DEVELOPMENTS AND APPLICATION OF NOVEL WATER TREATMENT
TECHNIQUES IN CSC

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SYNOPOSIS:

As a trustworthy steel company of global distinction that pursues growth together with environmental protection, China Steel Corporation (CSC) has developed and applied the electrodialysis reversal (EDR) and membrane bioreactor (MBR) techniques to decrease water usage and pollution emissions. An economical EDR desalination technique reclaimed 550 m$^3$ of cooling wastewater per day in hot rolling process with 80% conductivity removal rate, and 78% recovery rate. 540 m$^3$ of rinsed wastewater was reclaimed per day in electrolytic galvanizing line (EGL) and the conductivity of produced demineralized water was <10 µS/cm. On the other hand, high efficient MBR technique was applied to enhance COD removal in wastewater. The MBR system successfully reduced the COD discharge of 720 kg COD/day in coke oven wastewater and 449 kg COD/day in cold rolling wastewater. In addition, a new sludge conditioning method using sol-gel technique was tested on organic sludge produced from Coke Oven WWTP. The water content of the dewatered sludge reduced from 67% to 51% without mixed with inorganic sludge, and the amount of sludge cake sent to the incinerator could reduce 85%. Overall, CSC is very active in innovation, and has strong capability to put the innovations into practice.

Keywords: EDR, MBR, water reclamation, COD removal, sludge reduction

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1. Introduction

China Steel Corporation (CSC), located at Kaohsiung, Taiwan, was founded in 1971, with annual production around 10 million tons of crude steel. CSC is the largest integrated steel maker in Taiwan. Integrated steel production needs water for cooling, de-rust, lubrication, and dust washing. The source of raw water used in CSC is from Kaohsiung Fengshan Reservoir (FSR) effective capacity 3.4 Mt, which provides 0.3 Mt of industrial water daily. With effective water management, recycling and reuse, and energy integration in Linhai Industrial Park, the daily raw water consumption for production has reduced to 130,500 m³ in 2016, which is less than half of the supply of FSR. In CSC, process water recycling rate has reached 98.3 %, and the water intensity was reduced to 4.73 m³/tCS in 2016.

The other main task of CSC is water pollution control. The CSC wastewater treatment facility with 79,600 t/day capacity treats wastewater to effluent standards and discharges to the ocean through a 60-meter channel. In addition, a 40,000 m³ runoff wastewater collecting pool with 36,000 m³/day capacity for the raw material yard treats runoff wastewater from heavy rain to the effluent standards. In 2016, the total discharge was 13,629,000 m³. The Chemical Oxygen Demand (COD) concentration was 55.3 mg/L and Suspended Solids (S.S.) concentration was 5.8 mg/L much lower than statutory effluent standards of 100 mg/L and 30 mg/L.

In order to reclaim the process water and reduce the water pollution, the electrodialysis reversal (EDR) and membrane bioreactor (MBR) techniques were used in CSC. In addition, the wastewater treatment plants (WWTPs) produce great amount of sludge when processes wastewater. A new conditioning method was tested to reduce the amount of organic sludge produced from coke oven WWTP.

EDR is an electrodialysis reversal water desalination membrane process that arranges ion exchange membranes alternately in a direct current field. It has been extensively used for the removal of salt from a variety of water sources including industrial and municipal wastewater, groundwater, seawater as well as component separation and concentration, such as acid recovery and salt production. Several studies have provided EDR’s feasibility and high performance in the desalination of brackish water. Among industrial applications, EDR is effective in reducing the total dissolved solids (TDS) from the textile wastewater, produced water from oil and gas extraction, steel manufacturing process water, and semiconductor manufacturing wastewater. In addition, EDR has been demonstrated benefits under certain feed water and operational conditions when compared to other membrane techniques for desalination such as reverse osmosis (RO). EDR technique was selected to reclaim direct cooling water in hot rolling mill and to recycle wastewater from Electrolytic Galvanizing Line (EGL) in CSC based on the conductivity of these two streams of water.

