Development of Oily Wastewater Treatment Technologies Using Ceramic Flat-Sheet Membranes

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Abstract

Development of new energy resources is presently being promoted in many places around the world. For the mining of unconventional oil and natural gases represented by shale gas, it requires very special technologies to increase artificial permeability and fluidity by forcing hydraulic pressure or steam heat from the ground surface. As such, production of unconventional natural resources calls for a huge volume of water. From the viewpoint of securing sufficient water and preventing water contamination, it is a major initiative to recycle the recovered wastewater.

Meiden developed a Ceramic Flat-sheet Membrane (CFM) that has specific features and is quite different from the conventional membranes. Our membrane can be used in other industrial fields where it has been difficult to apply for other conventional membranes. Recently, we applied the newly developed ceramic membrane for the treatment of oily wastewater and confirmed its effectiveness.

1 Preface

Development of new energy resources is currently being positively promoted in many places throughout the world. Unconventional natural gases and oils represented by shale gas require very special techniques for extraction[(1)(2)]. When a well is dug from the ground level to reach a target earth layer, conventional resources will naturally be released and can be extracted. Unconventional resources cannot be extracted, however, unless artificial permeability and fluidity are imposed by applying hydraulic pressure or steam heat from the ground surface.

As suggested above, production of unconventional natural resources calls for a huge volume of water. From the viewpoint of securing sufficient water and avoiding water contamination, it is a major initiative to reuse the extracted wastewater.

The generated wastewater contains a small amount of oil, clay, and chemicals. In this connection, a membrane separation process can be an effective treatment technology.

Meiden-developed Ceramic Flat-sheet Membrane (CFM) offers the following features:

(1) Construction is simple and resistant to contamination.

(2) Even when contaminated, cleaning is easy to achieve.

(3) Chemical resistance, thermal resistance, and physical strength are high.

This paper introduces oily wastewater treatment technologies using CFMs.

2 Construction and Features of the CFM

Fig. 1 shows the construction of the CFM. The outer surface of the ceramic part comes in a two-layer structure consisting of a highly permeable supporting

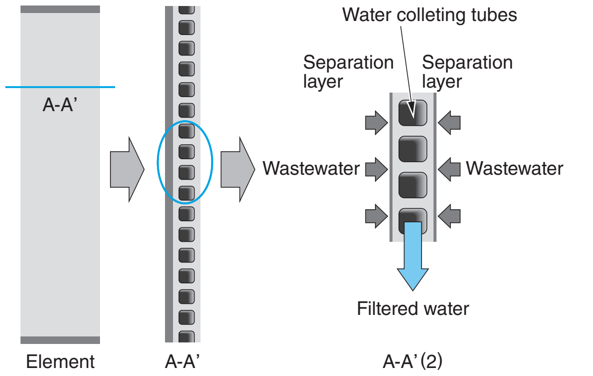

Fig. 1 Construction of CFM

Construction of the CFM is shown.

medium and a separation layer with micro filtration pore size. All of the external surface area can be used as a filtration surface. The inner surface of the ceramic part is provided with tubular air holes functioning as the water colleting tubes. The header has a bundle of water collecting tubes and the water intake port is positioned on the secondary side of the filtration. When wastewater is led into the inside, filtered water after passing through the process of solid-liquid separation is gathered into the water collecting tubes. The major features and service conditions of the CFM are itemized below.

(1) Nominal pore size: 0.1μm (MF membrane)
(2) Initial pure water permeability flux: 40m^3/(m^2·d) (25℃, 100kPa)
(3) Particle capturing ability: 95% (0.1μm standard particles, 100kPa)
(4) Pressure: −100～100kPa
(5) Temperature: −20～80℃
(6) pH: 2～12

The other features of the CFM are described below.

(1) High flux (permeability flux) and stable filtration can be attained.
(2) Thermal resistance and chemical resistance are superb, and mechanical strength is outstanding.
(3) Membrane filtration performance can be favorably recovered by chemical cleaning and backwash.
(4) Physical cleaning is possible with high-pressure cleaning water and brushes.
(5) Long-time storage is possible without taking any special measures.
(6) Used membranes can be recycled as raw materials for pottery.

As described above, the CFM is physically and chemically durable, and suitable for filtration at a high flow rate, backwash, and chemical cleaning. It can, therefore, assure high-efficiency membrane treatment even in the case of an oily drainage treatment.

3 Application to Oily Drainage Treatment

Generally speaking, oily drainage contains oil components, suspension substances, dissolved organic matter, and others. The oil component is present in the form of fine oil grains adsorbed to suspension substances.

Prior to the application of a treatment to an oily drainage, testing water for simulant drainage has been investigated from the viewpoint of filtration stability and reduction of fouling (effect of reducing the permeability flux). **Table 1** shows the filtration conditions of a CFM (resin-made membrane formed into a flat-sheet) and polymeric membrane, **Fig. 2** shows the fouling characteristics of simulated oil drainage during membrane filtration, and **Table 2** shows the result of water quality analysis for simulated oil contained drainage. Judging from this figure, the ceramic membrane assures stable filtration even at a high flux. Even when oily drainage is treated, we could

Table 1 Filtration Conditions of CFM and Polymeric Membrane

The filtration conditions of the CFM and the polymeric membrane are shown.

