

Lead and Zinc Smelting Wastewater Treatment and Reclamation by Coagulation-Flocculation-Sedimentation, Ultrafiltration and Reverse Osmosis Technique

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Abstract: The typical smelting wastewater is with characteristics of high concentration of TDS, conductivity, heavy metal ions, and low concentration of COD. The ultrafiltration (UF) and reverse osmosis (RO) is an attractive technology to reclaim and reuse this kind of wastewater. In this work, Coagulation-flocculation-sedimentation (CFS) and multi-media filter (MMF) was used as the pretreatment processes. UF, RO and concentration RO (CRO) processes was applied as the advanced treatment processes to reclaim the smelting wastewater. To enlarge the recovery of RO and CRO units, the influences of increasing the feed temperature by waste heat from the smelting plant and the feed pressure by change the operating frequency of the high pressure pumps were investigated. The optimize operation parameters of RO and CRO units were obtained. To understand the operation CIP cycle time of UF, RO and CRO membrane units in a long term operation, the trans-membrane pressure (TMP) and permeate flux difference were investigate. Good system operation stability, permeate flux recovery after CIP and qualified treated water were obtained in the recommend operation parameters. The results of this work can benefit to the designing of reclaiming the smelting wastewater by UF-RO-CRO approach within the Lead and Zinc smelting industrial application.

Keywords: Wastewater Reclamation, Smelting Wastewater, Coagulation-flocculation-sedimentation, UF, RO

1. Introduction

Lead and Zinc is the fundamental material in society development, it is widely used in electrical industry, machinery industry, military industry, metallurgy industry, chemical industry, light industry and medical industry [1-3], etc. It is abundant with Lead and Zinc resources in China and the need for Lead and Zinc increased rapidly with the rapid development of economic. The formal Lead and Zinc industry base was located in the central, northeast and southwest of China, some new factories were built in the south, northwest and Sichuan province in decades [4-9]. However, the rapid development of Lead and Zinc smelting industry also brings some serious environmental problems, such as water resources pollution [10, 11], air pollution [12] and soil pollution [13, 14], different heavy metals are one of the main

factors for these serious problems [15]. The wastewater drainage policies became more and more strict due to the serious water pollution, the rise in the high quality water price and responsibilities on society for these companies. These factors made the wastewater reclamation and reuse became a quite important issue for Lead and Zinc smelting companies to carry on.

The Lead and Zinc ores are always accompany with Ag, Cu, Cd, etc. [16, 17], these elements are contained in the wastewater during the fabrication processes of Lead and Zinc. So the smelting wastewater are characterized with very high total dissolved solids (TDS) concentration due to these heavy metal ions (Ag^+ , Cu^{2+} , Pb^{2+} , Zn^{2+} , Hg^{2+} , etc) and other metal ions (Ca^{2+} , Mg^{2+} , Na^+ , etc.). Besides, there are waste acid (mainly H_2SO_4 , As^{3+} , F^- , Cd^{2+} , Zn^{2+}) discharged from the H_2SO_4 fabrication workshop. Thus, the major pollutants of

wastewater coming from the Lead and Zinc smelting industry are heavy metals and dirty acid wastewater with complicated containments [18-21]. The heavy metals may cause serious health problems and do harm to the Lead and Zinc smelting processes as well [22, 23]. To remove the heavy metals, reduce TDS and containments of dirty acid are the main targets for reclamation and reuse of the wastewater. In previous studies on Lead and Zinc smelting wastewater treatments processes, it was focus on the chemical dosing [24, 25], neutralization [26] and coagulation-flocculation-sedimentation (CFS) processes [27]. Lime, sodium sulfide (Na_2S), sodium carbonate (Na_2CO_3) and flocculants were dosed in these processes. The metal ions and OH^- , S^{2-} , CO_3^{2-} can be combined to sediments, with the dosage of coagulants by which some metal ions can be removed. But different external ions (such as Na^+ , HCO_3^- , S^{2-} etc.) were introduced to the wastewater during the chemical dosing at the same time. However, the effluent water of these processes is the saturated solution of different ions, such that kind of effluent water cannot be reused to smelting processes and cannot match the requirements of local wastewater drainage codes as well. Hence, in order to reclaim the wastewater and to build a water saving smelting plant, advanced treatment methods should be conducted to solve the problem.

The dual-membrane technology combining UF and RO has been widely applied to the reclamation of municipal wastewater [28], textile dyeing wastewater [29], oilfield produced water [30], metal finishing wastewater [31], phenolic wastewater [32], and many other kinds of wastewater. However, few studies have been conducted to evaluate the feasibility of reclaiming the wastewater from Lead and Zinc smelting processes by UF-RO dual-membrane technology. And there is no report on concentration RO (CRO) process for further concentrate the drainage from RO units and enlarge the water recovery rate of the whole reclamation system. Little research has been devoted to optimize the best operation parameters for UF, RO and CRO membrane units, to evaluate the stable operation cycle time and the quality permeate water for smelting processes.

In this work, a four stage processes system was developed for wastewater reclamation in Lead and Zinc smelting processes reuse. The system was included two stages CFS process and multi-media filter (MMF) as the pretreatment processes, followed by UF-RO dual-membrane units and the CRO unit as the advanced treatment processes. The key processes for reclamation and reuse were the UF-RO-CRO approach. The waste heat from the smelting plant was used to heat the wastewater and enlarge the water recovery of RO and CRO units. The main objectives of this work including: (1)

study the typical characteristics of smelting wastewater and the efficiency of the pretreatment processes for the UF-RO-CRO processes, (2) analyze the effects of feed temperature and pressure on the recovery of RO and CRO units, to get the optimize operation parameters, (3) investigate the wastewater recovery rate, salt, conductivity and heavy metal ions rejection rate and permeate waster quality of the whole reclamation system.

2. Materials and Methods

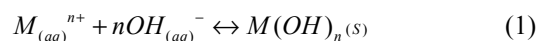
2.1. Wastewater

The source of wastewater was come from a Lead and Zinc smelting plant located in the central-south of China. The wastewater was mainly included two streams: smelting process wastewater and the dirty acid wastewater from sulfuric acid workshop, total influent wastewater flow rate was $200 \text{ m}^3/\text{h}$.

