

Application of EDR for Wastewater Reclamation and Reuse in Electrolytic Galvanizing Line

PO-HSUN LIN*, MAO-SUNG YEH* and KUAN-CHUNG CHEN**

**New Materials Research & Development Department*

***Rolling Mill Department III*

China Steel Corporation

The amount of the used demineralized water (DMW) and discharged wastewater in the electrolytic galvanizing line (EGL) were both at the 1st place in the No. 2 cold rolling mill. The daily usage of DMW reached approximately 1600 m³ as the production line was being fully operated. Unfortunately, the wastewater was discharged into the cold rolling mill wastewater treatment plant even though it had potential for reclamation and reuse. Therefore, the reclaimable wastewater streams from the EGL were selected, and an applicable and economic reclamation process was investigated. The full-scale wastewater reclamation plant equipped with coagulation, flocculation, sedimentation, filtration, EDR, and Ion Exchange processes for desalination was constructed and supplied 538 m³/day of reclaimed water to the EGL in 2012. The quality of reclaimed water has achieved the DMW standards, and its cost is lower than the DMW generated by regular China Steel processes. Furthermore, the problems with regard to the wastewater quantity, quality and temperature were successfully overcome during system commissioning. The annual benefit of the EGL wastewater reclamation was greater than 11.6 million NTD, and the investment cost was expected to be recovered in 4–5 years.

Keywords: Electrodialysis reversal, Electrolytic galvanizing line, Desalination

1. INTRODUCTION

Galvanizing is an attractive and economical means of corrosion protection for a wide variety of commercial and industrial steel articles. Cold-rolled steel strip produced by the electrolytic galvanized line (EGL) at China Steel (CSC) requires alkali and hydrochloric acid to remove anti-rust oil, rust, and other impurities for strip surface cleaning during the production process. Subsequently demineralized water (DMW) is used to rinse the remaining acid and alkali on the strip surface for high production quality. The usage of demineralized water (DMW) and discharged wastewater in the EGL were both at the 1st place in the No. 2 cold rolling mill. The daily usage of DMW reaches approximately 1600 m³ when the EGL is fully operated. However, the wastewater was discharged into the cold rolling mill wastewater treatment plant even though it had potential for reclamation and reuse. Therefore, the treatment processes including coagulation, flocculation, sedimentation, filtration, electrodialysis reversal (EDR), and ion exchange (IX) processes were applied to treat the selected EGL wastewater streams for DMW production, which can reduce EGL production cost and achieve the goal of wastewater reclamation at CSC.

Electrodialysis reversal (EDR) is a membrane separation and desalination process that has been extensively used for the removal of salt from a variety of industrial, municipal and ground water sources as well as component separation and concentration in pharmaceutical and food production⁽¹⁻³⁾. Previous laboratory-scale results have shown that electrodialysis is effective in reducing the TDS of saline water from various sources, including textile industry effluent, reclaimed water from oil and gas extraction, domestic wastewater and brackish ground water⁽⁴⁾. In addition, several studies have demonstrated the benefits of the technique under certain feed water and operational conditions when compared to other membrane techniques for desalination such as reverse osmosis (RO).

Aqueous ions in electrodialysis are migrated through a system of solutions and ion-exchange membranes by an applied electric potential gradient from two platinum electrodes (anode and cathode). Between the electrodes there are a series of semi permeable ion-selective membranes that are cation and anion-exchange membranes, separated by thin plastic manifolds (spacers) to create a channel for liquid flow (Fig.1). Cation-exchange membranes are permeable to positively charged ions but not to negatively charged

ones, and anion-exchange membranes are permeable to negatively charged ions but not to positively charged ones. The membranes alternate between anion transfer and cation transfer which produce product and concentrate streams. As the charged species migrate through the stack and transfer across the membranes, they become trapped in the concentrate channel and are depleted from the product (Fig. 1).

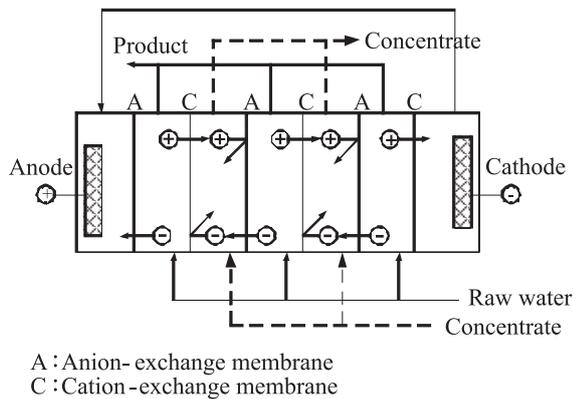


Fig.1. Schematic diagram of EDR system.