Membrane bioreactor (MBR) is the combination of a membrane process like microfiltration or ultrafiltration with a suspended growth bioreactor, and is now widely used for municipal and industrial wastewater treatment. The microorganisms in MBR system remove organic pollutants and reduce the COD concentration in wastewater. The membrane process in MBR system separates water from suspended solids. The combination of membrane process and bioreactor enhances the concentration of microorganisms in the system and improves the processing efficiency. MBR technique was used in CSC to treat coke oven wastewater and cold rolling wastewater and the concentration of COD and suspended solids in wastewater reduced.

The organic sludge from coke oven WWTP is mixed with inorganic sludge from the industrial WWTP in CSC and the polymer is added. The treated sludge is dewatered using belt press and the water content is reduced from 99% to 67%. The sludge cake is sent to the Industrial Waste Incinerator in CSC. Since the inorganic sludge could be reused in cement
factory, CSC was seeking a technique to dewater organic sludge without adding inorganic sludge. Therefore, the organic sludge and inorganic sludge could be treated separately and the amount of sludge sent to the incinerator would be minimized. The new conditioning method using a sol-gel technique with the combination of various chemical agents was tested. The cell walls of microorganisms in sludge are broken down first and the water within the cells is released. The organic sludge undergoes hydrolysis, polymerization, and forming a tightly hydrophobic structure. The organic sludge can be dewatered using plate and frame filter press without adding inorganic sludge.

2. Materials and Methods

2.1 The EDR wastewater reclamation system

The characteristics of the EDR ion exchange membranes as given by supplies are as follow: the surface area is 1.28 m$^2$. The production process is heterogeneous. The thickness of the membrane is 0.45 mm for cation membrane and 0.42 mm for anion membrane. The general permselectivity is \( >45\% \) for cation membrane and \( >40\% \) for anion membrane. The surface resistance is \( >10,000 \Omega \cdot \text{cm}^2 \). The supporting layer is polyethylene. The tensile strength is \( >0.3 \text{ kg/cm}^2 \). The chemical stability is between pH 1~13. The ion exchange capacity is \( >1.8 \text{ Mol/m}^2 \). The Hot Rolling mill has three EDR sets and each EDR set includes one stage membrane stack with 300 cation and anion exchange membrane pairs. The EGL has four EDR sets and each EDR set includes one stage membrane stack with 350 cation and anion exchange membrane pairs.

2.2 Selection of reclaimable EGL wastewater

Seven streams of EGL wastewater were considered, and the streams with conductivity \( >2,000 \mu\text{S/cm} \), chloride concentration \( >400 \text{ ppm} \), and flow rate \( <24 \text{ m}^3/\text{day} \) (1 m$^3$/h) were eliminated. Three streams of wastewater were selected including hot water rinse, pickling rinse wastewater, and condensate water as the reclaimable sources. The mixture of three streams has following characteristics: total flow rate: 768 m$^3$/day, conductivity: 300~700 \( \mu\text{S/cm} \), chloride: 120~180 ppm, T-Fe: 40~70 ppm. After coagulation, sedimentation, and fiber filtration, the particles \( >5 \text{ um} \) would be removed and the T-Fe concentration reduced to \(<0.1 \text{ ppm} \).

2.3 The MBR system in the coke oven WWTP

The coke oven WWTP has five lines of MBR and each line contained 3 cassettes. The total surface area of one cassette is 1.642 m$^2$. The material of the membrane is PVDF with 0.04 um pore size. The chemical stability is between pH 5~9.5. The maximum operating temperature is 40°C. The TMP range is between -55 to 55 kPa. The flux is set to 12.5 LMH. The MLSS concentration in the MBR system is controlled at 10,000 mg/L. The flow rate of the MBR system is 7,200 m$^3$/day and the HRT is 21 hours.

