The Advantage of Mixed Salt Crystallizers in Zero Liquid Discharge (ZLD) Wastewater Treatment Systems

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Summary

The crystallization process has long been used in the manufacture of commodity chemicals. However, unlike commodity production where only one salt precipitates, reducing industrial waste to dryness involves crystallizing multiple salts. A mixed salt crystallizer requires significantly different design parameters to avoid foaming and scaling. This paper will examine four types of mixed salt crystallizers used to reduce industrial wastewater to dry solids.

Introduction

Environmental regulations have mandated true ZLD wastewater treatment in a large number of industries, including power, manufacturing, refining, mining, pulp and paper and chemical processing. This means all industrial wastewater at a site is reduced to dry solids and recycled or sent to a landfill. Any useable water recovered from the waste treatment process is reused in the plant. Typically, large flow rates of wastewater are preconcentrated using a falling film evaporator, a membrane process such as reverse osmosis or both. Volumes of concentrated wastewater range from 3 to 100 gpm (0.01 to 0.38 m^3/minute) containing 100,000-300,000 mg/l total solids. This volume is then reduced to dry solids using a forced-circulation crystallizer.

The crystallization process has long been used in the manufacture of commodity chemicals such as sodium chloride and sodium sulfate. However, unlike commodity production where only one salt precipitates, typical reduction of industrial waste to dryness involves crystallizing multiple salts. This type of mixed salt crystallizer requires significantly different design parameters to avoid problems such as severe foaming and rapid scaling. Furthermore, mixed salt solutions have significantly high boiling point rises requiring detailed attention to design parameters when sizing vapor compressors, should a mechanical vapor recompression (MVR) cycle be desired.

Finally, innovative filtering techniques have been developed to reduce the cost of smaller crystallizer systems. Typical operating crystallizer systems will be reviewed, illustrating steam and MVR cycles, different solids separation devices and systems suitable for low flow rates. The critical use of testing, even with synthetic waters, will be reviewed. Data will be presented from operating plants to illustrate points presented in the paper.

There are about 15 wastewater crystallizers in operation in North America, most of which have been installed since 1989. Previous to this period,

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most plants involved in ZLD concentrated their liquid wastes to 20-30% total solids using a falling film evaporator of the seeded type and discharged a liquid brine to solar ponds. With increasing regulations on liners and monitoring wells, the construction cost of solar ponds has increased dramatically, making crystallizers a cost-effective alternative. Since many zero discharge plants are located where solar ponds are not technically feasible, crystallizers have been the process of choice to obtain solids from the concentrated liquid waste.

Mixed Salt Crystallization

Chemistry Example

In a commodity crystallizer producing, for example, sodium chloride or ammonium sulfate, a single salt is precipitated. If there are other salts present, these leave the evaporator system as a liquid purge which is often deep well injected, discharged to the environment or processed further. Using the Orlando Utilities Commission Stanton Power Station as an example, the following typical wastewater is processed (Table 1).

Table1: Table 1: Wastewater Composition Stanton Station (mg/l)

Dissolved Solids	Feed to Evaporator (after PH adjustment)	Feed to Crystallizer
Ca	335.0	1,300
Mg	56.0	2,800
Na	550.0	27,500
K	70.0	3,500
SO$_4$	1,279.0	26,900
Cl	658.0	32,900
NO$_3$-N	18.0	900
NH$_4$-N	0.8	40
PO$_4$-P	6.0	300
SiO$_2$	126.0	200
TDS	3,175.0	100,200

Suspended Solids	Feed to Evaporator (after PH adjustment)	Feed to Crystallizer
CaSO$_4$		52,500
SiO$_2$		6,100
TSS	50.0	58,600
Flow, gpm	600.0	13

The feedwater, mostly cooling tower blowdown, is preconcentrated in a falling film evaporator and then crystallized to a mixed salt consisting of sodium chloride and double salts of sodium, mag-

