The State of "Zero Liquid Discharge"

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Abstract

As environmental and sustainability concerns continue to drive corporate decision-making, and effluent discharge criteria continue to become more strict, water management on mining sites has become increasingly crucial to the bottom line. To meet newer strict effluent standards, many companies have investigated "zero liquid discharge", or ZLD, as a way of meeting those criteria and creating a reusable water source for other mining needs. But what is ZLD and is it really necessary?

The concept of "zero liquid discharge" is a misnomer. Every ZLD technology has a waste stream, and each waste stream contains some amount of "liquid discharge", and the capital cost and operating cost of the technology depends directly on how close to zero liquid is contained in the waste stream. And these costs can be staggering. So, it is crucial that owners understand when a ZLD-type technology is required, and more importantly, when it is overkill. This paper will investigate this question and give an in-depth example showing how innovative process design can avoid a ZLD project in favour of targeted contaminant removal.

When ZLD is determined to be necessary, there are several different available technologies, with new technologies emerging every year. These technologies can come in many forms from passive evaporation, thermal treatment, membranes, solidification and other innovative technologies. This paper will review these different types of ZLD technologies and provide advantages and disadvantages of each. It will also include a case study of a thermal ZLD application with Class 3 estimates of three different variations on the level of ZLD. Finally, it is also important to understand the residuals management and handling considerations from different ZLD processes. The paper will review different residuals management considerations such as incineration, landfills, hauling logistics, and hazardous constituents.

Introduction

Zero liquid discharge was originally developed for the power industry to minimize the impact of increased salinity in the Colorado River and other arid environment water bodies. Recently, ZLD equipment represents a capital investment of $100-200 million annually (6) and growing. The drivers for ZLD systems include strict environmental regulations, high costs associated wastewater disposal, freshwater scarcity and a public demand for "sustainable" water use. All of these drivers are continuing to be more pronounced each year; hence the increased focus on ZLD. Many industrial users benefit from the implementation of ZLD by receiving drastically shorter permit review periods, availability of high quality reuse water and a reduction in fresh water demand to the facility.

While ZLD systems can offer benefits, the drawbacks are often prohibitive. ZLD systems include many different unit processes which make them complicated and difficult to operate. Many are highly energy intensive, and if a waste heat stream is not readily available, they can be cost-prohibitive to operate. As the dissolved solids in the water are concentrated through the ZLD process, both corrosivity and scaling potential become important to consider in material selection of the unit processes. The metal alloys necessary to handle the corrosive nature of concentrated salts make the capital cost of the equipment prohibitive. For this multitude of reasons, high capital costs and operating costs of ZLD systems often makes them impractical.

An additional consideration that is often overlooked with ZLD, is the waste stream. Every "zero liquid discharge" solution has a waste stream, and most of them contain some amount of liquid in the waste. Often the waste from a ZLD is an extremely concentrated brine (~60% solids) or even crystallized salt (85-95% solids), that when placed in a landfill immediately re-solubilizes to form a concentrated brine leachate that is very difficult to handle. The transportation of brine requires either corrosion-resistant pumps or contained tanker trucks and the transportation of crystalized salts is difficult to avoid any moisture which can re-solubilize the salt. Some waste materials may contain radioactive contaminants which require the entire waste stream to be disposed of as a hazardous waste. When evaluating ZLD options, it is critical to consider the environmental impact and disposal costs associated with that method of ZLD.

The challenges associated with ZLD have driven considerable research into more efficient, less expensive ZLD alternatives, several of which will be discussed in this review. However, the least costly alternative is always to avoid ZLD if possible. This paper will review ways of avoiding ZLD if possible; and if not possible, evaluate several different ZLD alternatives, comparing the advantages and disadvantages of each alternative.