2.4 The MBR wastewater treatment system in the cold rolling WWTP

The cold rolling WWTP had two lines of MBR. The effective volume in each line is 750 m$^3$ and containing 10 cassettes for each line. There are 300 sets of membranes in each cassette. The total surface area for each cassette is 300 m$^2$. The material of the membrane is PVC. The chemical stability is between pH 5~9.5. The flux is set to 12.5 LMH. The MLSS concentration in the MBR system is controlled between 9,000~10,000 mg/L. The flow rate of the MBR system is 1,800 m$^3$/day and the HRT is 10 hours.
2.5 Examination of organic sludge and filtrate after conditioning

Several examinations, including pH, water content, capillary suction time (CST), volatile suspended solids (VSS), and heat value was performed on the sludge after conditioning and dewatering. Heat value was measured following CNS10835 standard procedure. On the other hand, concentration of COD, ions, suspended solids (SS), conductivity, and pH was examined in filtrate released from filter press. COD was measured following Taiwan national environmental analysis laboratory standard NIEA W515.54A procedure. Ion concentration was measured using two separate ion chromatography machines, one for anions and one for cations. Suspended solids were measured using following procedure. The samples were filtered through pre-weighted 0.45 μm filter paper and the filter paper was dried in 100 °C oven for 2 hours. The dried filter paper was weighted and the concentration of suspended solids was obtained with proper calculation.

3. Results

3.1 Direct cooling wastewater reclamation by EDR in hot rolling mill

The hot rolled coil is produce from slab by rolling under high temperature in hot rolling mill. The direct cooling water is used to control the temperature during the rough rolling and fine rolling processes. The direct cooling water flows back to cooling tower after heat exchange and the water is circulated and reused. The direct cooling water is concentrated due to evaporation and splashing out of the system. In order to control the water quality of cooling water to avoid scaling and corruption of the system, the water in cooling tower needs to be partially discharged and replaced with industrial water. EDR technique was selected to reclaim and reuse the discharged condensate water from cooling tower base on the conductivity of the condensate cooling water. The reclamation processes using EDR technique is illustrated in Figure 1.

![Figure 1 Reclamation of Direct Cooling Water in Hot Rolling Mill](image)

Four EDR stage membrane stack with 300 pairs of ion exchange membranes in each stack were established in hot rolling process to reclaim direct cooling wastewater (Figure 1).
The full-scale wastewater reclamation plant was constructed equipped with fiber filter and precision filter for pretreatment, and electrodialysis reversal (EDR) for desalination. The pretreatment process reduces the concentration of suspended solids to protect EDR membrane. The EDR systems reduce the conductivity of the pretreated wastewater from ~1,700 to 350 \( \mu \text{S/cm} \) (i.e., ~80% desalination rate). The plant is capable of supplying 550 m\(^3\)/day of reclaimed pure water to the hot rolling mill from condensate cooling water with the total flow rate of ~700 m\(^3\)/day (i.e., ~78% recovery rate). The cost of the reclaimed water is cheaper than the industrial water used by CSC. The annual saving of the reclamation system, including industrial water cost and wastewater treatment cost, was more than 6.6 million New Taiwan dollars (NT$). Furthermore, the calcium and chloride concentration in reclaimed water is lower than industrial water. The slipping number of fine rolling process decreases from 53 to 0 times per year due to the improvement of water quality.

3.2 Wastewater reclamation and reuse in EGL

Demineralized water (DMW) is used to rinse the strip surface for the galvanizing process. The usage of DMW and discharged wastewater of the EGL were both ranked the number one in CSC cold rolling mill. The daily usage of DMW reached approximately 1,600 m\(^3\) as the EGL was running at full capacity. The wastewater had potential for reclamation and reuse and EDR technique was selected to achieve the goal.

