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Physical-chemical property and filtration mechanism of the porous polyvinyl chloride composite membrane as filter for waste water treatment

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ABSTRACT

A porous polyvinyl chloride composite membrane with good filter effect for cooling water in continuous casting was designed and prepared. Physical-chemistry properties of the porous polyvinyl chloride composite materials, including surface microstructure, wettability (for water and oil) and permeability coefficient, were investigated. Filtration effect of the porous polyvinyl chloride composite tube filter was enhanced compared with the traditional filter due to the adjustment of wettability and permeability for water and oil. It was found that particle size and pore size distribution for exine and intine of the composite tube are almost the same. Particle size is about 50–120 μm while pore diameter is about 20–60 μm. Water droplets exhibit good wettability on the porous composite materials, while the oil droplets are not wetted. Due to the oleophilic/hydrophobic characteristics passage of water and adsorption of oil droplets, the porous PVC composite filter tube possesses good filter effect. As a result, water quality is remarkably improved after filtration by using the new filter.

Keywords: Polyvinyl chloride composite tube; Filter; Cooling water; Wettability; Penetration

1. Introduction

In iron and steel industry, a large amount of circulating cooling water is used (water withdrawal 3.2 m^3/t). Waste water usually contains a range of potential hazards with fouling, corrosion and microbial breeding. In order to optimize the allocation of water resources in iron and steel enterprises by recycling the waste water in circulating cooling water system, waste water must be purified to mitigate or eliminate these hazards for stable and safe operation in a long-term [1,2]. The traditional filter is prone to agglomerate and produce a blind spot in the continuous casting process, which affects the production and the quality of products. Therefore, in order to reduce water consumption and the risk of water pollution for the steel industry, it is necessary to develop new filters for water purification and recycling in continuous casting.

Polyvinyl chloride (PVC), a thermoplastic material, is extensively used in many fields, such as wire and artificial leather, medical devices, bathroom curtains, flooring and wire cable insulation, due to its low price, high chemical stability, durability, abrasion resistance and excellent mechanical properties [3–9]. Development of high performance porous PVC composite membrane filters will provide a new solution for continuous casting cooling water treatment. After filtration, the continuous casting cooling water quality is improved, leading to reduce of the energy consumption, water consumption and sewage. As a result,

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the production problems induced by clogging of the cooling water nozzle could be solved. In addition, porous PVC composite membrane filter has advantages over traditional filter in long service life, simple operation and less system downtime, which could ensure smooth operation of circulating water in a long term.

In this paper, a porous polyvinyl chloride composite tube filter was designed and prepared. The difference of the internal structure between the porous polyvinyl chloride composite tube filter and the traditional filter was discussed. Physical-chemistry properties of the porous polyvinyl chloride composite materials, including surface morphology (particle size, pore size), chemical composition, wettability (for water and oil) and permeability coefficient, were studied. The enhanced filtration mechanism of the porous polyvinyl chloride composite materials was analyzed based on the adjustment of the wettability and the permeability coefficient for water and oil on the porous polyvinyl chloride composite materials. The filtration effect of the porous polyvinyl chloride composite tube filter for the continuous casting cooling water was also test.

2. Experimental method

Polyvinyl chloride was used as the main material. The lead stearate and calcium stearate were used as the compound stabilizer. A small amount of the stearic acid and paraffin were used as the lubricant. The low temperature organic matter methyl methacrylate was used as a pore-forming agent. Polyvinyl chloride, pore-forming agent, stabilizer and lubricant were placed in the high-speed mixer, heated to 100–200°C for about 20–30 min, and then cooled down to 40–50°C. Afterwards, the granulations were performed in a granulator with collected materials, followed by putting in the hopper of extruder. The screw of extruder pushed the plasticized polyvinyl chloride mixture to the head in the barrel, which achieved the homogenization of compacting, melting and mixing. Finally, the PVC tube was obtained after cooling, pitching and cutting.

