WASTEWATER FROM CARBON CAPTURE — SPECIAL CONSIDERATIONS FOR WASTEWATER TREATMENT

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ABSTRACT

Carbon capture is a critical concern for power plants. The amine process generates a wastewater that can present several concerns for treatment and discharge. The stream is warm, and exhibits a low pH. If required, the stream can be pH-adjusted to a neutral pH prior to delivery for further treatment. The amine in the stream may be any one of the three amines that can be used as a carbon capture solvent. For the purposes of this paper, the amine is assumed to be monoethanolamine (MEA). Amines and ammonia exhibit odors characteristic of decay and the nitrogen present in the stream is a nutrient for organisms in the plant-receiving streams and is frequently regulated in NPDES (National Pollutant Discharge Elimination System) permits. Nitrogen adversely affects the environment by causing increased biological productivity, resulting in low dissolved oxygen and eutrophication of lakes, rivers, and estuaries.

1. BACKGROUND

Carbon capture systems (CCS) associated with fossil-fueled power generating facilities often employ a low-pH amine chemistry to remove carbon dioxide (CO_2). The amine and ammonia species that are used to recover the CO_2 from the flue gas are absorbed into a low-pH water solution, rather than being vented to the atmosphere. To maintain the solution's capacity to absorb the amines and ammonia, a portion of it must be removed from the circulation loop on a regular basis and replaced with fresh solution.

Amines and ammonia exhibit odors characteristic of decay. In addition, the nitrogen present in the stream can be a nutrient for organisms in the plant discharge estuary. Nitrogen causes significant problems in the environment by bringing about increased biological productivity, resulting in low dissolved oxygen and eutrophication of lakes, rivers, and estuaries. The portion discharged from the CCS must then be treated to remove ammonia.

This paper discusses several options available in the power industry for removal of amines and ammonia from CCS wastewater, offering insight into the advantages and disadvantages of each.

2. TREATMENT OPTIONS FOR LOW-pH AMINE BLOWDOWN STREAM

For the purposes of this report, two amine stream qualities are discussed, dilute (Stream A) and concentrated (Stream B). The various characteristics used as the basis for the comparison are listed in Table 1. Stream A assumes that the CCS operations and materials of construction do not

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allow the system to concentrate the amine absorbent. Stream B assumes that CCS system is capable of operation at a 10 times higher concentration than that for Stream A.

Table 1. Amine Blowdown Stream Chemistry

Parameter	Dilute Stream (A)	Concentrated Stream (B)
Temperature, °F	>110	>110
Pressure, psia	14.7	14.7
pH	4.0	3.5
Amine, ppm	<1500	<15,000
H_2SO_4, ppm	<1800	<18,000
NH_3, ppm	<200	<2000
Flow rate, gpm	40	4.0

Both of these types of streams are warm and exhibit a low pH. These streams may require neutralization with sodium hydroxide (NaOH) prior to delivery to the treatment system.

Four primary treatment options, including multiple variants, as applicable, for removing amines and ammonia from the wastewater are presented in turn below:

- Incineration
  - Direct incineration in dedicated furnace
  - Cofiring with fuel
- Ion exchange
- Nitrification/Denitrification in a bioreactor
  - Activated sludge/sequential batch reactor (SBR)
  - Membrane biological reactor (MBR)

2.1 Direct Incineration in Dedicated Furnace

The concentrated waste stream could be fed directly to a dedicated waste incinerator to guarantee destruction of the amines. However, incineration will result in the amines being oxidized in the flame, which will add a NO_X emission source. This new NO_X emission may require a modification to the facility's air permit.

2.2 Cofiring with Fuel

As shown above in Table 1, both the dilute stream and concentrated stream are primarily water. As such, the waste stream could feasibly be sprayed on the coal for dust suppression, with the amine portion of the stream ultimately being destroyed in the boiler during combustion.

