**Wastewater and wastewater treatment in steel plants**

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Steel plants use large amounts of water for cooling， dust suppression， cleaning， temperature control (heat treatment)， transportation of waste materials (ash， sludge， scale， etc.) and other purposes. Water is an important component of a number of processes， such as the water content of coking coal， granulation of sinter mixes， green pellets in the production of iron ore pellets， steam production and power production， and granulation of blast furnace slag.

The use of large amounts of water also generates large amounts of wastewater， which may contain suspended matter and many dissolved substances and chemicals. The quality of the wastewater depends on the process in which the water is used and the purpose for which it is used.

If untreated wastewater from a steel mill is discharged into a receiving water body， the main environmental impacts are: (1) toxicity to aquatic organisms; (2) reduction of dissolved oxygen; (3) siltation due to suspended matter; (4) taste and odor problems; (5) temperature rise affecting dissolved oxygen; (6) impact on aquatic organisms; and (7) oil slick formation due to floating oil， etc.

The large volumes of process water that come into direct contact with raw materials， products and exhaust gases require treatment for water reuse， water recirculation， or removal of pollutants to regulatory levels prior to discharge.

The quality of wastewater can be controlled by using improved technologies developed today for different processes. Technologies are also now available to treat wastewater for recycling in the same process or in other processes. The treatment of wastewater also leads to the recovery of some solid wastes that can be recycled into the process or undergo some further treatment， thus contributing to the conservation of natural resources.

In order to protect water as a resource， there is a movement to not only prevent pollution from wastewater， but also to treat it and recycle it in a closed system to reduce fresh water consumption.

Treatment of wastewater

The main processes requiring wastewater treatment in integrated steel plants include coking， ironmaking， steelmaking， hot and cold rolling and other operations such as pickling， electrolytic tinning and other coating processes.

The most important parameters are suspended solids， grease， phenol， cyanide， ammonia and heavy metals such as lead， zinc， chromium and nickel， which are generally regulated by statutory bodies. In addition， several organic compounds used in coking and cold rolling operations are also regulated. The normal wastewater treatment processes used to effectively treat steel mill wastewater are described below (Figure 1).



Figure 1 Wastewater treatment process

Control of suspended matter

Removal of suspended matter from wastewater is practically necessary for all production plants in a steel mill， from coking to finishing. Solid particulate matter is suspended in the process water stream during flue and exhaust gas cleaning and cooling， slag granulation， descaling， roll and product cooling， flume flushing in mills， and product flushing in finishing operations.

The methods typically used to remove suspended material are (i) sedimentation， (ii) centrifugal separation， and (iii) filtration.

Sedimentation， also known as clarification， involves settling by gravity. The process is usually carried out in a clarifier or inclined plate separator designed for a specific application. Clarifiers are usually circular， but can also be constructed as rectangular. One advantage of inclined plate separators over clarifiers is that they require much less floor space. However， care needs to be taken when using them when the concentration of oil and grease in the wastewater is high. The disadvantage of inclined plate separators is that the sludge storage capacity at the bottom of the separator is small.

Both the clarifier and the inclined plate separator are designed to remove the collected sludge continuously from the bottom of the unit. Underflow sludge is usually thickened by gravity and then further dewatered in several types of sludge dewatering equipment (e.g. filter presses， belt presses or centrifuges， etc.). This is done to reduce the sludge volume so that the sludge can be easily and economically disposed of during disposal. Coagulants， such as alum， ferric chloride， ferric sulfate， ferrous sulfate， ferrous chloride and commercial organic polyelectrolytes are often added to the wastewater prior to clarification to promote flocculation of the solid particles. This increases their effective size and thus improves their settling rate.

Centrifugal separation is a technique that uses centrifugal force to remove suspended matter from the water column. This separation technique is sometimes referred to as cyclone separation. The process is highly dependent on particle size and specific gravity. Larger particles and higher particle density will improve separation performance.

Multi-media or single-media filtration by pressure or gravity are other methods for removing fine suspended particles， and these methods are often applied to wastewater from steel mills. Wastewater is passed through a filter medium in a vessel. The system usually consists of several individual filtration units working in parallel. Sometimes sidestream filtration is utilized to treat a portion of the wastewater， which is then mixed with the unfiltered portion. Typically， filtration systems are designed to have the highest feasible flow rate through the filter media， thereby minimizing the required size and cost.