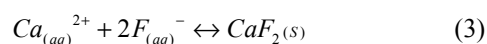
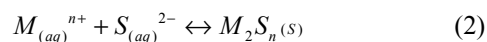
2.2. CFS Process

CFS process was the fundamental pretreatment process for the whole reclamation system. Different chemicals were dosed to the two streams of wastewater to remove the suspended solids (SS), small particles, contaminants and heavy metal ions [33-35].

In the first stream, lime solution was dosed to the wastewater, the heavy metal ions and OH^- combined to insoluble particles.



In the second stream, Na_2S -lime were dosed to the wastewater to remove the As^{3+} , F^- , Cd^{2+} , Zn^{2+} , Cu^{2+} , etc.



Then the coagulant (PAC, poly aluminum chloride) and coagulant aid (PAM, polyacrylamide) was dosed to the wastewater to form the flocculation. The contaminant of ions deposits and suspended solids were removed and sent to sludge tank. Effluents of first stage sedimentation tank flow into the wastewater regulation basin.

The effluents water quality from the wastewater regulation basin is shown in the Table 1.

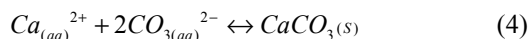
Table 1. The characteristics and wastewater concentrations of containments in the wastewater regulation basin.

Parameters	Unit	Data	Requirements for reuse*
Ca^{2+}	mg/l	600~900	<25
Zn^{2+}	mg/l	1.5~5.0	<1.0
NH_4^+-N	mg/l	4.0~10.0	<10.0
Total Fe	mg/l	0.4~0.7	<0.3
Total Mn	mg/l	/	<0.2
Cu^{2+}	mg/l	0.1~0.5	/
Pb^{2+}	mg/l	0.2~1.2	/

Parameters	Unit	Data	Requirements for reuse*
Hg ²⁺	mg/l	0.01~0.1	/
Cd ²⁺	mg/l	0.3~0.9	/
As ³⁺	mg/l	0.3~0.5	/
Ba ²⁺	mg/l	0.025~0.035	/
Sr ²⁺	mg/l	0.2~0.4	/
F ⁻	mg/l	8~15	/
Cl ⁻	mg/l	100~800	<50
SO ₄ ²⁻	mg/l	2500~5000	/
COD _{Cr}	mg/l	10~50	<60
BOD ₅	mg/l	/	<10
TDS	mg/l	4000~7000	<1000
pH	/	9~12	6.0~9.0
Turbidity	NTU	50~100	<2
SS	mg/l	40	<30
Total hardness (CaCO ₃)	mg/l	<2100	<450

* Code for design of wastewater reclamation and reuse of China, GB/T 50335-2002

Results show that wastewater was abundant with Ca²⁺, Zn²⁺, Cu²⁺, Pb²⁺, Hg²⁺, Cd²⁺, As³⁺, F⁻, Cl⁻, SO₄²⁻, etc. The wastewater from the regulation basin was pumped to the second stage sedimentation tank, and followed by MMF for removing tiny suspended solids. In order to reduce the scaling risk of the following membrane units, Na₂CO₃ aqueous, PAC and PAM was dosed to the second stage sedimentation tank to reduce the concentration of Ca²⁺ in wastewater.



The sludge from the sedimentation tanks were sent to filter separator for separation. The filter drainage was sent to the intake basin and the dry sludge was sent to the solid waste management system for further treatment.

2.3. MMF Process

The effluent from the second sedimentation tank contains high concentrations of dissolved and suspended solids, which affects the operation of UF process. MMF is a qualified choice for the pretreatment of UF. MMF guaranteed the best emitter performance with poorly treated wastewater [36-38]. Suspended materials were trapped by the filter decrease the water flow rate across the filter and eventually the sand media filter must be cleaned by backwashing [39]. Automatic backwashing can be controlled by time and/or by head loss across the filter [40]. The effluent water from MMF was used as backwashing water. To ensure the recovery effectiveness, compress air was blow to the filter media during the backwashing process, enhance to remove the contaminants on the surface of filter media.

There were four MMFs in this work, with the diameter of 3.0m. The effluent of each MMF was 55m³/h and the normal filter speed was 7.8 m/h. The filter speed was increase to 10.5m/h when one of the MMF was backwashing. The water backwashing strength was 11.5L/m²·s, the compress air blow strength was 15L/m²·s.

2.4. UF-RO Dual Membrane Process

UF can effectively remove colloids, particles, pathogenic microorganisms, and viruses from water [41]. It was studied

that the treatment of spent rinsing water from metal plating using RO meets the requirements for reuse as alkaline rinsing water. The results shown that UF, as a pretreatment for RO, reduced the fouling and increased the flux by 30~50% and that the treated effluent could be used as alkaline rinsing water [42]. A multiple membrane separation process was presented, where UF and MF were used for RO pretreatment [43]. UF membrane guaranteed a constant water quality at low cost, virtually independent of the feed water quality [44]. The Poly Vinylidene Fluoride (PVDF) was choosing as the UF membrane material and the operation mode was outside-inside.

There were two lines of UF units arranged, each unit can be operated separately or simultaneously. The UF unit devices were divided into the following equipments: feeding pumps, UF devices, UF backwash unit, UF enhanced backwash unit, cleaning in place (CIP) unit and integrity detection unit. The permeate flux of UF module is set less than 55 L/ m²·h (lmh). Hydrochloric acid was dosed into the influents of UF units to adjust the pH value of wastewater.

The application of RO technology for the treatment of wastewater containing copper and cadmium ions was investigated in [45]. The results showed that high removal efficiency of the heavy metals could be achieved by RO process (98% and 99% for copper and cadmium, respectively). It was believed that the RO technology would be an efficient process to remove the heavy metals, conductivities and reclaim the smelting wastewater.

There were two lines of RO units arranged, each unit can be operated separately or simultaneously. In order to balance the permeate flux of two stages in the RO equipment, booster pump was set between the stages and pump head was 0.3MPa. The RO units contained the following equipment: feeding pumps, 5μm cartridge filters, high pressure pumps, RO device, booster pumps, RO flushing unit and cleaning in place (CIP) unit. The permeate flux of RO membrane was less than 20 lmh. The membrane material is polyamide thin film composite (PA-TFC), and the water recovery rate was from 60%~74% due to the feed temperature and pressure difference. Anti-scaling chemicals and deoxidizer (NaHSO₃) dosed to the RO units during the operation.

