Advanced Integrated ZLD Systems

The Hybrid ZLD approach pairs the best of membrane and thermal technology to make ZLD affordable, yet robust and reliable.

By Ajanta Sarkar

Over the past decade, the Hybrid ZLD systems i.e. integrated zero liquid discharge (ZLD) systems have emerged as the most effective ZLD approach for dealing with the most difficult to treat wastewaters in many industries including power, refining, and chemicals. The Hybrid ZLD approach pairs the best of membrane and thermal technology to make ZLD affordable, yet robust and reliable. The Hybrid ZLD process incorporates advanced membrane technology, HEROTM (High Efficiency Reverse Osmosis) based Reverse Osmosis system as a pre-concentration step followed by evaporation and crystallization technologies.

Hybrid ZLD

Wastewater streams are known to be rich in silica, high heavy metals, TOC, hydrocarbons, and sparingly soluble salts, etc. A conventional RO system is limited by its chemistry to provide high yields and produces large quantities of brine for either treatment or disposal.

The patented HERO™ Technology is used to overcome these chemistry related issues and generate high yields of product water, thereby reducing the quantity of the reject/brine stream to less than 5-10% of the total wastewater for the thermal based ZLD system that follows. The high recovery is especially important for plant economics as the more water that can be recovered, the lesser the evaporation requirement downstream. This leads to significant energy efficiency as compared to a more conventional system.

The evaporation technology provided is usually a Mechanical Vapor Compression (MVC) based Brine Concentrator followed by a Forced Circulation Crystallizer, where the concentration of the waste stream exceeds the solubility limits of the major dissolved salts, thereby producing salt slurry. Solids are removed from the slurry using a belt filter press. The mother liquor that is separated goes back to the crystalyzer while the salts separated are suitably disposed.

The permeate from the advanced membrane based pre-concentration step can be used as cooling tower make-up or can be further polished and used as ultra high purity process makeup. The high purity distillate produced from the thermal portion in this system is also acceptable for demineralizer makeup.

The feed to the thermal system consists of HERO™ reject. An advantage of this process is that it operates at relatively high recovery generating less reject compared to a conventional RO. This leads to the generation of a very small concentrate stream/feed for the thermal system or evaporation pond, therefore making it possible to achieve a true ZLD status.

Thermal Process

The plate and frame feed/distillate heat exchanger preheats the feed with outgoing hot distillate. The preheated feed is sprayed into the deaerator, which further heats the feed with low-pressure evaporator vent vapors and boiler steam.

A small fraction of water from the feed is vaporized and vented from the system along with the non-condensable gases like carbon dioxide and oxygen. Removal of the carbon dioxide and oxygen from the feed stream minimizes corrosion in the system. Typical dissolved oxygen content in the deaerated feed is 10ppb.

The feed then flows to the Falling Film Evaporator. The feed is mixed with the brine and circulates over the tube surface. Water in the brine is converted into steam by absorbing the latent heat in the compressor discharge. Brine is discharged from the system to maintain the concentration in the evaporator system.

Vapor flows through an external mist eliminator which removes entrained droplets of brine from the vapor before it flows to the compressor. The mechanical compressor increases the vapor saturation pressure and temperature so that it can be used as heating steam in the evaporator. The compressed vapor transfers its latent heat to the brine circulating on the inside of the tubes. This generates vapor to be fed to the compressor. The vapor is condensed on the outside of the tubes and the condensed vapor (distillate) is pumped through the feed distillate heat exchanger and out of the system.