nesium and potassium sulfate. A phase diagram for the sodium, magnesium, chloride and sulfate system at 105° C is shown in Figure 1. The crystallizer feed composition and the expected concentrate composition are shown on the diagram. Based on this data, as the solution is concentrated the double salt Vanthoffite (3Na$_2$SO$_4$.MgSO$_4$) precipitates along with sodium chloride. In addition to the sodium, magnesium, chloride and sulfate, there is a significant amount of potassium present in the feed water that is expected to precipitate. Literature data is available for the system sodium, magnesium, potassium, chloride and sulfate, but it is difficult to represent in a two-dimensional diagram. Based on literature data, the double salts Langbeinite (K$_2$SO$_4$.2MgSO$_4$) and Glaserite (3K$_2$SO$_4$.Na$_2$SO$_4$) are also expected to precipitate.
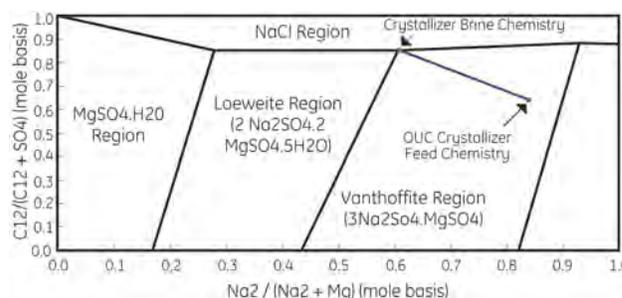

Figure 1: Na, Mg, Cl, SO$_4$ Phase Diagram (105° C)

The formation of mixed salts including double salts requires different design parameters than commodity salt crystallizers, some of which have been used for 100 years. Before discussing this, a review of the equipment is presented.

Mixed Salt Crystallizers

Crystallizers typically have an external heater, a two-pass horizontal or one-pass vertical, in which the solution is heated by steam in the shell. The heated solution then flashes into a large vessel called a vapor body. The heater tubes are flooded, with boiling water in the tubes suppressed by the liquid elevation in the vapor body (submergence). A slipstream is drawn off into a solids separation device (typically a centrifuge or automatic pressure filter) and crystals are removed. Different energy sources are used. Four types of devices are shown in Figures 2-5.

a) Steam Driven

In this schematic (Figure 2) steam is introduced into the heater shell. The steam use is about one pound of evaporation per pound of steam and this can lead to expensive operating costs. Cooling water is also required to condense the vapor that is generated.
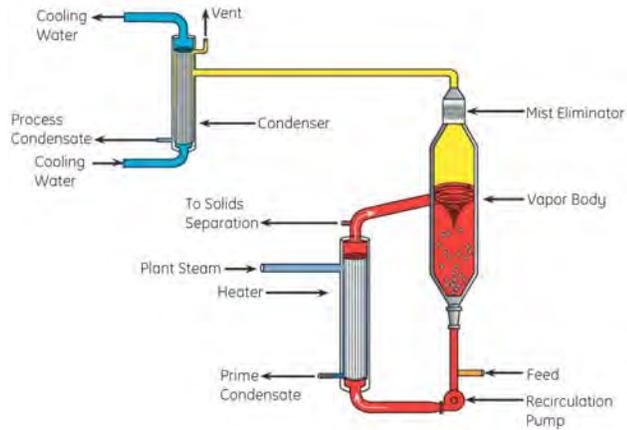

Figure 2: Steam-driven Crystallizer

b) Thermocompressor Driven

If higher pressure steam is available, a thermocompressor can be used to decrease the amount of steam required as shown in Figure 3. A portion of the vapor that is evaporated in the vapor body is recycled to the suction of the thermocompressor. Typically 150 - 200 psig steam is used as the motive steam. This configuration typically results in 20 - 30% reduction in steam usage. A condenser is still required to condense the remainder of the vapor that is not recycled to the thermocompressor.
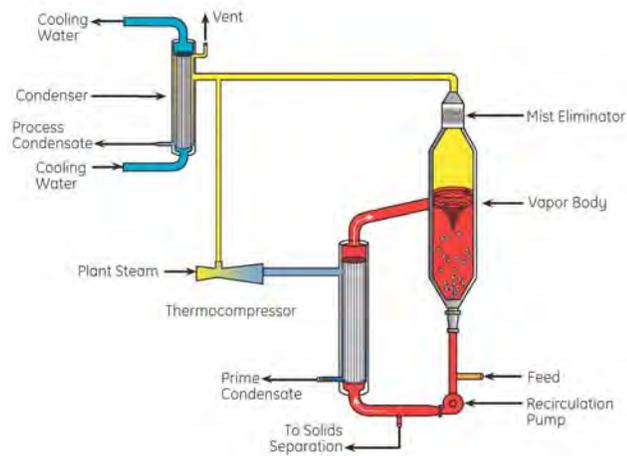

