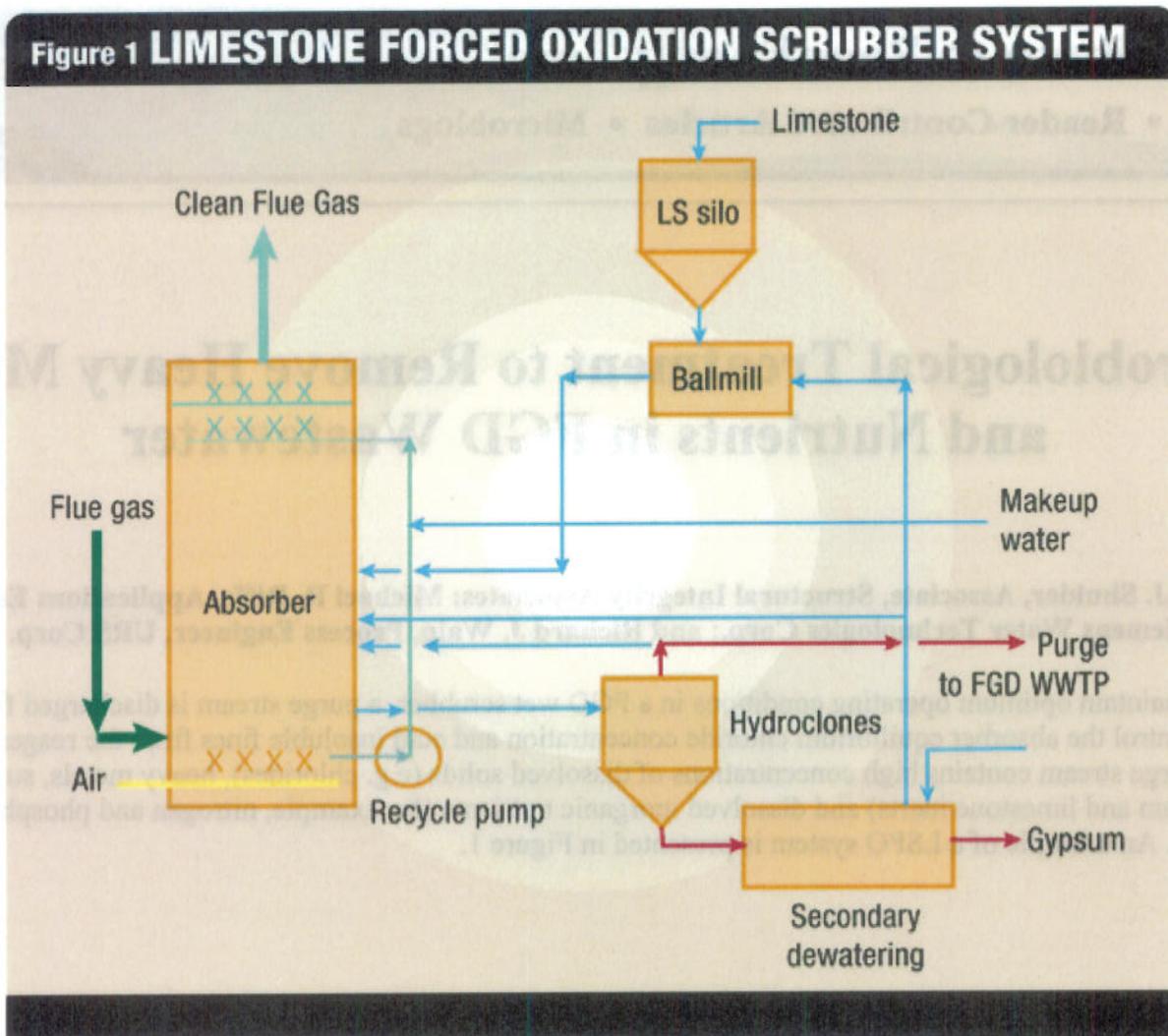


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Microbiological Treatment to Remove Heavy Metals and Nutrients in FGD Wastewater

By Stephen J. Shulder, Associate, Structural Integrity Associates; Michael R. Riffe, Applications Engineering Manager, Siemens Water Technologies Corp.; and Richard J. Walp, Process Engineer, URS Corp.

In order to maintain optimum operating conditions in a FGD wet scrubber, a purge stream is discharged from the system to control the absorber equilibrium chloride concentration and acid insoluble fines from the reagent limestone. The FGD purge stream contains high concentrations of dissolved solids (e.g. chlorides), heavy metals, suspended solids (gypsum and limestone inerts) and dissolved inorganic nutrients (for example, nitrogen and phosphorous compounds). An example of a LSFO system is presented in Figure 1.



Wastewater (Purge Stream) Characteristics

The quantity and quality of the wastewater stream varies with the type of coal, limestone composition, type of scrubber, make-up water and the gypsum dewatering system. In an increasing number of plants, the source of make-up water is recycled wastewater.

The purge stream is treated prior to discharge into a receiving stream to remove suspended solids, metals and nutrients. The treated water typically has discharge limits similar to other National Pollutant Discharge Elimination System (NPDES) monitoring locations including TSS and pH. More specific limits are based on the particular receiving stream. These often include heavy metals such as mercury, selenium or nutrient compounds. A number of treatment options may be considered though physical/chemical is the primary approach for TSS and some metals removal. Biological treatment has been demonstrated to effectively reduce selenium and certain nitrogen compounds.