The brine concentrator is designed with a very low ΔT (temperature difference between the heating medium and

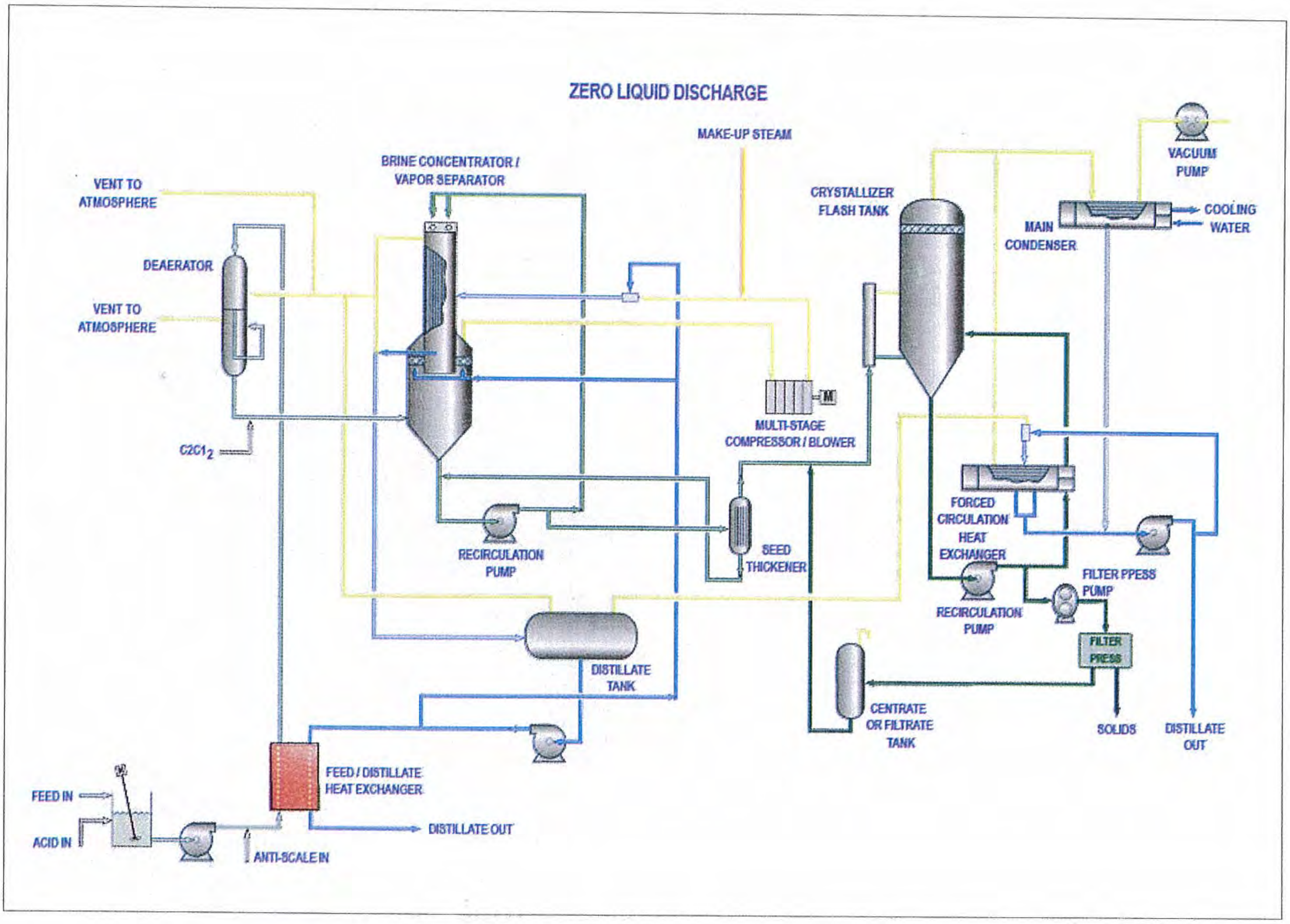

Figure 1: Typical process flow diagram of integrated system

the boiling brine) and a high recirculation rate. The two main benefits are reduced scaling rate and a lower compressor power requirement. Energy efficiency is maximized by utilizing the outgoing distillate and vent steam to preheat the incoming feed.

