

FGD Scrubber Wastewater ZLD Solid Waste Characterization and Disposal Options

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ABSTRACT

In the electric utility industry, new steam effluent guidelines are driving development of new water treatment technologies. Zero liquid discharge technologies are being considered as an economically feasible technology for disposing of FGD scrubber wastewater. However, little consideration has been given to the back end costs and risks of disposing of the solids produced by ZLD systems. FGD wastewater contains significant amounts of salts that once evaporated pose unique issues when it comes to disposal. Consideration needs to be given to how and if utilities want to dispose of such materials and how the associated costs affect the economics of the use of a ZLD system.

INTRODUCTION

Coal fired electric generating units are facing a myriad of challenges due to many new regulations which are being proposed at the federal level. Chiefly among them are the recently promulgated Mercury and Air Toxicity Standards which are putting pressure on gaseous emissions. On the water side, proposed changes to Steam Effluent Guidelines are quite stringent and will require much research and capital investment to be compliant if the rule is finalized in its current form. Of chief concern is the ability of flue gas desulfurization (scrubber) wastewater to be treated to the proposed standards. All of the commercially available technologies that are being proposed for scrubber water treatment are costly and could potentially be susceptible to upset conditions that could lead to noncompliance.

An alternative option for scrubber wastewater treatment is the use of a zero liquid discharge technology (ZLD). In the most generic sense, this approach would avoid having to be compliant with discharge regulations by evaporating the wastewater. ZLD technologies are commercial in other industries and are included, and incentivized, in the proposed changes to the effluent guidelines. However, inherent to all zero liquid discharge technologies is the creation of solid waste which must be disposed of. Currently, little thought has been given to the characteristics of these

byproducts, the long-term risks of their disposal, nor any technologies developed such that the material could be disposed of in a responsible way. In addition, the potential need to modify landfill practices for these new materials needs to be considered in the economics of installing a ZLD solution.

OPERATION OF ZLD SYSTEMS

Thermal ZLD systems, chiefly brine concentrator and thermal evaporator technologies, operate on the principal of evaporating water to avoid discharge. However, the residual in this process is a byproduct that consists of the dissolved and suspended solids that were in the wastewater. For the case of flue gas desulfurization wastewater, these byproducts are likely to be a calcium chloride salt, with the calcium being chiefly derived from the limestone used in the scrubber and the chloride coming from the combustion of coal. Also, of particular consequence to thermal ZLD systems, the scrubber wastewater could still contain a significant amount of calcium sulfate or sulfite.

Due to the presence of dissolved and suspended solids, there are significant challenges associated with the ZLD process. Of most consequence are scaling issues within the system as water is evaporated away. As the water evaporates, many of the constituents precipitate and can cause significant amounts of scaling

within a brine concentrator or evaporator that can impair the system to the point of shutdown.

To combat these scaling issues, a softening process could potentially be used to remove calcium ions. However, it is expected that this wouldn't completely prevent scaling. Additionally, the cost of a softening process need to be full considered. Inherent to softening is the use of a softening additive in which the calcium chloride in the wastewater is exchanged with sodium, producing a sodium chloride salt as well as calcium carbonate. When considering the system as a whole, this means that the softening process requires the purchase of additional materials as well causes the volume of waste material to increase significantly. To date, the electric utility industry has had little operational experience with brine concentrator and evaporator systems. The issue of scaling during long term operation is not yet defined, much less solved technically.

PROPERTIES OF ZLD MATERIALS

Traditionally, electric utilities have preferred to store and dispose of their coal combustion byproducts onsite at their own facilities wherever feasible. Due to being legally responsible for proper disposal and avoidance of any environmental issues, it is preferred that materials be disposed of onsite. If ZLD technologies are employed, they will in most cases be disposed of in

onsite landfills just as other byproducts are.