Objectives of Treatment

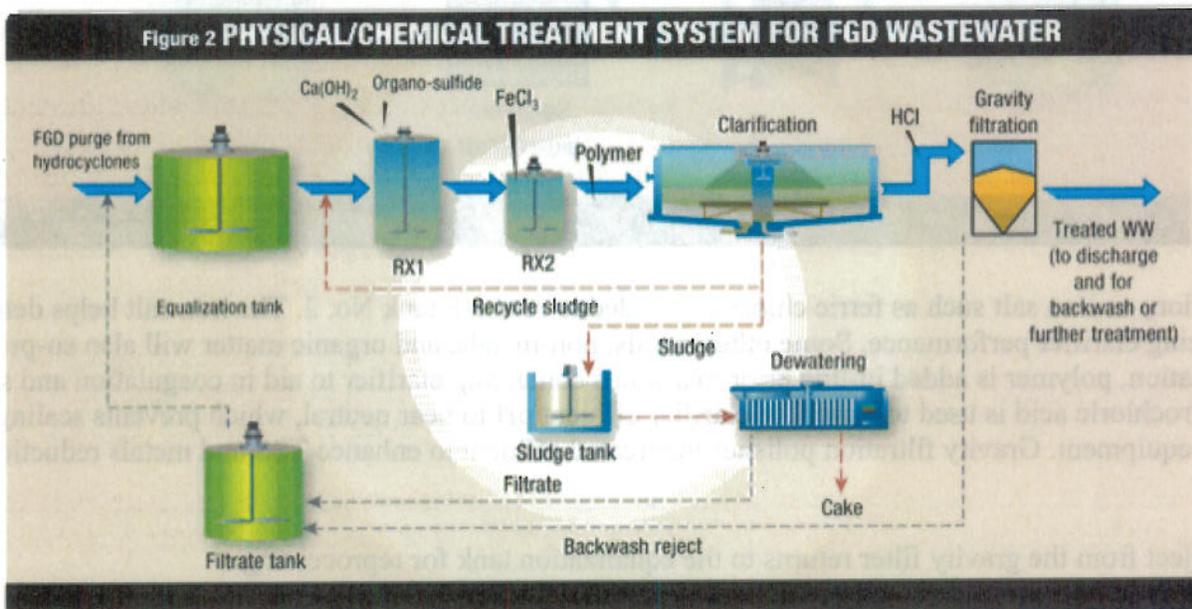
The FGD wastewater treatment system needs to be designed to meet the applicable discharge requirements with a high degree of reliability. The treatment objectives are:

- De-saturate the wastewater

- Reduce suspended solids
- pH Adjustment
- Reduce specific contaminants
- Solids dewatering to minimize disposal volume
- Produce treated water that meets the plant's discharge permit

Physical/Chemical Process

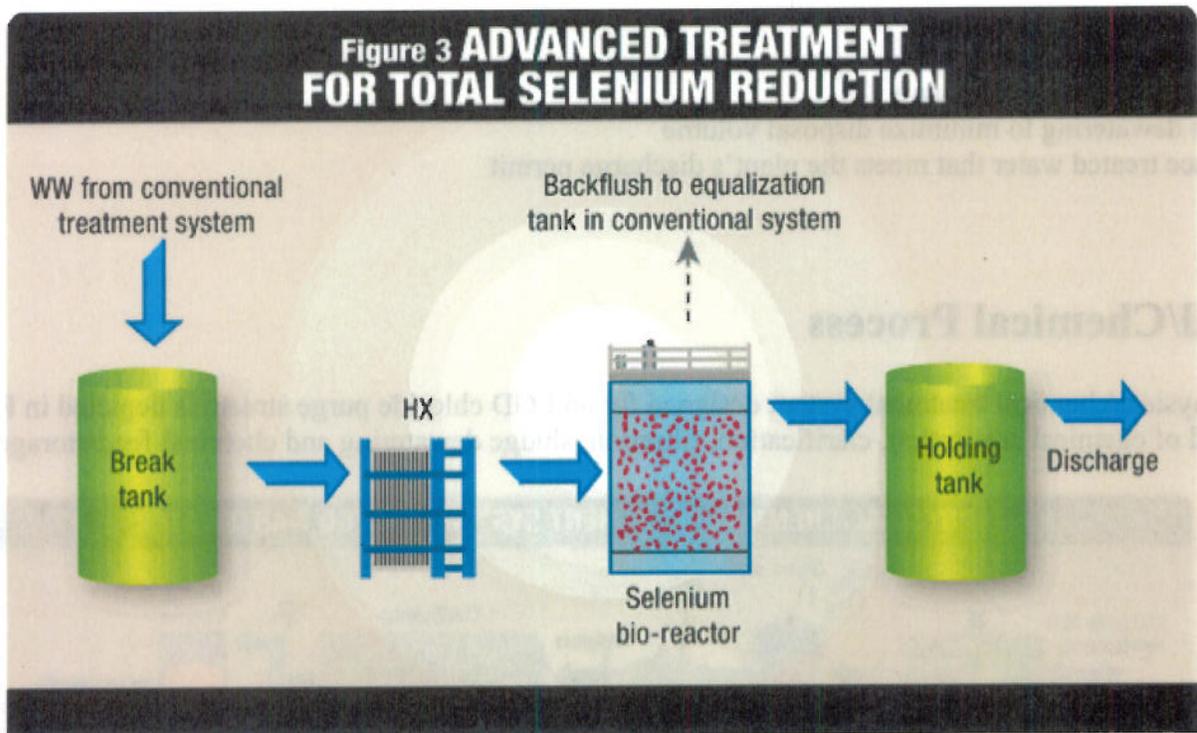
A typical physical/chemical treatment system designed for an FGD chloride purge stream is depicted in Figure 2 and is comprised of chemical adsorption, clarification, filtration, sludge dewatering and chemical feed/storage facilities.