2.5. CRO Process

The purpose of CRO process was to enlarge the water recovery rate of the whole wastewater reclamation system. The concentration of RO process was used as the feed water of CRO unit. It can learn from Table 1 that the TDS of wastewater was between 4000-7000mg/l, after the wastewater was treated by RO process, the concentration TDS of RO process was between 14000-26000mg/l, it was suitable for brine RO membrane for further concentration.

There was one CRO unit arranged. The equipment of the CRO unit was the same as the RO units, but the pump head of booster was 0.4MPa. The permeate flux of CRO membrane was less than 13 lmh and the water recovery rate was from 45%~60% due to the feed temperature and pressure difference.

2.6. Flow Chart

Figure 1 presents the flow chart of the Lead and Zinc smelting wastewater reclamation and reuse system.

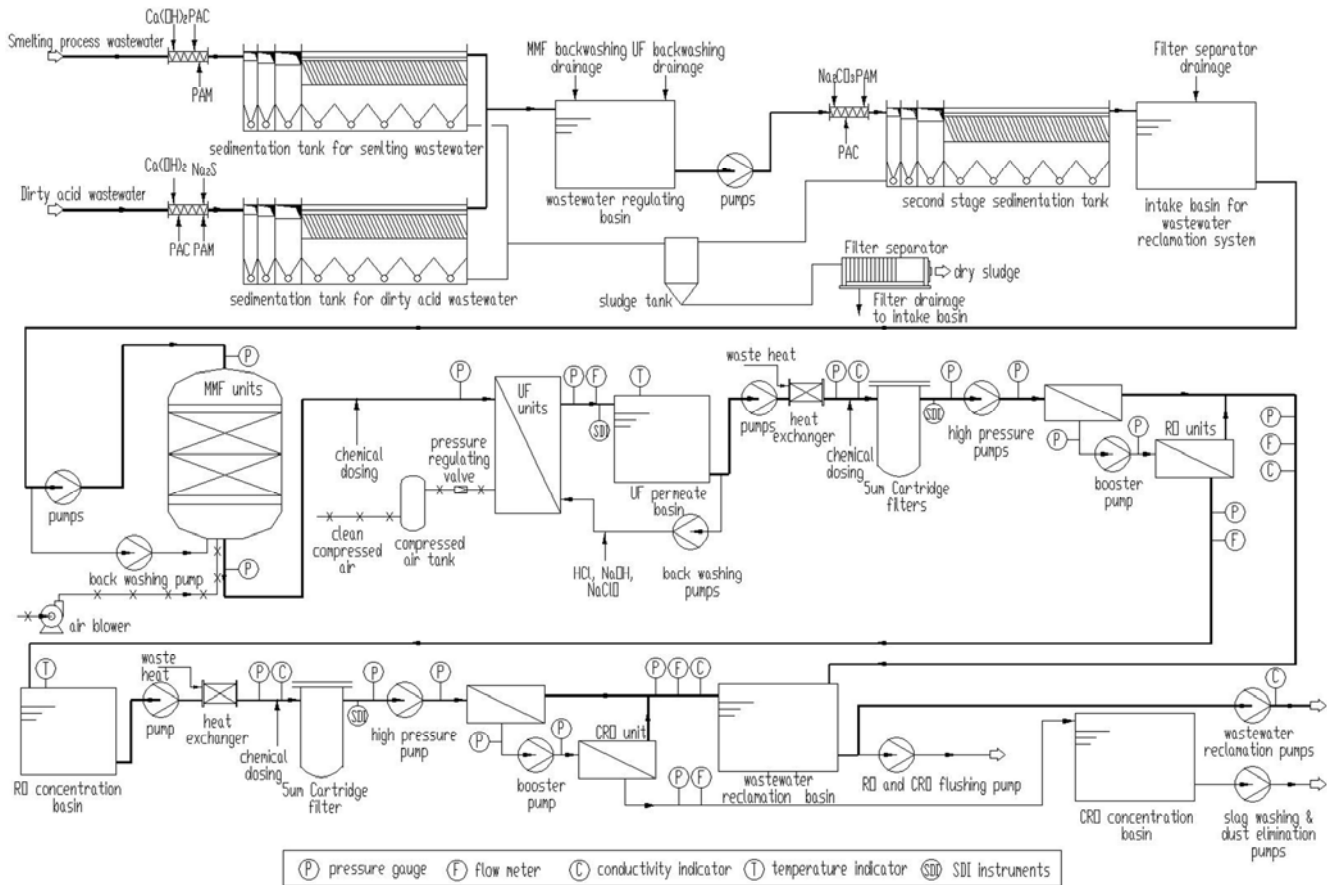


Figure 1. Flow chart of the smelting wastewater reclamation system.

The smelting process wastewater and dirty acid wastewater was pretreated by chemical dosing CFS processes separately. Then the effluents from each stream were mixed together and pumped to the second stage sedimentation tank. After the wastewater was dosed with sodium carbonate and coagulations to reduce the concentration of Ca^{2+} , SS and other metal ions in the wastewater, it was pumped to the MMF followed by UF-RO and CRO units. The whole system was operated in continuous mode. The backwashing drainage from MMF and UF membrane units was recycled to wastewater regulation basin to minimize the drainage water and enlarge the recovery rate of the whole system. The permeate water from RO and CRO units were mixed up in the wastewater reclamation basin, and reclaim to the Lead and Zinc smelting processes. The concentration of CRO unit was sent to wash the slag and for dust elimination in the plant.

2.7. Analytical Methods

The following parameters in the wastewater treatment and reclamation system were analyzed: pressure, temperature, pH, conductivity, TDS, turbidity, concentration of Ca^{2+} (CaCO_3 hardness) and 15-minute silt density index (SDI_{15}). The water pressure, temperature, pH, turbidity, concentration of Ca^{2+} and conductivity were measured by online instruments, SDI_{15} was manual measured periodically during the operation. TMP (Transmembrane Pressure Difference) was used to verify the operation stability and cycle time of the UF, RO and CRO units.

