Analysis of UF Membranes at the Industrial Wastewater Purification Plant at China Steel

YU-CHUN SU*, JINN-CHERN WU* and CHIUNG-HSUN LIN**

*New Materials Research & Development Departmen
**Utilities Departmen
China Steel Corporation

In 2009, an Industrial Wastewater Purification Plant (IWWPP) was built at China Steel (CSC) which is the first steelmaking wastewater treatment plant to use a dual membrane Ultrafiltration/Reverse Osmosis (UF/RO) process for wastewater reclamation in the world. However, UF membranes suffered from severe fouling after 3 years of operation resulting in frequent membrane cleaning. Therefore, the objective of this study was to analyze the UF for the major foulants for identification. The fouled UF membranes were cut and analyzed by Scanning Electron Microscope/Energy Dispersive Spectrometer (SEM/EDS) and resistance-in-series model. The results showed that the fouling cake layer on the UF surface was mainly metallic oxide. The resistance caused by irrecoverable fouling dominated in the UF accounting for 46.44% of the total resistance. The cause of irrecoverable fouling could be attributed to oxidation of iron and manganese into oxide particles. To reduce irrecoverable fouling caused by Fe and Mn, pretreatment such as oxidation is needed for the UF.

Keywords: Membrane fouling, Ultrafiltration (UF), Wastewater reclamation

1. INTRODUCTION

Taiwan is located in a subtropical area with extremely high rainfall. Although Taiwan's average annual rainfall is about 2,500 mm, 2.5 times the global average, the average annual precipitation per capita is just one-sixth of the global average[1]. This can be attributed to Taiwan's steep terrain, limited water storage facilities, uneven rainfall distribution, pronounced wet and dry seasons, and large fluctuations in river flow volumes. China Steel (CSC) is located in Kaohsiung city of southern Taiwan and an integrated steel mill which consumes a large amount of water for cooling, rust cleaning, lubrication, dust washing etc. The source of water for CSC is from Fengshan Reservoir and the daily industrial water consumption was about 126,000 tons in 2014, which takes up 42% of the industrial water consumption of Fengshan reservoir. In order to secure a reliable water supply and achieve a sustainable water resource development, CSC is dedicated to reinforcing pipeline management and to recycle and reuse water. In 2014, the process water recycling rate had risen to 98.3% reducing water consumption to 5.02 ton/ton crude steel, which is far below the global average, 28.6 ton/ton crude steel[2].

In 2003, CSC started to evaluate membrane puri-fication, Reverse Osmosis (RO) and other advanced techniques and processes for wastewater recycling. An Electrodialysis Reversal (EDR) water desalination membrane process facility was first built to recycle direct cooling water in hot rolling mills in 2008 and its design capacity was 560 m^3/day. In 2009, an Industrial Waste Water Purification Plant (IWWPP) was set which is the first steelmaking wastewater treatment plant using dual membrane Ultrafiltration (UF)/RO process for wastewater reclamation in the world. The design of the IWWPP was to reuse the treated wastewater for high-pressure boilers in the power plant of CSC. To meet the high quality requirement of the demineralized water for high-pressure boilers, UF, RO as well as an ion exchange system were implemented to remove suspended solids, ions and other impurities from the wastewater.

However, UF membrane suffered from severe fouling after 3 years of operation resulting in frequent membrane cleaning. Imposed flow rate also decreased from 350 m^3/hr to 270 m^3/hr to reduce the membrane fouling rate. Due to the complexity of the iron and steel making wastewater, little is known about the major cause of UF membrane fouling. As a result, adequate pre-treatment methods to remove foulants from the influent wastewater were not able to be adopted. Fou-

lants which were continuously received by the UF membrane would deteriorate the membrane performance. Moreover, lack of knowledge of membrane foulants would make chemical cleaning less effective. The choice of chemical cleaning agents and the timing of membrane cleaning were usually guess work as a rule of thumb. In this IWWPP, conventional alkaline and acid chemical cleaning were performed to restore membrane performance. Although this chemical cleaning was recommended by the membrane supplier, it had not been proven whether it was suitable for the iron and steel making wastewater. Therefore, the membrane foulants identification was urgent for UF fouling mitigation.