The wastewater originates from the gypsum dewatering system's two-stage hydrocyclone unit and will contain about 0.5 to 2.0 percent TSS. An equalization tank receives the absorber purge promoting flow and chemical stabilization to minimize frequent fluctuations to the downstream treatment process. Pumps transfer the wastewater from the equalization tank to reaction tank No. 1, where hydrated lime is added to raise the pH to about 8.5 to 9.2 and for gypsum de-saturation. pH control is essential to optimize the effectiveness of the reagents added to precipitate heavy metals and to avoid magnesium precipitation.

Recycle of seed sludge from the clarifier to reaction tank No. 1 provides sites for gypsum crystal growth to aid in the de-supersaturation, which prevents scale on the downstream equipment. The alkali also precipitates abundant metals, such as aluminum, iron, and heavy metals as metal hydroxides.

Metal sulfides have much lower solubility than metal hydroxides. Thus, in order to meet the low effluent requirements for heavy metals, organosulfide is dosed into the reaction tank No. 1 to further precipitate the heavy metals.



For flocculation, an iron salt such as ferric chloride is added to reaction tank No. 2. The iron salt helps denser flocs form, enhancing clarifier performance. Some other metals, non-metals, and organic matter will also co-precipitate. After flocculation, polymer is added in-line prior to a solids contacting clarifier to aid in coagulation and solids settling. Hydrochloric acid is used to lower the clarifier effluent pH to near neutral, which prevents scaling in downstream equipment. Gravity filtration polishes the treated effluent to enhance TSS and metals reduction prior to discharge.

Backwash reject from the gravity filter returns to the equalization tank for reprocessing.

Pumps transfer the settled clarifier sludge, usually in the range of 10 to 20 percent by weight, to an agitated sludge holding tank prior to being dewatered in filter presses on a batch basis. The sludge tank volume is sized consistent with the utility's plans for filter press operation.

The most common filter press being used for FGD wastewater sludge is the recessed chamber press. The dewatered solids or "filter cake" is discharged from filter presses at 40 to 55 percent by weight solids to roll-off boxes or to truck trailers and are disposed of in non-hazardous lined landfills. A more detailed discussion on FGD wastewater treatment is provided in reference 1.

Advanced Treatment for Selenium Reduction – Process Description

A fixed-film biological treatment system has been developed to reduce selenium in a bio-reactor². It is a continuous process based on hydraulic retention time of approximately 6 to 8 hours. Activated carbon is used as a support media on which site-specific naturally occurring bacteria will grow. Since the carbon content of the wastewater is not sufficient to promote growth, a carbon source is needed to promote growth of a stable microbiological population. Under anoxic or anaerobic conditions, the oxidized forms of selenium, selenite and selenate are reduced to form elemental selenium and captured on the media bed. The selenium reduction process is arranged as a two-stage process consisting of two or more primary bio-reactors followed by second stage bio-reactors for polishing.

The pH adjusted effluent from the physical/chemical system flows by gravity to a break tank. The temperature should be reduced to less than 100 F using a non-contact heat exchanger.

Each bio-reactor contains a bio-matrix (medium) for microbial growth. Activated carbon is used as the media on which selected microorganisms will grow and be retained within the system. Activated carbon is employed due to the very large surface area available for microbial growth. Moreover, a majority of the surface area is protected within crevices of the carbon particles, thus sheltering biomass growths from shear and abrasive forces. Nutrient-containing microbial cultures and other process balancing compounds are injected into the influent to each stage to promote microbial cell growth. Blending of the nutrient feed with the flow stream is achieved by an inline static mixer.

The effluent from the first stage bio-reactors flows by gravity to second stage transfer tanks for subsequent transfer by the second stage transfer pumps to the second stage bio-reactors. The effluent from the second stage bio-reactors flows by gravity to the treated effluent (backwash) storage tanks and subsequent discharge. Subject to the final effluent discharge required, the advanced treated effluent may be conveyed to the point of discharge or be transferred to downstream gravity filters for enhanced TSS and metals reduction prior to discharge.

Periodically, the bio-reactors will undergo a backwash cycle to remove captured elemental selenium and suspended solids. The source of the backwash water shall be the treated effluent stored in the backwash storage tank. The backwash wastewater generated during a backwash cycle shall be conveyed to the backwash waste holding tank for subsequent transfer by the backwash waste return pumps at a low hydraulic rate to the equalization tank of the physical/chemical treatment system for subsequent reprocessing.

Advanced Treatment for Nitrogen

Nitrogen will exist in a number of forms including ammonia, nitrite, nitrate, and complex sulfur-nitrogen compounds. The sulfur-nitrogen compounds will not be removed by the biological treatment process. Total nitrogen reduction is a more complicated biological process than that for selenium reduction as it requires a series of denitrification/nitrification steps. The process of converting ammonia nitrogen to nitrate is referred to as nitrification and is carried out in an aerated environment. Denitrification converts nitrates and nitrites to nitrogen gas in an anoxic environment. The SBR system is an activated sludge process in a true batch mode. The treatment system consists of influent and effluent storage (equalization) tanks, bio-reactors, blowers, continuous backwash gravity filters for additional suspended solids and phosphorus reduction, and associated chemical feed and storage equipment³.

The pH adjusted effluent from the physical/chemical system flows by gravity to a break tank. The temperature is reduced using a non-contact heat exchanger or dilution water.