The permeate flux of UF, RO and CRO units can be presented in the equation (5).

$$\text{flux}_{\text{Permeate}} = \frac{Q_{\text{permeate}}}{A_{\text{membrane}}} \times 1000 \quad (5)$$

Where, $\text{flux}_{\text{permeate}}$ is the permeate flux of UF/RO/CRO units (lmh), Q_{permeate} is the UF/RO/CRO permeate flow rate (m^3/h), A_{membrane} is the total UF/RO/CRO membrane effective area of the unit (m^2).

DOW Chemical ROSA software Version 9.1 was used as the analyzing method for RO and CRO operation and permeate quality verification.

3. Results and Discussion

3.1. Operational Performance of Two Stages Sedimentation

Different heavy metals were removed in some extent in the first stage CFS process, but the concentration of Ca^{2+} increased because of the lime solution dosage. With the dosage of Na_2CO_3 in the intake wastewater of second stage CFS process, effluent concentration of Ca^{2+} decreased to 50mg/l in the operation. The pH value was stay around 11, high pH value guaranteed the concentration of Ca^{2+} remove efficiency. Lower concentration of Ca^{2+} guaranteed the feed water quality for the following membrane system.

The concentration of PAC aqueous was 10% and PAM was 0.1%, it was dosed to the intake wastewater from the wastewater ragulation basin after Na_2CO_3 was dosed. In order to enhance the turbidity removal efficiency, the PAM was dosed in 60 seconds after PAC. The recommend PAC and PAM dosage was 40 mg/l and 0.3 mg/l. When the turbidity of the feed wastewater was 60NTU, the effluent turbidity was 5.6 NTU, 90.6% removal efficiency can be achieved.

3.2. Operational Performance of MMF and UF Units

SDI_{15} and turbidity were chosen as the MMF and UF units operation parameters. Figure 2 presents the permeate quality of MMF and UF, and the operation conditions of UF units.

In Figure 2(a), the permeate SDI_{15} of MMF was between 4 and 5.2 in 30 days operation, turbidity was around 1 NTU. The MMF backwashing was implemented every 24 hours. Figure 2(b) shows that the permeate SDI_{15} of UF was between 1.6 and 2.7, turbidity was around 0.1 NTU. The UF backwashing was implemented every 25-35 minutes. The chemical enhance backwashing (CEB) was carried out every 24 hours, HCl, NaOH and NaClO solution were dosed to the backwashing pipeline respectively during the CEB operation. Figure 2(c) shows the operational performance of UF units in the year of 2015. The TMP of UF membrane was less than 80kPa and permeate flux was between 55 and 41 lmh during the 47 days operation.

After 47 operation days, cleaning in place (CIP) was implemented. The fouling on the UF membrane surface were different metal deposits because of the wastewater characteristics. HCl solutions was chosen as the acid to clean the UF membrane units and recover the metal deposits fouling. NaOH and NaClO solutions were chosen as the alkali and oxidant to clean the UF membrane after acid cleaning. After CIP, the permeate flux recover to 54.8 lmh, the flux recovery rate of UF unit can reach to 99%. The UF units were running in a good condition and permeate flux of UF membrane can recover to the right parameters after CIP. The best CIP cycle

time was chosen around 47 days.

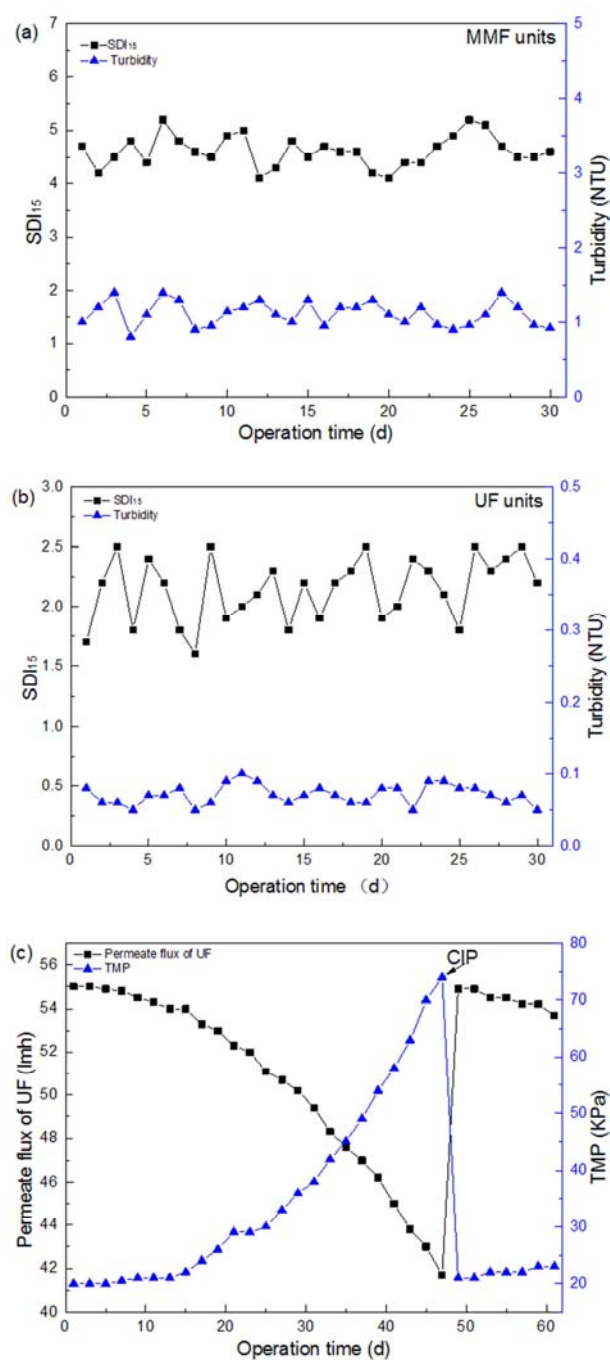


Figure 2. (a) The permeate water quality of MMF, (b) the permeate water quality of UF, (c) permeate flux and TMP of the UF units.

3.3. Operational Performance of RO and CRO Units

After the smelting wastewater was pretreated by CFS, MMF and UF processes, the effluents can meet the feed requirements of RO units, but it should be noted that the UF effluent was no suitable for reuse in the smelting process because of the high TDS and conductivity. RO and CRO units were the key processes to reduce the conductivities for the smelting wastewater reclamation process. Theoretically and practically, the permeate quality of RO and CRO

membranes is much better than the conventional smelting process feeding water and the requirements for reclamation wastewater (Table 1*).). So the key target of this wastewater reclamation system was to find the suitable way to maximize the recovery rate, to minimize the rate of drainage of the RO and CRO units, and keep the system running in a stable condition at the same time.