The advantage of EDR over conventional ED resides in the ability to invert the electrodes polarity to reduce concentration polarization and scaling on the membrane surface⁽⁵⁾. This process of reversal (generally running from 15 to 30 min) is important to control the scaling of ionic species prone to deposition, such as calcium phosphate or carbonate, that require aggressive and costly cleaning treatments to remove. Membrane fouling has been reported to be a problem occurring in EDR systems, with the main compounds responsible being calcium sulphate (CaSO_4), calcium phosphate ($\text{Ca}_3(\text{PO}_4)_3$) and high molecular weight charged organic molecules⁽⁶⁾. In addition, electrolysis occurs on the surface of each platinum electrode producing a mixture of chlorine and oxygen gas helping to further reduce fouling.

2. MATERIALS AND METHODS

2.1 Selection of reclaimable rinse wastewater

The DMW used by the EGL requires conductivity $< 10 \mu\text{S/cm}$ and chlorine concentration $\leq 5 \text{ mg/L}$. Seven streams of EGL rinse wastewater were considered, and then streams with conductivity $> 2000 \mu\text{S/cm}$, chlorine concentration $> 400 \text{ mg/L}$, and flow rate $< 1 \text{ m}^3/\text{h}$ were eliminated. As a result, the CSC New Materials R&D team selected 3 streams of wastewater including rinse wastewater, pickling wastewater and condensate water as the reclaimable sources. The flow rate, conductivity, and chlorine concentration of the 3 streams were approximately $770 \text{ m}^3/\text{day}$, $1000 \mu\text{S/cm}$, and 150 mg/L , respectively. Additionally, a post desalination process is required. The desalination processes mainly used globally include reverse osmosis (RO), EDR, multi-stage flash distillation (MSF), multiple-effect distillation (MED) and the IX process. The New Materials R&D team applied EDR as a desalination process for rinse wastewater because of its economic and technical feasibility⁽⁷⁻⁹⁾. In addition, the EDR influent required a less strict standard than RO, the recovery rate is better than RO, and the energy consumption is less than MSF and MEE; furthermore, unlike IX, EDR does not generate chemical waste.

2.2 The EGL rinse wastewater reclamation system

The rinse wastewater reclamation system in EGL (Fig.2) consisted of a pretreatment process that included coagulation, sedimentation and fiber filtration. The entire pretreatment process can remove total iron (T-Fe) from $40\sim 70$ to $< 0.1 \text{ mg/L}$, and prevent irreversible damage to the cation-exchange membranes caused by iron (II) ions in the rinse wastewater. Iron ions were oxidized to iron oxides during coagulation, and large iron oxide particles were removed by sedimentation. Then the fiber filtration was capable of filtering particles with size $\geq 5 \mu\text{m}$ so that the filtered effluent could achieve the EDR influent standard. After EDR the conductivity of the EGL rinse wastewater

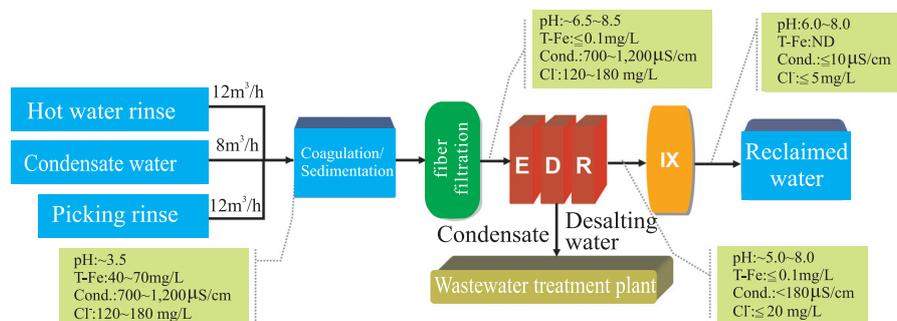


Fig.2. The process of wastewater reclamation and reuse in EGL.

decreased from 1200 to $<180 \mu\text{s}/\text{cm}$. Eventually, the EDR product water was refined by the IX process (activated carbon, cation, and anion exchange resins), after which the conductivity and chlorine concentration of reclaimed water were $<10 \mu\text{s}/\text{cm}$ and 5 mg/L, respectively.