In a typical multi-media system， the wastewater first passes through a relatively coarse media layer (e.g.， anthracite) and then through a fine media layer (e.g.， sand). Most of the particles are removed by the coarse media layer， while the fine media layer provides a final polishing of the wastewater. Multi-media filters are generally used when the wastewater has a high content of oil and grease. High concentrations of oil and grease can cause media fouling and/or clogging in both single and multi-media filters.

Collected particulate matter is regularly removed from the filter media by backwashing. In the backwash operation， the inflowing wastewater is stopped and the treated water stream， and sometimes air， is allowed to pass through the filter media in the opposite direction， flushing the collected solids away.

By installing a number of filter units in parallel， a unit can be cycled through the backwash without causing an interruption in the continuous treatment of the wastewater stream. The backwash stream is usually settled in a backwash holding tank and the solids are processed through a thickener and sludge dewatering equipment. Both single-media and multi-media filters produce a high degree of clarity in the wastewater stream. However， clarifiers are typically used to pretreat wastewater containing large amounts of solids in order to remove most particles prior to filtration. If the solids content of the wastewater is low， a separate filter can be used without prior clarification.

The amount of suspended and other particulate matter discharged to the receiving stream can often be greatly reduced by recirculating the water back into the process. However， the degree of recirculation that is feasible is limited by the amount of suspended matter in the wastewater and the increased concentration of dissolved solids in the system， which can eventually lead to sedimentation and clogging in pipes and equipment. Therefore， some portion of the recirculated water volume always needs to be released as a blowdown to control the concentration of dissolved solids to an acceptable level.

Oil and grease control

Oil and grease are commonly found in the wastewater from continuous casting mills， hot and cold rolling mills， pickling， plating and coating operations. These oils come from equipment， product lubricants and coolants， hydraulic systems and， in some processes， anti-corrosion coatings applied to the product. Oil and grease are typically removed from wastewater by several methods， including skimming， gravity separation， air flotation， filtration and ultrafiltration. If the oil is insoluble in water， it is removed from the wastewater by gravity separation and skimming. Gravity oil separators typically have a rectangular chamber in which the velocity of the wastewater stream is slowed sufficiently to provide time for oil and grease to float to the surface， where they are removed by the various skimming devices available. Some examples of skimming devices are rotary drum skimmers， rope and belt skimmers， and scrapers， which are also used to scrape off heavier solids that settle on the bottom. Insoluble oils can also be removed along with suspended solids in a multi-media filter. If the oil is emulsified or water-soluble， such as found in spent cold rolled liquor or rinse water， it needs to be treated with an acid or emulsion breaker to break the emulsion， followed by gravity settling and skimming， or with air flotation and/or membrane separation techniques.

Skimming can be used for any wastewater containing components that float on the surface and is typically used to remove free oil， grease and soap. Skimming is often used in conjunction with air flotation or clarification to improve the removal of sediment and floating materials. The removal efficiency of a skimmer is a function of the density of the material to be floated and the residence time of the wastewater in the tank. Gravity separators tend to be better suited for use where the amount of surface oil flowing through the system is quite large and stable.

Air flotation processes are typically used to separate floatable material whose density is close to that of water， and therefore cannot be effectively separated by gravity alone. During flotation， air bubbles (usually air) released from the wastewater attach to the oil and fine solid particles， causing them to float to the surface more quickly and be skimmed off as foam. Sometimes chemical additives are used to improve the performance of the flotation process.

The ultrafiltration process involves the use of pressure and semi-permeable polymer or ceramic membranes to separate emulsified or colloidal materials suspended in the liquid phase. The membranes used in ultrafiltration units form a molecular sieve that retains molecular particles based on their differences in size， shape and chemical structure. The membrane allows the passage of solvents and molecules of low molecular weight. In the ultrafiltration process， the wastewater is pumped through a tubular membrane unit. Water and some low molecular weight substances pass through the membrane at pressures ranging from 0.7 kg/cm2 to 7 kg/cm2. Emulsified oil droplets and suspended particles are retained， get concentrated and are continuously removed.

Control of heavy metals

Regulatory agencies typically restrict heavy metal discharges from blast furnace shops in steel mills， steel smelters， and process water from pickling， cold rolling， plating and hot coating operations. The usual method used to remove these trace metals is chemical precipitation followed by clarification or filtration.