Lee et al. used Microfiltration (MF) and RO to treat secondary treated steel wastewater for reuse[3]. However, fouling in MF unit was not mentioned in that study. This might be due to the short period of time of their test (180 min) in their pilot scale experiment. Choi et al. used an UF/RO process for reclamation of wastewater from the iron and steel industry[4]. They concluded that algal and bacterial bio-fouling were dominant in the UF modules. Nevertheless, their experiments were also tested in a pilot scale and over a relative short period (max. 16 days). Therefore, in order to increase the application of membrane filtration in iron and steel making wastewater, there was a strong need for investigating membrane fouling in long-term field experiments. Based on the results, further recommendations for pre-treatment and chemical cleaning methods can be made with confidence[5]. The aim of this study is to analyze the fouled UF for identification of major foulants. To the best of our knowledge, this is the first study to analyze fouled UF membrane treating iron and steel making wastewater in a full-scale plant.

In this study, the fouled UF membrane was directly cut from the UF modules in the IWWPP after operating for 5 years and was sent to the laboratory for membrane foulants analysis by Scanning Electron Microscope (SEM) / Energy Dispersive Spectrometer (EDS). Loss on Ignition (LOI) was measured to determine the ratio of organic and inorganic foulants. The fouled UF membrane after cleaning was also analyzed by SEM/EDS to distinguish reversible, irreversible and irrecoverable foulants. A single hollow fiber module was used to measure different types of fouling resistance.

2. EXPERIMENTAL METHOD

2.1 Wastewater treatment process of the industrial wastewater purification plant

The IWWPP process flowchart is illustrated in Fig.1. Blast Furnace (BF) /Basic Oxygen Furnace (BOF) gas wet scrubbing wastewater and cooling water treated with coagulation, flocculation and sedimentation are the main influent of wastewater of the IWWPP. First, the influent was treated with the fiber filter process to remove suspended solids. Second, the influent was treated with UF membranes to reduce Silt Density Index (SDI) to less than 2. The UF unit includes three trains with a total of 12 cassettes of GE ZeeWeed® 500D submerged hollow fiber membrane modules. The ZeeWeed® 500D membrane is made of Polyvinylidene Fluoride (PVDF) with surface hydrophilic modification. The nominal pore size of the ZeeWeed® 500D membrane is 0.04 μm, which is in the range of the UF. The UF membrane was operated at the constant flux of 30 L/m^{2}hr with an on-off mode (15 min-on and 1 min-off). The UF permeate was then treated with RO to remove most dissolved matters. An ion exchange resin system was the last process to remove ionized species from the water by exchanging them for H^+ and OH^- ions. The design capacity of the IWWPP is 26,000 m^3/day producing 4,500 m^3/day of RO permeate and 9,000 m^3/day of demineralized water.

UF maintenance cleaning was implemented once a week using 100 or 250 mg/L NaOCl and 2,000 mg/L citric acid. Recovery cleaning was performed using 250 or 1,500 mg/L NaOCl and 2,000 mg/L citric acid to restore UF membrane performance once the Trans-Membrane Pressure (TMP) exceeded -40 kPa.
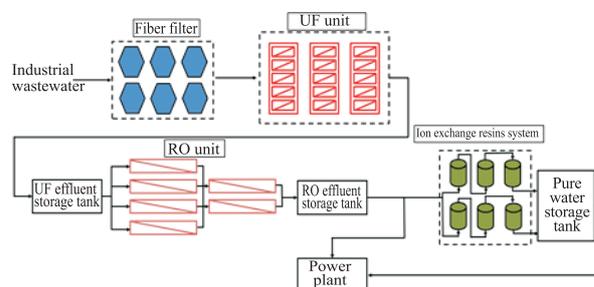

Fig.1.   Flow diagram of the industrial wastewater purification plant at CSC.