The feed lowest temperature for RO and CRO units were 12°C, it was the designing temperature. However, higher wastewater temperature can increase the permeate flux and recovery rate, and higher operation pressure can increase the flux as well. So we find the two possible methods to enlarge the recovery rate [46]: 1) take the advantage of the waste heat in the smelting plant to heat the wastewater in influents of RO and CRO units. The viscosity of wastewater will decrease with the temperature increased. Lower viscosity could enhance the recovery rate of RO and CRO units. 2) Increase the high pressure pumps' operation frequency and pressure. the higher pressure will provide a higher driving forces for RO membrane, and benefit to the recovery rate of the RO and CRO units as well.

3.3.1. The Influent Characteristics and Quality of RO Units

After the wastewater was pretreated, different chemicals were dosed to the wastewater, the wastewater characteristics and quality changed in many aspects. Table 2 gives a typical feed wastewater characteristics and quality for RO units.

Table 2. Typical influents characteristics and quality for RO units.

Parameters	Unit	Data	Parameters	Unit	Data
Ca ²⁺	mg/l	49	Sr ²⁺	mg/l	0.4
Mg ²⁺	mg/l	15	F ⁻	mg/l	14.5
Zn ²⁺	mg/l	0.8	Cl ⁻	mg/l	403
Na ⁺ +K ⁺	mg/l	2103	SO ₄ ²⁻	mg/l	3037.1
NH ₄ ⁺ -N	mg/l	5	COD _{Cr}	mg/l	15
Total Fe	mg/l	0.2	BOD ₅	mg/l	/
Cu ²⁺	mg/l	0.12	TDS	mg/l	6358.1
Pb ²⁺	mg/l	0.4	pH*	/	7.5
Hg ²⁺	mg/l	0.03	Turbidity	NTU	<0.3
Cd ²⁺	mg/l	0.4	SS	mg/l	<1
As ³⁺	mg/l	0.2	SDI ₁₅	/	<3
Ba ²⁺	mg/l	0.036	Total hardness (CaCO ₃)	mg/l	<130

* The pH value decreased because of the HCl is dosed to the feed of UF units to adjust the value.

In Table 2, comparing with the smelting wastewater quality (Table 1), the concentration of Ca²⁺ and other heavy metal ions decreased a lot, but the concentration of Na⁺ increased because of the Na₂CO₃ was dosed to the sedimentation tank. The concentration of Cl⁻ and SO₄²⁻ did not change much.

3.3.2. The Operation Temperature and Pressure Influence on the Recovery of RO Units

DOW chemical ROSA 9.1 software was used to analyze the feed temperature and pressure influence on the performance of RO units. To evaluate the permeate TDS, pH, flux, power consumption for each line of RO units. The feed temperature influence on the recovery rate of RO units is shown in Table 3.

Table 3. The feed temperature influence on the recovery rate of RO units in stable feed pressure.

Feed Temperature (°C)	Feed Pressure (bar)	Recovery	Permeate flux (lmh)	Permeate TDS (mg/l)
12	15.49	61.2%	15.83	57.49
13	15.41	62.5%	16.17	61.28
14	15.39	64.0%	16.55	65.35
15	15.47	65.8%	17.02	69.79
16	15.49	67.3%	17.41	74.64
17	15.46	68.5%	17.72	79.86
18	15.44	69.7%	18.03	85.52
19	15.48	71.0%	18.37	91.72
20	15.45	72.0%	18.62	98.32
21	15.45	73.0%	18.88	105.49
22	15.47	74.0%	19.14	113.29
23	15.53	75.0%	19.40	121.79

Table 3. Continued.

Concentrate TDS (mg/l)	Specific Energy (kWh/m ³)	Feed pH	Permeate pH	Concentrate pH	Warning
17100.03	0.98	7.5	5.78	7.64	None
17682.23	0.95	7.5	5.80	7.64	None
18406.12	0.93	7.5	5.82	7.63	None
19358.33	0.90	7.5	5.84	7.62	None
20228.52	0.88	7.5	5.86	7.61	None
20988.87	0.86	7.5	5.89	7.60	None
21800.86	0.85	7.5	5.91	7.59	None
22755.80	0.83	7.5	5.93	7.58	None
23545.36	0.82	7.5	5.95	7.57	None
24391.53	0.80	7.5	5.97	7.55	None
25300.73	0.79	7.5	6.00	7.54	None
26279.91	0.78	7.5	6.02	7.52	Warning*

* CAUTION: The concentrate flow rate is less than the recommended minimum flow.

Table 3 shows the relationship between the feed temperature and recovery during the feed pressure was around 15.39~15.53 bar. When the feed pressure kept stable, the feed temperature increase from 12°C to 22°C, the recovery was increase from 61.2% to 74%, increased by 21% in data. The permeate flux increased from 15.83 to 19.14 l/h. But when the feed temperature reach to 23°C, the recovery reaches to 75%, there was a warning shown by the software, the concentrate flow rate is less than the recommended minimum flow, so the 75% recovery rate was not suitable for the RO unit stable operation. The specific energy changed from 0.98 to

0.78 kWh/m³ because of the permeate flow rate increased. It was clear that increase the feed temperature by waste heat is an energy friendly way to enhance the RO unit recovery. The permeate TDS increased from 57.49 to 121.79 mg/l, even it increased by 112%, but it is still much better than the requirements of Code for design of wastewater reclamation and reuse of China (GB/T 50335-2002). The pH value of permeate and concentrate changed a little.

The feed pressure influence on the recovery rate of RO units in feed temperature 12°C is shown in Table 4.

Table 4. The feed pressure influence on the recovery rate of RO units at 12°C feed temperature.

Feed Pressure (bar)	Recovery	Permeate flux (l/h)	Permeate TDS (mg/l)	Concentrate TDS (mg/l)
15.18	60%	15.52	57.66	16590.14
15.96	63%	16.3	57.33	17926.38
16.51	65%	16.81	57.27	18943.89
17.09	67%	17.33	57.35	20038.98
18.03	70%	18.11	57.74	22089.4
18.70	72%	18.63	58.2	23658.98
19.05	73%	18.88	58.5	24530.84
19.41	74%	19.14	58.85	25969.3
19.80	75%	19.4	59.25	26482.68

Table 4. Continued.