The influent tank provides storage of the physical/chemical clarifier effluent which is continually mixed. Dilution water may be added to reduce the level of TDS, controlled by online conductivity, and temperature to a range of 20,000 to 30,000 $\mu\text{S}/\text{cm}$ and less than 95 F, respectively. A carbon "food" source is typically added to the inlet of each SBR on a batch basis. Carbon addition is necessary since the wastewater does not contain sufficient organic matter to sustain biological growth. Foam may develop in the process and is generally an indication of a problem. Either a spray system or chemical defoamant feed system may be utilized to control the level of foam.

The batch biological process consists of five basic cycles that take place in the SBR tanks: anoxic fill and aerated fill, react, and settling, decant, and idle/sludge wastage. Acclimation or growth of microorganisms will begin almost immediately once seeding has taken place. Each step is described briefly below.

Anoxic Fill/Denitrification: During this step, effluent from the SBR is loaded with food from the influent tank using SBR feed pumps without aeration. The influent comes into contact with the settled biomass in the sludge blanket to create a high food to mass (F:M) ratio. Soluble biochemical oxygen demand (BOD) is absorbed and stored in the

biomass. The facultative organisms will utilize and consume the available nitrate as an oxygen source as the dissolved oxygen level will be low.

Aerated Fill/Nitrification: During this step, the blowers are used to add oxygen and the organisms convert the available ammonia nitrogen to nitrate. The biomass metabolizes the food (soluble BOD) that has been stored referred to as a ‘feast’ environment”. The dissolved oxygen level will be high. The jet motive pumps circulate the biomass and incoming wastewater. The SBR feed pumps are shutoff at the end of the fill process.

Denitrification: A secondary denitrification phase may be utilized in the fill cycle if the concentration of nitrates is elevated. The blowers are turned off while the jet motive pumps continue to mix the biomass and incoming wastewater. The system will return to an anoxic state where nitrates are used as the oxygen donor and the food source is relatively high from the wastewater.

React: This process involves a number of nitrification and denitrification steps to convert any remaining ammonia and nitrite to nitrate followed by nitrate conversion to nitrogen gas. The filling cycle is complete and no more food (influent) enters the SBR. During nitrification, the blowers are turned on and the biomass metabolizes food it has absorbed. The dissolved oxygen will be high during the nitrification stage and is controlled by a combination of online DO and ORP measurements. During denitrification, the blowers are turned off while the jet motive pump continues to circulate the tank contents. The dissolved oxygen level will be low and the ORP will decrease (become negative). The number of nitrification/denitrification steps is determined by grab sample testing and analyzing for ammonia, nitrite, and nitrate. The last step in the react sequence is gas stripping to remove the nitrogen gas formed from the conversion from NO_3 to N_2 (g). Blowers are turned on to aerate the reactor. The biomass will break up and allow the trapped nitrogen gas to escape into the atmosphere. The ORP should not be allowed to go to reducing (negative) in the denitrification phase to avoid anaerobic growth of sulfate reducing bacteria and the formation of hydrogen sulfide.

Settle: Following the react step, the blowers and jet motive pumps are idle and the biomass is allowed to settle. No influent is introduced or effluent decanted. The reactor is under true quiescent conditions and the liquids and solids will separate with 100 percent of the reactor available for settling.

Decant: Once the separation is complete, the decant step is initiated to remove water from the upper section of the SBR. The initial flow is returned to the SBR inlet tank with a higher level of suspended solids in the decant pipe and the remainder going to the SBR effluent tank. The decant step is not a timed event and the control valve closes when the bottom water level is reached. The vessel will await the next batch in the idle mode with the jet motive pump off.

Idle/Sludge Wasting: As the amount of biomass continues to grow, a percentage needs to be removed. The process can be performed once per day or during each batch cycle with the varying amount of time based on sludge level. The sludge is combined with the sludge from the physical/chemical process. Sludge removal can also occur during the decant step.

During shutdowns periods or when the influent flow is significantly lower than design (infrequent batches), additional steps are necessary to sustain the biomass. A nitrate source should be added such as sodium nitrate along with the carbon source to the SBR. The react sequence should be followed with reduced operating times and likely only a single nitrification/denitrification cycle.

Biological treatment systems can be utilized successfully to reduce certain heavy metals and nutrients found in FGD wastewater. The following issues should be considered in the system design:

- Dilution water to reduce the temperature and TDS levels (chloride) of the inlet water.
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- Verify analytical test methodology for nitrogen compounds in the discharge permit. The total kjeldahl nitrogen procedure will measure all of the nitrogen compounds including the sulfur-nitrogen compounds.

