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Preliminary Assessment of a Thermal Zero Liquid Discharge Strategy for Coal-Fired Power Plants

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ABSTRACT

The authors performed a preliminary analysis of the possible advantages and disadvantages of developing a thermal zero liquid discharge (ZLD) system for use in treating flue gas desulphurization (FGD) wastewater from coal-fired power plants. Research included a general survey of existing application of the technology to FGD wastewater, discussions with vendors, and basic engineering calculations based on a model case. The authors conclude that, because of the many factors that can affect wastewater composition, each facility must make an individual assessment of the feasibility and risk associated with ZLD technology. They also conclude that further research and development is necessary before ZLD technology can be applied to FGD wastewater.

FGD systems have been widely used to remove sulfur dioxide and other pollutants from the flue gas generated by coal-fired power plants. As a result, some of the pollutants that were emitted from the stack are collected in the FGD blowdown. Mercury, selenium, arsenic, boron, nutrients, and organics are the main pollutants of concern in FGD wastewater. In some states, selenium, mercury, total dissolved solids (TDS), or nitrates have already been regulated, and other pollutants are being investigated for regulation.

Currently, the United States Environmental Protection Agency (EPA) is collecting data on FGD wastewater in the utility industry. The EPA is evaluating current FGD wastewater treatment technologies at eight coal-fired power plants belonging to multiple utilities as part of its development of new steam electric effluent guidelines by early 2014. The new effluent guidelines will set more stringent wastewater limitations for FGD wastewater.

The technologies that the EPA is evaluating include settling ponds, physical/chemical treatment, biological treatment, constructed wetlands, and thermal ZLD. In a recent guidance document, the EPA concluded the settling ponds are unlikely to be best available technology (BAT) for FGD wastewater because more effective treatment technologies have been demonstrated. It has further concluded that physical/chemical treatment is not effective at removing selenium, nitrogen compounds, and certain elements (such as calcium, magnesium, and sodium). Additionally, EPA finds (1) physical/chemical treatment followed by biological treatment substantially reduces nitrogen and/or selenium, but not the TDS, boron, sodium, and magnesium, and does not remove mercury to single-digit part per trillion (ppt) levels; (2) constructed wetland treatment is able to remove selenium and mercury, but does not perform better than other biological treatment systems. These conclusions and findings are based on a limited data set and all aspects of the EPA's conclusions/findings need further research.

Other technologies that have been applied to FGD wastewater treatment, such as deep well injection and solar ponds, have not been the focus of the EPA's evaluations.

A thermal ZLD system is a candidate technology for FGD wastewater treatment. A ZLD system usually includes one or more brine concentrator(s) with/without crystallizer(s). Some ZLD systems also include a spray dryer and a bag house to achieve ZLD. In theory, a thermal ZLD system can transform almost all the pollutants from the liquid phase into a solid phase. Thermal ZLD systems for FGD wastewater treatment are not common in the U.S.; only a few designs have been applied to coal-fired power plants since the 1970s.

Thermal ZLD processes for FGD wastewater treatment in coal-fired power plants are currently installed at nine coal-fired power plants: One in the U.S., six in Italy, one in China, and one in Japan.

In the 1990s, the first U.S. ZLD for FGD wastewater was demonstrated at Miliken Station, NY. The demonstration experienced many problems and the system was abandoned. In Centralia, Washington, at the Big Hanaford Plant, a brine concentrator for FGD wastewater was installed and operated for about three months before it was abandoned. The latest ZLD installation for FGD wastewater treatment is at Iatan Generating Station, which is owned and operated by Kansas City Power and Light. The current operational situation at Iatan is unclear.

Of all six thermal ZLDs in Italy, four have been successfully demonstrated to treat FGD wastewater in coal-fired power plants since 2008. The other two plants have installed ZLD technology but are not running the ZLD systems because the site does not require it.

The thermal ZLD in China's coal-fired power plant has been in operation to treat FGD wastewater since 2009. This ZLD system is unique because it does not include a brine concentrator, but applies a 4-stage crystallizer.

Japan's coal-fired power plant started to operate a thermal ZLD in 2002. No crystallizer is applied in this system.

WHAT IS A BRINE CONCENTRATOR?

The brine concentrator is the primary water evaporator in the process. It typically is a seeded slurry falling film system in which the wastewater slurry is recirculated from a sump in the bottom of the brine concentrator vessel to the top of the vessel. The waste slurry falls through heating tubes where a portion of the wastewater is evaporated and the remainder returned back to the sump. The evaporated vapor is piped to a vapor compressor or turbo fan where the vapor is compressed, adding heat to the process. The heated vapor is used to heat the brine concentrator tubes to drive the evaporation process. After exchanging its heat, the vapor condenses and is collected and pumped to a collection tank for disposal or reuse at the power plant.

In our case, we assume a plant will burn Illinois basin coal. We evaluated a ZLD system that is capable of treating 410 gpm FGD wastewater with 40,000 ppm chloride in the water. The 40,000 ppm of chloride was the maximum chloride concentration in the scrubber because of materials of construction and operating concerns.

Based on tests with an equipment supplier, we calculated that for our study application, the brine concentrator will reduce our wastewater flow by approximately four times and the TDS in the concentrated brine will be approximately four times that of the inlet water. Figure 1 is a typical flow diagram for a brine concentrator and figure 2 is a typical picture of brine concentrator.