3. EDR TROUBLESHOOTING DURING FULL-SCALE FINAL ACCEPTANCE TEST (FAT)

The full-scale EDR system once built encountered problems regarding rinse wastewater quantity, quality, and temperature due to the low EGL production rate and the varying operating conditions of the evaporators. The cause of these problems and the troubleshooting details are described below.

3.1 Quantity

The incoming wastewater quantity of the EGL reclamation system was significantly decreased on 2010 because of the insufficient orders for steel products. The capacity utilization was approximately 50%, which reduced the wastewater quantity to 32 m³/h. After discussion with the engineers in the Continuous Annealing and Coating Mill, the EDR internal recycle system would be activated when the quantity of rinse wastewater was too low. At this stage, EDR influent and the discharge of concentrate and product water were all terminated, and the concentrate and product water were mixed and desalinated alternately for internal recycling (Fig.3).

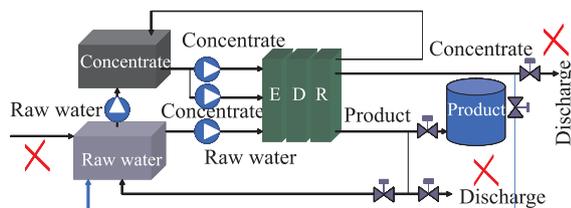


Fig. 3. The mechanism of EDR internal recycling.

3.2 Quality

The EGL recycled wastewater included a stream of condensate water. When the evaporator was initially started or the operating conditions varied, it was at an unstable condition in the first half hour which caused part of electroplating solution to be drawn into the evaporator with steam. This resulted in an extraordinary quality of condensate water in which the concentrations of suspension solids, Cl^- , Zn^{2+} and K^+ , and the conductivity were significantly increased, higher than the designed treatable conductivity of wastewater reclamation system (i.e., $\sim 1200 \mu\text{s}/\text{cm}$). Therefore, we

suggested that the Continuous Annealing and Coating Mill install solenoid valves (the dashed line in Fig.4) and alter the control method — when the conductivity meter showed the conductivity of the condensate water to be $>200 \mu\text{s}/\text{cm}$, the solenoid valve was opened and discharged the condensate water into the sump pit. According to the results, shown in Fig.5, before the improvement there was a conductivity spike, and afterwards the quality of the incoming wastewater was stable and within the required standard.

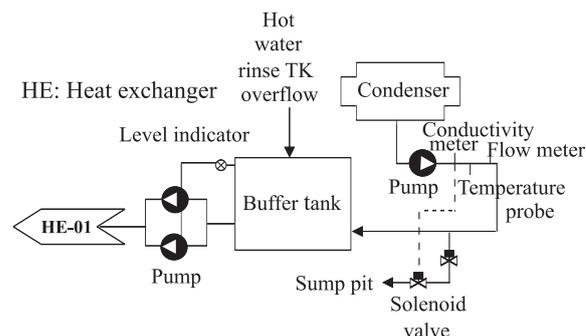


Fig.4. The improvement of control method for wastewater qualities.

3.3 Temperature

During one month's temperature monitoring for the EGL wastewater reclamation system, the highest temperature of the incoming wastewater reached 56°C, higher than the endurable temperature (45°C) of both the EDR membrane and the ion exchange resin. We installed a two-stage heat exchanger (HE) ahead the reclamation system to reduce wastewater temperature and increase heat loss recovery. The incoming wastewater temperature after the HE was expected to be reduced to $<40^\circ\text{C}$ (Fig.6). The DMW produced from the EGL wastewater reclamation system was used as cooling water, and its temperature rose to 44°C, which can be directly utilized in the EGL production processes to decrease the usage of steam and recover heat loss. Figure 7 shows temperature the trend of incoming wastewater. The temperature of wastewater was consistently controlled between 30 to 35°C, which indicated that the temperature problem was completely solved.