Surface morphology and chemical composition of the porous polyvinyl chloride filtration membrane were examined by using scanning electron microscopy (SEM) (Zeiss EVO MA 10LS 10) and energy dispersive spectroscopy (EDS), respectively. Au-topore IV-9500 automatic pressure pump was used to examine the porosity of the tube. A self-designed intravenous drier was employed to measure the wettability of water and oil droplets on porous composites. The experimental materials were mechanically polished for 20 min, followed by ultrasonic cleaning for 15 min. Afterwards, an imaging system was used to record the pictures of the water droplets and oil droplets on the porous composite.

To measure the permeability coefficient of porous PVC composite tube, an experiment was designed as shown in Fig. 1. The bottom of the tube filled with water was sealed and placed in the pool. The height of the tube is H, and the height of water in the pool is H_1. Above the surface of the water, the outer wall of tube was sticked by waterproof glue and clamps to prevent the water pouring out. The distance between the surface of water and the nozzle is H_2 in the

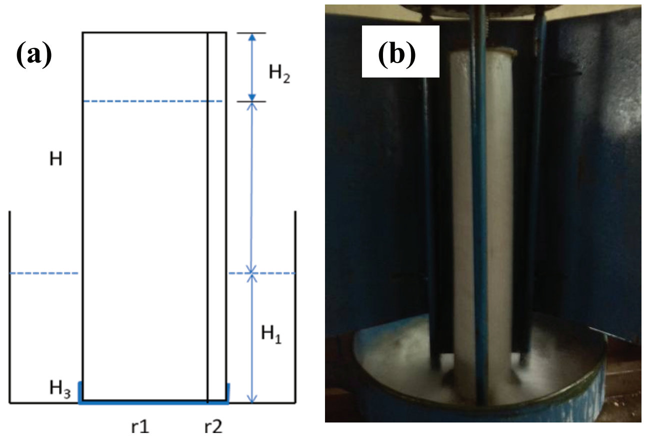

Fig. 1. (a) Schematic illustration of the experiment to measure the permeability coefficient and (b) a photograph of composite tube.

inner tube, and the height of the hoop is H_3 in the lower part of the tube. The height L of filter section can be expressed by

$$L = H_1 - H_3 \quad (1)$$

Among them, the height of tube H is 100.06 cm, the height of water H_1 is 22.07 cm, the height of hoop H_3 is 3.84 cm.

The average seepage time Q can be calculated by Darcy formula (2):

$$Q = KAJ = 2K\pi rL\frac{\Delta h}{\Delta r} \quad (2)$$

where A is the surface area of flow cross section; J is the hydraulic gradient; K is the permeability coefficient. Among them, $A = 2\pi r\mathrm{d}x$, $J = \Delta h/\Delta r$.

3. Analysis of porous PVC composite membrane

3.1. Comparison of filters

During continuous casting the circulating cooling water system is one of the important systems to ensure the continuous operation. The secondary cooling [10] generally adopts fresh industrial water or sewage water from clean circulating system, which increases the pH and scaling ions. Large suspended solids and oil are apt to block the nozzle at high temperature. Traditionally, cobbles, quartz sands, cokes and fibers are used as filters. However, the performance of ϕ 4000 × 6400 traditional filter (single treatment of water 400 m^3/h) is very poor and prone to agglomerate and produce a blind spot in the continuous casting process. As a result, the production and quality of products are affected. In backwashing, it is easy to bring the filter into the pool and circulating water system, damaging the strainer and the recirculation channels, and clogging the nozzles. Some problems of the filter may directly affect the cooling effect of the continuous casting machine, and sometimes even deteriorate the surface quality of continuous casting billet. Fig. 2 shows the difference between the traditional filter and the PVC filter.

In the newly designed filter, a composite membrane filter tube replaces the quartz sand for the internal filter. A top plate and a bottom plate were added. A net coil and oil drain were placed to clean the tube. The core equipment of the new filter has many outstanding properties, such as small aperture, high strength, high temperature and corrosion resistance. The new filter integrates the functions of filtration, backwashing and slag discharge. The cost of the porous PVC composite tube is low, and the porosity and pore size are different from the traditional filter. The strength is also in accordance with the conditions required for the research.