2.2 Foulants identification

A SEM equipped with EDS (1540 XB Crossbeam, Zeiss, Germany) was used to observe the membrane foulants and determine the elemental composition of the membrane foulants. All the UF membrane samples were coated with a thin gold film to increase their conductivity before SEM/EDS examination.

To understand the extent and spatial distribution of foulants in the UF membranes pores was critical because it was much more difficult to be cleaned than the foulants deposited on the membrane surface. In order to observe the foulants in the membrane pores, a cross-section of the UF membrane was examined by

SEM/EDS. However, mechanical cuts would create compression and tearing which may severely distort the fine structure of the membrane. To avoid destruction, the wet UF membrane sample was directly frozen in liquid nitrogen making it brittle. The frozen UF membrane sample was then quickly fractured by sharp scissors[6].

LOI analysis was performed to determine the organic content of the foulants. First, membrane foulants were washed out from the UF membrane by ultrasonic cleaning. Second, LOI was determined by comparing the weight of the sample before and after the foulants had been ignited at 550℃. Then, the LOI was calculated by the following equation (1).

$$LOI = \frac{weight(dry) - weight(550°C)}{weight(dry)} \quad .... (1)$$

2.3 Fouling resistance analysis

In order to evaluate membrane fouling, a resistance-in-series model was used based on Darcy's law (2)：

$$J = \frac{TMP}{\mu(R_m + R_{re} + R_{irr} + R_{irc})} \quad .... (2)$$

Where, J is flux through the membrane (m^3/m^2 sec), TMP is the trans-membrane pressure (Pa), μ is the dynamic viscosity of the permeate (Pa・S), R_m is the membrane resistance (m^{-1}), R_{re} is the reversible fouling resistance (m^{-1}), R_{irr} is the irreversible fouling resistance (m^{-1}) and R_{irc} is the irrecoverable fouling resistance (m^{-1}). In this study, fouling is classified into reversible, irreversible, and irrecoverable fouling. Reversible fouling is the fouling which can be removed by physical cleaning；Irreversible fouling is the fouling which can only be removed by chemical cleaning；Irrecoverable fouling is the fouling which cannot be removed by physical or chemical cleaning[7].

First, pure water was filtered through the virgin UF membrane to determine R_m. Second, pure water was filtered through the fouled UF membrane to determine $R_{re}+R_{irr}+R_{irc}$. Physical cleaning (such as backwashing, pressure relaxation and air scouring) was then performed to measure the R_{re}. Afterward chemical cleaning was implemented to determine the R_{irr}. Once R_{re} and R_{irr} were obtained, R_{irc} can be calculated by subtracting them in $R_{re}+R_{irr}+R_{irc}$.

3. RESULTS AND DISCUSSION

3.1 Identification of membrane foulants

The UF membrane fibers after operating for 5 years were directly cut from the IWWPP. The UF membrane fibers were dried at 50℃ overnight and then coated with gold before SEM/EDS analysis. Figure 2(a)

shows the SEM image of the fouled UF membrane surface. A dense fouling cake layer resulting in TMP increase can be clearly observed. The elemental composition of the cake layer formed on the membrane surface was analyzed by EDS as shown in Table 1. C and F dominated in the composition were mainly derived from PVDF material. Except C and F, the order of abundance of elements in the fouling cake layer is as follows: O > Fe > Ca > Cl > Al > Mn > Mg > Zn. The results suggest that the fouling cake layer might be metallic oxide such as iron oxide. Figure 2(b) is the SEM image of the cross-section of the fouled UF membrane. The structure of the UF membrane can be obviously divided into supporting layer and active layer. The active layer possessing separation function is where membrane fouling occurred. The elemental composition of the cross-section of the fouled UF active layer is revealed in Table 1. Compared with the elemental composition of fouled UF surface, S and Si were not detected on the membrane surface. This result indicates that foulants containing S and Si might penetrate through the cake layer and be retained in the pores.