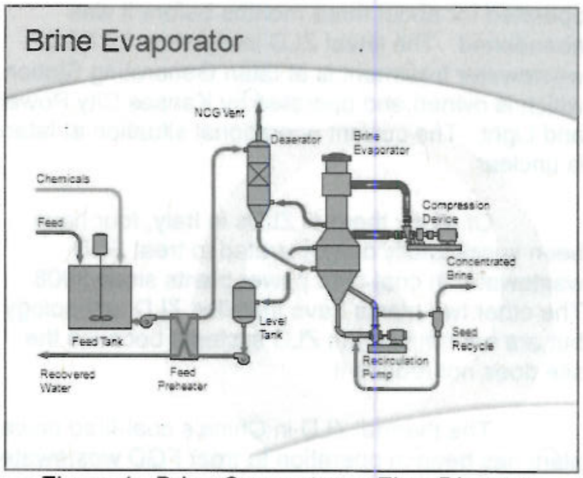

Figure 1. Brine Concentrator Flow Diagram. Courtesy Veolia/HPD

Figure 2. Brine Concentrator. Courtesy Veolia/HPD

WHAT DOES A CRYSTALLIZER DO?

It is our understanding that the crystallizer is the largest user of energy in the ZLD process because it must evaporate the brine concentrate from such a concentrated solution to produce a slurry that can be dewatered. Concentrated brine is pumped from the brine concentrator to the crystallizer. The brine slurry is recirculated from the crystallizer vessel to a heat exchanger and back to the crystallizer body where salt crystal formation will take place. Depending on the type of model chosen, the heat exchanger can be a horizontal or a vertical design. Crystallizer materials of construction can range from rubber-coated carbon steel to titanium. Crystallizer designs can include multiple effects, depending on the economics of the project. For our model case, multiple effect crystallizers were evaluated to conserve energy. Figure 3 is a typical crystallizer flow diagram and figure 4 is a typical picture of a crystallizer. Figure 5 is a flow diagram of a two-effect crystallizer and figure 6 is a typical diagram of a brine concentrator and a crystallizer in series.

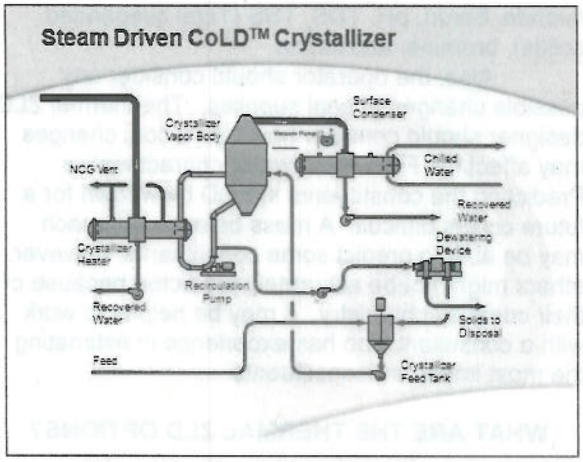

Figure 3. Crystallizer Flow Diagram.
Courtesy Veolia/HPD

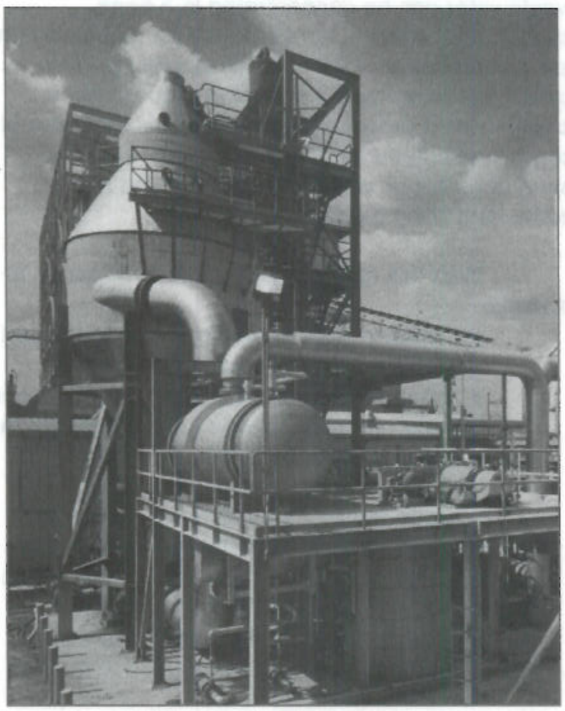

Figure 4. Crystallizer.
Courtesy GE

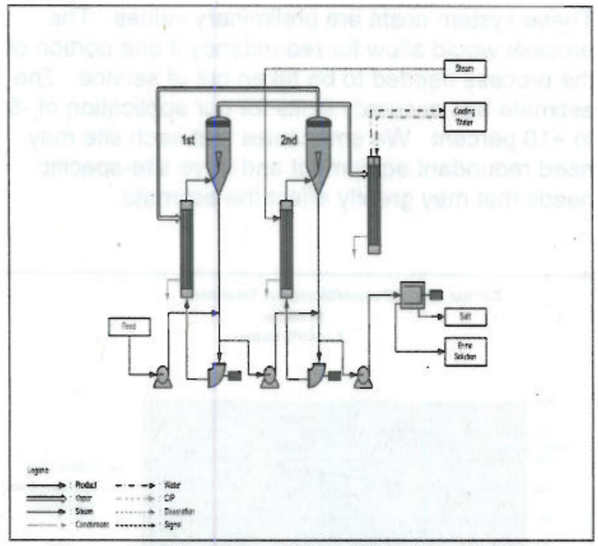

Figure 5. Diagram of Two-Effect Crystallizer.
Courtesy IGEA

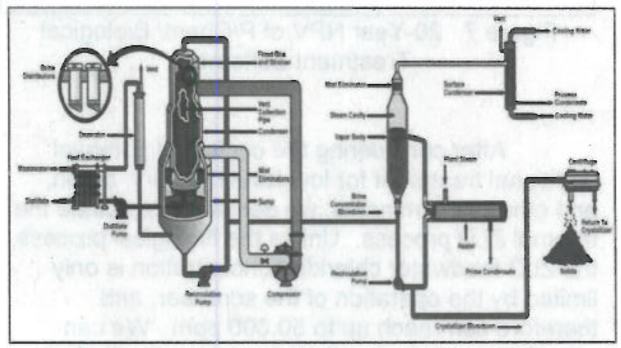

Figure 6. Brine Concentrator and Single Effect Crystallizer.
Courtesy GE

WHY ARE WE EVALUATING ZLD SYSTEMS FOR OUR FGDS?