References

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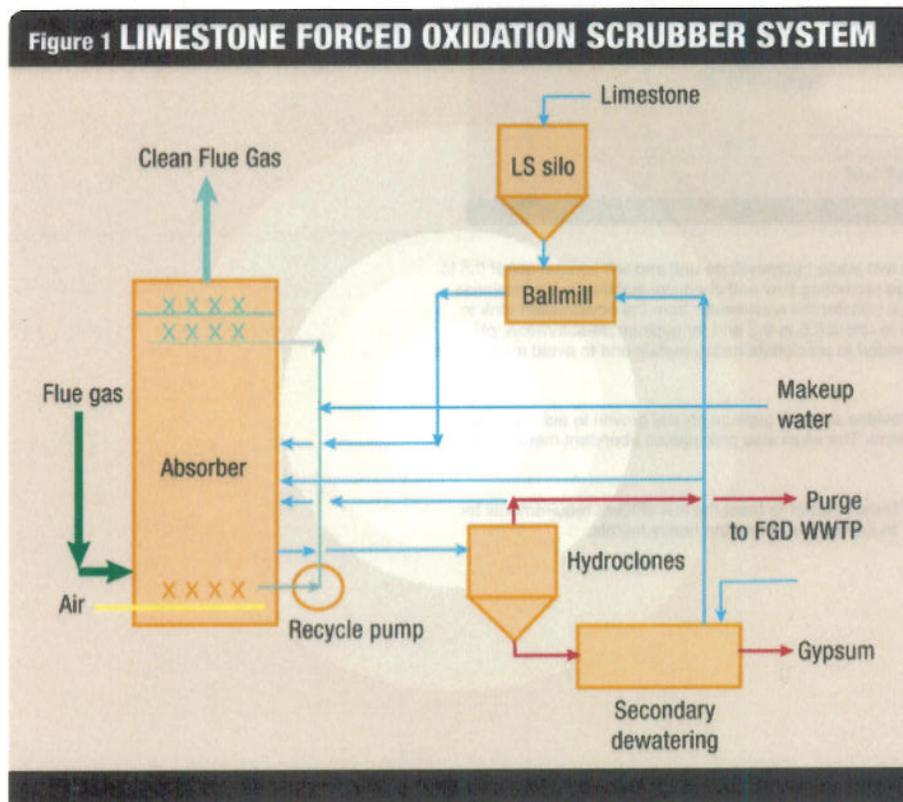
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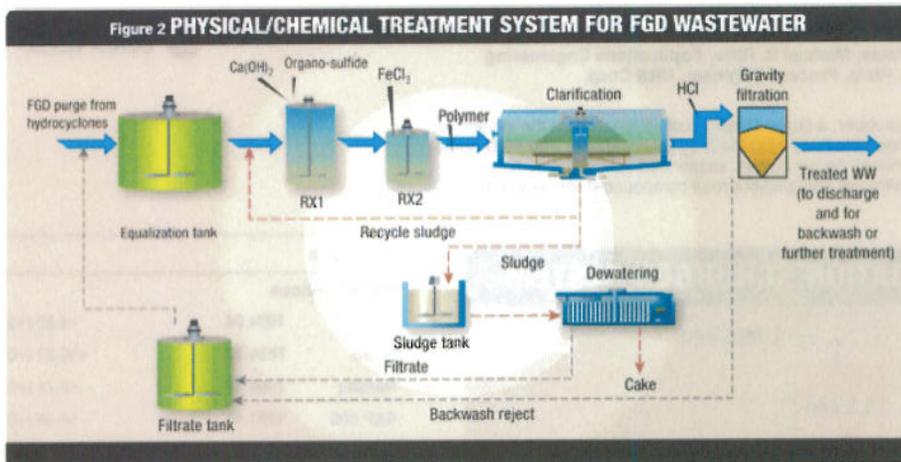
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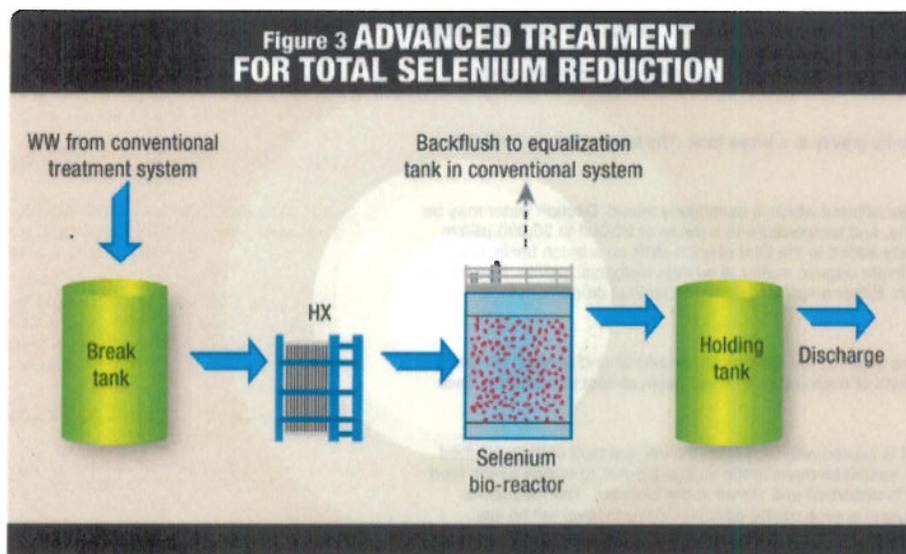
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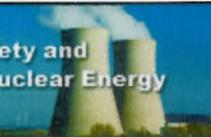
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09/01/2010

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In order to maintain optimum operating conditions in a FGD wet scrubber, a purge stream is discharged from the system to control the absorber equilibrium chloride concentration and acid insoluble fines from the reagent limestone. The FGD purge stream contains high concentrations of dissolved solids (e.g. chlorides), heavy metals, suspended solids (gypsum and limestone inerts) and dissolved inorganic nutrients (for example, nitrogen and phosphorous compounds). An example of a LSFO system is presented in Figure 1.

