COKE PLANT WASTEWATER TREATMENT
AT BAOSHAN STEEL, SHANGHAI - CHINA

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ABSTRACT

The Baoshan Steel Group (Baosteel), Shanghai, China is currently in the startup phase of its Phase 3 expansion to produce 4.0 million metric tons of coke per year. Chester Engineers (Chester) was retained to provide design engineering, equipment procurement, equipment installation oversight, and startup services for the Phase 3 coke plant wastewater treatment facilities. These facilities include ammonia steam stripping, sequential PAC activated sludge nitrification and faced film denitrification biological treatment, sequential chemical precipitation of cyanide and fluoride and sludge dewatering. The paper discusses the design criteria for the various processing operations, startup and current operating experience of the facility.

KEYWORDS: Coke Plant Wastewater, Ammonia Steam Stripping, Aerobic Biological Treatment, Denitrification Filter, Precipitation Cyanide and Fluoride.

INTRODUCTION

The Baoshan Steel Group started production at its Phase 3 coke plant expansion last December 1997. This expansion was designed to produce 4.0 million metric tons of coke per year. Chester Engineers was retained to provide design engineering, equipment
procurement, equipment installation oversight, and start-up service for the Phase 3 coke plant wastewater treatment facilities.

The wastewaters produced by this coke plant include:

- **Flushing Liquor**: 70 m³/hr
- **Final Cooler, Light Oil and Desulfurizer Blowdowns**: 25 m³/hr
- **COG Seal Pots Blowdown**: 10 m³/hr
- **Chemical Plant Blowdown**: 30 m³/hr
- **Phosam Process Blowdown**: 6 m³/hr

The total wastewater flow was estimated at 141 m³/hr, and the combined composition of these wastewater streams was estimated as shown in Table 1.

**Table 1: Combined Composition of Coke Plant Wastewater.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoride (F)</td>
<td>20 – 40 mg/L</td>
</tr>
<tr>
<td>Total Ammonia</td>
<td>2,700 mg/L</td>
</tr>
<tr>
<td>Free Ammonia Nitrogen (NH₃-N)</td>
<td>2,170 mg/L</td>
</tr>
<tr>
<td>Organic Nitrogen</td>
<td>170 mg/L</td>
</tr>
<tr>
<td>Volatile Phenol</td>
<td>215 mg/L</td>
</tr>
<tr>
<td>Thiocyanate (SCN-)</td>
<td>285 mg/L</td>
</tr>
<tr>
<td>Cyanide (Total)</td>
<td>130 mg/L</td>
</tr>
<tr>
<td>Chemical Oxygen Demand (Dichromate)</td>
<td>4,000 mg/L</td>
</tr>
<tr>
<td>Oil and Grease</td>
<td>100 mg/L</td>
</tr>
<tr>
<td>pH</td>
<td>8.5 – 9.5</td>
</tr>
</tbody>
</table>

These wastewaters were to be treated to meet the requirements shown in Table 2.

**Table 2: Required Discharge Effluent Water Quality.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoride (F)</td>
<td>≤ 10 mg/L</td>
</tr>
<tr>
<td>Ammonia Nitrogen (NH₃-N)</td>
<td>≤ 15 mg/L</td>
</tr>
<tr>
<td>Total Reduction of Nitrogen Removal</td>
<td>&gt; 70 %*</td>
</tr>
<tr>
<td>Nitrite (NO₂⁻)</td>
<td>&lt; 10 mg/L</td>
</tr>
<tr>
<td>Volatile Phenol</td>
<td>≤ 0.5 mg/L</td>
</tr>
<tr>
<td>Cyanide (Free)</td>
<td>≤ 0.5 mg/L</td>
</tr>
<tr>
<td>COD Permanganate, MN</td>
<td>≤ 40 mg/L</td>
</tr>
<tr>
<td>COD (Dichromate, CR)</td>
<td>≤ 100 mg/L</td>
</tr>
<tr>
<td>Oil and Grease</td>
<td>≤ 5 mg/L</td>
</tr>
<tr>
<td>Total Suspended Solids (TSS)</td>
<td>≤ 200 mg/L</td>
</tr>
<tr>
<td>PH</td>
<td>6 – 9</td>
</tr>
<tr>
<td>BOD</td>
<td>≤ 25 mg/L</td>
</tr>
<tr>
<td>Aniline</td>
<td>≤ 2 mg/L</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>≤ 3 mg/L</td>
</tr>
<tr>
<td>Pyridine</td>
<td>≤ 2.0 mg/L</td>
</tr>
</tbody>
</table>

* Removal percent between ammonia still effluent and final treatment plant effluent.
These water quality requirements required reductions/controls on ammonia, BOD, COD (permanganate and dichromate), cyanide, fluoride, phenol, oil and grease, and suspended solids.