ZLD systems should be evaluated for our FGD wastewater treatment for several reasons. First, it could be an effective, long-term FGD wastewater treatment system at some sites. Second, if it is effective, it will reduce water usage by recycling the condensate. Third, if it is effective, it would allow removal of all pollutants and eliminate any wastewater discharge concerns, such as the treatability of boron and TDS. Fourth, we are concerned with the economics of ZLD installation.

We compared the costs of a physical/chemical/biological process to the thermal ZLD process. For the biological treatment system, chloride concentrations in the scrubber must be maintained at less than 25,000 ppm. The graph in figure 7 illustrates the estimated 20-year net present value (NPV) costs from a physical/chemical/biological treatment process.

These system costs are preliminary values. The process would allow for redundancy if one portion of the process needed to be taken out of service. The estimate has accuracy limits for our application of -5 to +10 percent. We emphasize that each site may need redundant equipment and have site-specific needs that may greatly affect the estimate.

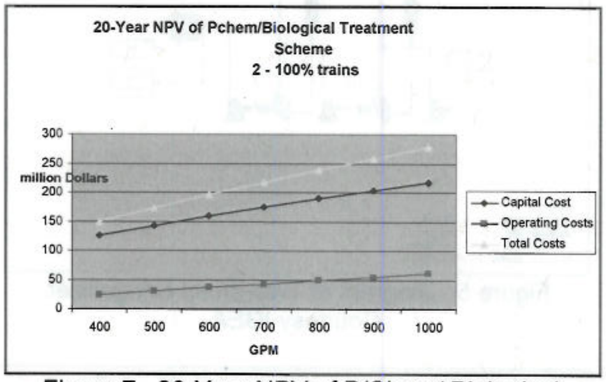

Figure 7. 20-Year NPV of P/Chem/ Biological Treatment Scheme.

After considering the costs and potential additional treatment for low-level mercury, boron, and other contaminants, we decided to evaluate the thermal ZLD process. Unlike the biological process, the ZLD feedwater chloride concentration is only limited by the operation of the scrubber, and therefore can reach up to 50,000 ppm. We can effectively recycle the distillate captured with the ZLD process, which is about 80 percent of the FGD blowdown flow, thus reducing the amount of water withdrawn by the plant.

WHAT ARE THE KEY FACTORS FOR A ZLD DESIGN?

The FGD wastewater flow rate is a key parameter in determining the ZLD footprint and heat/energy usage. The design flow rate is directly related to the chloride concentration required for the scrubber, plus any margin needed for equipment fouling, system operation, and recovery from system down times. The lower the flow rates, the lower the capital and operating costs will be. At lower flow rates, the equalization tank and pretreatment system are smaller as well.

Unlike cooling tower blowdown, FGD wastewater is chemically complex. Prior to design, the vendor should measure or estimate the concentrations of the following elements: calcium, magnesium, sodium, potassium, chloride, sulfate, nitrate, carbonate, bicarbonate, carbon dioxide, fluoride, boron, pH, TDS, TSS (Total suspended solids), bromine, and iodine.

Also, the operator should consider any possible changes to coal supplies. The thermal ZLD designer should consider how future coal changes may affect the FGD wastewater characteristics. Predicting the constituents in FGD blowdown for a future coal is difficult. A mass balance approach may be able to predict some constituents; however, others might not be accurately predicted because of their complex chemistry. It may be helpful to work with a consultant who has experience in estimating the most important constituents.

WHAT ARE THE THERMAL ZLD OPTIONS?

1. **BRINE CONCENTRATOR WITH ASH CONDITIONING.** If sufficient ash is available, FGD wastewater can be concentrated in a brine concentrator and the concentrated brine mixed with ash to produce a moist solid for landfilling. This option does not need a softening process nor a crystallization process, which simplifies the thermal concentration and salt dewatering process. The brine does not go away but is held in the ash to make land filling possible.

With this option there are several issues to consider.

- Should the brine be pumped to the ash or the ash be brought to the brine?
- Should the brine be stored in a tank? In our model case, ash mixing applications would occur 5 days a week only. Wastewater treatment would be a 24/7 operation. As a result, we would have to be able to store the brine in a tank.
- How to prevent brine from solidifying in the storage tank or in the pipeline?
- What affect will the brine have on the pug mill (carbon steel) used to mix the brine and ash?
- How much brine can be mixed with the ash?
- Are there leaching issues with the ash/brine mixture?
- How will you treat the leachate from the mixture?

A third-party bench test has been performed to answer some of these questions. FGD wastewater from a coal-fired power plant was collected and evaporated in a brine concentrator. After the thermal treatment, the brine had a concentration of 150,000 ppm chlorine and 215 ppm selenium. The compaction test showed that for this brine, the conditioned fly ash had a maximum dry unit weight at 18.3 percent moisture content. A TCLP (toxicity characteristic leaching potential) test further showed that selenium in the leachate (2.0 mg/L) exceeds the EPA's standard (1.0 mg/L), which means a potential environmental impact. Another permeability test indicated that chloride is rapidly dissolved in significant concentrations in the permeant and will be collected in the leachate collection system. Sulfate is readily dissolved in the permeant as well. Therefore, the leachate collection system needs to be carefully designed considering these constituents. More research is needed to evaluate brine concentrations and leachate collection and handling.