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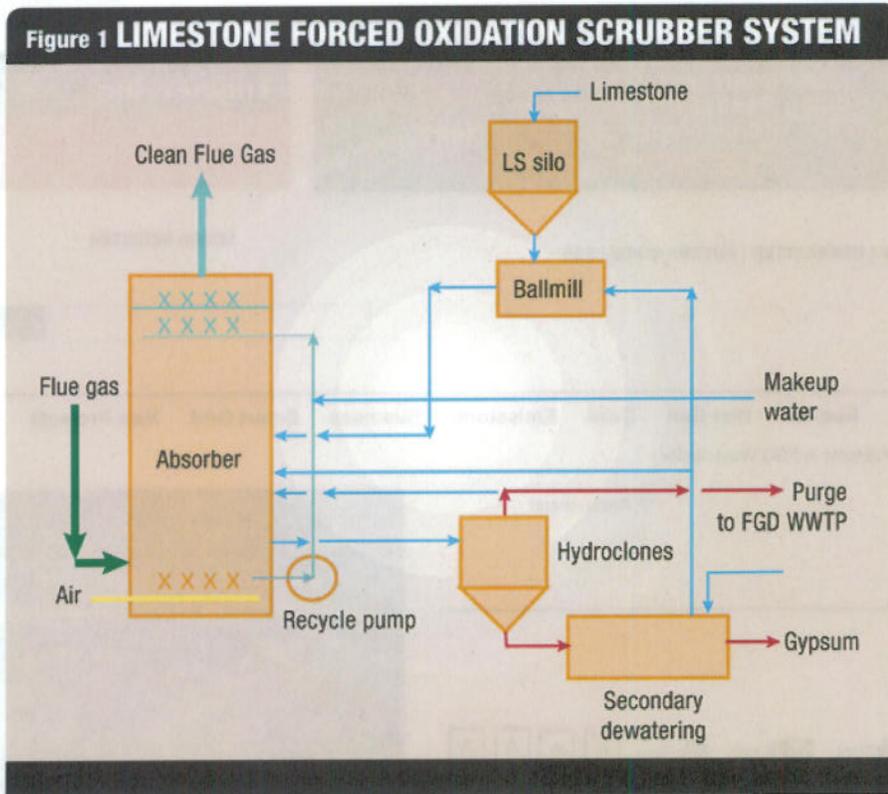


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Wastewater (Purge Stream) Characteristics

The quantity and quality of the wastewater stream varies with the type of coal, limestone composition, type of scrubber, make-up water and the gypsum dewatering system. In an increasing number of plants, the source of make-up water is recycled wastewater.

The purge stream is treated prior to discharge into a receiving stream to remove suspended solids, metals and nutrients. The treated water typically has discharge limits similar to other National Pollutant Discharge Elimination System (NPDES) monitoring locations including TSS and pH. More specific limits are based on the particular receiving stream. These often include heavy metals such as mercury, selenium or nutrient compounds. A number of treatment options may be considered though physical/chemical is the primary approach for TSS and some metals removal. Biological treatment has been demonstrated to effectively reduce selenium and certain nitrogen compounds.

Objectives of Treatment

The FGD wastewater treatment system needs to be designed to meet the applicable discharge requirements with a high degree of reliability. The treatment objectives are:

- De-saturate the wastewater
- Reduce suspended solids
- pH Adjustment
- Reduce specific contaminants
- Solids dewatering to minimize disposal volume
- Produce treated water that meets the plant's discharge permit

Physical/Chemical Process

A typical physical/chemical treatment system designed for an FGD chloride purge stream is depicted in Figure 2 and is comprised of chemical adsorption, clarification, filtration, sludge dewatering and chemical feed/storage facilities.

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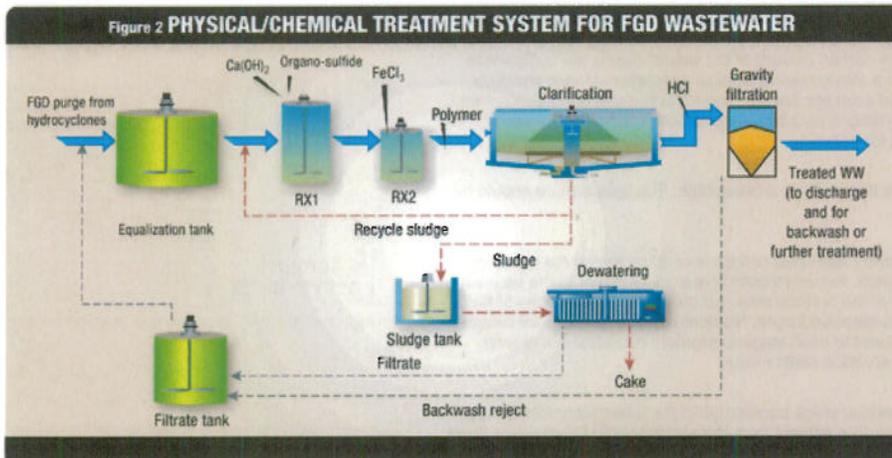
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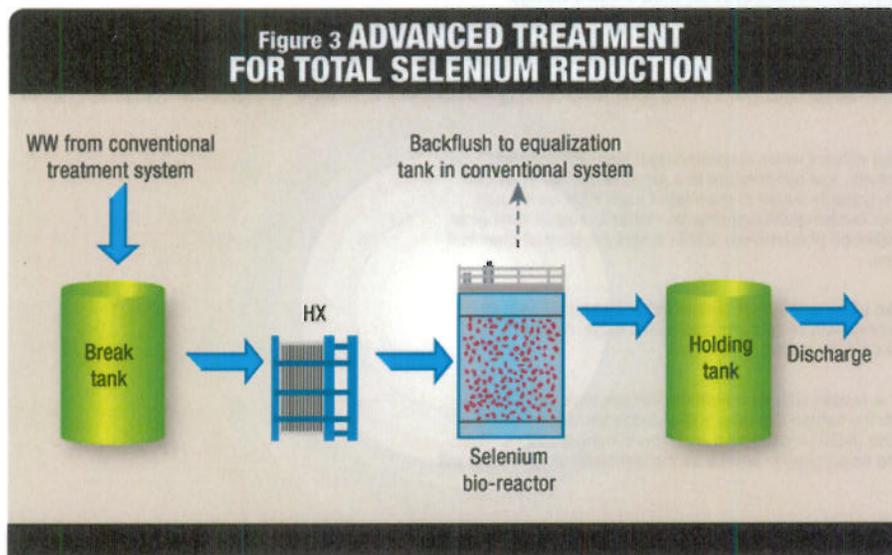
3DS SIMULIA