4. THE ESTABLISHMENT OF OPTIMAL PRETREATMENT CONDITIONS

The pretreatment processes of the EGL wastewater reclamation system included buffering, oxidative coagulation, sedimentation (i.e., reaction tank, pH adjustment tank and flocculation tank), and fiber filtration. However, the operating configurations were based on results obtained from the pilot test but not adjusted

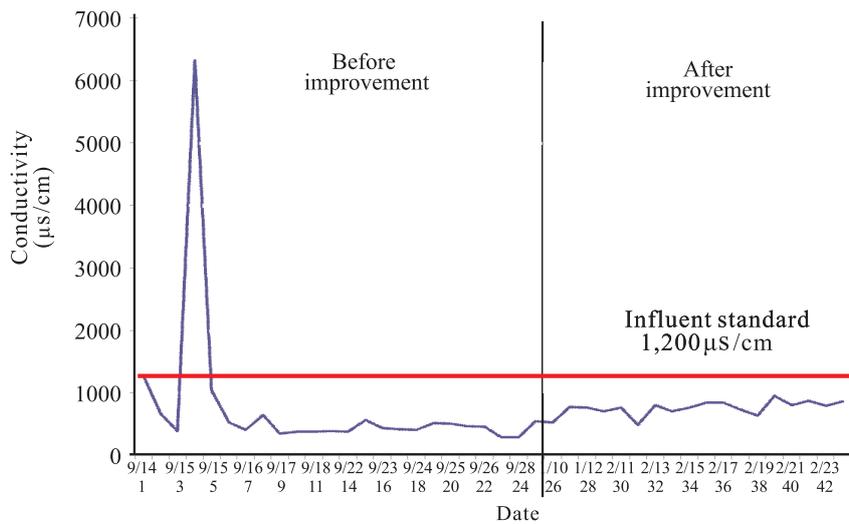


Fig.5. The trend of wastewater conductivity as a function of time.

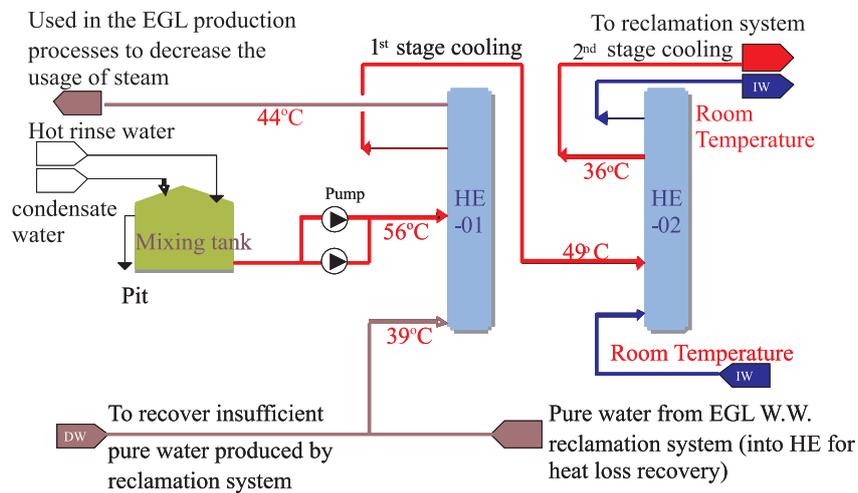


Fig.6. The configuration of two-stage heat exchanger for reducing wastewater temperature.



Fig.7. The trend of wastewater temperature as a function of time.

to the optimal conditions after the construction engineering was completed. As a result the T-Fe concentration of the pretreated effluent did not achieve the required standard of ≤ 0.1 ppm. The details of adjustment in each pretreatment process to optimize the system are described in the following two paragraphs.

Figure 8 presents the original operating conditions of the pretreatment process. The pH in the buffer tank was controlled between 5~6 by NaOH. Thirty L/h of polyaluminum chloride (PACl) was dosed for coagulation in the reaction tank, and the oxidation reduction potential (ORP) was maintained at ~ 250 mV by NaOCl. Then, in the pH adjustment tank, the pH was controlled between 7~8. Furthermore, 75 L/h of polyacrylic acid (PAA) was added for flocculation, and the flow rate of fiber filter was 40 m³/h. According to the pretreatment conditions described above, the T-Fe concentration in the pretreated wastewater was >0.1 ppm, and the quality was instable. In order to optimize the pretreatment conditions, we conducted a series of jar tests to provide reference points for the field.

