributor, collector, valving, flow control, and internal design details for the columns. Many times, these details are part of vendor or operating companies' intellectual property as many different schemes have been developed over the years which effect the economics of the systems. Poor management of particle degradation either by the use of weak particle or poor hydrodynamic control will affect the system capacity, recovery and performance.

There is one other step that must be considered, that is of replacement of the particles. This is usually considered a heavy maintenance operation and not part of the regular daisy chain or merry go round sequence of steps. The replacement step would occur with the column locked out and valved off from any of the other steps. The access to the column internals and the loading of the new material in the column are an operation unto itself. Many times a portion of the bed is replaced versus a whole column being emptied and replenished with new material. There are both dry load and wet slurry load methods. The detail design of the column internals to allow these operations are a topic for another write up, but they are critical to the integration of the overall operation of the system. Particle life cycle is critical is usually on the order of a year.   Since particle synthesis is a significant operation unto itself and has significant cost, this must be part of the consumables budget in the overall system OpEx. In this example scenario, a budget of $10MM for replacement particles would not be unreasonable.

Whether intercalated alumina or a more traditional organic backbone resin, these packed bed column systems work on very similar principles. If using a liquid for the capture, this would be a solvent extraction system, which is still a type of DLE. In the case of SX, however, an immiscible fluid would be used as the capture material versus a solid particle. Instead of column daisy chains, there would be a series of mixer and settlers that would allow the immiscible liquids to contact on another. The lithium would transfer from the aqueous phase to the organic phase in the series of mixer settlers. This system would look like a very common traditional SX system found in many mining operations. The lithium selectivity, equilibrium and disengagement dynamics of an SX system is a topic for another article. A as general comment here is to caution that a lithium SX system would be very large. The specific details of the brine must be studied to determine the best DLE type for the various applications. Most likely, the intercalated alumina will come out as the more economical system in the majority of cases, even with all its complexity.