The wastewater originates from the gypsum dewatering system's two-stage hydrocyclone unit and will contain about 0.5 to 2.0 percent TSS. An equalization tank receives the absorber purge promoting flow and chemical stabilization to minimize frequent fluctuations to the downstream treatment process. Pumps transfer the wastewater from the equalization tank to reaction tank No. 1, where hydrated lime is added to raise the pH to about 8.5 to 9.2 and for gypsum de-saturation. pH control is essential to optimize the effectiveness of the reagents added to precipitate heavy metals and to avoid magnesium precipitation.

Recycle of seed sludge from the clarifier to reaction tank No. 1 provides sites for gypsum crystal growth to aid in the de-supersaturation, which prevents scale on the downstream equipment. The alkali also precipitates abundant metals, such as aluminum, iron, and heavy metals as metal hydroxides.

Metal sulfides have much lower solubility than metal hydroxides. Thus, in order to meet the low effluent requirements for heavy metals, organosulfide is dosed into the reaction tank No. 1 to further precipitate the heavy metals.



For flocculation, an iron salt such as ferric chloride is added to reaction tank No. 2. The iron salt helps denser flocs form, enhancing clarifier performance. Some other metals, non-metals, and organic matter will also co-precipitate. After flocculation, polymer is added in-line prior to a solids contacting clarifier to aid in coagulation and solids settling. Hydrochloric acid is used to lower the clarifier effluent pH to near neutral, which prevents scaling in downstream equipment. Gravity filtration polishes the treated effluent to enhance TSS and metals reduction prior to discharge.

Backwash reject from the gravity filter returns to the equalization tank for reprocessing.

Pumps transfer the settled clarifier sludge, usually in the range of 10 to 20 percent by weight, to an agitated sludge holding tank prior to being dewatered in filter presses on a batch basis. The sludge tank volume is sized consistent with the utility's plans for filter press operation.

The most common filter press being used for FGD wastewater sludge is the recessed chamber press. The dewatered solids or "filter cake" is discharged from filter presses at 40 to 55 percent by weight solids to roll-off boxes or to truck trailers and are disposed of in non-hazardous lined landfills. A more detailed discussion on FGD wastewater treatment is provided in reference 1.

Advanced Treatment for Selenium Reduction – Process Description

A fixed-film biological treatment system has been developed to reduce selenium in a bio-reactor². It is a continuous process based on hydraulic retention time of approximately 6 to 8 hours. Activated carbon is used as a support media on which site-specific naturally occurring bacteria will grow. Since the carbon content of the wastewater is not sufficient to promote growth, a carbon source is needed to promote growth of a stable microbiological population. Under anoxic or anaerobic conditions, the oxidized forms of selenium, selenite and selenate are reduced to form elemental selenium and captured on the media bed. The selenium reduction process is arranged as a two-stage process consisting of two or more primary bio-reactors followed by second stage bio-reactors for polishing.

The pH adjusted effluent from the physical/chemical system flows by gravity to a break tank. The temperature should be reduced to less than 100 F using a non-contact heat exchanger.

Each bio-reactor contains a bio-matrix (medium) for microbial growth. Activated carbon is used as the media on which selected microorganisms will grow and be retained within the system. Activated carbon is employed due to the very large surface area available for microbial growth. Moreover, a majority of the surface area is protected within crevices of the carbon particles, thus sheltering biomass growths from shear and abrasive forces. Nutrient-containing microbial cultures and other process balancing compounds are injected into the influent to each stage to promote microbial cell growth. Blending of the nutrient feed with the flow stream is achieved by an inline static mixer.

The effluent from the first stage bio-reactors flows by gravity to second stage transfer tanks for subsequent transfer by the second stage transfer pumps to the second stage bio-reactors. The effluent from the second stage bio-reactors flows by gravity to the treated effluent (backwash) storage tanks and subsequent discharge. Subject to the final effluent discharge required, the advanced treated effluent may be conveyed to the point of discharge or be transferred to downstream gravity filters for enhanced TSS and metals reduction prior to discharge.

Periodically, the bio-reactors will undergo a backwash cycle to remove captured elemental selenium and suspended solids. The source of the backwash water shall be the treated effluent stored in the backwash storage tank. The backwash wastewater generated during a backwash cycle shall be conveyed to the backwash waste holding tank for subsequent transfer by the backwash waste return pumps at a low hydraulic rate to the equalization tank of the physical/chemical treatment system for subsequent reprocessing.

Advanced Treatment for Nitrogen

Nitrogen will exist in a number of forms including ammonia, nitrite, nitrate, and complex sulfur-nitrogen compounds. The sulfur-nitrogen compounds will not be removed by the biological treatment process. Total nitrogen reduction is a more complicated biological process than that for selenium reduction as it requires a series of denitrification/nitrification steps. The process of converting ammonia nitrogen to nitrate is referred to as nitrification and is carried out in an aerated environment. Denitrification converts nitrates and nitrites to nitrogen gas in an anoxic environment. The SBR system is an activated sludge process in a true batch mode. The treatment system consists of influent and effluent storage (equalization) tanks, bio-reactors, blowers, continuous backwash gravity filters for additional suspended solids and phosphorus reduction, and associated chemical feed and storage equipment³.