We concluded that using a brine concentrator with ash conditioning is not feasible because we plan to sell part of our ash and; not enough ash would be available for disposal to make this option work.

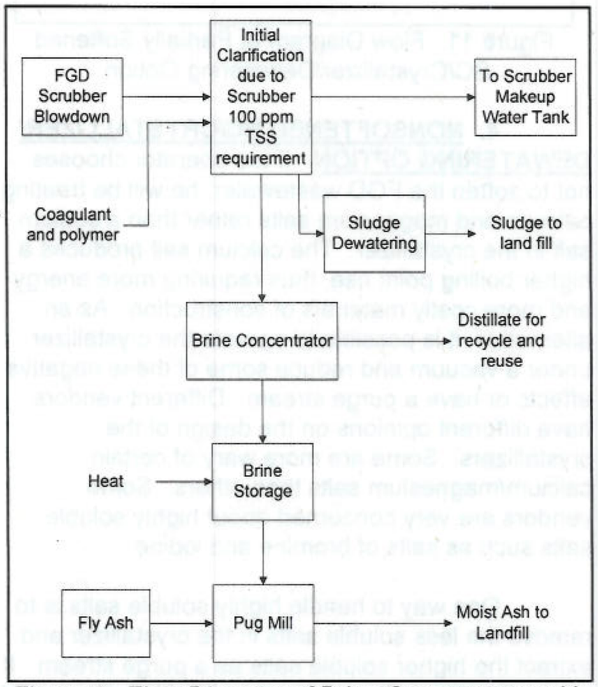

Figure 8. Flow Diagram of Brine Concentrator with Ash Conditioning.

2. SOFTENED BC/CRYSTALLIZER/ DEWATERING OPTION. Another option is to use a treatment chain consisting of a softened brine concentrator, crystallizer, and dewatering equipment. This process allows for treatment of the FGD wastewater on the front end of the process by softening to produce a sodium salt, which is a more treatable salt on the back end of the process. This process consumes a large amount of lime and soda ash and produces a large amount of sludge. By our estimates for our model case, we would need to feed 40 tons of lime and 80 tons of soda ash per day, resulting in a chemical cost of approximately $17 million per year. Some of this reagent cost can be reclaimed as calcium carbonate and fed to the scrubber. The cost of chemicals and sludge handling will need to be compared to the cost of a spray dryer operation to determine if this option is practical. As with all other cost figures in this paper, these numbers are preliminary and may not reflect the full range of costs associated with this option.

The large amount of chemicals needed and the large amount of sludge produced are disadvantages to this process.

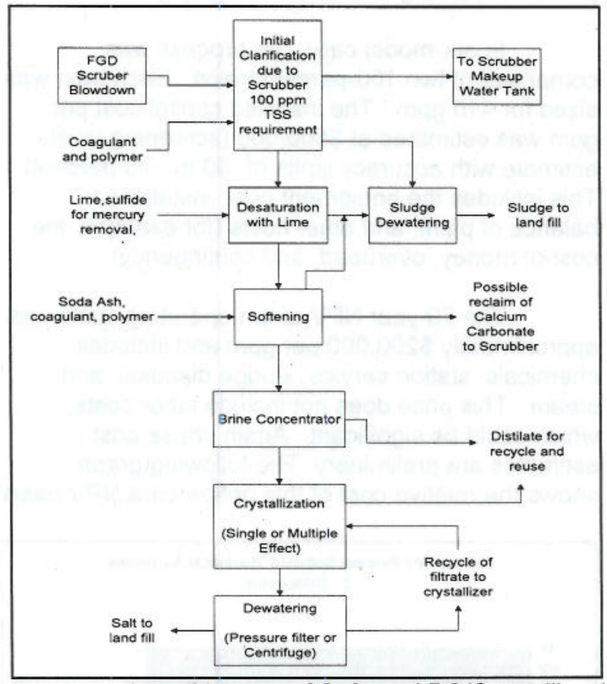

Figure 9. Flow Diagram of Softened BC/Crystallizer/ Dewatering Option.

3. PARTIALLY SOFTENED BC/ CRYSTALLIZER/DEWATERING OPTION. In this approach, magnesium is removed from the feedwater to a level needed to produce a defined salt in the crystallizer. The advantages of this approach are: (1) by removing the magnesium, the crystallized salts are easier to dewater; and (2) it is possible to lower the slurry boiling point rise. In our model case, the partially softened chemical usage rate was approximately $6 million per year. The partially softened process may require a purge stream that must be evaporated in a spray dryer or mixed with ash.

A bench scale test showed that raising the pH to 11 in the partial softening process is necessary to precipitate soluble magnesium to an acceptable level. In our case, about 3 tons of lime would be consumed per day for partial softening. The $Mg(OH)_2$ sludge could not be directly dewatered. A high-pressure recess chamber (225 psi) would be required to dewater this sludge and 3 to 4 hours would be needed for each dewatering cycle.

A bench crystallization test indicated that crystals can be successfully produced and dewatered. Calcium chloride dehydrate ($CaCl_2*2H_2O$) is the main crystal with smaller amounts of sodium chloride and calcium sulphate. During the crystallization test, iodine gas emission was observed at low pH operation. To inhibit iodine formation, pH should be controlled to greater than pH 8. No foaming was observed during the test.

In our model case, the process was comprised of two 100-percent trains. Each train was sized for 410 gpm. The installed capital cost per gpm was estimated at $500,000 (screening level estimate with accuracy limits of -30 to +70 percent). This includes the equipment cost, installation, balance of plant, and other costs (for example, the cost of money, overhead, and contingency).