Figure 3: Crystallizer with Thermocompressor

c) Vapor Compression Cycle

A much more energy efficient system is shown in Figure 4, where the crystallizer energy is supplied by a vapor compressor driven by electricity or a gas or steam turbine. The water that is evaporated is compressed to raise its temperature of condensation to slightly above the boiling temperature of the recirculating brine on the inside of the tubes. The compressor discharge steam condenses on the outside of the tubes. The compressor is typically a positive displacement rotary blower, or for larger flows a single stage centrifugal compressor can be used.
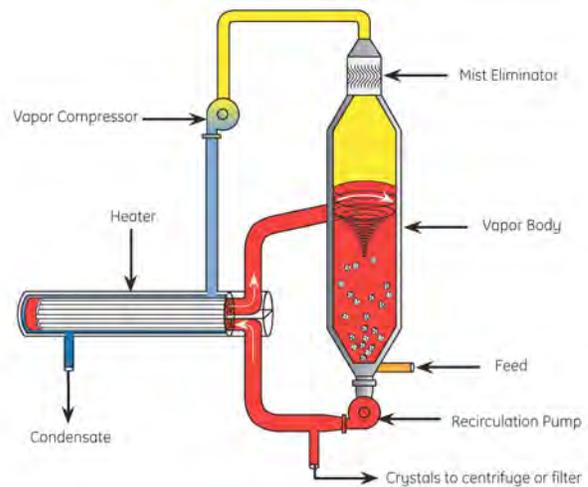

Figure 4: Vapor Compression Crystallizer

d) Calandria Crystallizer with Salt Basket

For smaller flow applications, a calandria crystallizer can be used as shown in Figure 5. This
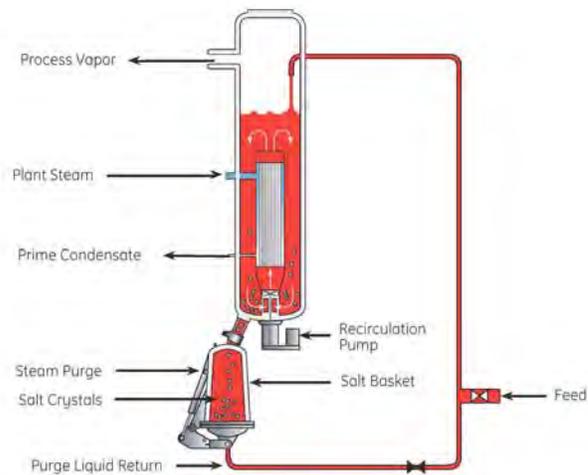

Figure 5: Calandria Crystallizer

provides a compact design with the heater inside the vapor body. The calandria crystallizer uses low pressure steam as an energy source. The vapor is either vented to the atmosphere or condensed. A propeller pump located in the lower portion of the crystallizer forces flow up through the heater where the condensing steam (shell side) gives up its latent heat to the rising liquid. Upon reaching the surface, the heated liquid (brine) releases its vapor and recirculates back to the propeller suction. The patented salt basket is a vertical vessel used to accumulate solids during crystallizer operation. To dewater and discharge the salts from the basket the following steps are followed:

1. The basket is isolated from the vapor body (calandria).

2. The brine is drained out of the salt basket.

3. Steam is used to dewater the solids in the basket.

4. The flanged lid is opened to discharge the salts. The salt basket works well for mixed salts that contain mostly large crystal salts such as sodium sulfate or sodium chloride that are easily dewatered. For more difficult filtering applications, the calandria crystallizer can be supplied with a pressure filter or centrifuge instead of a salt basket.

Special Design Parameters

Operating Characteristics

Foaming almost always occurs in mixed salt crystallizers. It can be a result of the presence of fine crystals or other contaminants such as organics. It can also be a result of improper pH control. If the cause of foaming cannot be identified and stopped, the foaming can be controlled with the addition of antifoam. Laboratory testing can be performed to identify an appropriate antifoam agent. Small doses of antifoam can be metered into the process on a continuous basis. Foam detection probes of the capacitance type are installed so that if an upset occurs, a larger dose of antifoam can be automatically pumped into the vapor body. In a vapor compression system, the foam probes can be interlocked to the compressor to protect it from severe foamovers. Foaming is severely enhanced by vacuum operation.