Avoiding ZLD – Selective Contaminant Removal

In many instances ZLD is investigated because discharge regulations are strict for a particular contaminant that may be difficult to treat using conventional treatment approaches. In these cases, many industries see ZLD as the only option to manage their wastewater stream. However, if a novel treatment approach is developed specifically for the removal of that contaminant, ZLD can be avoided altogether.

One typical example of such a contaminant is sulfate. Sulfate is difficult to remove from water because the solubility of sulfate is between 1,500 and 2,000 mg/L, while regulations (when applicable) tend to limit sulfate to 250 to 500 mg/L. High pressure membranes such as nanofiltration (NF) or reverse osmosis (RO) membranes are often evaluated for this situation, but because of the high potential for irreversible scaling from calcium sulfate in the concentrate stream, the membrane recovery cannot be run high enough to meet stringent discharge limits and membranes are not selected as the final solution. Figure 1 demonstrates the difficulty of using NF membranes to meet a discharge limit of 250 mg/L sulfate.

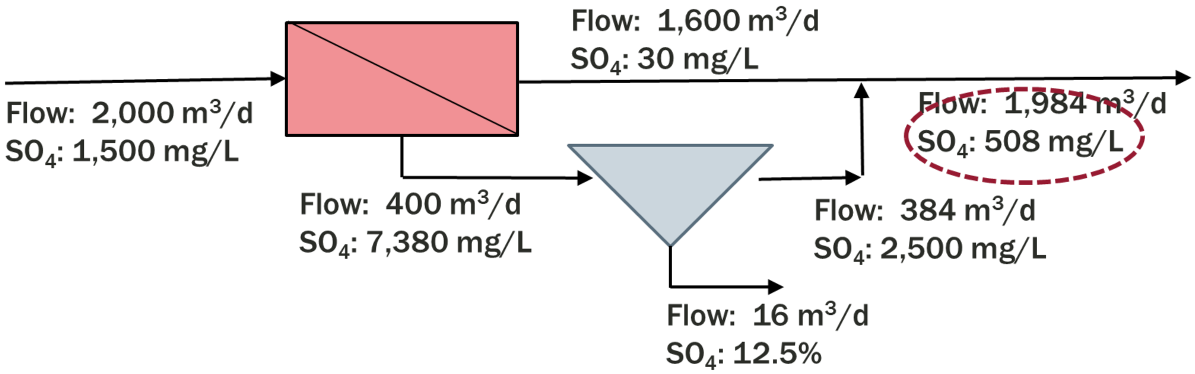

Figure 1: Example of NF membranes to a sulfate limit of 250 mg/L

Figure 1 shows that even with a two pass NF system, the treatment requirement of 250 mg/L cannot be achieved with a simple membrane design. This may lead someone to think that ZLD is best approach. However, if a treatment system is specifically designed to maximize sulfate removal, it is possible to see how the treatment target can be achieved with just a slight modification to the overall treatment system (see Figure 2).