In order to determine the relative abundance of organic and inorganic constituents, membrane foulants were washed out and subjected to a LOI test. The LOI results shown in Fig. 3 depict that more than half of the foulants were inorganic matter (55.12%). As a result, inorganic foulants such as the aforementioned metallic oxide mainly contributed to UF fouling in the IWWPP.

Table 1 Elemental analysis of the fouled UF membrane determined by EDS

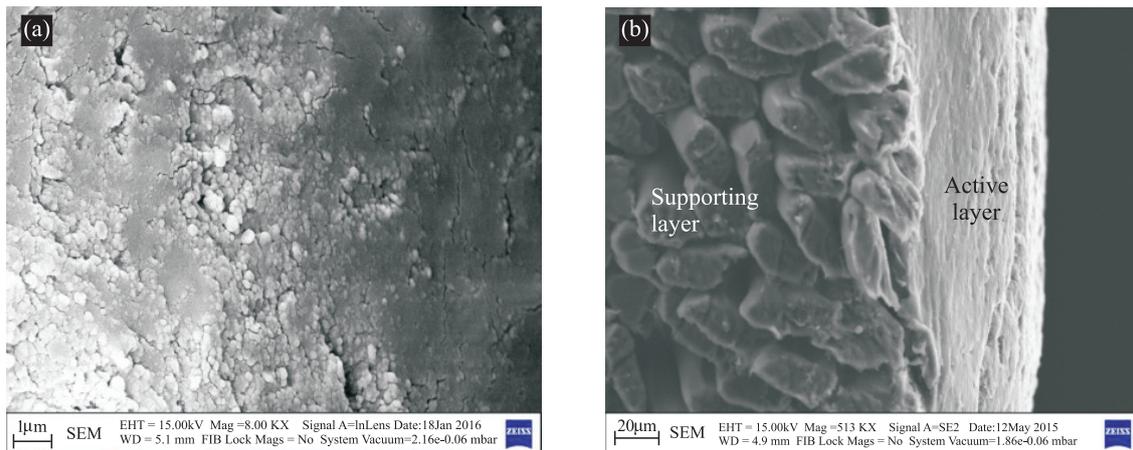| Element	Atomic % (surface)	Atomic % (cross-section)
C	38.62	-
O	26.24	35.99
F	19.95	2.96
Mg	0.27	1.83
Al	1.46	3.84
Si	-	2.83
S	-	1.96
Cl	1.42	3.64
Ca	2.34	11.27
Mn	0.80	1.81
Fe	8.73	31.54
Zn	0.17	0.45

Fig.2. SEM images of the fouled UF membrane: (a) surface (magnification, 8,000×); (b) cross-section (magnification, 512×).
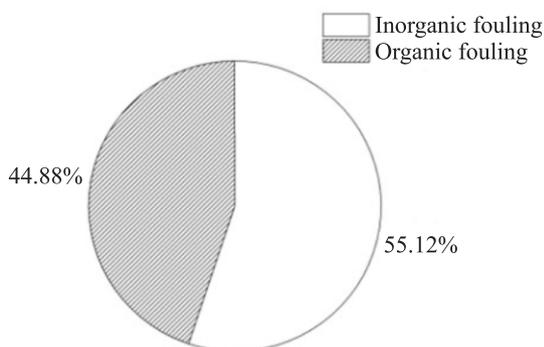

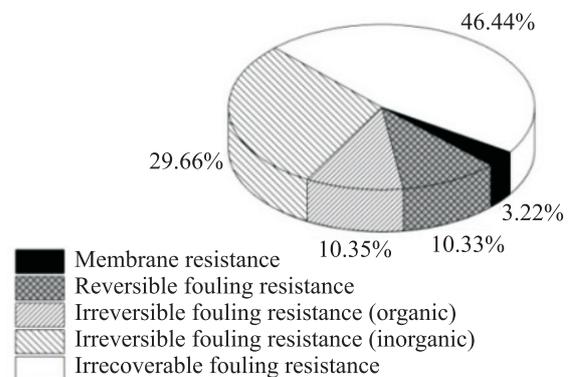**Fig.3.** LOI measurement of membrane foulants.

Fig.4. Fouled UF membrane resistance analysis.