Figure 9 illustrates the improved pretreatment conditions in which the pH in the buffer tank was raised to 8~10 to increase alkalinity and enhance oxidation efficiency. This resulted in the ORP increasing from 250 to 350 mV so that the dosage of PACl was reduced from 30 to 14 L/h. Moreover the addition of PAA could also be decreased from 75 to 36 L/h thereby reducing the chemical costs. Finally, the flow rate of fiber filtration was adjusted to 32 m³/h to minimize the system rebooting frequency and to stabilize the quality of the filtered wastewater. After the optimized conditions were employed, the T-Fe concentration of the pretreated effluent could consistently achieve the required standard of ≤ 0.1 ppm.

5. SYSTEM COMMISSIONING AND FAT RESULTS

Since the quantity, quality, and temperature problems of the rinse wastewater were troubleshot, and the establishment of optimal pretreatment conditions in the full-scale EDR system was completed, the R&D team

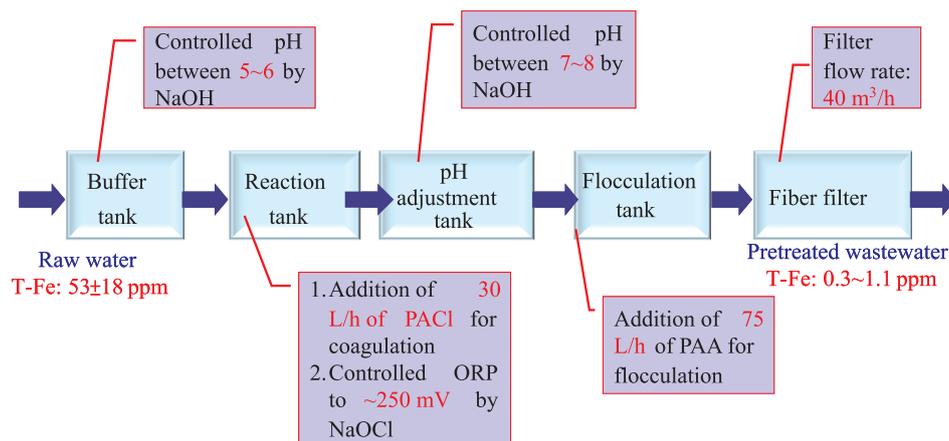


Fig.8. The original operating condition of pretreatment process.

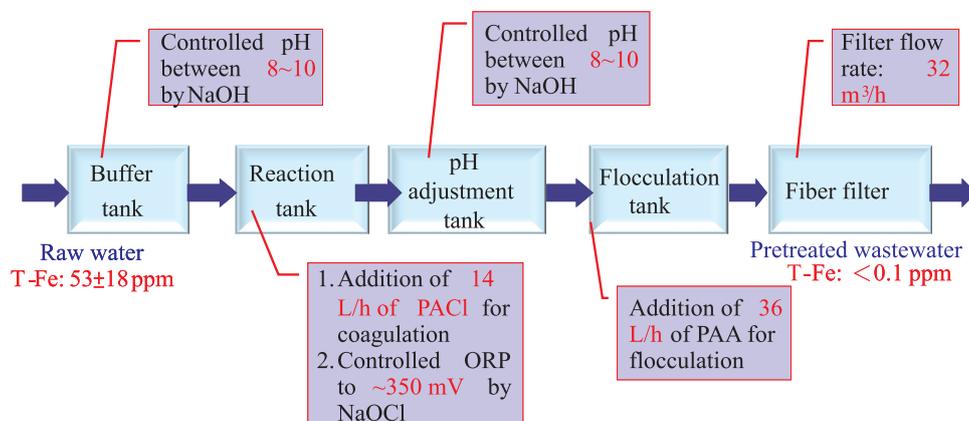


Fig.9. The improved operating condition of pretreatment process.

immediately began system commissioning and FAT. The date tested, analyzed samples, water quality guidelines, and results are listed in Tables 1 to 4, which indicate that the fiber filter effluent, EDR product water, and IX effluent all achieved the required standards of system commissioning and FAT. In addition, the EDR desalination system was able to continuously produce water of 50000 m³/5cycle. The system required chemical cleaning when the water production volume was \geq

10000 m³, and the acid and alkali cleaning times were \leq 7 hours (mainly alkali cleaning/10000 m³ water; and alkali and acid cleaning/40000 m³ water). The cycle time of IX resin was approximately 40 hours, and regeneration time was \leq 3 hours. Lastly, the entire recovery rate of the EGL wastewater reclamation system was \geq 70%. Based on the results shown, the efficiency of the system fully accomplished the requirements of system commissioning and FAT.