The 20-year NPV of the operating costs was approximately $200,000 per gpm and includes chemicals, station service, sludge disposal, and steam. This price does not include labor costs, which could be significant. Again, these cost estimates are preliminary. The following graph shows the relative cost of this option on a NPV basis.

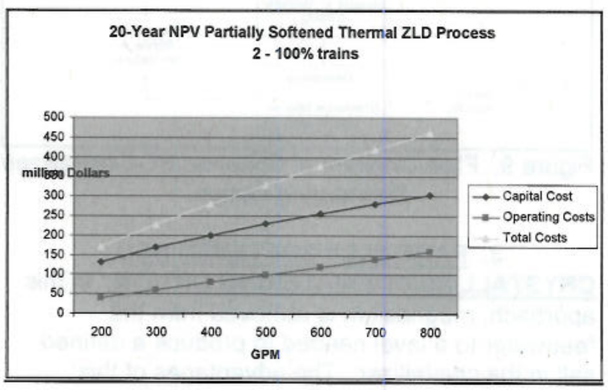

Figure 10. 20-Year NPV Partially Softened Thermal ZLD Process.

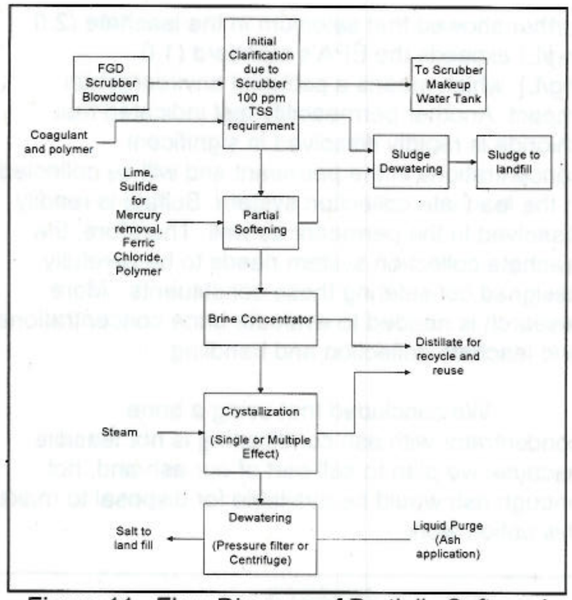

Figure 11. Flow Diagram of Partially Softened BC/Crystallizer/Dewatering Option.

4. **NONSOFTENED BC/CRYSTALLIZER/ DEWATERING OPTION**. If the operator chooses not to soften the FGD wastewater, he will be treating calcium and magnesium salts rather than a sodium salt in the crystallizer. The calcium salt produces a higher boiling point rise, thus requiring more energy and more costly materials of construction. As an alternative, it is possible to operate the crystallizer under a vacuum and reduce some of these negative effects or have a purge stream. Different vendors have different opinions on the design of the crystallizers. Some are more wary of certain calcium/magnesium salts than others. Some vendors are very concerned about highly soluble salts such as salts of bromine and iodine.

One way to handle highly soluble salts is to remove the less soluble salts in the crystallizer and extract the higher soluble salts as a purge stream. It is possible to mix the purge stream with ash, or send the purge stream to a spray dryer - bag house system, or design a crystallizer with sufficient vacuum to produce a salt without the purge stream.

Some vendors have concerns about the deliquescent nature of calcium chloride salt. Others say pure calcium chloride will not be formed in the crystallizer but that instead a double salt that will not absorb water as would pure calcium chloride is formed and is easier to handle.

A bench test was performed using high vacuum in crystallization to generate crystals without softening. The test successfully produced crystals, mainly composed of calcium chloride and magnesium chloride hydrate, together with calcium sulfate and boron. The crystals are hydroscopic, very easy to take moisture from the ambient air. The amount and quality of the crystals appears to depend on the crystallizer concentrate pH. The distillate quality also appears to depend on the crystallizer concentrate pH.

For our model case, the treatment process was comprised of two 100-percent trains. Each train was sized for 410 gpm. The installed capital cost per gpm was estimated to be in the range of \$500,000 to \$600,000 (screening level estimate with accuracy limits of -30 to +70 percent). This includes the equipment cost, installation, balance of plant, and other costs (for example, the cost of money, overhead, and contingency).

The 20-year NPV of the operating costs was approximately \$130,000 to \$150,000 per gpm and included chemicals, station service, sludge disposal, and steam. The cost does not include labor or maintenance for existing equipment affected by the high-chloride brine solution.

The following graph shows the relative cost of this option on a NPV basis at various flows.

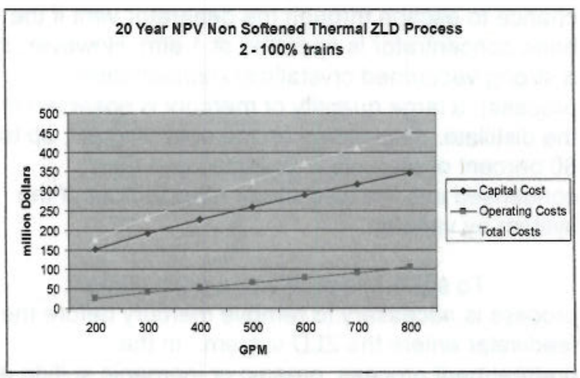

Figure 12. 20-Year NPV Nonsoftened Thermal ZLD Process.