As outlined above, inherent to the ZLD process is the production of solid byproducts. These byproducts will chiefly be salts; either calcium or sodium based depending on whether or not the system is softened. Characteristically as will be described below, the properties of these byproducts will require specialized equipment, procedures, and technologies; none of which have been commercially vetted over long operational periods. However, of most importance is the need to recognize that in order for a process to be truly called ZLD, disposal of byproducts is an integral and significant part of the ZLD process and cannot be disregarded. Until issues related to solids disposal are demonstrated in a technical, environmental, and economically feasible way, thermal ZLD technologies cannot be considered commercially available for the electric utility industry.

The basic chemical properties of salts, especially calcium chloride, suggest that there could be significant issues related to the handling and placement of ZLD materials into a landfill. In regions of the country where there is significant humidity, salts are naturally hygroscopic and will readily absorb moisture from the air. Data suggest that at typical summer temperatures and high humidity, a pound of calcium can absorb seventeen pounds or more of water from the atmosphere (Dow 2003). For

the case of calcium chloride, it will absorb ambient moisture to the point of liquefying and producing free water. Therefore, in a humid environment, research is needed to determine if ZLD byproducts would be able to pass paint filter tests in order to be considered a solid waste. Beyond potential paint filter test issues, little research has been conducted on transporting ZLD materials to onsite landfills as many utilities would plan to do. Due to the moisture affinity of the material, the potential to clog silos and conveyance lines needs further investigation. Finally, due to the salt content and the corrosive nature of salts, it is expected that care will need to be taken in selecting materials of construction.

DISPOSAL RISKS

Assuming that the material can be cost effectively transported and placed into the landfill, when considering disposal of ZLD materials, the largest unanswered issue is the long term fate of the material. As stated above, due to the high affinity for moisture, much research needs to be performed on whether ZLD byproducts will remain in the landfill over long timespans. As water infiltrates the landfill and comes in contact with the material, little data exists on whether the ZLD materials will remain in place or leach out. Also, given the affinity for ambient moisture, the potential for additional moisture collection from the air which could translate to additional landfill leachate exists. For calcium chloride, the

hygroscopic gain of moisture is an exothermic process. That can generate over one hundred degrees Fahrenheit of additional heat (Dow, 2003). It remains to be seen whether this could have negative effects on landfills.

As a corollary to ZLD disposal in landfills, in some instances wastewater as well as brine concentrator wastewater has been mixed with or used to condition fly ash before landfill disposal. However, there is apprehension within the industry with this approach. Much work has been performed by researchers in South Africa concerning the mixing of cooling water brines with fly ash. While data from that research at times shows that ash can sequester constituents from the wastewater in the ash, over time the brine migrates back out of the ash and produces a higher TDS leachate (Fatoba et al. 2011). Among other risks, the fact that the brine comes back out of the ash doesn't appear to be a true ZLD process. Therefore, if ZLD salts are disposed of, research needs to be conducted such that the assurances are made that the material won't migrate out of the landfill.

Also, very little work has been performed throughout the industry to determine the effects of ZLD materials on landfill geotechnical properties. Questions such as slope stability, compaction properties and dusting all need to be explored. Additionally, if ZLD materials lead to leaching and production of higher TDS leachates,

this could lead to scaling and clogging of leachate collection systems.

TECHNOLOGY DEVELOPMENT

Given the physical properties of ZLD wastes, if ZLD technologies are to be deployed, technologies need to be developed and evaluated so that the material can be disposed of in a responsible fashion such that they remain a solid and are stable in the landfill. Technology development toward additives and research on performance needs to be conducted to ensure that ZLD materials can be permanently sequestered in a landfill. Of most promise is development of solidification and stabilization technologies to mitigate the properties of ZLD byproducts. If a technology can be developed that reduces the leachability of the salts as well as offers favorable geotechnical properties, it could be of great benefit. Although stabilization has been employed in other fields for many years, to date not much work has been done to evaluate stabilization of ZLD materials along with coal ash. Cement as well as lime are traditional stabilization additives used in other fields and are likely of use for ZLD materials. It is expected that since coal ash is a common cement additive, it should have some benefit toward stabilization.