3.2 Characterization of membrane fouling

In this study, membrane fouling was categorized into reversible, irreversible and irrecoverable fouling as mentioned in 2.3. Recoverable fouling which can be easily removed by physical cleaning is not a big problem for membrane filtration. On the other hand, irreversible and irrecoverable are the major obstacle hindering membrane application. Frequent chemical cleaning resulting in operating cost increase and permeate and membrane lifespan reduction is required to eliminate irreversible fouling. Irrecoverable fouling which cannot be removed by any cleaning methods would reduce membrane effective pores for filtration and then shorten membrane lifespan.

Figure 4 shows the classification of the fouled UF fouling resistance. It is not surprising that resistance caused by irrecoverable fouling was dominant in membrane fouling after operating for 5 years. The resistance caused by irrecoverable fouling accounted for 46.44% of the total resistance, which means that almost half of the membrane performance has been lost. The resistance

caused by irreversible fouling accounted for 40.01% of the total resistance, which is the second largest part of the total resistance. In the irreversible resistance, resistance caused by inorganic foulants accounted for 29.66% of the total resistance; resistance caused by organic foulants accounted for only 10.35% of the total resistance. This result is in agreement with Table 1 and Fig.3, which show that inorganic matters such as metallic oxide might be the major UF foulants. Therefore, inorganic fouling of the UF membrane will be discussed in depth in the next section. The resistance caused by reversible fouling also accounted for 10.33% of the total resistance but it can be easily removed by physical cleaning (backwashing here). It may not cause serious adverse effect on membrane filtration. The resistance caused by membrane itself accounted for only 3.22% of the total resistance.

3.3 Analysis of irrecoverable fouling

As mentioned previously, irrecoverable fouling is defined as the fouling which cannot be removed even

by chemical cleaning and will deteriorate the membrane performance. In this study, 1,500 mg/L NaOCl and 2,000 mg/L citric acid were used in series to clean the fouled UF. The remaining foulants on/in UF membrane caused the irreversible fouling. Figure 5(a) shows the SEM image of the fouled UF membrane surface after chemical cleaning. Compared with Fig.2(a), the fouling cake layer was found to be removed by chemical cleaning. Some membrane pores can be observed after chemical cleaning, which represents that NaOCl and citric acid were effective in removing the fouling cake layer. Figure 5(b) shows the SEM image of the cross-section of the fouled UF membrane after chemical cleaning. The membrane pore structure cannot be observed due to the limited SEM resolution. The elemental analysis of the chemical cleaned UF membrane is as shown in Table 2. Compared with Table 1, most metallic elements were removed. Except C and F, only O, Ca and Fe remained on the membrane surface. The results reveal that calcium oxide or calcium fluoride and iron oxide deposited on the membrane surface cannot be totally cleaned out. On the other hand, it is surprising that Fe was dominant in the cross-section of the UF accounting for 49.3% of the total elements. It means that iron oxide fouled in the membrane pores cannot be effectively removed by chemical cleaning. Ca, however, was not found in the cross-section of the UF membrane. The result suggests that calcium oxide or calcium fluoride in the membrane pores could be chemically removed but still remained on the membrane surface. It is interesting that Mn accounted for about 1% of the total elements in the membrane pores but it was not found on the membrane surface. Because foulants in the membrane pores were thought to be irrecoverable[8], Fe and Mn were responsible for the irrecoverable fouling in the fouled UF.

Table 2 Elemental analysis of the UF membrane determined by EDS after chemical cleaning

Element	Atomic % (surface)	Atomic % (cross-section)
C	47.68	36.09
O	15.52	8.08
F	32.24	5.54
Ca	2.69	-
Fe	1.87	49.30
Mn	-	0.99