The brine is concentrated to approximately 15-18% total solids in the evaporator to achieve a very high recovery factor. Blowdown from the sump flows to the crystallizer unit, maintaining the solids balance in the system,

The Forced Circulation Crystallizer is specially designed to precipitate, grow, and handle crystals in the brine as water is continuously evaporated. In a properly designed forced circulation evaporation system, recirculated brine is pumped through the forced circulation heat exchanger where it is heated above its boiling point. Boiling of the brine in the heat exchanger is suppressed by backpressure exerted by sufficient static head. It is important to suppress boiling in the heat exchanger tubes to prevent precipitation of the saturated salt(s) in the tubes.

Precipitation of salts in the tubes can lead to plugging and poor performance. High recirculation rates are used to maintain high velocity on the heated tube surface, which keeps the contact time low, avoiding scale formation on the heat transfer surface. High velocity through the tubes also increases turbulence, which increases heat transfer efficiency. The heated brine flows into the flash tank, where it flashes to its saturation temperature.

The Forced Circulation Crystallizer uses a thermocompressor to minimize the amount of steam required and the amount of cooling water used in the condenser while maximizing the amount of evaporation. This improves the reliability of the system by eliminating a potential point of failure while not significantly increasing the cost of the operation.

A Crystallizer Recycle Pump and associated piping is provided to continuously recirculate crystallizer slurry to/from the Belt Filter Press. This recirculation loop is provided to prevent slurry from the gravity settling in the feed piping to the Belt Filter Press. The Recycle Pump recirculates the slurry at velocities high enough to prevent the slurry from gravity settling in the lines.

The density of the Crystallizer recirculating slurry is monitored and controlled. On high density, the concentrate salt slurry is taken to the Belt Filter Press for separation. The Belt Filter Press dewaters and discharges the salt cake. Filtrate —which is actually the highly concentrated mother liquor from the crystallizer and from the Belt Filter Press— gravity flows back to the Forced Circulation Feed Tank where it is mixed with blowdown from the Brine Concentrator. The salts exit the system as salt cake from the Belt Filter Press unit.

An important aspect of the evaporation as well as crystalyzer system design is the issue of foaming. The feed to the evaporator/crystallizer may foam. Foaming is undesirable in the system, as it results in loss of heat transfer surface available

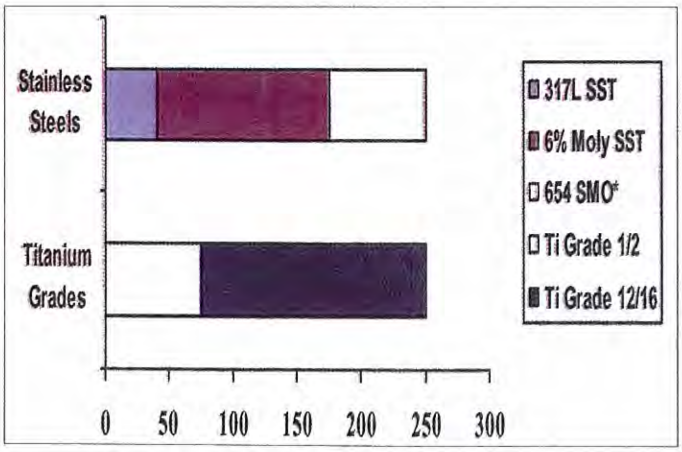

Figure 2: Materials as a function of Chloride Concentration for 110 C Deaerated Solutions, pH>6

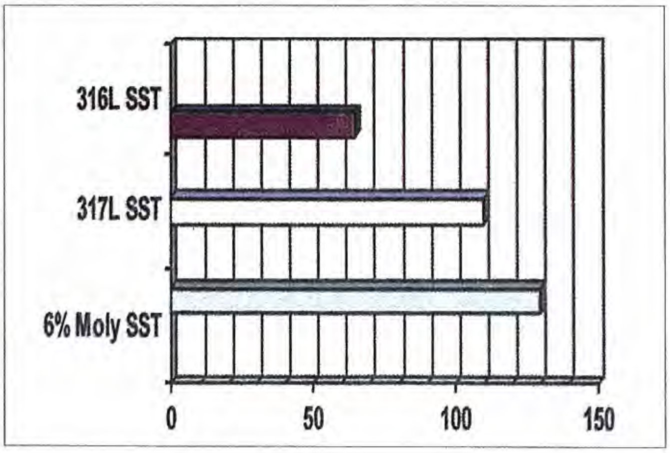

Figure 3: Materials Selection as a Function of Temperature Deaerated Solutions, Chloride Concentrations from 1,000 to 20,000 ppm, pH > 6

Figure 4: Brine Concentrator

for evaporation, thereby reducing the efficiency of the system. To control foaming in these units, an antifoam dosing is necessary.