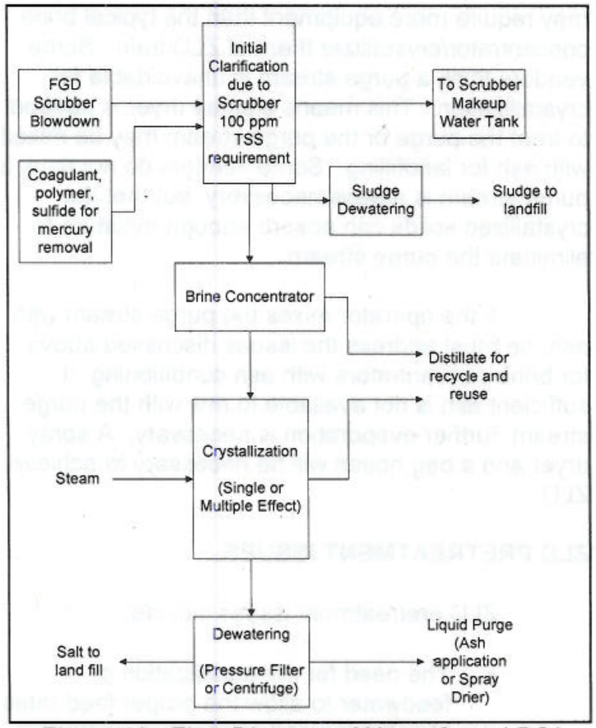

Figure 13. Flow Diagram of Nonsoftened BC/ Crystallizer/Dewatering Option.

COST COMPARISON BETWEEN PHYSICAL/ CHEMICAL/BIOLOGICAL SYSTEM AND ZLD SYSTEM

There are other treatment options for FGD wastewater. Physical/chemical plus biological treatment appears to be less expensive than a ZLD system. The actual cost difference will be site-specific. For our example, we assumed that a 20,000 ppm chloride blowdown stream could be concentrated to 40,000 ppm chloride in the scrubber and we compared the costs. That does not take into consideration the plant costs for operating at the higher chloride level (such as higher operator attention and corrosion of the plant equipment and infrastructure, such as steel and concrete components that come into contact with the higher chloride water). When taking those costs into account, the actual difference in cost will be greater because the thermal plant will have a smaller flow rate. Each site must look at its individual situation and pick from the options available to determine which process is the best suited for the site. Other options such as deep-well injection may also merit consideration. Also, further research and development is necessary before ZLD technology can be readily applied to FGD wastewater.

CAN THE SYSTEM ACTUALLY RESULT IN ZLD?

Whether the system can be operated as a ZLD system depends on wastewater chemistry and may require more equipment than the typical brine concentrator/crystallizer thermal ZLD train. Some vendors think a purge stream is unavoidable for crystallization. This means a spray dryer is needed to treat the purge or the purge stream may be mixed with ash for landfilling. Some vendors do not think a purge stream is always necessary, but that the crystallized solids can absorb enough moisture to eliminate the purge stream.

If the operator mixes the purge stream with ash, he must address the issues discussed above for brine concentrators with ash conditioning. If sufficient ash is not available to mix with the purge stream, further evaporation is necessary. A spray dryer and a bag house will be necessary to achieve ZLD.

ZLD PRETREATMENT ISSUES.

ZLD pretreatment issues include:

- The need for the equalization of feedwater to allow the proper feed rates of softening and clarification chemicals.
- The control of suspended solids that may clog the inlet heat exchanger.
- The ability to dewater and haul solids produced by the pretreatment process from the site.
- The removal of some heavy metals if needed.

For our model case, a settling pond and clarifier with the option for sulfide addition will be designed as the pretreatment for the thermal ZLD.

WHAT SALTS ARE FORMED AND ARE THEY TREATABLE?

The characteristics of the salts formed in the crystallizer depend on the crystallization process picked. With a fully softening process, the salt is mainly composed of sodium chloride, which is not hygroscopic. The ZLDs in Italy and China generate this kind of salt.

A partially softened process generates salt with a hygroscopic nature, as it is composed mainly of calcium chloride hydrate. A nonsoftened process produces a similar salt that is composed mainly of calcium chloride and magnesium chloride hydrate. Both salts tend to melt down in a short period of time (minutes to hours).

The produced salt generally could be sold, landfilled or stored at a geologically stable mine. Of all the operational ZLDs, only China's ZLD site is able to sell its salt as a product (high purity NaCl). In some European countries such as Italy and the Netherlands where landfilling is not allowed, salts (mainly sodium chloride) are exported to German mines. In the U.S., a landfill may be a more realistic disposal choice. The landfill site should be well-lined and have a leachate collection system. However, chloride leaches out very easily and could flow into the leachate collection system. If the leachate is returned to the landfill without a chloride removal treatment, chloride will accumulate in the leachate and reach a very high concentration and cause corrosion problems. More studies are needed regarding salts delivery and handling.

DOES MERCURY ESCAPE FROM THE PROCESS?

Since mercury is volatile, questions remain about mercury's fate during the process. We theorize that mercury stays with the salts, but mercury might be released to the atmosphere through the brine concentrator's deaerator, or the crystallizer's vacuum system (if used). It might fall to distillate as well, and recycle in the power plant as the water is reused.

Limited tests show that mercury has little chance to escape through the deaerator vent if the brine concentrator is operated at 1 atm. However, in a strong vacuumed crystallizer (nonsoftened process), a large quantity of mercury is observed in the distillate. Depending on the operating pH, up to 80 percent of mercury is volatized and then condensed into the distillate or released out of the system by vacuum.

To solve this problem, a pretreatment process is necessary to remove mercury before the feedwater enters the ZLD system. In the pretreatment process, organic or inorganic sulfide is added to precipitate mercury. By this method, a high portion of the mercury could be removed. Ion exchange resin or absorbent could be used to treat mercury as well.