Specific Energy (kWh/m ³)	Feed pH	Permeate pH	Concentrate pH	Warning
0.98	7.5	5.78	7.64	None
0.98	7.5	5.78	7.64	None
0.97	7.5	5.77	7.64	None
0.97	7.5	5.77	7.64	None
0.97	7.5	5.77	7.64	None
0.97	7.5	5.77	7.63	None
0.98	7.5	5.77	7.63	None
0.98	7.5	5.77	7.62	None
0.98	7.5	5.76	7.62	Warning*

* CAUTION: The concentrate flow rate is less than the recommended minimum flow.

Table 4 shows, the feed pressure increase from 15.18 to 19.41 bar, the recovery was increase from 60% to 74%, increased by 23% in data. The permeate flux increased from 15.52 to 19.14 l/h. But when the feed pressure reached to 19.8 bar, the recovery reached to 75%, the same warning was shown as Table 3. The specific energy almost stay at 0.97 kWh/m³ because of the permeate flow rate increased while the feed energy increased. The permeate TDS increased from 57.66 to 59.25 mg/l, it changed a little, the permeate quality was better than Table 3. The pH value of permeate and concentrate changed a little.

It is clear that the increasing on the feed temperature and

pressure have a great impact on the recovery. Considering the operation margin, energy consumption and stability, we choose the feed temperature as the main factor to enhance the recovery. The best operation parameters was feed temperature 20°C, feed pressure 15.45 bar, the permeated flux 18.62 l/h, recovery 72%.

3.3.3. The Operation Temperature and Pressure Influence on the Performance of CRO Unit

The concentrate of RO units in the best operation parameters was used as the feed water for CRO unit. The feed temperature influence on the recovery rate of CRO unit is shown in Table 5.

Table 5. The feed temperature influence on the recovery rate of CRO unit in stable feed pressure.

Feed Temperature (°C)	Feed Pressure (bar)	Recovery	Permeate flux (l/h)	Permeate TDS (mg/l)
20	25.01	52.8%	12.11	300.78
21	25.04	53.2%	12.20	319.20
22	25.02	53.5%	12.27	338.70
23	25.02	53.8%	12.34	359.52
24	25.01	54.0%	12.39	381.64
25	25.01	54.3%	12.46	404.64
26	25.01	54.5%	12.50	429.33

Feed Temperature (°C)	Feed Pressure (bar)	Recovery	Permeate flux (lmh)	Permeate TDS (mg/l)
27	25.00	54.7%	12.55	455.25
28	25.06	55.0%	12.62	482.11

Table 5. Continued.

Concentrate TDS (mg/l)	Specific Energy (kWh/m ³)	Feed pH	Permeate pH	Concentrate pH	Warning
49291.01	1.80	7.49	6.01	7.47	None
49675.81	1.79	7.49	6.03	7.46	None
49982.69	1.77	7.49	6.05	7.45	None
50275.85	1.76	7.49	6.07	7.45	None
50471.22	1.76	7.49	6.10	7.44	None
50763.56	1.74	7.49	6.12	7.43	None
50952.57	1.74	7.49	6.14	7.43	None
51149.90	1.73	7.49	6.16	7.42	None
51445.84	1.72	7.49	6.18	7.41	None

The data in Table 5 shows, the feed perssure stay around 25bar, the recovery increase from 52.8% to 55.0% when the feed temperature increased from 20 to 28°C, the recovery increased only by 4.2%. But the permeate TDS increased from 300.78 to 482.11 mg/l. It is clear that the temperature does not have great effectiveness on the recovery, the possible

explanation for this is that the viscosity did not changed a lot with the temperature increase in that high salt concentration. The permeate quality decreased in a large extend at the same time.

The feed pressure influence on the recovery rate of CRO unit in feed temperture 22°C is shown in Table 6.

Table 6. The feed pressure influence on the recovery rate of CRO units at 22°C feed temperature.

Feed Pressure (bar)	Recovery	Permeate flux (lmh)	Permeate TDS (mg/l)	Concentrate TDS (mg/l)
21.50	45%	10.32	371.04	42294.30
22.64	48%	11.01	357.84	44714.54
23.46	50%	11.47	350.22	46493.24
24.77	53%	12.16	340.17	49449.89
25.76	55%	12.62	334.61	51624.76
26.83	57%	13.07	329.63	54016.76
27.43	58%	13.30	327.39	55296.18
28.02	59%	13.53	325.27	56631.41

Table 6. Continued.

Specific Energy (kWh/m ³)	Feed pH	Permeate pH	Concentrate pH	Warning
1.87	7.49	6.11	7.44	None
1.82	7.49	6.09	7.45	None
1.80	7.49	6.07	7.45	None
1.78	7.49	6.05	7.45	None
1.77	7.49	6.04	7.46	None
1.77	7.49	6.03	7.46	None
1.77	7.49	6.02	7.47	None
1.77	7.49	6.02	7.47	Warning*

* CAUTION: The concentrate flow rate is less than the recommended minimum flow.

The data in Table 6 shows, the the feed temperature stay in 22°C, the recovery increased from 45% to 58% when the feed pressure increased from 21.50 to 27.43 bar. The recovery increased 28.9% when the energy consumption increased 27.58%. The permeate TDS decreased from 371.04 to 327.39 mg/l, the permeate quality was better. The specific energy decreased from 1.87 to 1.77 kWh/m³ due to the permeate flow rate increasing. But when the feed pressure reach to 28.02 bar, the recovery reach to 59%, the same warning as Table 3 and 4 is shown by the software, so the 59% recovery rate is not suitable for the CRO unit stable operation.

It is clear that the efficiency of increasing on the feed temperature on the recovery was limited, but feed pressure was effective. Considering the operation margin, effectiveness

and stability, we choose the feed pressure as the main factor to enhance the recovery. The best operation parameters was feed temperature 22°C, feed pressure 25.76 bar, the permeated flux 12.62 lmh, recovery 55%.

3.3.4. The Permeate Quality of RO and CRO Unit, the Mixed Water Quality for Reuse

Figure 3 shows permeate of RO, CRO unit and the mix up permeate quality in the chosen operation parameters in 30 days continuous operation in the year of 2015.