The integrated systems are designed for automatic steady state operation and require little operator attention. The typical process flow diagram is illustrated in Figure 1.

Major Equipment Description

Vertical Tube Falling Film Evaporator

Falling film vertical tube evaporators use vertical tube bundles with brine evaporating from a thin film on the inside of the tubes. Brine is distributed in a thin film down the inside of the tubes. The brine absorbs heat from condensing water vapor on the outside of the tubes. The latent heat of vaporization transfers from the water vapor through the tube wall to the thin brine film on the inside of the tube. For every kilogram of water vapor that condenses, approximately one kilogram of water is evaporated from the brine film.

The vapor condensing on the tube bundle is primarily water vapor but can also contain air and other non-condensables. These non-condensables stay in the vicinity of the tube walls and impede heat transfer unless swept away by sufficiently high vapor velocities. A vent on the evaporator body continuously removes the non-condensables to maintain high heat transfer coefficients and to prevent loss of driving force (differential temperature) through excess subcooling of the heating vapor.

The brine is introduced at the top of the vessel and flows in a downward direction as a falling film. The brine is uniformly and generously directed to the full circumference of each tube as a thin film. Because the recirculation rate is many times greater than the evaporation rate, only a small change in concentration occurs down the tube length as evaporation takes place. The recirculation rate is chosen conservatively to ensure that the heat transfer surface is well wetted and localized drying is not encountered.

A proprietary inlet feed distributor ensures that the liquid is evenly distributed to the tubes. This design has been proven to be much less susceptible to plugging than other designs, including individual weir inserts or swirler inserts. Loss of flow to the tube is a primary cause of scaling. The proprietary design

Figure 5: Waste salt from ZLD

feature greatly reduces the potential for loss of flow to a tube and increased scaling.

Careful design eliminates areas where solids and impurities may collect and impede liquid flow and heat transfer. Design features include large holes in the distribution system, sloped bottoms, and smooth entrance to pump suctions.

Mechanical Vapor Compression

Vapor compression is a highly efficient process using mechanical energy input to achieve evaporation and condensation. The fundamental difference between the vapor compression unit and the conventional evaporator is that the latent heat of vaporization is fully utilized in the VC evaporator. Since the evaporator also serves as the condenser, essentially all of the latent heat is recycled, with no rejection of heat to cooling water.

The evaporated vapor flows through the mist eliminator to the suction of the compressor. The compressor does work on the water vapor increasing the saturation pressure of the water vapor so that when it condenses, it does so at a higher temperature. The compressed vapor flows to the heating side of the evaporator. As it condenses, it transfers the latent heat of vaporization back to the liquid film on the tube side.

The compression process produces discharge vapors that are superheated (i.e. hotter than the corresponding saturation temperature). Scaling, excessive fouling, and stress corrosion can occur if the superheated vapor is allowed to condense on the evaporator tube bundle. This scaling would occur as the sensible heat is transferred through the tube. To remove the superheat in the compressed vapor discharge, de-superheated water (in the form of distillate) is sprayed into the vapor stream. This distillate is at saturation temperature so latent heat is not removed from the vapor stream and can be used for the evaporation process.

A low speed centrifugal compressor is used for the mechanical compressor for the brine concentrator. This is a very simple and easy-to-maintain machine and it has a long history of successful operation in mechanical vapor compression evaporator systems. All components of the compressor in contact with the vapor are constructed of stainless steel for resistance to corrosion.