For coal-fired plants, this method of treatment may result in having to re-permit the unit that utilized the sprayed coal, as a new waste product would be incinerated in the boiler. The additional NO_X generated in the boiler would need to be included in the loading for any flue gas

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NO_X removal system, such as selective non-catalytic reduction (SNCR) or selective catalytic reduction (SCR).

2.3 Ion Exchange

Deionization in a resin bed is a commonly used method to remove ionic contaminants from a wastewater stream. Ion-exchange resin beads have a highly developed structure of pores that contain numerous sites with easily trapped and released ions. Trapping ions of interest takes place simultaneously with the release of other ions; thus, the process is called ion-exchange. There are several types of ion-exchange resin, which may be fabricated to selectively prefer one or several different types of ions. The type of resin most effective for removal of amines and ammonia is the strong acid cation (SAC) type. In the hydrogen form, SAC resin sites are initially occupied by H^+ ions.

The SAC resin has a higher selectivity for the amine and ammonia constituents in the wastewater stream than for the acid constituents. This is not true for alkali in the wastewater; therefore, neutralization with sodium hydroxide, potassium hydroxide, or other caustic chemical is not recommended until after ion-exchange treatment.

Ions trapped on the resin are, in turn, *exchanged* with new ions entering the resin bed. Through the exchange mechanism, ions migrate through the resin bed and eventually separate, or “break”, from the downstream resin interface. To prevent the separation, the resin is regenerated on a set throughput measured in gallons.

Both the dilute and concentrated amine wastewater streams contain high concentrations of amine and ammonia. The gallons of throughput before separation occurs for each vessel will be limited. In order to increase the throughput, a custom-designed resin vessel, which reduces the hydraulic loading and increases the depth of the resin bed, will be required. The lower limit of hydraulic loading for a resin vessel in order to prevent channeling through the resin bed is about 5 gpm/ft^2. Treating the dilute stream, at 40 gpm, the maximum vessel diameter is 40 inches. Deeper resin beds induce greater pressure drop across the resin bed. The practical maximum resin bed depth is six feet. Due to the very low hydraulic loading, the concentrated stream, at 4 gpm, cannot be practically treated with ion exchange.

The regeneration waste will be an amine/ammonia stream that is concentrated by five to ten times, a level of concentration similar to that of the wastewater stream. For this reason, the ion-exchange treatment is not preferred.

2.4 Nitrification/Dentrification in Bioreactor

Nitrification/Denitrification is a set of well-understood biologically mediated processes that ultimately produce molecular nitrogen (N_2) through a series of intermediate nitrogen compounds. Table 2 is a list of common bioreactor system configurations.

Table 2. Bioreactor Process Summary

Process Name	Process Description	Nitrogen Removal Effectiveness
Modified Ludzack-Ettinger (MLE)	Continuous flow, suspended growth, two stages, in separate tanks anoxic → aerobic	Good
Bardenpho	Continuous flow, suspended growth, four stages, in separate tanks, anoxic → aerobic → anoxic → aerobic	Excellent
Sequencing Batch Reactor (SBR)	Batch-suspended growth, four stages, time-sequenced in one tank, anoxic → aerobic → anoxic → aerobic	Moderate
Oxidation Ditch	Continuous flow, suspended growth, three stages, time-sequenced in one looped channel, anoxic → aerobic → anaerobic	Excellent

Ammonia is first converted to nitrate (nitrification), and then nitrate is reduced to nitrogen gas (denitrification). The conversion of ammonia to nitrate is strictly an aerobic process. Conversion of nitrate to nitrogen gas is an anaerobic process. These processes are routinely performed in sanitary wastewater treatment plants using one of the processes listed above. However; the high concentrations of nitrogen expected from the CCS waste stream will require optimization. It is expected that additional carbon sources and micronutrients will be needed to maintain the nitrification/denitrification process.

Nitrification is a two-step process, wherein nitrifying bacteria convert ammonia and ammonium to nitrite and then to nitrate. Two different types of bacteria are required to complete the process and both are strictly aerobic, in effect attaching oxygen to the nitrogen molecule. The nitrifying reactions normally are coupled and move quickly to nitrate, so nitrite generally will not accumulate in the bioreactor.