Membrane type	Polymeric membrane	Ceramic membrane
Pore size (μm)	0.4	0.1
Permeability flux (m^3/(m^2·d))	0.5	0.5～1.0
Operating conditions	Filtration: 9 min Relax: 1 min	Filtration: 9 min Backwash: 1 min

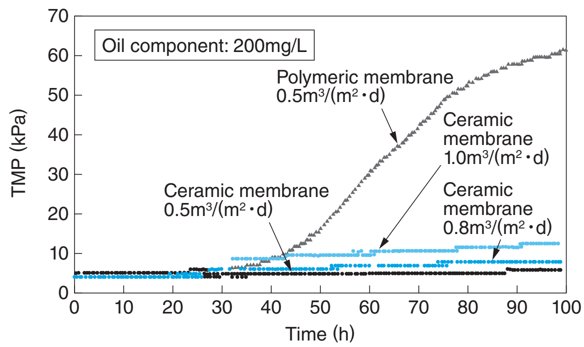

Fig. 2 Fouling Characteristics of Simulated Oil Drainage during Membrane Filtration

The results show stable characteristics even in case where the permeability flux of the ceramic membrane is changed. When the CFM is compared with the polymeric membrane under the same conditions, it shows the ceramic membrane's greater stable performance.

Table 2 Results of Water Quality Analysis for Simulated Oily Drainage

This shows the results of water quality analysis before and after filtration by the CFM. It also shows that oil components and suspended solids were removed to the lower quantitative limits.

Item	Raw water	Filtered water
BOD	6	4
COD	12	7
SS	104	<1
Oil	140	<1

Notes: BOD: Biochemical Oxygen Demand
COD: Chemical Oxygen Demand
SS: Suspended Solids

confirm that no sudden fouling occurred and operation can be continued with a Trans Membrane Pressure (TMP) kept at a low level. As a result of chemical cleaning after the completion of testing, we could confirm that initial characteristics can be recovered.

4 Development of Technology for Actual Wastewater Application

4.1 Oil Refinery Wastewater Treatment by Membrane Bioreactor (MBR)

We are continuing the MBR verification test using the CFM in Japan. Since 2011, stable operation has been observed[3]. As an application of this technology, we investigated the treatment of oil refinery wastewater by using the MBR. Table 3 shows the operating conditions of an aerobic tank and Table 4 shows the filtration conditions of the hollow fiber PVDF membrane (semipermeable membrane made of a tubular PVDF) and the CFM. In addition, Fig. 3 shows the fouling characteristics of oil refinery wastewater during membrane filtration and Table 5 shows the result of water quality analysis for oil refinery wastewater. During two weeks after the start of testing, there was no occurrence of a jumping phenomenon (sudden rise of TMP) due to membrane contamination. Transition of TMP on the ceramic membrane looked favorable and stable. The result of chemical cleaning of the ceramic membrane after the completion of testing confirmed that we could recover it at the initial characteristics. As Table 5 shows, the water quality results in terms of Chemical Oxygen Demand (COD) and oil content level.

4.2 Application of Oilfield Injection Water Reclamation Process

We investigated the application of the injection water reclamation process in an oilfield. Crude oil from this oilfield is a heavy oil with high viscosity. The crude oil is pumped up by injecting hot water to increase fluidity. A large quantity of water is there-

Table 3 Operating Conditions of Aerobic Tank

The operating conditions of the aerobic tank are shown.

Item	Value
MLSS (g/L)	7
MLVSS/MLSS	>0.75
DO (mg/L)	3~5
pH	7~8
HRT (h)	16

Notes: MLSS: Mixed Liquor Suspended Solids
MLVSS: Mixed Liquor Volatile Suspended Solids
DO: Dissolved Oxygen
HRT: Hydraulic Retention Time

Table 4 Filtration Conditions of Hollow Fiber PVDF Membrane and CFM

The operating conditions of hollow fiber PVDF membrane and CFM are specified.