Table 1 System commissioning description

		Samples analyzed		
Commissioning date	1st stage	2012.01.09~01.15	7 sets of results	
	2nd stage	2012.02.10~02.23	14 sets of results	
Analyzed samples	Buffer tank raw water	Fiber filter effluent	EDR product water	IX product water
Water quality guidelines	NA	pH 7.5±1 T-Fe \leq 0.1 ppm	pH 5.0~8.0 Cond.<180 μ s/cm T-Fe \leq 0.1 ppm	pH 7±1 Cond.<10 μ s/cm

Table 2 System commissioning results

	Buffer tank raw water	Fiber filter effluent	EDR product water	IX product water
pH	7.92±0.86	8.08±0.36	6.35±0.31	6.45±0.42
Conductivity (μ s/cm)	398±128	801±125	126±18	0.8±1.0
T-Fe (ppm)	—	<0.1	<0.1	—
Achieve standard	○	○	○	○

Table 3 The description of final acceptance test (FAT)

		Samples analyzed		
Commissioning date	1st stage	2012.01.13~02.23	EDR product during commission was included in FAT	
	2nd stage	2012.02.24~06.04	12 sets of results	
Analyzed samples	Buffer tank raw water	Fiber filter effluent	EDR product water	IX product water
Water quality guidelines	NA	pH 7.5±1 T-Fe \leq 0.1 ppm	pH 5.0~8.0 Cond.<180 μ s/cm T-Fe \leq 0.1 ppm	pH 7±1 Cond.<10 μ s/cm

Table 4 Final acceptance test results

	Buffer tank raw water	Fiber filter effluent	EDR product water	IX product water
pH	9.45±1.18	7.93±0.34	6.48±0.64	6.45±0.24
Conductivity (μ s/cm)	684±265	819±218	105±26	3±2
T-Fe (ppm)	—	<0.1	<0.1	—
Achieve standard	○	○	○	○

6. ECONOMIC EVALUATION

The benefit of constructing the EGL rinse wastewater reclamation system includes saving the cost of pure water usage and decreasing the wastewater treatment cost. Given an EGL operating rate of 85% and a wastewater reclamation rate of 85%, the annual benefit of the EGL wastewater reclamation system could be greater than 11.6 million NTD, and it was estimated that the investment cost could be recovered in 4~5 years.

7. CONCLUSIONS

1. During full-scale FAT, the EGL rinse wastewater had the following problems: (1) low EGL production rate caused by an insufficient wastewater quantity; (2) a varying operating condition of the evaporator resulting in a higher conductivity; and (3) a higher temperature. The R&D team overcame the problems by: (1) activating the internal recycling system; (2) installing solenoid valves and modifying the control programs; and (3) installing a two-stage heat exchanger and designing a heat loss recovery system.
2. The pretreatment optimization of the EGL rinse wastewater reclamation system, system commissioning, and FAT were fully accomplished, and the wastewater treatment flow rate is now able to reach 768 m³/day.
3. The conductivity of the pure water produced is <10 $\mu\text{s}/\text{cm}$, and the system recovery rate is $\geq 70\%$. The plant has been producing pure water for EGL and creating cost-reduction profits since March 2012.

REFERENCES

1. B. Pilat: *Desalination*, 2001, 139(1-3), pp. 385-392.
2. J. M. Ortiz, J. A. Sotoca, E. Expósito, F. Gallud, V. García-García, V. Montiel and, A. Aldaz: *Journal of Membrane Science*, 2005, 252(1-2), pp. 65-75.
3. T. Xu and C. Huang: *AIChE Journal*, 2008, 54(12), pp. 3147-3159.
4. T. Sirivedhin, J. McCue and L. Dallbauman: *Journal of Membrane Science*, 2004, 243(1-2), pp. 335-343.
5. Y. Kim, W. S. Walker and D. F. Lawler: *Water Research*, 2012, 46(7), pp. 2042-2056.
6. F. H. Meller: "Electrodialysis (ED) & electro dialysis reversal (EDR) technology, Ionics Incorporated", 2000.
7. Y. M. Chao: Report No. TS-95677, China Steel Corporation, 2006.
8. Y. M. Chao: Report No. TE-96625, China Steel Corporation, 2007.
9. Y. M. Chao, J. F. Wu and T. P. Yang: Report No. PJ-95610, China Steel Corporation, 2007. □