It is well known that the solubility of heavy metals in water is a function of pH. Typically， the solubility of metals decreases as the pH increases. Therefore， to remove the dissolved metals， the wastewater is treated with alkaline materials in a mixing tank with a pH controller. In most chemical precipitation processes， heavy metals are separated by hydroxide and sulfide precipitation. In hydroxide precipitation， lime， which is the cheapest reagent， is usually used， although caustic soda， magnesium hydroxide or other alkaline substances are sometimes used for this purpose. After the pH has been raised to a level where the dissolved metal precipitates as hydroxide， the water is passed through a clarifier and/or through a filter to remove the precipitated metal hydroxide. The addition of a coagulant is usually required. The use of coagulants， such as ferric chloride， at alkaline pH levels results in the formation of a hydroxide surface， which enhances the additional removal of metals by adsorption. Other coagulants， such as alum， ferrous sulfate and polymeric flocculants can also be used to improve particle formation.

If chromium is present in the hexavalent form， it must first be chemically reduced to the trivalent form before it can be precipitated. The rate of this reduction reaction is a function of the pH conditions of the system. For example， if sulfur dioxide， sodium bisulfite or spent acid wash is used as the reducing agent， the pH of the system is adjusted in the range of 2.0 and 3.0. Hexavalent chromium can also be reduced to trivalent chromium with sodium bisulfite at relatively high pH values (from 8.5 to 9.5). The reduced trivalent chromium ions are converted to insoluble chromium hydroxide and removed by precipitation.

Dissolved metal ions and certain anions are usually chemically precipitated and removed by physical means such as precipitation or filtration. In addition to the use of alkaline compounds， the following are other reagents that can be used

1. Metal sulfides - With the exception of chromium sulfide， the solubility of metal sulfides is lower than that of metal hydroxides. Therefore， the use of sulfide precipitation process can improve the removal rate of dissolved metals. Soluble sulfides， such as hydrogen sulfide or sodium sulfide， and insoluble sulfides， such as ferrous sulfide， can be used to precipitate many heavy metal ions as insoluble metal sulfides. The use of organic sulfides for wastewater treatment is now a popular practice. Usually， the process of sulfide precipitation includes clarification and filtration.

2. Carbonate-Carbonate precipitates can be used to remove metals by direct precipitation using carbonate reagents (e.g.， calcium carbonate) or by converting hydroxides to carbonates using carbon dioxide.

Chemical precipitation as a mechanism for removing metals from wastewater is a complex process that usually involves two steps， namely (i) precipitation of unwanted metals， and (ii) removal of precipitates. After complete precipitation， a small amount of metal is usually dissolved in the wastewater. The amount of dissolved metals remaining depends on the treatment chemicals used， the solubility of the metals and the co-precipitation effect. The effectiveness of this method in removing any particular metal depends on the fraction of the wastewater that is metal-specific (and therefore includes the precipitates) and the effectiveness of the removal of suspended solids.

Biological treatment

Biological oxidation is the technique commonly used to treat coke oven and by-product plant wastewater. These wastewaters contain significant amounts of phenol， cyanide， thiocyanate and ammonia， as well as lower concentrations of other organic compounds， mainly due to the condensation of the raw coke oven gases containing these substances. Biological treatment is a traditional method used to treat wastewater from coke ovens and by-product plants before treatment.

Since biological oxidation is very sensitive to fluctuations in constituent loading and pH， the wastewater is first passed through an equilibrium tank to equalize concentration， temperature and flow rate. Conventional bio-oxidation methods typically include a single-stage or two-stage system. In a single-stage system， the process is designed to reduce organic compounds and ammonia in the only stage of the process. In a typical two-stage system， the first stage is designed to reduce organic compounds and the second stage is typically used for nitrification (ammonia removal). Sometimes， with careful control， carbide and nitrogen treatment can be performed in the same aeration tank. Often， biological treatment of thiocyanates results in an increase in ammonia in the wastewater. This needs to be considered in the design of the bio-oxidation treatment plant.

Both aeration systems typically utilize the activated sludge method followed by a clarifier. The activated sludge process is a suspended growth process similar to that applied in wastewater treatment plants. In an aeration system， a large number of microorganisms or biomass in the form of suspended solids (called activated sludge) are supplied with oxygen， which allows it to reduce the biodegradable components of the wastewater. Microbial populations can be developed that can effectively degrade phenol and other organic matter， thiocyanate， free cyanide and ammonia.