METHODS OF PROVIDING HEAT TO THE BRINE CONCENTRATOR.

The brine concentrator system will scale with time and will lose heat transfer capacity, which will manifest itself in a reduction of treatment flow capacity. If the brine concentrator is designed with additional heat transfer capacity, it may be possible to maintain flow and operate on the margin as the system scales. Research will be necessary to find the optimum balance of heat transfer area and compressor or fan capacity.

There are three primary means for providing energy to the brine concentrator and the crystallizer: compressors or turbo fans, thermo compressors, and direct steam feed. Compressors or turbo fans typically provide energy to the recirculating brine in the brine concentrator or a crystallizer. This appears to be the most energy efficient way for heating the brine. This approach, however, is limited to the capacity of the compressor or fan. If feedwater conditions change and the system experiences an additional boiling point rise, it may not have enough compressor capacity to input the necessary heat required to boil the slurry.

The thermo compressor is more energy efficient than steam heating, but it is limited by the capacity of the ejector to input heat into the process.

The use of steam for operating the brine concentrator and crystallizer is another option. This option is the least efficient but allows for the most flexibility. As the water conditions change, the operator can turn up the steam flow and achieve higher boiling points.

For FGD wastewater applications, because of the possibility of changing feedwater conditions, we prefer the turbo fans for the brine concentrator and direct steam injection for the crystallizer. If the operator experiences a boiling point rise caused by changes in the feedwater, he can increase the steam flow and inject more heat into the crystallizer process.

CHOOSING AMONG DEWATERING DEVICES.

Belt pressure filters and centrifuges appear to be the most popular means of dewatering the salt slurry formed in the crystallizer. Each has advantages and disadvantages. The dewatering device recommended by the ZLD equipment vendor will be based on the vendor's experience and the size of the project. Preliminary investigations indicate the centrifuge costs more to repair, but needs maintenance work less often. Pressure filters cost less to repair, but must be maintained on a more regular basis. The amount of salt that must be processed will also determine which device is chosen. The centrifuge's handling capacity is higher than the pressure filters.

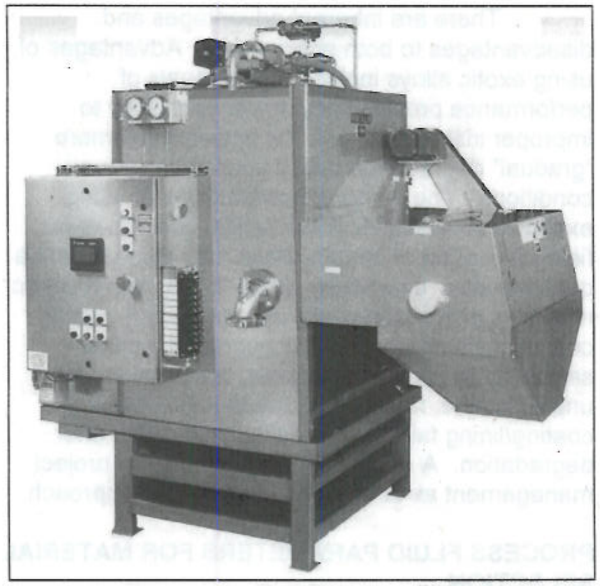

Figure 14. Belt Pressure Filter.
Courtesy Veolia/HPD/Oberlin

ZLD SYSTEM MATERIALS SELECTION CONCERNS.

Materials selection is a primary concern when designing scrubber-effluent ZLD systems. High system reliability is often necessary to sustain permitted operation of the coal plant it serves. Thus, unanticipated material degradation that causes equipment failure can have severe consequences. The most important driver affecting materials selection in these systems is process water composition.

Scrubber effluent is quite aggressive; further cycling this liquid in the ZLD process severely compounds the problem. Exotic materials are often required to resist process conditions in several components of the ZLD process, such as concentrator tubing and crystallizer vessel. Since components can be quite large for a ZLD system serving a large coal plant, material costs become a major portion of total system costs. Therefore, selection of the proper materials is critical to striking the balance of maximizing system reliability and minimizing both initial capital and life-cycle costs.

Since raw material cost is a significant portion of the total project cost, there is an incentive to reduce the use of exotic materials wherever possible. Manufacturers are of two schools of thought on this subject:

(1) handle aggressive conditions with conservative alloy selection; or
(2) handle aggressive conditions with inert non-metallic surfaces wherever possible.

There are inherent advantages and disadvantages to both approaches. Advantages of using exotic alloys include higher levels of performance predictability, lower sensitivity to improper installation, and the possibility of more "gradual" degradation under unanticipated conditions. The primary disadvantage of using exotic alloys is higher initial capital cost; however, field fabrication of certain alloys may also present a qualified labor availability issue. Using non-metallic materials and coatings allows lower initial capital cost. Disadvantages of this approach include sensitivity to installation quality; the potential for unpredictable, rapid degradation in the event of coating/lining failure; and difficulty in repair after degradation. A decision must be made by project management as to the most appropriate approach.

PROCESS FLUID PARAMETERS FOR MATERIAL SELECTION.

Scrubber effluent chemistry is complex in that a large number of elements are present and the effluent composition constantly varies with coal and limestone composition. Important process liquid characteristics that affect corrosivity of typical ZLD materials include chloride concentration, pH, dissolved oxygen, and fluoride concentration.

Since the total system cost is strongly linked to hydraulic capacity, minimizing the volume of water in the system is a key consideration. Thus, there is an incentive to increase cycling in the scrubber vessel itself. Cycling has the potential to raise chloride levels of the incoming water stream into the tens of thousands ppm. In any case, the incoming liquid will eventually be increased in composition to the practical limit of titanium and nickel-based materials under ZLD process conditions (approximately 180,000 ppm chlorides) using a brine concentrator.