**TREATMENT TECHNOLOGIES**

To achieve the required water quality limits a treatment facility which embodied the following technologies was designed:

- Ammonia steam stripping to reduce and recover wastewater ammonia
- Activated sludge aerobic biological treatment with PAC addition to remove BOD, COD, volatile phenolics, and oxidize ammonia
- Fixed film denitrification to remove nitrite and nitrates using an external carbon source
- Chemical precipitation to remove cyanide using ferrous sulfate and fluoride using calcium chloride
- Support facilities included wastewater storage/equalization and sludge collection and dewatering

Figure 1 presents a schematic diagram of the Baoshan Coke Plant wastewater treatment facility.

**AMMONIA STEAM STRIPPING**

In water, ammonia exists in equilibrium with ammonium ion according to the following mass action equation:

\[
\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+ \quad \text{equation (0)}
\]

This equilibrium is very dependent on pH and temperature. In the Baoshan operation, the collected wastewater is steam stripped in a still fitted with caustic addition to raise the pH of the wastewater to about 9 to 10 and direct steam injection.

The wastewater streams collect in two 5,000-m³ storage/equalization tanks where free and emulsified oils are allowed to separate out of the wastewaters. This oil-free wastewater is pumped to the ammonia still via heat interchangers to recover heat from the still bottoms. This 2.6 m diameter, 19.5 m tall ammonia still is designed to process 145 m³/hr of wastewater; it is fitted with 26 valve trays.
Low pressure steam (15,000 kg/hr) and 30 percent sodium hydroxide (1,530 kg/hr) are injected directly into the still to facilitate the release of ammonia from the wastewater into a gaseous stream which exits the top of the stripping tower. Other volatile constituents in the wastewater (e.g., benzene, hydrogen cyanide, and hydrogen sulfide) are also stripped from the wastewater.

The wastewater leaving the ammonia still contains about 100 mg/L of ammonia and about 60 mg/L of total cyanide. This hot ammonia stripped wastewater (about 94°C) is pumped to the 8,500 m³ biological treatment storage/equalization tank via heat interchangers and coolers which cool the wastewater to about 38°C.

**ACTIVATED SLUDGE AEROBIC BIOLOGICAL TREATMENT**

Generally, for ammonia stripping, two stills are installed. This allows uninterrupted processing while one still is being serviced. Only one still is installed at Baoshan Steel. To counter the eventuality of the ammonia still being out of service, the activated sludge aerobic treatment system was designed to process the high ammonia strength (> 2,000 mg/L) wastewater.

The activated sludge aerobic treatment system is comprised of two treatment trains; each train is made up of four aeration compartments as shown in Figure 2.
The first compartment of each train is designated as a “Pre-Aeration” chamber where essentially all organic constituents are degraded to carbon dioxide and water according to the following reaction equation:

$$\text{ORGANIC MATTER} + \text{O}_2 \xrightarrow{\text{microbes}} \text{CO}_2 + \text{H}_2\text{O} + \Delta H$$  \hspace{1cm} \text{equation (1)}

Where $\Delta H_f$ is energy produced by the microorganisms to sustain their metabolic activities including growth and reproduction.

At a design flow of 170 m$^3$/hr, each pre-aeration basin provides about 9 hours of hydraulic retention time (HRT) and a total of 18 hours HRT.

The subsequent treatment compartments, designated as Aeration Basins, were intended for the oxidation of the inorganic constituents, (e.g., ammonium-nitrogen, cyanide, thiocyanate, and sulfide) and removal of residual biodegradable organics. These reactions progressed according to the following equations:

$$\text{NH}_4^+ + 1.5 \text{O}_2 \xrightarrow{\text{microbes}} \text{NO}_2^- + 2 \text{H}_2^+ + 2 \text{H}_2\text{O} + \Delta H_f$$  \hspace{1cm} \text{equation (2)}

$$\text{NO}_2^- + 0.5 \text{O}_2 \xrightarrow{\text{microbes}} \text{NO}_3^- + \Delta H_f$$  \hspace{1cm} \text{equation (3)}

$$\text{CN}^- + \text{O}_2 \xrightarrow{\text{microbes}} \text{NH}_4^+ + \text{CO}_2 + \text{H}_2\text{O} + \Delta H_f$$  \hspace{1cm} \text{equation (4)}

$$\text{SCN}^- + \text{O}_2 \xrightarrow{\text{microbes}} \text{NH}_4^+ + \text{S}^= + \text{CO}_2 + \text{H}_2\text{O} + \Delta H_f$$  \hspace{1cm} \text{equation (5)}

$$\text{S}^= + 2 \text{O}_2 \xrightarrow{\text{microbes}} \text{SO}_4^{2-}$$  \hspace{1cm} \text{equation (6)}
At the design flow rate of 170 m$^3$/hr each Aerobic treatment train (three compartments) provides a HRT of 37 hours and a total of 74 hours HRT. Both Pre-Aeration and Aeration Basins are fitted with full floor coverage fine bubble aeration devices to distribute air from low pressure air blowers (three units operating and two spares). Each blower is rated at 4,590 m$^3$/hr at 147 kPa discharge pressure. These treatment basins are also fitted with controls for dissolved oxygen, pH, and temperature.