The solutions that are concentrated in mixed salt crystallizers are very corrosive, typically containing high concentrations of chlorides. Special consideration must be given to the selection of materials of construction. Titanium Grade 12, 254SMO, AL6XN, C-276 and 625 are among the alloys usually used in mixed salt crystallizers.

A mixed salt crystallizer operates in a scaling environment. Several design parameters such as high tube velocities are incorporated to minimize the scaling rate. Nonetheless, frequent cleaning is required. Since the salts in a mixed salt crystallizer are typically very soluble, a hot water rinse or boil-out using distillate or service water can be performed to periodically clean the system. For mixed salt applications the crystallizer typically runs 2 to 6 weeks between boilouts. The boilout takes about 1 shift to perform and must be figured into the design capacity and feed storage capacity. Regular boilouts can prevent the need for more rigorous cleaning such as chemical cleaning or hydroblasting.

Mixed salt crystallizers have varying amounts of soluble impurities. If these impurities are not removed from the crystallizer their concentration will increase and may cause operating problems such as a high boiling point rise or a solution that is difficult to filter or that does not crystallize. Soluble impurities are removed with the liquid that is occluded with the solid cake. Sometimes the solids moisture can be controlled in the solids separation device to remove excess soluble impurities. If the soluble impurities build up to unacceptable levels that cannot be removed with the solids, a liquid purge stream may be required. Sometimes this is required to maintain the boiling point rise at a level where vapor compression can be used and sometimes this is required so as not to interfere with crystallization of salts. For example, a crystallizer with high organics levels may require a purge because when the organics impurities reach certain levels, crystal formation may not occur. The presence of calcium chloride in the mixed brine often leads to a system purge. Computer modeling of the chemistry or laboratory testing of the brine (or even a synthetic brine) can often be used to determine if a purge is required.

Heater Design Parameters

The heater for a mixed salt application will be larger than for a pure salt application. When designing a heater for a mixed salt application, the lower heat transfer coefficient that occurs at the end of an operating cycle must be used for sizing the heater. Typically the heat transfer coefficient degrades to about 50% of the clean value before the heater must be boiled out. The tube velocity is generally higher for mixed salt crystallizer applications than for pure salt applications. The higher velocity helps to prevent salt deposits on the tube walls to prolong the length of the operating cycle.

Vapor Body Design Parameters

Vapor bodies for mixed salt applications are also larger than for pure salt applications. The height and diameter are larger to mitigate foaming problems. The liquid velocity through the vapor body must not be too high to prevent excessive short circuiting losses. The diameter must also be large enough to minimize liquid entrainment with the vapor. Sufficient residence time must be present to promote crystal growth. All of these factors must be considered when designing the vapor body.

Compressor Characteristics

When vapor compression is used for crystallizers, special consideration must be taken for compressor selection. One of the most critical parameters for specifying the compressor is accurate prediction of the boiling point rise of the brine. This is easy to determine for pure salt mixtures from literature data. However, for mixed salts it is not as easy to determine. Computer programs have been developed to predict boiling point rises and often testing can be done in the laboratory with either the actual solution or a synthetic solution. Another phenomenon that must be accounted for is short circuiting loss or slip. This is a result of vapor bubbles that are not released at the vapor/liquid interface and get trapped in the recirculating liquid. This can add a few degrees to the overall temperature difference that the compressor must overcome. Additionally, the proper fouled heat transfer coefficient must be used when determining the compressor requirements so that the system can meet capacity under fouled conditions.

Typically vapor compressors for mixed salt applications have high compression ratios. For smaller systems, rotary positive displacement blowers can be used. These are rugged machines that can tolerate occasional foaming. For higher flow rates, a single stage centrifugal compressor is used. These machines have higher tip speeds in order to achieve the required compression ratios. Protection from carryover of mist or foam is very important for these systems. Typically two stages of mist elimination and a foam detection system are required to protect the compressor.

Solids Separation

Crystal sizes can vary significantly in mixed salt crystallizers. When the crystallizer operation is started from dilute feed, relatively pure salts such as sodium sulfate or sodium chloride with large crystal sizes (several hundred microns) may be formed. These solids can be separated easily. However, as the solution is concentrated, the composition of the crystals changes as the more soluble components begin to precipitate. The soluble impurities increase and mixed salts, often double salts, begin to precipitate. The particle sizes are often quite small and may not be easily separated by devices such as pusher centrifuges that are used for larger particle (pure salt) applications. Two types of solids separation devices are typically used for mixed salt crystallizers. These are automatic pressure filters and solid bowl decanter centrifuges.