The waste liquids enter into the collection chamber from the inlet of the composite membrane filter, collecting the carried oil at the top of collection chamber. When the accumulation reaches a certain amount, it can be discharged from the oil drain. The waste liquids penetrate into the filtration chamber by means of the filter tube of porous PVC composite membrane, and discharge via the liquid outlet under the external pressure. Meanwhile the impurities are trapped and deposited in the sediment chamber, and discharged from the sewage outfall at a certain amount of accumulation. Whereas, with the increase of filtration time, some of the impurities will adhere to the tube surface and plug the pores, which will reduce the flow rate and increase the difference of pressure. When the pressure difference is greater than 0.05 MPa, the backwashing device starts to work. The backwashing water pump passes the purified water through the backwash passage into the porous PVC composite membrane filter tube. By penetration, impurities adhering to the filter tube surface could fall off to the bottom of the filtration along the penetrant, and separate from the sewage channel.

3.2. The performance of porous PVC composite filtration membrane

3.2.1. Morphology

Pore size and particle size of the filter medium have significant effect on filtration pattern, filtration flux and filtration efficiency. The morphology of the exine and intine of porous PVC composite tube are shown in Figs. 3a and b, respectively. It can be clearly observed that particle size and pore size distribution of exine and intine is almost the same. Particles are in the range of 50–120 μm, while pores are about 20–60 μm. Besides, the exine

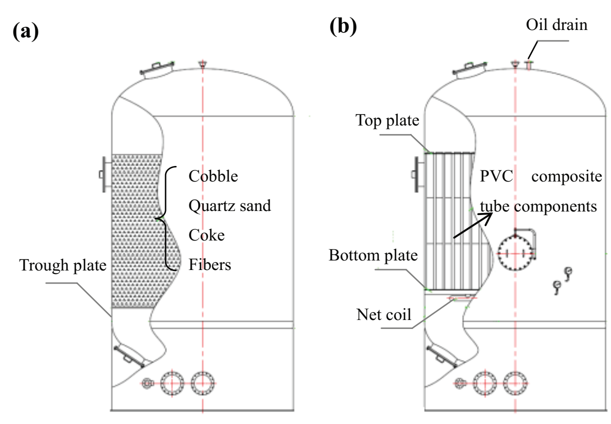

Fig. 2. The internal structure for (a) a traditional filter and (b) a porous polyvinyl chloride composite tube filter.

and intine of porous PVC composite tube exhibit similar porosity. After usage for 3 years, the exine and intine of porous PVC composite tube are shown in Figs. 3c and d, respectively. As can be seen, particles on the surface are destroyed.

The EDS spectrums of the composite tube exine and intine are shown in Fig. 4. The main chemical components of both exine and intine are C, Cl and Au. Trace metals such as Ca are contained during sintering. Au is attributed to the gold spray.

3.2.2. Wettability

It is well known that the filtering effect is determined by the wettability of filters, which is influenced by the chemical properties of the material surface. When the wettability of the filter material is good for the oil, the filtering effect is good. Conversely, the filtering effect is poor [11,12]. In order to evaluate the filtering effect of porous PVC composite filter tube, wettability tests were performed on the intine of porous PVC composite filter tube with a diameter of 13.7 cm by water and oil droplets (Figs. 5 and 6). The dropmeter software analysis results shown in Fig. 5 reveal the relationship between the wettability of lubricating oil droplets from the roll and time on porous composites materials. At the initial 1200 s, the contact angle of oil droplets on porous composite materials decreases slowly with time (from 138° to 93° after 1200 s). When the time comes to 1500 s, the contact angle no longer changes (93°). During the whole process, the contact area of liquid-solid interface increases slightly, and the volume of the oil droplets has no significant change. It can be concluded that the oil droplets are not wetted on the porous composite materials.

The wettability of water droplets on porous PVC composite filter tube with different time are given in Fig. 6. The water droplets spread rapidly on the surface of the porous composite materials, and the contact angle decreased from 104° to 35° after 25 s. Besides, the contact area of liquid-solid interface expands several times, demonstrating that the water droplets have good wettability on the porous composite materials.