Nitrification requires dissolved oxygen, a long retention time; a low food-to-microorganism ratio (F:M); a high mean-cell residence time (MCRT or sludge age); adequate buffering (alkalinity); alkalinity in the range of 50-100 mg/L; a very strict temperature range; and a very strict pH range.

For example, conditions used to remove the ammonia found in sanitary wastewater typically has an extended aeration system with 24 hours of hydraulic detention time; a sludge age of approximately 30 days; temperatures in the range of 85°F to 95°F; and pH values between 7.5 and 8.5.

The warm temperature of the blowdown stream is a potential advantage to maintaining the biological nitrification process, as long as optimal temperatures are not exceeded.

The conditions necessary for denitrification of sanitary wastewater include depleted dissolved oxygen levels; a sufficient concentration of carbon, such as the ethanol from the amine; pH values between 7.0 and 8.5, and temperatures in the range of 40°F to 85°F. The organic amines may provide some carbon for this process, but supplemental carbon is expected to be required.

In some wastewater treatment plants, small amounts of micronutrients are provided by a small waste stream from the plant sewage treatment plant, or through direct augmentation. Denitrification produces nitrogen, carbon dioxide, and an activated sludge byproduct that must be separated from the effluent water in a settling tank or clarifier. The sludge will be disposed in a landfill. In order to meet any low discharge limits for total suspended solids (TSS), it is recommended that sand filters or other solids removal equipment be installed to polish the effluent before discharge.

The carbon dioxide evolved in the bioreactor will slightly reduce the total carbon dioxide removed by the plant.

High concentrations of salts in the wastewater can have a negative effect on the bacteria in the treatment system. Salt concentrations approaching that of seawater cause osmotic dehydration in the sludge bacteria, which inhibits respiration, and can kill the bacteria population. For this reason, the dilute stream, neutralized by the CCS vendor, is favored for activated sludge treatment. Over time, the bacterial population can be acclimatized to higher concentrations of salt. Trace metals from the fuel may scrubbed from the flue gas by the amine; high concentrations of these trace metals may inhibit the nitrification/denitrification process.

Pilot testing is recommended to optimize the system design for the high concentrations of ammonia and nitrate to be treated. Some vendors will perform pilot testing to determine the proper mix of bacteria, appropriate sludge age, and recycle flow to design the capital treatment system.

The membrane bioreactor is a technology that combines biological degradation of waste products with membrane filtration. The membrane bioreactors may be anoxic or aerobic and arranged in the same fashion as the processes in Table 2, above. The membranes act as a solid-liquid separation to replace secondary clarifiers and polishing filters.

3. CONCLUSION

The treatment options available for the amine-containing blowdown stream are: incineration, ion exchange, and nitrification/denitrification.

Incineration, either directly or with the fuel in the boiler, is not recommended due to the potential increase of site NO_X emissions and air permit impacts.

Ion exchange is not recommended due to the TDS concentration in the waste stream. The TDS is too high to practically treat without regenerating the ion exchange resin on site; thus, only concentrating the waste stream rather than removing nitrogen. For this reason, ion exchange is not recommended.

Nitrification/denitrification in a bioreactor converts amines in the wastewater to elemental N_2. The waste streams that the system generates are a gaseous N_2 and a solid filter cake. Neither of these wastes would require further treatment; nitrogen would be vented to the atmosphere and the filter cake should be suitable for landfill disposal. Therefore, biological nitrification/denitrification treatment of the amine waste stream is preferred.

There is an additional disposal method available for this waste stream that does not require equipment installation. This method involves sending the amine waste stream to a publicly owned treatment works (POTW). The POTW typically is a municipal sewage treatment plant that uses activated sludge to denitrify the ammonia in the sewage before tertiary treatment. A local POTW may have the capacity and margin to treat the amine waste stream. It is recommended that waste stream disposal to a local POTW be investigated before preparation of capital treatment equipment procurement documentation is considered.