The discharge requirements for this plant include a limit of 100 mg/L of COD (dichromate). Generally biological treatment of coke plant wastewater produces effluent COD levels about 300 mg/L (including about 100 mg/L of TSS which contribute to COD measurement). In an attempt to produce compliance with this very stringent COD limit, facilities for powdered activated carbon (PAC) addition (450 kg/day) is provided.

Overflow from the aerobic treatment trains enter gravity solids separation clarifiers. There are two 20 m diameter clarifiers which operate at an overflow rate of 6.5 m$^3$/day/m$^2$. Sludge from the clarifier underflow is returned to the Pre-Aeration influent splitter box and a fraction to a sludge holding tank by sludge recycle pumps. There are three horizontal centrifugal pumps rated at 170 m$^3$/hr at 20 meters TDH; normally two pumps are running and one on standby. Overflow from the biotreatment clarifiers is pumped to the Denitrification Filters.

**DENITRIFICATION FILTERS**

The Denitrification Filters provided controls to achieve compliance with nitrite/nitrate discharge limits of 10 mg/L. This system utilizes an external carbon source, methanol, to drive the nitrite and nitrate dissimilation reactions.

\[
2 \text{NO}_2^- + \text{CH}_3\text{OH} + \text{H}_2\text{CO}_3 \rightarrow \text{N}_2 + 2 \text{HCO}_3^- + 2 \text{H}_2\text{O} + \Delta H_f \quad \text{equation (7)}
\]

\[
2 \text{NO}_2^- + \text{CH}_3\text{OH} + \text{H}_2\text{CO}_3 \rightarrow \text{N}_2 + 2 \text{HCO}_3^- + 2 \text{H}_2\text{O} + \Delta H_f \quad \text{equation (8)}
\]

Figure 3 presents a schematic diagram of the denitrification filter system.

The four Denitrification Filters are designed to operate at a filtration rate of 1.9 m$^3$/hr/m$^2$ based on 170 m$^3$/hr of wastewater flow. Methanol is added to the filter feed sump; the methanol feed pumps are rated to deliver 11 to 110 L/hr of 98% methanol. These Denitrification Filters are filled with 1.8 meters of media (1 meter sand and 0.8 meters gravel). Bacterial growth attaches to the surface of both the sand and gravel, and mediates the denitrification reactions. To complement the denitrification operation, facilities for fluffing and backwashing the filter media are provided. The filter media is periodically fluffed by pumping air through the media when the filter begins to exceed high water level alarm. This same high water level alarm also triggers the backwash cycle. Overflow from the Denitrification Filters flow through a backwash holding tank and then to a re-aeration tank. Overflow from the re-aeration tank flows by gravity to the Chemical Treatment section.
CHEMICAL TREATMENT

To achieve compliance with the cyanide and fluoride chemical precipitation technologies are provided. This processing is arranged to firstly precipitate cyanide using ferrous sulfate at pH about 6.5 to 7.0 followed by fluoride precipitation using calcium chloride at pH about 7.0 to 7.5. These precipitation reactions proceed according to the following reaction equations:

**Cyanide:**  \[ 6 \text{CN}^- + \text{Fe}^{+2} \rightarrow [\text{Fe(CN)}_6]^{4-} + \frac{1}{2} \text{O}_2 \rightarrow [\text{Fe(CN)}_6]^{3-} \]  

**Fluoride:**  \[ 2 \text{F}^- + \text{CaCl} \rightarrow \text{Ca(F)}_2 + 2 \text{Cl}^- \]

The reactions depicted in both Equation 9 and 10 are pH dependent. Figure 4 presents a schematic diagram of the chemical treatment train.

In the system shown in Figure 4, the cyanide and fluoride in the coke plant wastewater are converted to insoluble constituents and are remove by gravity settling with the aid of alum and a polymer. The clarified wastewater is discharged at an outfall into Shanghai Bay. The sludge from the bottom of the final clarifier is pumped to the sludge holding tank for dewatering.

SLUDGE DEWATERING

Waste activated sludge, backwash solids from the denitrification filter, and chemical precipitation solids are collected in a 200-m³ sludge holding tank; this tank is fitted with an agitator to keep solids in suspension and to mix ferric chloride added to the sludge for conditioning. The waste sludge in the sludge holding tank is pumped to a belt filter press.
for dewatering; prior to entry to the belt filter press and polymer is added to the sludge to further enhance dewatering.

Two 1.5-meter filter presses are provided, and with the ferric chloride and polymer conditioning, sludge cake with 20 percent solids is anticipated.

**SUMMARY / CONCLUSIONS**

The Baoshan Steel Phase 3 coke plant wastewater treatment system was started-up last December 1997 and has been in operation since that time. It is producing effluent quality which meets the required discharge limits.

This treatment system is by far the most complex and advanced treatment system in the world. This complexity is by virtue of its requirements to meet stringent limits on nitrite/nitrate, cyanide, and fluoride in addition to limits on ammonia, BOD, COD, and phenol.