The pH adjusted effluent from the physical/chemical system flows by gravity to a break tank. The temperature is reduced using a non-contact heat exchanger or dilution water.

The influent tank provides storage of the physical/chemical clarifier effluent which is continually mixed. Dilution water may be added to reduce the level of TDS, controlled by online conductivity, and temperature to a range of 20,000 to 30,000 $\mu\text{S}/\text{cm}$ and less than 95 F, respectively. A carbon "food" source is typically added to the inlet of each SBR on a batch basis. Carbon addition is necessary since the wastewater does not contain sufficient organic matter to sustain biological growth. Foam may develop in the process and is generally an indication of a problem. Either a spray system or chemical defoamant feed system may be utilized to control the level of foam.

The batch biological process consists of five basic cycles that take place in the SBR tanks: anoxic fill and aerated fill, react, and settling, decant, and idle/sludge wastage. Acclimation or growth of microorganisms will begin almost immediately once seeding has taken place. Each step is described briefly below.

anoxic Fill/Denitrification: During this step, effluent from the SBR is loaded with food from the influent tank using SBR feed pumps without aeration. The influent comes into contact with the settled biomass in the sludge blanket to create a high food to mass (F:M) ratio. Soluble biochemical oxygen demand (BOD) is absorbed and stored in the biomass. The facultative organisms will utilize and consume the available nitrate as an oxygen source as the dissolved oxygen level will be low.

Aerated Fill/Nitrification: During this step, the blowers are used to add oxygen and the organisms convert the available ammonia nitrogen to nitrate. The biomass metabolizes the food (soluble BOD) that has been stored referred to as a "feast" environment". The dissolved oxygen level will be high. The jet motive pumps circulate the biomass and incoming wastewater. The SBR feed pumps are shutoff at the end of the fill process.

Denitrification: A secondary denitrification phase may be utilized in the fill cycle if the concentration of nitrates is elevated. The blowers are turned off while the jet motive pumps continue to mix the biomass and incoming wastewater. The system will return to an anoxic state where nitrates are used as the oxygen donor and the food source is relatively high from the wastewater.

React: This process involves a number of nitrification and denitrification steps to convert any remaining ammonia and nitrite to nitrate followed by nitrate conversion to nitrogen gas. The filling cycle is complete and no more food (influent) enters the SBR. During nitrification, the blowers are turned on and the biomass metabolizes food it has absorbed. The dissolved oxygen will be high during the nitrification stage and is controlled by a combination of online DO and ORP measurements. During denitrification, the blowers are turned off while the jet motive pump continues to circulate the tank contents. The dissolved oxygen level will be low and the ORP will decrease (become negative). The number of nitrification/denitrification steps is determined by grab sample testing and analyzing for ammonia, nitrite, and nitrate. The last step in the react sequence is gas stripping to remove the nitrogen gas formed from the conversion from NO_3 to N_2 (g). Blowers are turned on to aerate the reactor. The biomass will break up and allow the trapped nitrogen gas to escape into the atmosphere. The ORP should not be allowed to go to reducing (negative) in the denitrification phase to avoid anaerobic growth of sulfate reducing bacteria and the formation of hydrogen sulfide.

Settle: Following the react step, the blowers and jet motive pumps are idle and the biomass is allowed to settle. No

influent is introduced or effluent decanted. The reactor is under true quiescent conditions and the liquids and solids will separate with 100 percent of the reactor available for settling.

Decant: Once the separation is complete, the decant step is initiated to remove water from the upper section of the SBR. The initial flow is returned to the SBR inlet tank with a higher level of suspended solids in the decant pipe and the remainder going to the SBR effluent tank. The decant step is not a timed event and the control valve closes when the bottom water level is reached. The vessel will await the next batch in the idle mode with the jet motive pump off.

Idle/Sludge Wasting: As the amount of biomass continues to grow, a percentage needs to be removed. The process can be performed once per day or during each batch cycle with the varying amount of time based on sludge level. The sludge is combined with the sludge from the physical/chemical process. Sludge removal can also occur during the decant step.

During shutdowns periods or when the influent flow is significantly lower than design (infrequent batches), additional steps are necessary to sustain the biomass. A nitrate source should be added such as sodium nitrate along with the carbon source to the SBR. The react sequence should be followed with reduced operating times and likely only a single nitrification/denitrification cycle.

Biological treatment systems can be utilized successfully to reduce certain heavy metals and nutrients found in FGD wastewater. The following issues should be considered in the system design:

- Dilution water to reduce the temperature and TDS levels (chloride) of the inlet water.
- Dechlorination system for dilution water that may contain free available chlorine.
- Available heating system for operation in winter months or if low FGD purge flow allows temperature to drop below optimal level for biogrowth.
- Provide redundant analyzers for key control parameters which should include pH, ORP and DO.
- Ability to keep biomass in dormant, viable state during low flow conditions that may require carbon and nitrogen sources.
- Installation of a maintenance tank that may be used as either an inlet or effluent tank in the event one of the two is not available or needs to be out of service for repair.
- Multiple reactors to provide flexible operation and maintenance.
- Verify analytical test methodology for nitrogen compounds in the discharge permit. The total kjeldahl nitrogen procedure will measure all of the nitrogen compounds including the sulfur-nitrogen compounds.

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Editor's Note: The topic was first presented at the University of Illinois' 2010 Electric Utility Chemistry Workshop .

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