Forced Circulation Evaporator

Forced Circulation Crystallizers are specially designed to precipitate, grow, and handle crystals in the brine as water is continuously evaporated. In a properly designed forced circulation evaporation system, recirculated brine is pumped through the forced circulation heat exchanger at a high velocity where it is heated above its boiling point. Boiling of the brine in the heat exchanger is suppressed by backpressure exerted by sufficient static head.

There is no boiling or concentration in the Forced Circulation Heat Exchanger. This minimizes the scaling and fouling that would be found in thin film evaporators, where there is a concentration change within the evaporator body. Therefore, it is important to suppress boiling in the heat exchanger tubes to prevent precipitation of the saturated salt(s) in the tubes. Precipitation of salts in the tubes can lead to plugging and poor performance. High recirculation rates are used to maintain high velocity on the heated tube surface, which keeps the contact time low, avoiding the formation of scale on the heat transfer surface.

Since hard sodium chloride crystals are also in the recirculating fluid, these assist in limiting the buildup of scaling salts on the heat transfer surface by providing a scouring action. High velocity through the tubes also increases turbulence, which increases heat transfer efficiency.

Heated brine flows into the flash tank, where it flashes to its saturation temperature. The vapor then flows through the mist eliminators and downstream to the condenser. Feed brine is mixed with the concentrated brine in the Flash Tank where they are mixed and recirculated through the Forced Circulation Heat Exchanger.

Key Operational Features

- Proven thermal Brine Concentrator utilizing Mechanical Vapor Compression for energy efficiency.
- The system provides for a deaerator to remove oxygen from the feed and reduce the corrosion that would otherwise be caused by the high chloride brine.
- High efficiency mist elimination to provide high quality water, on a consistent basis, for reuse and blending.

- External configuration of the mist eliminator allows the removal and cleaning of the internals without the need to get into the evaporator vessel thus providing ease of maintenance.
- Provision for remote operational monitoring of the process for troubleshooting by the vendor.
- The Brine Concentrator is designed with a low ΔT across the heat transfer surface to minimize scaling and extend times between cleanings.
- The Forced Circulation Crystallizer is designed with a high flowrate through the tubes to minimize scaling and maximize the times between cleaning.

Construction Materials

The thermal based ZLD systems are very sensitive to construction materials, as they face some of the most hostile corrosive environment in water treatment in terms of high chlorides as well as high temperatures. In case of high chlorides in the feed, the environment in the equipment can be very conducive to stress and crevice corrosion.

Other factors inducing corrosion are pH and dissolved oxygen. These are mostly tackled in the system by way of optimal pH operation and provision of a deaerator for removal of dissolved salts along with other corrosion causing non-condensable gases.

Components in contact with brine in the Brine Concentrator are titanium and 2507 Super Duplex SST; these extend life and resist corrosion. Super Duplex 2507 SST is designed to operate at high chloride environments and has been proven in evaporators designed and operated by Aquatech.

The Forced Circulation Crystallizer components are titanium tubes and 2507 Super Duplex SST; these provide excellent corrosion resistance.

Conclusion

In a world where extreme water scarcity often intersects environmental responsibility, ZLD is fast becoming a common need of the industry. The need for affordable and reliable ZLD has been a true challenge and over the past decade Aquatech has met this challenge by developing a Hybrid ZLD approach which focuses on pre-concentrating as much of the wastewater as possible before taking the balance waste though a proven and reliable thermal evaporation plant. It is important to note that the design and metallurgical selection of the evaporation plant must be done carefully to ensure process robustness and reliability as well as longevity of the overall system. This approach has been proven on dozens of projects globally.

About The Article

Ajanta Sarkar graduated from LIT Nagpur as a Chemical Engineer and completed Post Graduation in Management from Symbiosis Pune. She has nearly 21 years of experience in the field of process design and estimation of water treatment, sea water desalination and wastewater recycle and reuse systems. She has been working in Aquatech for the past 13 years in their Indian office as the Deputy General Manager Application Engineering. Prior to this she worked in Thermax India Ltd. as Deputy Manager Proposals Engineering. www.aquatech.com