From the above results, it could be found that porous PVC composite filter tube is oleophilic/hydrophobic, which is favorable for the passage of water and the adsorption of oil droplets. However, accumulation of the adsorbed oil droplets and particulate matters will lead to serious decrease of the filtration efficiency. At this point, it is essentially important to start the backwashing. Generally, the super-hydrophobic surface with a water contact angle larger than 150° has seriously negative effects on the filtration performance [13–15]. However, at this time, the effect of backwashing is worse. When the oil concentration in the waste water is higher, the surfactant can be added to increase the wettability of the oil droplets on the surface of the porous composite materials. As a result, the filtration efficiency is improved.

3.2.3. Permeability coefficient

Compared with the common porous medium, the porous PVC composite filter tube possesses weak perme-

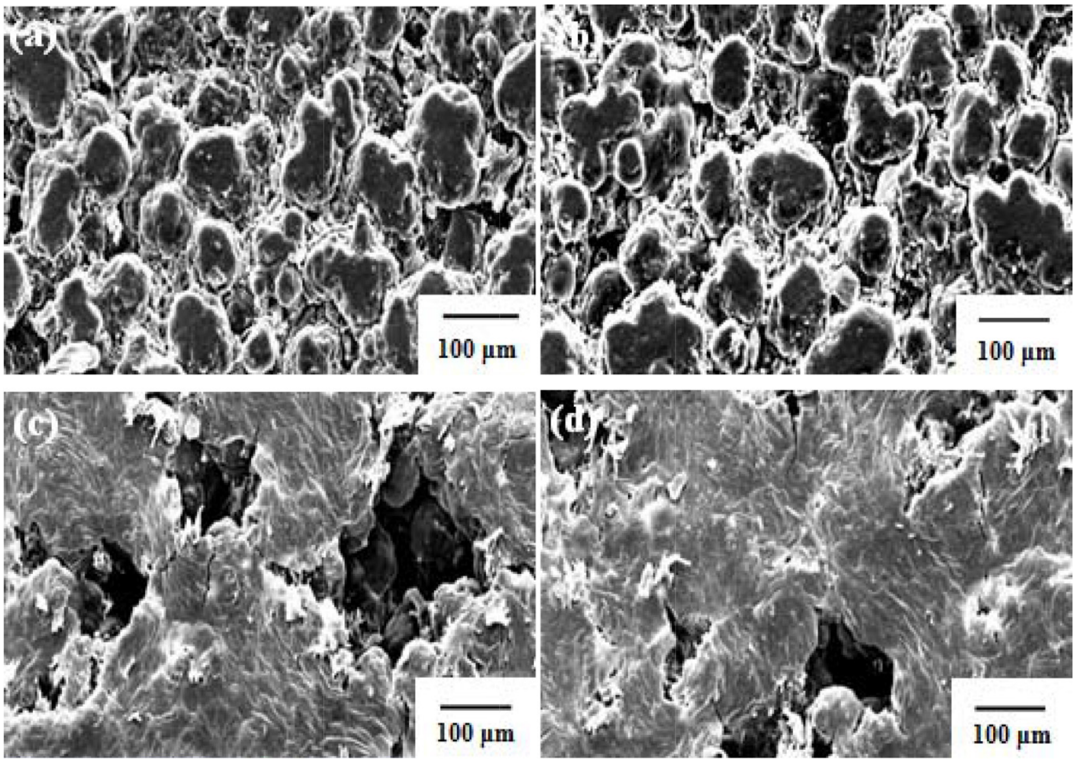

Fig. 3. Morphology of (a) the exine and (b) the intine of a porous PVC composite tube; Morphology of (c) the exine and (d) the intine of a porous PVC composite tube after usage of 3 years.