To investigate the effect of Fe and Mn on membrane fouling, the elemental mapping of the cross-section of the fouled UF after chemical cleaning was carried out by EDS and the results are as shown in Fig.6. In Fig.6 (d) and (e), it can be noted that Fe and Mn were evenly distributed in the supporting and active layer. Iron ions presented in the influent could be easily oxidized into ferric oxide particles under aeration and neutral pH[9]. The UF was operated under vigorous aeration to prevent the membrane from fouling and under a neutral pH. As a result, while penetration of iron ions into the UF membrane, iron oxide particles might be formed in the membrane pores resulting in irrecoverable fouling. Compared with iron ions, manganese ions are more difficult to be oxidized. In the IWWPP, chlorination was implemented prior to the fiber filer unit to reduce bio-fouling. Chlorination would promote oxidation of manganese ions, and then gradually formed oxide particles in the membrane pores[10].
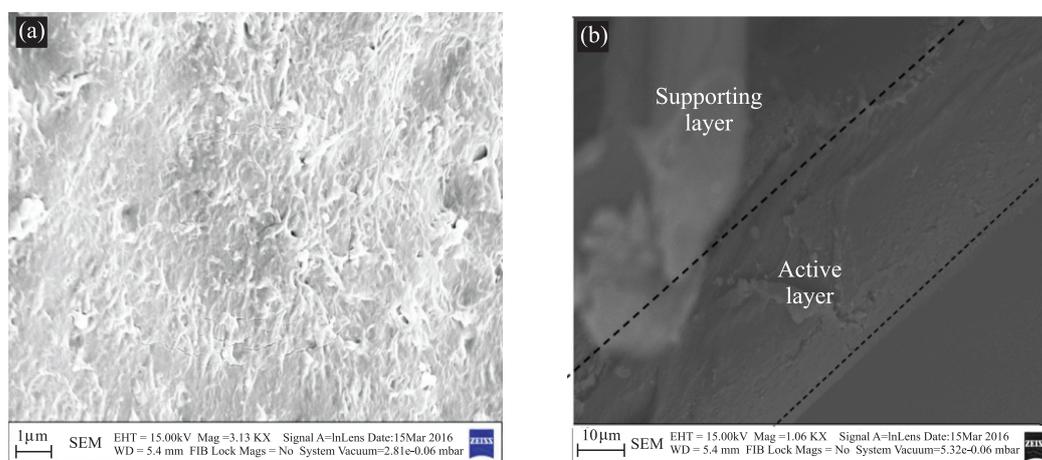

Fig.5. SEM images of the fouled UF membrane after chemical cleaning: (a) surface (magnification, 3,130×); (b) cross-section (magnification, 1,060×).