Membrane type	Hollow fiber PVDF	Ceramic membrane
Pore size (μm)	0.02	0.1
Permeability flux ($m^3/(m^2 \cdot d)$)	0.19	0.38
Operating conditions	Filtration: 4 min Relax: 2 min	Filtration: 11 min Backwash: 1 min
Chemical cleaning	Nil	Nil

Note: PVDF: Polyvinylidene Difuluoride

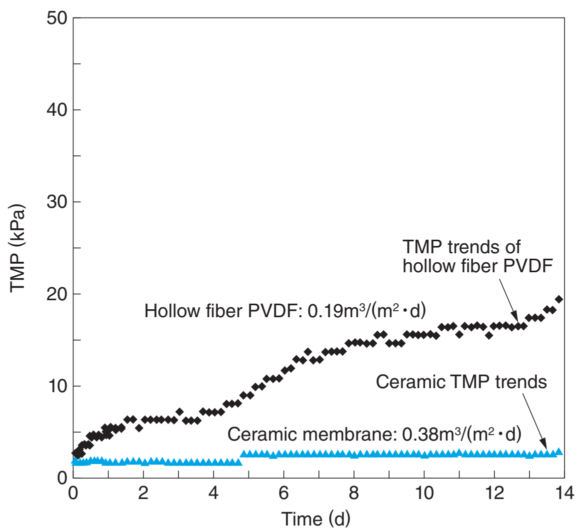

Fig. 3 Fouling Characteristics of Oil Refinery Wastewater during Membrane Filtration

This diagram shows that comparing the performance between the ceramic membrane and hollow fiber, the ceramic membrane with high permeability flux feature can operate in more stable way.

Table 5 Result of Water Quality Analysis for Oil Refinery Wastewater

This table shows the water quality of raw water and filtered water in the case of filtration through the hollow fiber PVDF membrane and the ceramic flat-sheet membrane. The results show how it excels more than the standard values.

Item		Hollow fiber PVDF	CFM	Standard values※
Raw water	COD (mg/L)	267~549		—
	Oil (mg/L)	27~57		—
Filtered water	COD (mg/L)	25~29	34~39	<60
	Oil (mg/L)	3.8~4.8	3.5~6.3	<10

※ Overall wastewater release standard (Maximum permissible wastewater release level with the content of Class 2 pollutants)

Table 6 Filtration Conditions of CFM

The operating conditions of CFM are specified.

Membrane type	CFM
Pore size	0.1μm
Permeability flux	0.84m^3/(m^2·d)
Operating conditions	Filtration: 11 min Backwash: 1 min
Water temperature	50℃

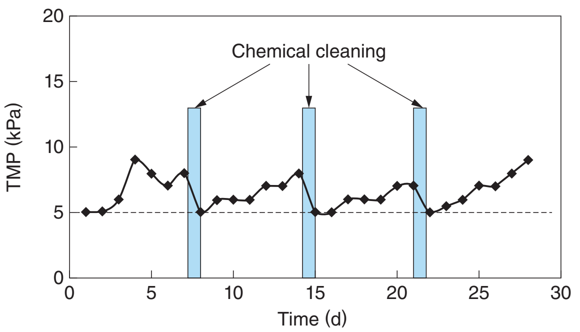

Fig. 4 Fouling Characteristics of Oilfield Injection Wastewater during Membrane Filtration

This diagram shows that after the execution of chemical cleaning, initial characteristics are recovered and stable operation is continued.

fore used for production. The used water is turned into wastewater containing oil components and clay. This wastewater is reused as the reclaimed water. As such, it is necessary to remove oil components and clay.

We investigated the possible replacement of the present process, from dissolved air floatation to coarse filter filtration adopted in the present system, by membrane filtration. When the present process is replaced by ceramic membrane filtration process, the entire process can be simplified and it produces space saving. As a result of this process modification, it will become possible to reduce chemicals like flocculation agents, scaling agents, and sterilizers, used in the process from dissolved air floatation to the flocculation reactor (chemical reaction tank).

Table 6 shows the filtration conditions of a CFM. **Fig. 4** shows the fouling characteristics of oilfield injection wastewater during membrane filtration and **Table 7** shows the result of water quality analysis. The capability of stable operation was confirmed under the operating conditions specified in the table and by performing chemical cleaning for a period of

Table 7 Result of Water Quality Analysis for Oilfield Injection Wastewater

This table shows the water quality of raw water and filtered water in the case of filtration through the CFM. The result meets the requirements of the relevant standard.

Item	Raw water	Filtered water	Standard value※
Oil component (mg/L)	20〜65	0.1〜1.0	<5
Quantity of SS (mg/L)	30〜110	0.1〜0.9	<1
Median particulate size (μm)	3.5〜8.6	0.1〜0.7	<1
Nephelometric Turbidity Unit (NTU)	150〜200	1.0〜1.8	—
COD (mg/L)	180〜267	88〜109	—
Hydrogen ion concentration (pH)	6.8〜7.2	7.1	—
Water temperature (℃)	45〜56	50	—
Volume of sulfate-reducing bacteria (N/mL)	1200〜2000	ND	—

※ Water quality standard on reinjection water from clastic sedimentation reservoir: SY5329-94 A1

one week. In regard to water quality, the injection water obtained by membrane filtration meets the requirements of the top class standard. We confirmed that the result assures the fact that the ceramic membrane can be applied to the injection water reclamation process.

5 Postscript

CFMs are a new and unique product with much potential in future applications. They are not only useful in the conventional field of membrane treatment but also applicable to other industrial fields not yet applied. Going forward, we will continue to develop new products and applicable technologies not only for the existing application fields but also in new special fields.

《**References**》

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