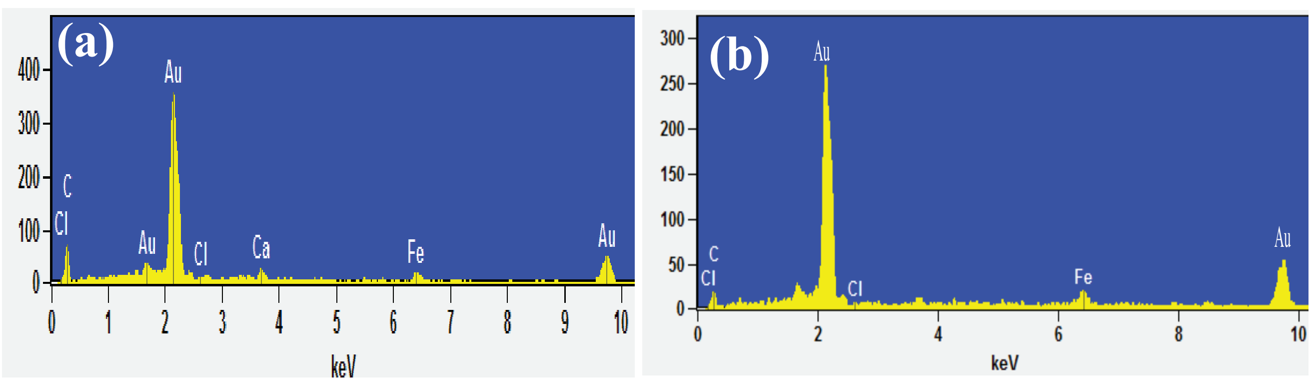

Fig. 4. The EDS spectra of porous PVC composite tube: (a) exine and (b) intine.

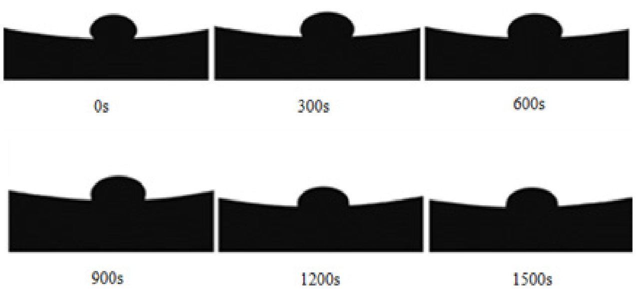

Fig. 5. Wettability of lubricating oil on the intine of porous PVC composite tube with different time.

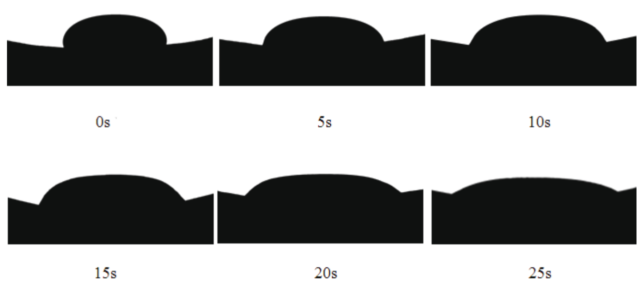

Fig. 6. Wettability of pure water on the intine of porous PVC composite tube with different time.

ability. The linear relationship between the unit time flow Q and the head difference Δh is simulated by using the origin results, and the intercept is set to zero (Fig. 7). From the linear relationship, it can be identified that the slope is 2.66 × 10^{-4}, the error is 5.91 × 10^{-6}, and the R^2 is 0.994. The relationship between the velocity of the fluid and the inner and outer pressure differential of the tube is consistent with the formula derived from Darcy's law. According to Eq. (3), the permeability coefficient K is 4.42×10^{-5} m/s.

$$K = \frac{Q\ln\frac{r_2}{r_1}}{2\pi(H_1 - H_3)(H - H_1 - H_2)} \quad (3)$$

4. Application of porous PVC composite tube filter

Usage of the porous PVC composite tube filter improves water quality. So, the operation is improved and the service life is increased. As a result, the operating costs and the system downtime are reduced. The morphology and the chemical composition of the sludge filtered by porous PVC composite tube filter are examined by SEM and EDS, respectively (Fig. 8). As shown in Fig. 8a, the dried sludge is composed of fluffy and porous structured particles with a size range from several microns to dozens of microns. The results indicate that the sludge can be separated through the porous composite tube. The main chemical components of sludge are C, O, Fe, Si, P, S, Ca and Al (Fig. 8b). Fe content of sludge is about 74.51 wt%, while other elements are impurities. It is considered that the collected sludge could be reused as a sintered raw material due to the high Fe content.