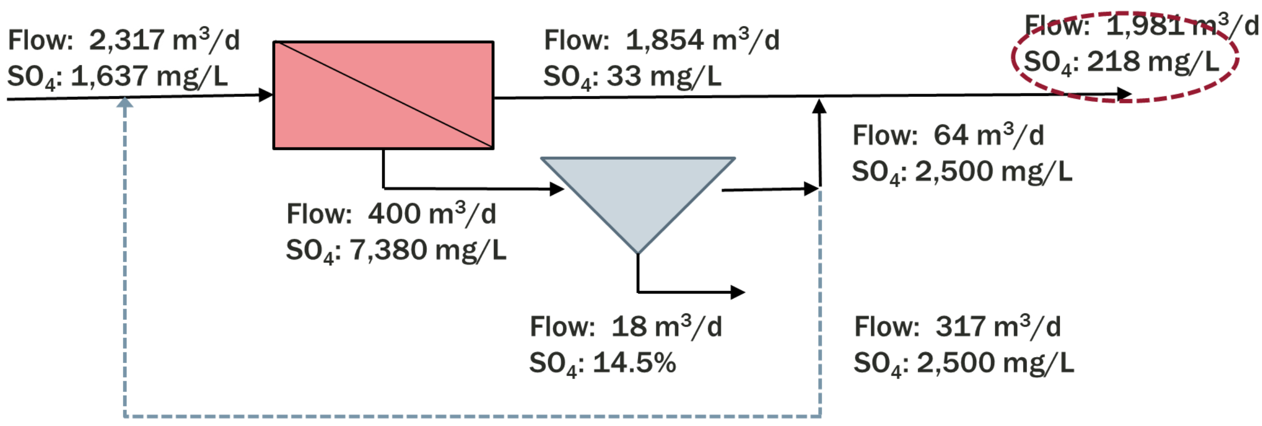

Figure 2: Membrane System Enhancement to meet sulfate limit of 250 mg/L

Avoiding ZLD – Other Potential Methods

In certain scenarios water treatment using membranes or other advanced treatment systems may produce effluent water quality capable of meeting water reuse or discharge requirements but leave a concentrated waste stream that cannot be discharged or landfilled. In these cases there are a number of potential methods of disposing of concentrated waste that do not require a ZLD solution. The following lists some of those potential disposal methods:

- **Open mining pits or underground mine workings** – this option depends on many different aspects of the mine site including the type of geology, location of groundwater table, mining plan, and other site-specific environmental concerns.
- **Deep well injection** – obtaining Underground Injection Control (UIC) Class I waste disposal well permits can be challenging in many locations due to concerns of enhanced earthquake activity, environmental concerns and/or a lack of viable locations for these wells. If a business can obtain an injection well permit, this option often has reasonable capital and operating costs and can be an attractive disposal option.
- **Land Application** – many mining sites have the ability to use waste water for dust control on roads. Some locations may also be able to use excess water for irrigation or disposed of through infiltration basins.
- **Ice dams** – in some cold-weather climates concentrated brine can be sprayed in layers which freeze during the winter. When ice melts, the water flows away leaving the solids and other contaminants in place (1). This method obviously requires a particular climate and is an emerging technology; however, it is an energy-efficient, low capital cost possibility.

Methods of Zero Liquid Discharge

When ZLD is unavoidable, it is critical to thoroughly review all of the potential options to find the best alternative for each particular application. There are dozens of potential ZLD options and this review paper will examine the following ZLD themes:

- Passive Evaporation
- Thermal Evaporation
- Membranes
- Solidification

Each of these four ZLD themes will be discussed in more detail in the following sections.

Passive Evaporation

Passive evaporation uses shallow, lined ponds to utilize areas of low humidity to evaporate water. These systems are typically installed in the southwest of the United States where climate is very dry and land area is plentiful. Design criteria for such a treatment system is for a climate with less than 0.3 meters (12 inches) of rainfall per year and where the evaporation rate is 1.0 meters (40 inches) per year or higher. The land area required is directly related to both the annual rainfall and the evaporation rate.

Evaporation ponds can be either lined or unlined. Depending on the contaminants present in the water or proximity to groundwater tables, regulations may require the ponds be lined to prevent solids migration into the groundwater. In some instances, the cost of lining the pond is offset with increased evaporation rate from solar radiation bouncing off the liner. Another method to increase the evaporation rate is add dark-colored dyes to the water to absorb more solar radiation. It is also possible to increase the evaporation rate by installing a forced evaporation system which pumps water through spray nozzles which create aerosol droplets with a high amount of surface area. This increased surface area provides allows much faster evaporation at a relatively low energy demand.