Figure 3(a) shows the permeate conductivity of RO was between 145 and 150 µS/cm, the salt and conductivity rejection was large than 98% in the 30 days continuous operation. The permeate conductivity of CRO is shown in

Figure 3(b), it was between 540 and 550 $\mu\text{S}/\text{cm}$, the salt and conductivity rejection was large than 97%.

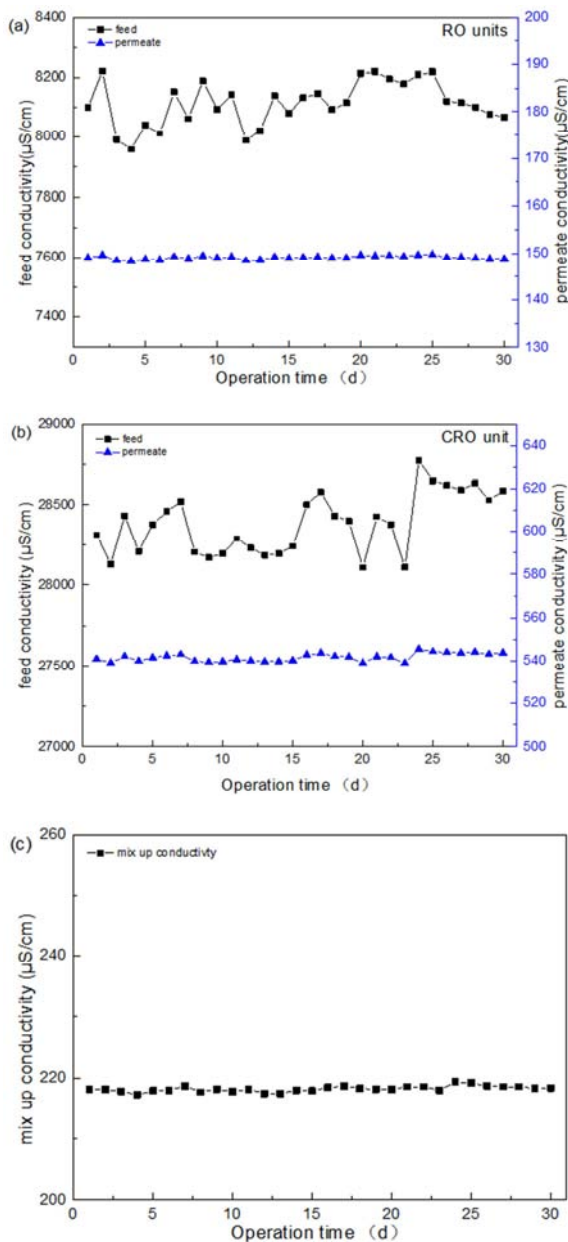


Figure 3. (a) The permeate water quality of RO units, (b) the permeate water quality of CRO unit, (c) the mixed up permeates quality.

The feed wastewater flow rate was $200 \text{ m}^3/\text{h}$, and the permeate water flow rate of RO was $144 \text{ m}^3/\text{h}$ and the permeate water flow rate of CRO was $30.8 \text{ m}^3/\text{h}$. the mixed water flow rate was $174.8 \text{ m}^3/\text{h}$, the whole recovery rate of the whole wastewater reclamation can reach to 87.4%. The mixed water conductivity of these two streams can be approximately presented in the equation (6):

$$C = \frac{C_1 \cdot Q_1 + C_2 \cdot Q_2}{Q_1 + Q_2} \quad (6)$$

Where, C is the mixed water conductivity, C_1 is the permeate conductivity of RO units, Q_1 is the flow rate of RO

permeate, C_2 is the permeate conductivity of CRO unit, Q_2 is the flow rate of CRO permeate. The mixed water conductivity is shown in Figure 3(c).

In Figure 3(c), the mix up conductivity was around 220 $\mu\text{S}/\text{cm}$, the salt, conductivity and heavy metal ions rejection percentage of the whole wastewater reclamation system was larger than 97%. The reclaimed water quality is much better than the municipal industrial water which was used as the feed water for smelting process. It can match the requirements of Code for design of wastewater reclamation and reuse of China (GB/T 50335-2002) at the same time.

3.4. The Operation Cycle of RO and CRO Unit

Figure 4(a) shows the operational performance of RO units in the year of 2015. The TMP was less than 272 kPa during the 55 days operation. The permeate flux was between 18.60 lmh and 16.80 lmh , the permeate flux decreased 9.67% when the TMP increased 12.86%.

After 55 operation days, cleaning in place (CIP) was implemented. The CIP reagent was HCl and NaOH solution, but the concentration was different to UF units. After the CIP, the permeate flux recover to 18.60 lmh , the flux recovery rate of RO unit can reach to 99%. The RO units were running in a good stable condition and the RO membrane permeate flux can recover to the right parameters after CIP. The best CIP cycle time was chosen around 55 days.

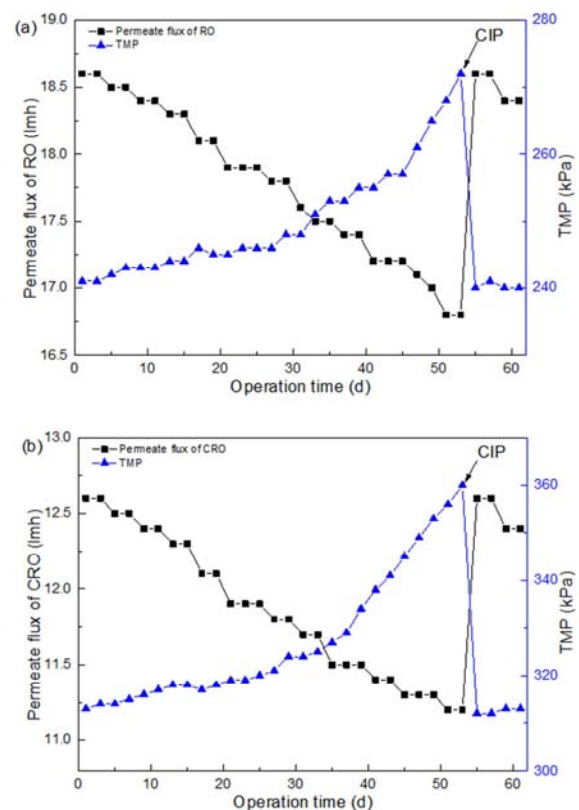


Figure 4. (a) Permeate flux and TMP of the RO units, (b) permeate flux and TMP of the CRO unit.