The pH of incoming scrubber effluent can vary depending on the scrubber technology, but is often between 5 and 6.5 for limestone-based scrubbers. Depending on the ZLD pretreatment used, this value can be increased, and the corrosive potential reduced. Incoming liquid can contain high levels of dissolved oxygen (DO), further increasing the corrosive potential.

Before process liquid enters the brine concentrator, deaerators are used to reduce DO to manageable levels. Titanium is typically used for tubing in falling film brine concentrators.

Since titanium is susceptible to fluoride pitting, fluoride levels can be a concern. Most manufacturers indicate that if sufficient elements are available to complex with fluoride ions, and pH is kept high enough, fluoride corrosion of titanium is controllable. Some high-fluoride applications may require the use of expensive palladium alloyed titanium grades such as Grades 7, 11, and 16 to control corrosion.

As the liquid proceeds through the ZLD process, the temperature increases from the scrubber outlet temperature to near the boiling point of the process liquid (over 212 °F, depending on the boiling point rise). Components wetted with aggressive process fluids at these temperatures require exotic materials to resist rapid corrosion failure.

In summary, halide content (chlorides, fluorides), and temperature aggravate the corrosion situation and drive materials selection to exotic alloys in many areas, while the use of deaerators to reduce DO and pretreatment to raise pH assist in mitigating those effects. Components with heat transfer surfaces, and any scaling, high-deposit areas, or areas with crevice geometry provide further aggressive conditions.

EQUIPMENT CONSIDERATIONS.

Equipment design and function also affect materials selection. Heat transfer surfaces require particular attention. Heat exchangers, brine concentrators, and crystallizers all have the ability to scale or accumulate deposits. Local conditions under these deposits are more aggressive than bulk liquid composition and thus more highly alloyed materials may be necessary than may initially have been predicted by bulk liquid composition. Plate and frame heat exchangers and any other components containing crevices also make the surface more prone to attack. Areas such as heat exchanger surfaces and tubes in falling-film brine concentrators contain thin wall sections. Thin wall areas are not able to tolerate any significant corrosion penetration that might occur due to pitting. Manufacturer experience with component performance is critical to choosing the correct alloy for areas of aggressive service.

SCALING ISSUES.

Both the brine concentrator and the crystallizer will scale. Calcium sulfate formation on the evaporation tubes in the brine concentrator is the primary scale in the brine concentrator. The formation of the scale reduces heat transfer and results in loss of capacity in the unit. The seed slurry design must control scaling by selectively providing crystals for the scale to preferentially form on. Over time additional scale that forms on the tubes will require cleaning. If the chemistry is not properly controlled, other salts will form in the brine concentrator. Some vendors are concerned about Glauberite (another salt) in the brine concentrator. Most vendors recommend cleaning the brine concentrator at least once a year. More frequent cleaning may be necessary, but the down time will reduce the amount of water that can be processed. Yearly cleaning would be a goal to be worked toward.

Salt formation is the purpose of the crystallizer. As a result, the crystallizer will scale up more frequently than the brine concentrator. The system is designed to allow salt formation in the crystallizer vessel and not on the system heat exchanger by maintaining a hydrostatic pressure at the heat exchanger which retards crystallization. By controlling the feed chemistry, pressure, purge stream rate, and temperature, the vendor determines which salts are formed and which must be purged from the process. Scales formed on the crystallizer are more soluble than those formed on the brine concentrator and can be more easily removed.

CLEANING.

Cleaning of a brine concentrator is a multiple-day event requiring the mechanical removal of the scale from the evaporation tubes by a hydro blast followed by a chemical cleaning of the vessel. Cleaning may take from three days to a week, depending on the level of scale and the expertise of the cleaner.

The crystallizer is cleaned more frequently than the brine concentrator. Cleaning typically will be in the range of weeks rather than months. Typically the cleaning of a crystallizer requires a boil out with fresh water and takes 8 to 12 hours.

BORON AND AMMONIA.

Boron is a major concern in some FGD wastewaters. At some plants, boron concentrations can be in the hundreds of ppm. The boron species formed depend on the pH of the wastewater. At low pH, boric acid is present. Boric acid is a volatile specie and will evaporate in the brine concentrator and crystallizer. At high pH, boron is present as borate and is not volatile.

Boron might cause problems in the brine concentrator and crystallizer. If a large concentration of boron is present in the feedwater, it may evaporate and be concentrated in the condensate. If the condensate is reused in the FGD, boron will build up within the system. Boron might also deposit in the mechanical compressor. One vendor provided us a design with a boron scrubber to solve this problem. The boron scrubber waste effluent could be treated via a spray dryer or ash conditioning.

Ammonia/ammonium in the FGD wastewater usually comes from the leakage of ammonia injected into the selective catalytic reduction (SCR) or selective noncatalytic reduction (SNCR), which is used to remove Nitrous oxides NOx in the flue gas. Operation of the brine concentrator or crystallizer at high pH will increase ammonia evaporation, causing ammonia carryover to the distillate. At low pH, the ammonium is dominant, which will precipitate as solids in the crystallizer and be removed with other salts.

SUMMARY

Choosing an appropriate FGD wastewater treatment technology is a site-specific exercise that requires a thorough review of engineering goals and objectives, feasibility, and costs. Thermal ZLD systems are not a proven technology for FGD wastewater in the U.S., as all U.S. installations with the exception of Iatan are no longer in operation. We do not have enough information to judge the effectiveness of the Iatan application. Further research and experience with ZLD applications to FGD wastewater are necessary prior to any large-scale use of this technology.