Electron Image 3

(a)   25 μm

C Kα1_2

(b)   25 μm

F Kα1_2

(c)   25 μm
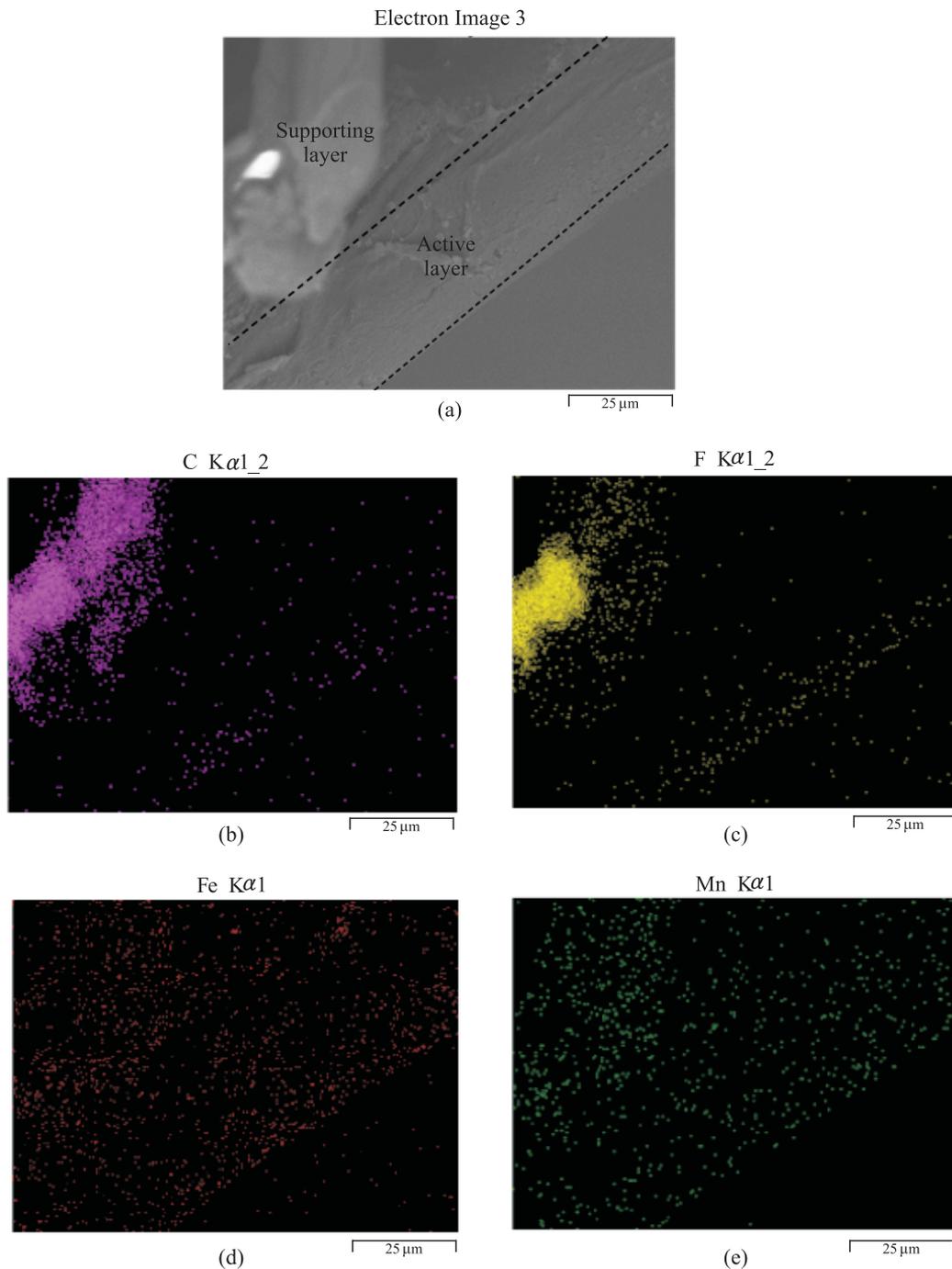
Fe Kα1

(d)   25 μm

Mn Kα1

(e)   25 μm

Fig.6. (a) SEM cross-section image and (b-e) the EDS mapping images of the fouled UF membrane after chemical cleaning.

In brief, the cause of irrecoverable fouling of the UF membranes can be attributed to oxidation of iron and manganese ions into oxide particles. Therefore, in order to reduce irrecoverable fouling caused by iron and manganese, pretreatment such as oxidation is needed for the UF in the IWWPP.

4. CONCLUSION

The UF membranes after operating for 5 years in the IWWPP were analyzed for identification of major foulants. According to EDS analysis, the fouling cake layer on the UF surface contained O, Fe, Ca, Cl, Al, Mn, Mg, Zn. Furthermore, the LOI results revealed that

inorganic fouling accounted for 55.12%. The results suggested that inorganic matters such as metallic oxide led to UF fouling. The resistance caused by irrecoverable fouling was dominant in the UF accounting for 46.44% of the total resistance. The resistance caused by irreversible fouling accounted for 40.01% of the total resistance, which is the second largest part of the total resistance. In the irreversible resistance, resistance caused by inorganic foulants accounted for 29.66% of the total resistance; resistance caused by organic foulants accounted for only 10.35% of the total resistance. After chemical cleaning, Fe and Mn were detected in the UF membrane pores. The results implied that the cause of irrecoverable fouling can be attributed to oxidation of iron and manganese ions into oxide particles. In order to reduce irrecoverable fouling caused by Fe and Mn, pretreatment such as oxidation should be taken into consideration in the IWWPP.

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