Figure 4(b) shows the operational performance of CRO unit. The TMP is less than 360 kPa during the 51 days operation. The

permeate flux is between 12.60 l/mh and 11.20 l/mh, the permeate flux decreased 11.11% when the TMP increased 15.02%.

After 51 operation days, cleaning in place (CIP) was implemented. After the CIP, the permeate flux recover to 12.62 l/mh, the flux recovery rate of CRO unit can reach to 99%. The CRO unit was running in a good condition and the CRO membrane permeate flux can recover to the right parameters after CIP. The best CIP cycle time was chosen around 50 days.

3.5. Scaling Analysis on RO and CRO System

The operation cycle (CIP) time of RO and CRO unit was determined by the TMP and the decrease on the permeate flux of RO and CRO membrane. In order to choose the suitable CIP chemicals, it is important to determine the contaminants on the surface of RO and CRO membrane surface. There were two SDI instruments set on the cartridge filter of RO and CRO units. Energy dispersive spectrometer (EDS) was conducted to characterize the scaling on the SDI membrane surfaces. The contaminants on the surface of SDI membranes were scraped and dried, and these kinds of contaminants can represented the scaling condition of RO and CRO membrane surface in some extent.

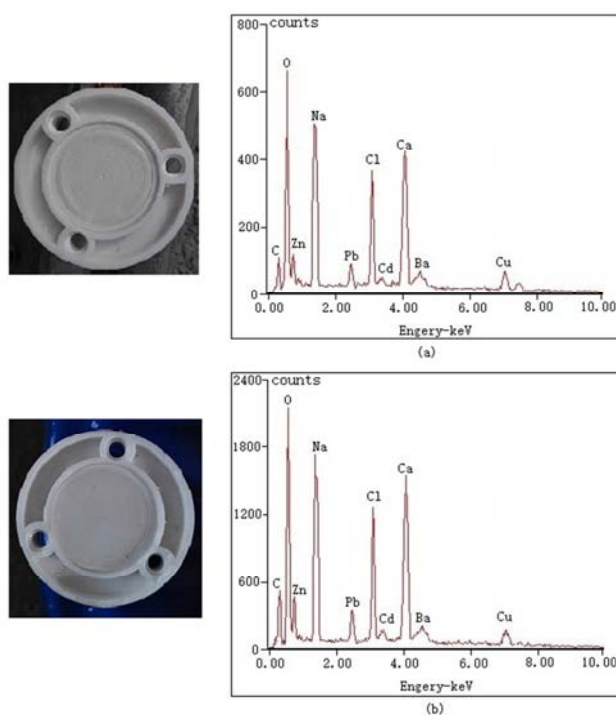


Figure 5. Contaminants precipitations by EDS on the fouled SDI membrane. (a) RO cartridge filter and (b) CRO cartridge filter.

According to EDS analysis in Figure 5(a), (b), there were similar contaminants chemical compositions and peak intensities on both cartridges filter SDI membrane of RO and CRO units. The main contaminants including Ca^{2+} , Na^{+} , Zn^{2+} , Pb^{2+} , Cu^{2+} , Cd^{2+} , etc. It can be determined that the feed water for RO and CRO unit was mainly fouled by the inorganic deposits, such as CaCO_3 , CaSO_4 , BaSO_4 , SrSO_4 , Pb(OH)_2 , Zn(OH)_2 , etc. The Ca^{2+} was come from lime solution dosing in the CFS process. The Zn^{2+} , Pb^{2+} , Cu^{2+} , Cd^{2+} was the inherent

contaminants of smelting wastewater. This kind of contaminants can be chemical cleaned by HCl and NaOH/EDTA solution [47].

4. Conclusion

In this work, a wastewater treatment processes consisting of the CFS, MMF and UF-RO-CRO membrane system was applied to reclaim smelting wastewater. Conclusions are drawn as follows:

- (1) The contaminates of wastewater from the Lead and Zinc smelting plant contains high TDS, conductivity, heavy metals, F^{-} , As^{3+} , and SO_4^{2-} , etc.
- (2) The UF-RO dual membrane technology to treat the Lead and Zinc smelting wastewater with good system stability and high contaminant removal efficiency. Increasing on feed pressure and temperature of RO units play a positive role to enlarge the recovery. The wastewater recovery of RO units was 72% with permeate conductivity around $150\mu\text{S/cm}$ in the recommend operation temperature and pressure. The best UF and RO CIP cycle time was around 47 and 55 days respectively.
- (3) The CRO unit was proved to be a feasible way to concentrate the RO concentration water with good system stability. The feed temperature increasing has little efficiency on the recovery. The best wastewater recovery of CRO unit was 55% with permeate conductivity around $540\mu\text{S/cm}$ in the recommend operation temperature and pressure. The best CRO CIP cycle time was around 50 days.
- (4) The wastewater recovery rate of the whole reclamation system was larger than 87.4%. The salt, heavy metal ions and conductivity rejection are more than 97%. The reclamation water conductivity was around $220\mu\text{S/cm}$, it is much better than the normal smelting process water and the requirements of Code for design of wastewater reclamation and reuse of China (GB/T 50335-2002).
- (5) The advanced treatment of Lead and Zinc smelting wastewater by the UF-RO-CRO membrane technology is feasible. It takes the waste heat of the smelting plant to heat the wastewater and enlarge the recovery rate and guarantee the permeate quality at the same time. It presents a novel way to explore the optimize operation parameters for RO and CRO membrane system. This work provides a deep understanding of treating the Lead and Zinc smelting wastewater by the technology for Lead and Zinc smelting industrial application.

5. Highlights

1. Coagulation-flocculation-sedimentation (CFS) and multi-media filter (MMF) as the pretreatment processes to guarantee the influent quality of UF and RO membrane processes.
2. Wastewater was heated by the waste heat from the smelting plant to enlarge the recovery of RO and CRO units.
3. Increasing in the feed pressure on RO and CRO units

play a positive role to enlarge the recovery.

4. Good operation stability of the reclamation system, permeate flux recovery after CIP and qualified treated water were obtained.

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