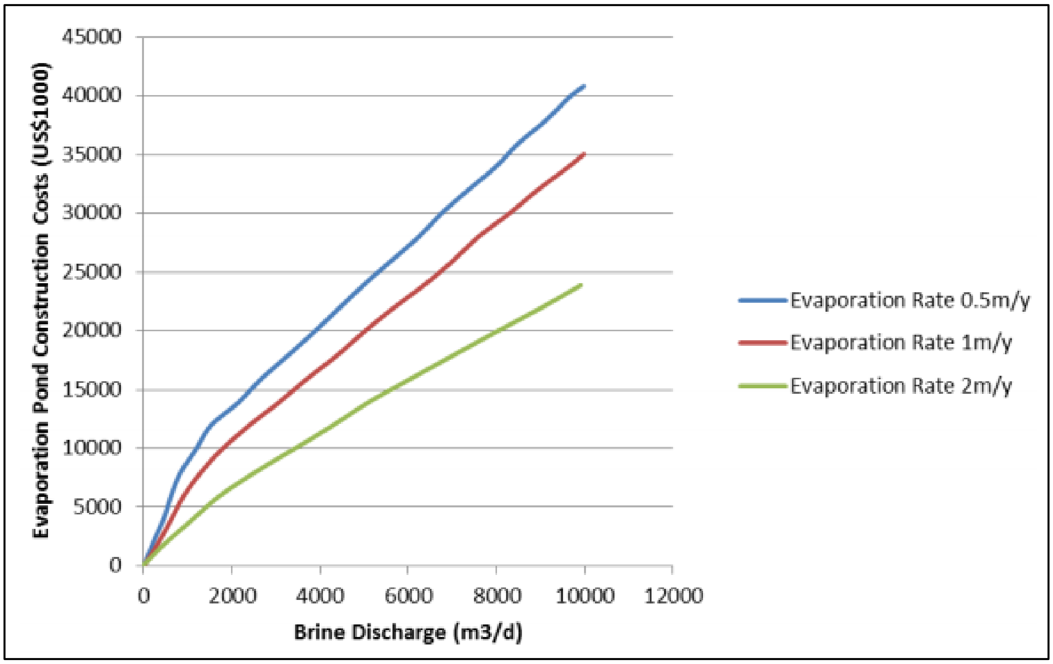

Figure 3 – Construction Cost of Evaporation Ponds (2)

One clear advantage of using evaporation ponds for ZLD is that the resulting solids do not require any direct solids handling as the solids remain in the evaporation pond. The final state of the solids is typically a salt slurry because as the water evaporates and the solids continue to concentrate in the remaining liquid, the evaporation rate decreases due to the increased salinity. Final closure of the evaporation pond would include significant earthworks to cap the pond.

Table 1 contains a summary of the advantages and disadvantages of passive evaporation.

Table 1: Advantages and Disadvantages of Passive Evaporation

Advantages	Disadvantages
Low OpEx	Geographically / climate constrained
Relatively low CapEx when compared to other ZLD alternatives	Large land area required
Low residuals handling, transportation, and disposal	Creates legacy residuals remaining in the lined ponds
Nearly zero greenhouse gas footprint	Highly visible
	Not applicable for reuse as the water cannot be recovered

Thermal Evaporation

Thermal evaporation is most commonly used form of ZLD because it is applicable in any climate or geography, it creates a nearly pure water for reuse, and it has a relatively small footprint compared to other ZLD technologies. Thermal evaporation typically has three main unit processes to achieve a true zero liquid discharge.

- Falling film evaporator or Brine Concentrator
- Brine crystallizer
- Solids centrifuge

For a thermal ZLD system, incoming wastewater is pumped through a heat exchanger that uses pure water distillate to pre heat the wastewater before entering the evaporator. The falling film evaporator is the most energy efficient evaporator available and is shown in the schematic in Figure 4. The system operates by pumping the brine solution to the top of a tall tower. The brine then falls through the inside of heat exchange tubes with compressed water vapor on the outside of the tubes. As the liquid falls down the tubes, a portion of the liquid evaporates with the remaining concentrated liquid falling back into the evaporator sump to be pump back to the top again. The evaporated water from the tubes is sent to a mechanical vapor compressor, which slightly compresses the water vapor and pumps it to the shell side of the falling film evaporator tubes. A brine concentrator operates at up to 60% solids in the brine, which offers a significant volume reduction at a relatively low energy input. Falling film evaporators utilizing mechanical vapor compressors operate between 20-39 kWh_c/m^3 of distillate (4). For some projects, users simply implement the evaporator portion of the ZLD system and send the concentrated brine to smaller evaporation ponds.