![Figure 2 Reclamation of wastewater in EGL](image)

Three wastewater streams including hot water rinse, pickling rinse wastewater and condensate water from the EGL were selected for reclamation base on the conductivity, chloride concentration and flow rate of the stream (Figure 2). The full-scale wastewater reclamation plant was constructed equipped with coagulation, flocculation, sedimentation, and filtration for pretreatment, and electrodialysis reversal (EDR) and ion exchange (IX) processes for desalination. The pretreatment processes reduce the total iron concentration in the wastewater from 40–70 ppm to <0.1 ppm to protect EDR membranes from fouling. The EDR systems reduce the conductivity of the pretreated wastewater from ~800 to 125 \( \mu \text{S/cm} \) (i.e., ~85% desalination rate). The plant is capable of supplying 540 m\(^3\)/day of reclaimed
pure water to the EGL from selected wastewater streams with the total flow rate of 768 m$^3$/day (i.e., ~70% recovery rate). The cost of the reclaimed water is cheaper than the DMW produced by regular processes in CSC. The annual saving of the reclamation system, including pure water cost and wastewater treatment cost, was more than 11.6 million New Taiwan dollars (NT$).

3.3 Application of MBR to treat coke oven wastewater

Coke oven wastewater and sanitary wastewater were mixed and treated together with activated sludge having >85% COD removal rate in coke oven WWTP. With the expansion of production line, the wastewater flow rate and COD amount were exceeding the capacity of the original design. The stability of the microorganisms in activated sludge was affected and the concentration of suspended solids together with COD in secondary effluent increased occasionally. In order to increase the capacity of the biological treatment process, MBR technique was tested and utilized in CSC (Figure 3).

Five commercial MBR membranes were tested in pilot plant and three of them reached the requirement of effluent criteria. The full-scale MBR system was implanted in the original coke oven WWTP to replace the sedimentation process. It’s the first full-scale MBR system used to treat coke oven wastewater in Asia with the total flow rate of 7,200 m$^3$/day. The MBR significantly improved COD and S.S. removal of coke oven wastewater. The secondary effluent COD decreased ~20% (from 277 to 219 mg/L), equal to 720 kg COD/day and the S.S. concentration decreased from $\geq$ 30 mg/L to $\leq$ 5 mg/L (Table 1). The COD removal rate of coke oven WWTP increased from 88% to 93%.

![Figure 3 The MBR module in coke oven wastewater treatment](image)

Table 1 COD concentration of secondary effluent before and after MBR established

<table>
<thead>
<tr>
<th></th>
<th>Secondary Effluent COD (mg/L)</th>
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<tbody>
<tr>
<td></td>
<td>Before MBR established</td>
</tr>
<tr>
<td>Average</td>
<td>277</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>59</td>
</tr>
</tbody>
</table>

3.4 Application of MBR to treat cold rolling wastewater

Cold rolling wastewater contains all different kinds of organic and inorganic pollutants including emulsifier, degreaser, lubricating oil, sulfide, etc and is hard to treat. The concentration of suspended solids and COD in the secondary effluent was over the standard occasionally. There are three streams of wastewater, including acid cleaning wastewater,
alkali containing wastewater, and oily containing wastewater, to be treated in cold rolling WWTP. Alkali containing wastewater and oily containing wastewater contribute 80% of COD in cold rolling wastewater. MBR technique was selected to treat these two streams of wastewater to increase the ability of cold rolling WWTP to remove COD and S.S. (Figure 4).

Three commercial MBR membranes were tested in pilot plant and only one of them reached the requirement of effluent criteria. The full-scale MBR system was constructed and the original treating processes in cold rolling WWTP were modified. The total flow rate is 1,800 m$^3$/day. The MBR significantly improved COD and S.S. removal of cold rolling wastewater. The COD concentration decreased from 1,590 mg/L to 56 mg/L, equal to 449 kg COD/day removal. The S.S. concentration decreased from 211 mg/L to 3 mg/L. The oil concentration decreased from 130 to < 3 mg/L fitting the <8 mg/L requirement.