The turbidimeter was employed to measure turbidity of water samples. To determine the content, the suspended matter should be dried and weighed. Table 1 lists the water samples deposited separately for 12 h before and after filtration. As can be seen, water quality has been significantly improved after filtration by the porous PVC composite tube. And the filtered water meets the cooling water purification requirements in continuous casting. The filtration effect is significantly improved compared with these of the traditional filtration equipment. Content of suspended matter in water is less than 8 mg/L, the oil removal rate is 60–80%, and the recycling rate of water reaches 99.9%. Capacity of water treatment increases from the original 400 m^3/h to 800 m^3/h. And the water no longer causes production problems such as clogging of the cooling water nozzles.

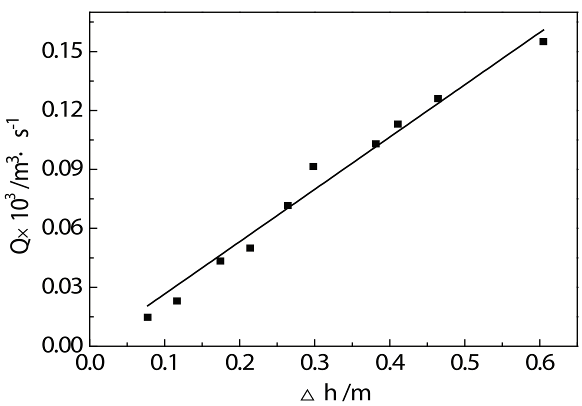

Fig. 7. The relationship of Q and Δh.

5. Conclusion

The following conclusions can be drawn on the basis of the above studies:

1) The porous PVC composite tube filter developed in the project can improve the quality of continuous casting cooling water. Content of suspended matter in water is less than 8 mg/L, the oil removal rate is 60–80%, and the recycling rate of water reaches

Table 1
Test results of water quality before and after filter/mg·L^{-1}

Number	Turbidity before filtration	Turbidity after filtration	Suspended matter before filtration	Suspended matter after filtration
1	194	10.2	695	13.7
2	208	7.9	834	9.5
3	187	9.3	656	12.3
4	195	9.5	753	10.6

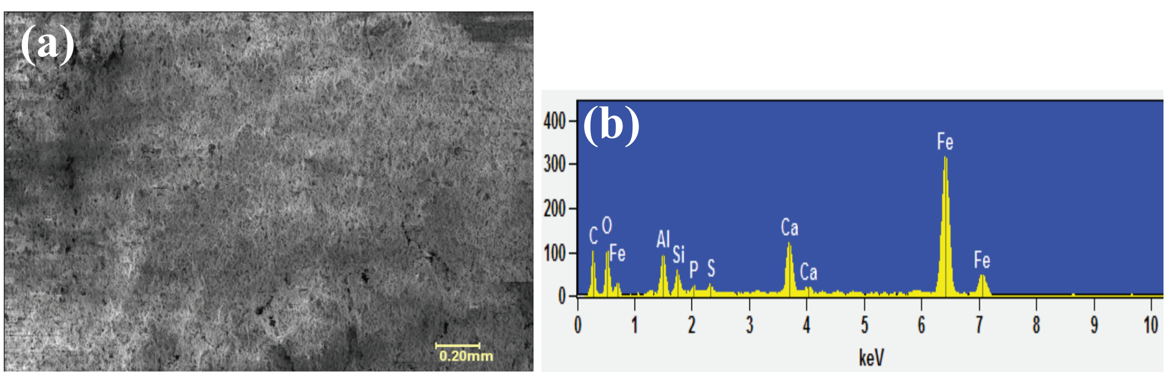

Fig.8. (a) SEM micrographs and (b) EDS spectrums of filter sludge.

99.9%. Capacity of water treatment increases from the original 400 m^3/h to 800 m^3/h. Application of PVC composite filters could solve the production problem induced by the clogging of the cooling water nozzle and ensure the long-term smooth operation of circulating water.

2) Particle size and pore size distribution of the porous PVC composite tube exine and intine are almost the same. The particle size of the surface is about 50–120 µm, the pore diameter is about 20–60 µm.
3) The water droplets have good wettability on the porous composite, while the oil droplets are not wetted on the porous composite material. The permeability coefficient K is 4.42×10^{-5} m/s, indicating that PVC composite tube is a weak permeable material compared with the common porous medium.

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