The automatic pressure filter operates in batches. The filter uses filter pump pressure to force liquid through the filter media and the filter cake as it builds up. When the cake is several inches thick, the feed is stopped and the cake is dried using pressurized air. The cake is automatically discharged by advancing the belt. The belt is automatically washed before it is used again. The sequence is automatic and is controlled by a series of timers that can be changed manually or automatically by input from the process operating parameters. The resulting cake is typically about 10% moisture. This can be somewhat controlled by adjusting the filtering and drying cycle times. The solid bowl decanter centrifuge is typically used for larger flow rate systems with higher solids loading. The resulting solids typically contain 5 - 10% moisture. The centrifuge operates continuously. The feed

rate to the centrifuge is adjusted to maintain the desired suspended solids concentration in the recirculating brine, typically 25%.

Typical Operating Systems

Steam Driven System

A steam driven crystallizer has been operating at Orlando Utilities Commission (OUC) Stanton Power Station since 1994. The feed to the crystallizer is cooling tower blowdown preconcentrated in a falling film evaporator. The crystallizer uses a thermocompressor to increase the steam economy of the system. A solid bowl centrifuge is used for solids separation. Two crystallizer systems are present in parallel so that if one is down for cleaning or maintenance, the other one can be used.

Figure 6 shows a printout of a screen from the control system for one of the crystallizers. The crystallizer brine return pumps feed the preconcentrated brine from the evaporator to the crystallizer recirculation line. The feed rate shown, 32 gpm, includes centrate that is recycled back to the system from the centrifuge. The recirculated brine enters the heater at 240° F and is heated to 243° F. It is then flashed in the vapor body operating at atmospheric pressure. About 76% of the vapor is condensed in the crystallizer product condenser and the remaining 24% goes to the thermocompressors. There are four thermocompressors of varying capacities in parallel. One or several thermocompressors can be valved into service to achieve the desired crystallizer capacity. This allows for efficient operation over a variety of flow rates.

The centrifuge is operated to control the suspended solids level in the crystallizer. The specific
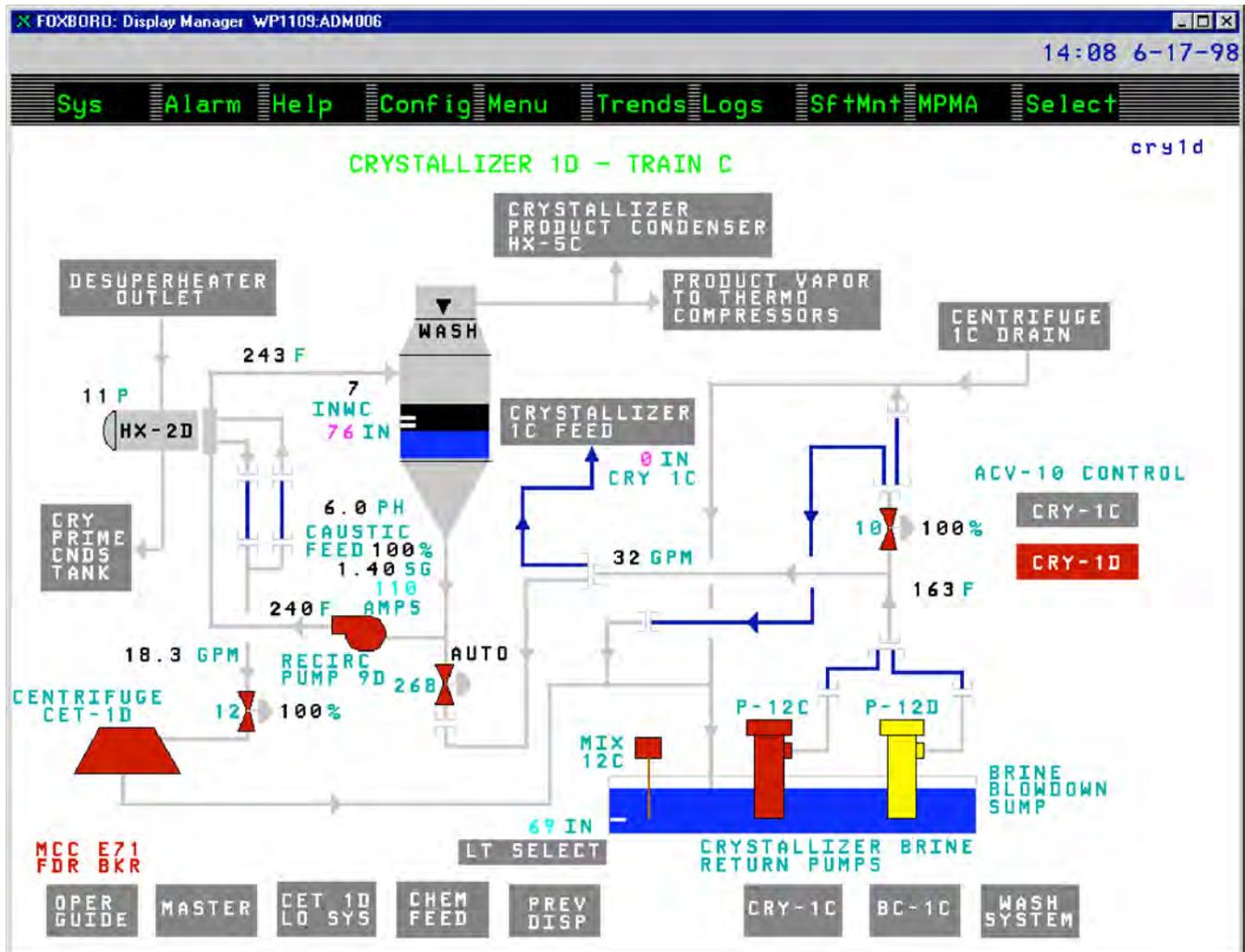