![Figure 4 The MBR system in cold rolling wastewater treatment](image)

3.5 Organic sludge reduction using a novel conditioning method

The coke oven WWTP treats 7,200 m$^3$ wastewater per day and contains active sludge and MBR system which produces 120 m$^3$ of organic sludge per day. The water content of the organic sludge is 98.4%. The organic sludge is mixed with inorganic sludge from the industrial WWTP in CSC and the polymer is added. The treated sludge is dewatered using belt press and the water content reduced to 67%. The coke oven WWTP produces 860 tons of sludge cake per month. The sludge cake is sent to the Industrial Waste Incinerator in CSC. The incinerator has been built for almost 30 years and the loading of the incinerator is increasing each year. The reduction of sludge cake sent to the incinerator is needed. Since the inorganic sludge could be reused in cement factory, CSC was seeking a technique to dewater organic sludge by itself without adding inorganic sludge. Therefore, the organic sludge and inorganic sludge could be treated separately and the amount of sludge sent to the incinerator could be minimized. A new conditioning technique is able to meet the requirements.

This new conditioning technique uses a sol-gel technique with the combination of various chemical agents. First, the agents break down the cell walls of microorganisms in sludge and the water in cells is released. Second, the sludge undergoes hydrolysis, polymerization, and form a tightly hydrophobic structure. Third, the organic sludge is dewatered using plate and frame filter press. The results of pilot scale test showed that the
water content of the dewatered sludge decreased to 57%. The heat value of the dewatered sludge cake was 3,992 kcal/kg so it is easily burned with the incinerator. The new conditioning technique was tested on site in our WWTP, the water content of the dewatered organic sludge could decrease to 51% (Table 1; Figure 5). If the water content was assumed to be 60%, the amount of sludge cake sent to the incinerator would be decreased to 144 tons per month which is 85% reduction compared to current process. The filtrate (Figure 5) released from the filter press could be pumped back to coke oven WWTP and be easily treated.

Table 2 Test results of new conditioning method

<table>
<thead>
<tr>
<th></th>
<th>Volume (L)</th>
<th>VSS (%)</th>
<th>CST (secs)</th>
<th>Water content (%)</th>
<th>pH</th>
<th>Plate Filter Press Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>before</td>
<td>after</td>
<td></td>
<td>before</td>
</tr>
<tr>
<td>Lab</td>
<td>10</td>
<td>62</td>
<td>71.5</td>
<td>4.6</td>
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<td>55.5</td>
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<tr>
<td>Pilot</td>
<td>2,000</td>
<td>62</td>
<td>64.5</td>
<td>8.9</td>
<td>98.9</td>
<td>56.8</td>
</tr>
<tr>
<td>On site</td>
<td>300,000</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>93</td>
<td>51</td>
</tr>
</tbody>
</table>

Figure 5 Sludge cake and filtrate released from plant and frame filter press

4. Discussion

The direct cooling water reclamation system was built in CSC and the amount of makeup water and discharged water in hot rolling mill decreased. It saved more than 6.6 million New Taiwan dollars annually. The quality of reclaimed water was better than industrial water and decreased the slipping number of fine rolling process. Moreover, the wastewater reclamation system was also built in EGL and the quality of reclaimed water fit the pure water standard. The annual saving cost was more than 11.6 million New Taiwan dollars. Together, 300,000 m³ of water was reclaimed annually by these two reclamation systems.

The MBR systems were established in coke oven WWTP and cold rolling WWTP, and successfully improved the processing efficiency. The concentration of COD and S.S. in secondary effluent both decreased significantly in these two WWTPs. Overall, the COD amount decreased 1,170 Kg-COD/day in the effluent of CSC after the implantation of these two MBR systems.

The dry solid in the sludge released from MBR system is around 2 tons per day. On site test results showed water content of organic sludge can be reduced form 98.4% to 51% without adding inorganic sludge. If we assumed the final water content to be 60%, the
amount of sludge after dewatering would be around 5 tons per day. The amount of sludge cake sent to the incinerator decreased 85% compared to current process with dewatering and not adding inorganic sludge. The heat value of the dewatered organic sludge was 3,992 kcal/kg, so it would be easily burned by the incinerator. The filtrate released from the filter press could be easily treated.

5. References