In addition to cement and lime additives, research is currently ongoing toward developing novel stabilization additives. Since any

additive that is used as well as a process to mix the material and stabilize it will increase costs, research is being directed toward developing low cost solutions that sequester the ZLD salts as well as the potential metals they may contain. Examples of such technologies are geopolymers as well as additives to create water repellent properties within materials (Daniels et. al., 2009)

On a second technology front, electric utilities need to evaluate the operation of their landfills and determine what steps need to be taken toward minimizing the interaction of rainwater with ZLD materials in the landfill. While the municipal landfill industry uses daily cover to achieve this, the utility industry needs to evaluate if this is necessary and determine if alternative covers that utilize ash and gypsum are feasible and more cost effective.

WASTE VOLUME AND ECONOMIC CONSIDERATIONS

Given the properties of ZLD materials and the potential need to add binders to solidify and stabilize the material, consideration must be given to the cost implications of such additives. In other industries, such as nuclear, salt waste stabilization requires additives of as much as 50%. Of those additives, fly ash is a commonly used along with cement and slag with cement typically constituting 10% of the total (Dixon et. al., 2008).

For a generic ZLD system operating on a 250gpm waste stream at 25,000ppm TDS, assuming all of the TDS becomes the waste material after the evaporative process would create 1.5 tons/hr of salt waste. Assuming a 10% cement addition at a current cement price of ~\$100/ ton (Cement Cost Adjustment Datasheet, 2013) would mean a cost of ~\$10/ton in cement addition alone. For comparison, onsite disposal costs for fly ash are typically in the range of ~\$10-30/ton. Considering the cost of cement additives alone could easily make disposal of ZLD materials twice as expensive as fly ash disposal. Additionally, in order to process the large volume of produced ZLD salts, mixing systems would be needed to mix ash, cement, or other additives in with the salts. Currently, the equipment and operational costs associated with such equipment is not considered as a part of the economics for ZLD systems.

Finally, consideration needs to be given to the costs associated with the extra volume of material from ZLD processes and how much valuable landfill space it consumes. Also, if landfill management practices have to be amended such that more aggressive techniques to prevent rainfall contact and infiltration, there will be additional operational cost that must be considered.

CONCLUSIONS

Whether electric utilities choose to employ ZLD technologies for

effluent guideline compliance or not, it is expected that ZLD is a technology path that will become ever more prevalent over time. As pressures increase around water quality and water consumption, the drivers for ZLD will become stronger. Therefore, it is prudent for the industry to start sooner rather than later to start evaluating the disposal implications of ZLD and start developing approaches to address those issues. In addition, the costs associated with landfill disposal needs to be factored into the overall costs of ZLD so that it can be properly compared to other wastewater treatment technologies.

References:

- Cement Cost Adjustment Datasheet. (2013): Engineering News Record.<http://www.ct.gov/dot/lib/dot/documents/dconstruction/cement_hist.pdf>.
- Daniels, J.L., Hourani, Mimi S., Harper, Larry S.(2009). Organo-silane chemistry: A water repellent technology for coal ash and soil. World of Coal Ash Conference- May 4-7, 2009. Lexington, KY. <www.flyash.info/2009/025-daniels2009.pdf>
- Dixon, K., Harbour J., Phifer, M. (2008). Hydraulic and Physical properties of Saltstone Grouts and Vault Concretes. SRNL-STI-2008-00421. <<http://sti.srs.gov/fulltext/SRNL-STI-2008-00421.pdf>>.
- Dow 2003. Dow Calcium Chloride Handbook. Published by Dow Chemical Company. August 2003.
- Fatoba, O. O., L. F. Petrik, W. M. Gitari, and E. I. Iwuoha. (2011). Fly Ash-Brine Interactions: Removal of Major and Trace Elements from Brine. *Journal of Environmental Science and Health, Part A*, 46, 1648–1666.