Figure 6: Crystallizer Control Screen

gravity, shown at 1.40, is an indication of the suspended solids level. Another quick test of suspended solids level can be done by taking a sample in a graduated cylinder and allowing the suspended solids to settle. Laboratory tests are done once per shift to measure the actual suspended solids level. The diagram shows the feed valve to the centrifuge 100% open. The separated solids are discharged to a bin and the centrate is returned to the crystallizer along with the feed via the brine blowdown sump.

Compressor Driven System

A vapor compression crystallizer was installed in 1990 at a chemical plant in central California. The actual wastewater to be treated was not available at the time the system was designed, so a synthetic material was made to simulate the actual wastewater. Glassware testing was performed to determine crystallization characteristics, boiling point rise and other system design parameters. The major salts present in the crystallizer were sodium sulfate, sodium chloride, sodium nitrite and sodium carbonate. Other minor constituents included fluoride, boron, hypochlorite and nitrate. Several organic constituents were also identified in the feed, the major components being sodium acetate, formic acid, formaldehyde, methanol and ethylene dichloride. Since the system was to use a vapor compressor, the boiling point rise of the solution was critical for system design. Since sodium nitrite, sodium nitrate and some of the organic constituents are very soluble and can have a big impact on the boiling point rise of the solution, testing was deemed necessary.

A synthetic solution was made and the solution was concentrated in a series of steps with intermediate solids removal. The resulting concentrated brine was about 65% total dissolved solids and the measured boiling point rise was 32° F.

Another concern was the emission of volatile components in the system vents. A computer program was developed using relative volatility data to predict the composition of the vents. A vent condenser using cooling water and a chilled water condenser were designed to condense the vents and minimize the emissions to the atmosphere.

A positive displacement rotary blower with a compression ratio of 2.37 was selected for this applica-

tion. The system was designed to treat 15 gpm of wastewater. When the system started with dilute feed at a low boiling point rise under clean conditions, the capacity was significantly higher than this, about 20 gpm. As the system became concentrated and the heater fouled, the system capacity dropped off to design capacity.

Over time, soluble impurities build up in the brine, increasing the boiling point rise and the total dissolved solids in the brine. Some of the soluble impurities leave the system with the moisture in the centrifuged solids. However during synthetic feed testing, the need for a purge was determined and quantified. In actual operation it was necessary to purge a small amount of liquid from the system to prevent the buildup of soluble compounds that did not crystallize, which increased the boiling point rise and resulted in excessive foaming. The actual amount of purge was very close to the quantity predicted by laboratory testing.

Conclusion

Mixed salt crystallization is a proven method of waste minimization. However a successful system requires design parameters and design features substantially different from classical single salt commodity crystallizers.

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