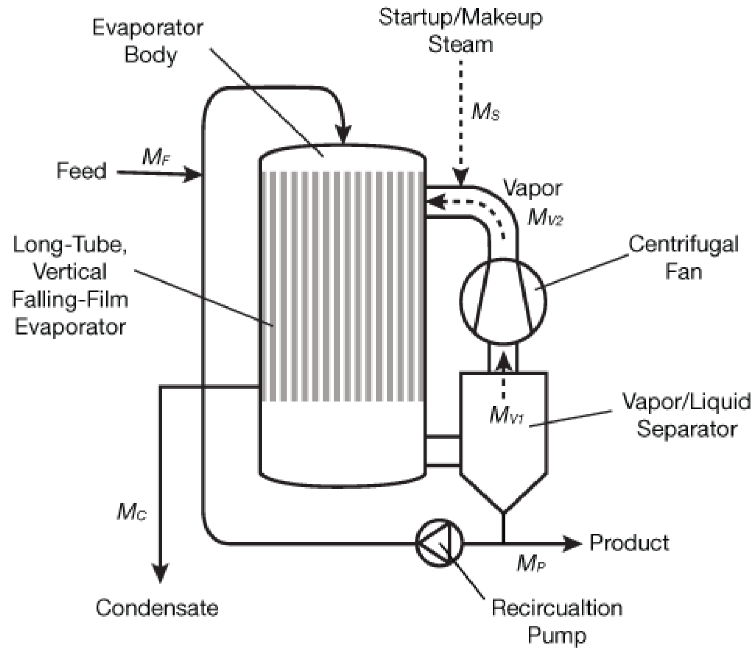

Figure 4 – Falling Film Evaporator Using Mechanical Vapor Recompression

For projects that require complete ZLD, the concentrated brine would be pumped to a brine crystallizer, which heats the brine solution to near its boiling point as it is pumped into the crystallizer tank where the liquid flashes. The distillate from the flashing is collected, used in the heat exchanger to heat the incoming concentrated brine, and is collected and reused. As the liquid flashes, salts crystallize out of solution and are collected in the bottom of the crystallizer. The solids are then dewatered through a centrifuge and recovered in a 95-98% solid product. Crystallizers require significantly more energy than evaporators, requiring 52 to 66 kWh_c/m^3 of distillate (4).

The brine in the crystallizer is around 80-90% salt solids, and this highly concentrated salt solution is extremely corrosive. Crystallizers must be constructed out of highly corrosion-resistant materials such as titanium which significantly increases the capital cost of the vessels when compared to even 316 stainless steel. Similarly to the crystallizer, the centrifuge, the pumps and all piping must also be constructed of corrosion-resistant and heat resistant material. The materials of construction make these unit processes extremely expensive capital costs and on-going maintenance and spare parts as everything is custom-fabricated.

Table 2 contains a summary of the advantages and disadvantages of thermal evaporation.