The required oxygen is provided by mechanical surface aerators or by diffusion of bubbles through the tank， also without the use of submerged turbine agitators. Treated water overflows from the tank to a clarifier where activated sludge is settled and recycled to the aeration tank. The overflow water from the clarifier is discharged. Other biological treatment processes can be used， including suspended growth processes with fixed membranes， packed towers， fluidized beds， and integral clarification.

Wastewater Treatment

There are two methods of treating wastewater in wastewater treatment plants. These methods are described below.

Conventional wastewater treatment consists of three stages， namely primary， secondary and tertiary treatment. Primary treatment involves temporarily holding the effluent in a still tank where heavy solids can settle to the bottom while oil， grease and lighter solids float to the surface. The settled and floating material is removed and the remaining liquid is discharged or subjected to secondary treatment. Secondary treatment removes dissolved and suspended biological material. Secondary treatment is usually performed by native， aquatic microorganisms in a managed habitat. Secondary treatment may require a separation process that removes microorganisms from the treated water prior to discharge or tertiary treatment. Tertiary treatment is often defined as something more than primary and secondary treatment. Treated water is sometimes chemically or physically disinfected (e.g.， through lagoons and microfiltration) before discharge， or used for horticultural purposes.

In the second method， known as ozone treatment， incoming raw sewage is passed through a bar screen chamber to remove coarse suspended matter， fibers， plastics， etc.， and is collected in a septic tank/shelter. The septic tank usually has a holding capacity of 24 hours to 48 hours with appropriate compartments to separate the heavy sludge solids present in the incoming effluent. A sewage transfer pump conveys the raw sewage to a manual self-cleaning filter， a pressure sand filter， and then to an ozone generator. Ozone is injected into the raw sewage and mixed into a contact chamber/holding tank. The ozone oxidizes the organic matter in the effluent， thereby reducing the BOD (Biological Oxygen Demand)/COD (Chemical Oxygen Demand) levels of the effluent to acceptable limits. The ozonated effluent is filtered through a pressure sand filter to remove trace suspended matter/turbidity， etc. The effluent can be appropriately reused for gardening， etc.

Terminal Treatment

A common practice for wastewater treatment within steel plants is to combine several different types of wastewater into a so-called terminal treatment plant for treatment. This practice has been particularly successful in treating wastewater from various finishing operations. These wastewaters typically contain suspended solids， free and emulsified oils from cold rolling， acids from pickling rinse water， and heavy metals from pickling and coating processes. In a typical system， the acid stream is mixed with an emulsified oil stream to break the emulsion. The combined waste is then passed through a gravity oil separator， neutralized with lime to remove the acid and precipitated heavy metals， and treated in a clarifier or filter to remove the solids and any remaining oil.

Breakpoint chlorination

Chlorination is one of the technologies used to treat ammonia， phenol and free cyanide. Chlorine has long been used as a biocide in drinking water treatment facilities and is known for its powerful oxidizing potential. When chlorine is added to water， the chlorine molecules undergo hydrolysis， producing hypochlorite and hypochlorite ions， which together make up the available free chlorine. Alkaline chlorination (pH greater than 9.5 in the presence of excess chlorine) is necessary to destroy free cyanide.

The term "breakpoint chlorination" comes from the observation of the point of maximum reduction of the remaining chlorine when the sample is dosed with increasing chlorine. Theoretically， the chlorine quantity ratio for treating ammonia is 7.6 parts chlorine to 1 part ammonia. In practice， quantity ratios of 8:1 to 10:1 are typically required. Optimum pH is usually between 6.0 and 7.0. Care needs to be taken to provide enough chlorine to complete the reaction to avoid the formation of chloramines. In addition， the competing needs of phenol， nitrite， ferrous， sulfite， hydrogen sulfide， free cyanide and other organics must be considered in the total chlorine requirement. Alkalinity may also need to be added to the wastewater in order to maintain the desired pH. For every 1.0 mg/L of ammonia nitrogen oxidized， approximately 14.3 mg/L of alkalinity (in terms of CaCO3) is consumed. Sometimes dechlorination of the final discharge is also required. This is usually done by adding sulfur dioxide， sodium bisulfite or activated carbon.

The advantages of this process are fairly stable process performance， low space requirements， and the ability to reduce ammonia concentrations in one step. The disadvantages of this treatment method are the potential formation of trihalomethanes (THMs)， increased total dissolved solids (TDS)， and relatively high operating costs. This is why this technology is usually only suitable for treating small concentrations of pollutants or as a polishing treatment.