Table 2: Advantages and Disadvantages of Thermal Evaporation

Advantages	Disadvantages
True ZLD application if crystallizer is implemented as pare of the thermal ZLD	High CapEx and OpEx
Small footprint	Complicated operation
"Dry" solids can be transported	Materials of construction incompatibilities
Pure water for reuse	Residuals management, disposal of large mass of solids
	High greenhouse gas footprint

Membranes for ZLD

Improvements in membrane technology have allowed membrane systems to approach ZLD. These "Minimal Liquid Discharge" (MLD) systems are popular for minimizing liquid wastes because they operate at relatively low energy requirements and a small system footprint. There are several types of MLD membrane configurations utilize enhanced RO membrane system designs including:

- **2 and 3 stage RO**: several RO stages can obtain water recovery up to 90%. Typically these systems require aggressive pretreatment to remove scaling potential in the membranes and significant chemical antiscalant and cleaning treatments.
- **Ultra-high-pressure RO**: utilizing pressures between 80 to 125 bar (1,200 to 1,800 psi) can concentrate solids up to the osmotic pressure of the salts, in the neighborhood of 130,000 mg/L total dissolved solids in the concentrate.
- **Closed circuit RO**: this type of RO system design utilizes a concentrate line recirculation in a semi-batch process to maximize water recovery, which can obtain 90-95% water recovery in many instances. Figure 5 shows a schematic of closed-circuit RO, courtesy of Desalitech's website.

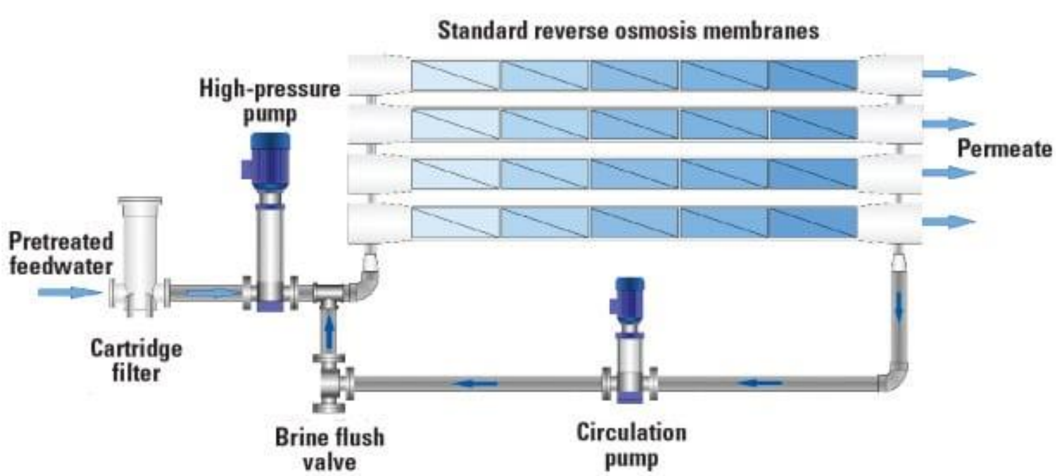

Figure 5 – Closed-Circuit RO Schematic

Another type of membrane that can be used to concentrate contaminants and create a clean reusable permeate is Forward Osmosis (FO). FO is an emerging technology that has been under development decades. The process uses a "draw solution", usually an amine/carbon dioxide-based liquid to draw pure water from a brine using the osmotic pressure of the brine solution to push the clean water through the FO membrane into the draw solution (see Figure 6). The pure water is then recovered from the draw solution by vaporizing the NH3/CO2 draw solution (and subsequently recovering that solution) and leaving pure water for potential reuse.

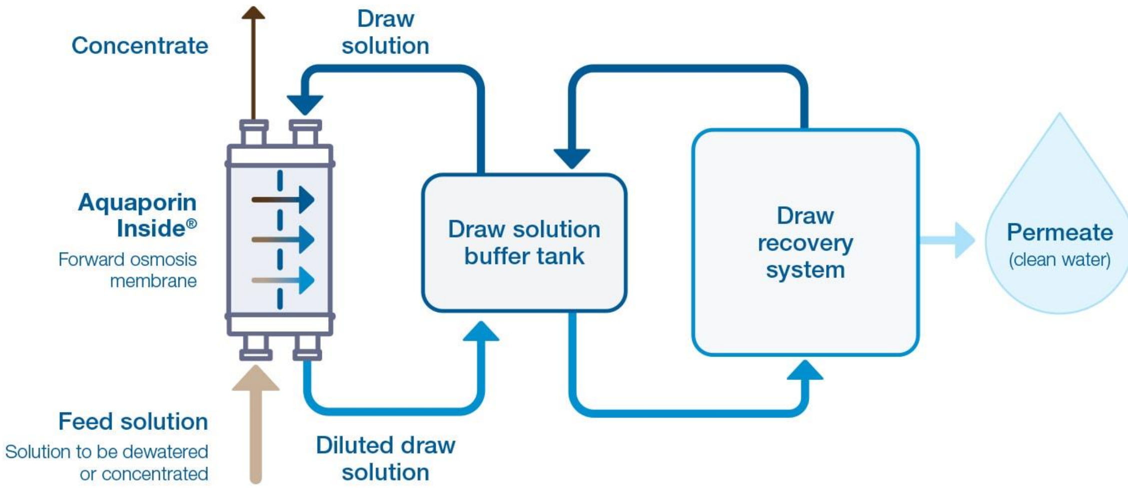

Figure 6 – Forward Osmosis Schematic, courtesy of Aquaporin

Forward osmosis has been shown to achieve a concentrate stream that is 200,000 to 230,000 mg/L TDS while modelling showed it would be capable of doing so utilizing only 21 kWh/m^3 of produced water (3). Table 3 summarizes the advantages and disadvantages of FO when applied to MLD.

Table 3: Advantages and Disadvantages of Forward Osmosis

Advantages	Disadvantages
Operates at low pressure	Like other membrane alternatives, not a true ZLD solution, still has a brine waste stream to manage
Small footprint	High CapEx
Capable of concentrating past osmotic pressure which can be upward of 230,000 mg/L TDS	Emerging membrane technology
Lower fouling propensity than conventional RO	Few full scale applications
Relatively low greenhouse gas contribution	

Solidification

Solidification is a ZLD alternative where a brine solution, perhaps from an RO membrane system, is mixed with an absorptive additive such as fly ash to create a thick slurry that can harden, encapsulating the contaminants into a solid state. In order to get the slurry to harden properly, it is idea to have a 1:1 ratio of brine to fly ash on a weight basis. This approach to ZLD has been recently adapted at power plants around North America to deal with coal combustion residuals and has been shown as an effective way of closing waste ponds. It is particularly attractive at power plants because there is a readily available source of fly ash. A few mining sites have been able to mix concentrated brine solutions in with the tailings waste, especially as mines move toward paste and filtered tailings.

Solidification of residuals is an attractive option if the cementation source is readily available because the contaminates are immobilized the solid matrix and do not leach back out of solution. Therefore, solidification is a permanent disposal solution for hazardous contaminants. However, if a source of fly ash and/or cement is not readily available, the option would become cost-prohibitive.

Table 4: Advantages and Disadvantages of Solidification

Advantages	Disadvantages
Dual disposal method for power plants with coal combustion residuals	Requires vast land resources
Permanent residuals management	Requires fly ash amendment
Low CapEx	Difficult to maintain concrete in slurry piping
No significant greenhouse gas contribution	

Conclusion

Zero Liquid Discharge is somewhat of a misnomer as all technologies have a waste stream that have some amount of liquid entrained in that waste stream. The cost of ZLD systems is related to many factors including the location of the facility and the type of contaminants needed to be removed, and the moisture content of the waste stream. Typically, the lower the moisture content the more expensive the operating cost of the ZLD system. The lowest cost option is always to avoid ZLD if possible.

If ZLD is required there are several alternatives available that depend on the location of the facility, the discharge requirements, availability of thermal energy sources, availability of land, and other site-specific factors. Each system has its advantages and disadvantages and there is no correct solution for every application. It is critical to thoroughly vet each ZLD for the particular factors at each application and it is recommended to engage knowledgeable consultants to assist in the selection of the best ZLD solution.

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