

Tuning the diffusion dialysis performance by surface cross-linking of PPO anion exchange membranes—simultaneous recovery of sulfuric acid and nickel from electrolysis spent liquor of relatively low acid concentration

Xu Tongwen*, Yang Weihua

Department of Chemistry, Laboratory of Functional Membrane, University of Science and Technology of China, Hefei 230026, China

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Abstract

The results of the development of the industrial diffusion dialysis technology and the unit based on it for sulfate acid recovery from nickel electrolysis waste have been considered. Unlike most acid recovery systems, this system has a relatively low acid concentration and the main aim is to recover both nickel and acid sulfate by recycling the waste and the recovered acid to the respective steps of electrolysis process. So the waste volume control seems to be the most important thing. To satisfy with this new request, the membrane is surface-cross-linked with aqueous ammonium to decrease waste volume expansion caused by the water osmosis. The results showed that the best membrane for such operation is the one that cross-linked at least 8 h with a volumetric expansion factor (volumetric ratio of waste to feed) less than 1.1.

Pilot diffusional runs were conducted with this membrane at various feed flow rate and flow ratio of stripping water and feed. After comprehensively considering all factors, the range of feed flow and the flow ratio has been recommended to be 1.2–1.8 l/h and 1.05–1.1, respectively. Under these conditions, nickel leakage can be controlled within 4% and the acid recover ratio can attain as high as 66–72%. The recovered acid can be recycled to the back-extraction step by mixing it with high concentration acid and the waste recycled to the initial leaching stage by adjusting the acid concentration to recover valuable metal nickel and the residual acid. Therefore, the new technology discards nothing and shows many advantages whether in environmental aspect or economical aspect and thus should be deserved attention. © 2004 Elsevier B.V. All rights reserved.

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1. Introduction

In conventional production of metal by electrolysis, i.e., hydrometallurgy, four basic steps should be conducted [1]: (a) metal-rich ore is leached with acid at a certain pH value such as $\text{pH} = 2\text{--}3$ under the condition of proper strain (bacteria) medium; (b) the metal is extracted from the leaching solution by proper organic extractant to obtain the metal-contained organic phase; (c) the metal-rich organic phase is back-extracted with acid (acid sulfate is commonly used) to achieve the electrolysis solution containing both acid sulfate and metal sulfate; (d) the metal is then obtained at the cathode by electrolysis invariably accomplished by certain quantities of dilute solution (electrolysis dilute solution). For example, in a nickel processing plant in western china, 80 m^3 per day of such solution which containing

H_2SO_4 : 40–50 g/l, Ni^{2+} : 70–80 g/l and other metal impurities such as rare earth metal, Na^+ , etc. was discarded [1]. Since the nickel-dilute solution containing a quantity of acid can neither be returned to step 1 which will acidifies the bath and further affect the leaching process, nor be returned to step 3 which causes a decline in the extraction performance, so the eventual disposal is necessitated. This disposal of spent liquor has posed a problem in the nickel processing and also the whole hydrometallurgy industries for long time and has prompted industries to give serious consideration to recover acid or useful components from spent liquors that are now going to wastes. Treatment of this hazardous waste solution has been rather difficult. A conventional and popular method is neutralization by suitable base. For example, in nickel hydrometallurgy process, to treat the waste, neutralization with base (ammonium hydroxide or lime) is a common practice. Such a neutralization process produce large quantity of sludge which cause serious ensuing disposal problem. Furthermore, in the neutralization process,

* Corresponding author. Tel.: +86-551-360-1587.

E-mail address: twxu@ustc.edu.cn (X. Tongwen).

resources materials such as acid, base and nickel are lost, which otherwise can be possibly recovered for reuse or avoided. Obviously, new method is strongly recommended if it can both improve the economics of the process and avoid nickel-containing hazardous waste disposal.

To satisfied with the situation, diffusion dialysis with anion exchange membrane seems to be a desirable treatment of such waste solution, which consumes no additional energy except pumping the waste. This technology has been exploited to recover inorganic or organic acid from waste solutions being generated in steel, metal-refining, ion exchange resin regeneration waste and electroplating industries [2–10]. In this operation, the anion exchange membrane is the linchpin. The membrane for this purpose differs a lot from ordinary membrane for electro dialysis. It is demanded that it should provide high proton permeability but strong rejection of salts, relatively high water content but poor water permeability and thus it must retain an appropriate fixed group concentration so as to functionalize efficiently in the recovery of acids by diffusion dialysis.

Recently, our lab has developed a new series of membranes from engineering plastics poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) for this purpose whose properties can be quantitatively adjusted by bromination and amination processes [11,12]. By changing the bromination content and position, a series of membranes with high water content were produced to recover sulfuric acid from titanium white production waste containing sulfuric acid and ferrous ions [9] and the analogous membrane with mediate water content produced to recover mixed acid ($\text{HNO}_3 + \text{HF}$) from titanium leaching liquor [10]. In those cases, the main aim is to recover the acid, i.e., let the acid transport enough from the waste and finally discard the waste. Nevertheless, if the purpose of the operation is to decrease the acid concentration of waste containing relatively low concentration acid and valuable metal ions and then recycle the waste to recover the metal, the said membrane does not definitely satisfy with the requests, e.g., when the membranes were used to recover acid and the nickel from the mentioned spent electrolysis nickel waste solution, our preliminary test showed a large volumetric expansion at the waste side due to the large transport of water osmosis from the stripping phase to the waste phase. This not only decreases the nickel concentration, but also increases the recycling volume. For this new purpose, the water permeability seems to be more important than acid recovery ratio. Therefore, in the present study, emphasis has been placed on examining the effect of membrane cross-linkage on the process performances with an aim to derive a desired membrane for such a process.

2. Experimental

2.1. Membrane preparation

Commercially obtained poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) of intrinsic viscosity equal to $0.57 \times$

$10^{-3} \text{ m}^3/\text{kg}$ (i.e. 0.57 dL/g) in chloroform at 25°C was dissolved in chlorobenzene to form a 8% solution and this solution was subjected to the benzyl bromination by some addition of bromine with molar ratio $\text{Br}_2:\text{PPO} = 4:3$ (theoretical substitution = 100%) for 8 h at boiling state [11]. After cooling down to ambient temperature, the solution was cast onto a polyvinyl chloride substrate to form a base membrane of 0.1–0.2 ml in dry thickness. This base membrane was surface-cross-linked in ammonium aqueous solution for different time and then functionalized with trimethylamine for additional 16 h by controlling the temperature at about $35 \pm 1^\circ\text{C}$. Unlike our previous papers [9–11], in which the intrinsic properties such as moisture content, ion exchange capacity, etc., were controlled by bromine substitution content and position, the series membranes properties in this paper were controlled by the surface-cross-linking degree.

2.2. Membrane characterizations

The main characteristics of the typical membranes detected in this paper including the fundamental properties such as ion exchange capacity (IEC), water uptake, wet thickness, area resistance, cross-linking degree and the diffusional features such as water osmosis coefficient and acid dialysis coefficient. These fundamental properties are determined completely in the same manner as our previous paper [11] except the cross-linking degrees of the membranes was calculated from the weight decrease after cross-linking. All the properties were evaluated at room temperature of $25 \pm 1^\circ\text{C}$ and the results were collected in Table 1.

2.3. Diffusional tests

The diffusional tests include the static dialysis tests for apparent water osmosis coefficient and the dynamic diffusional dialysis for acid recovery ratio, nickel leakage ratio, and dialysis coefficients, etc.

The unit for apparent water osmosis coefficient is shown in Fig. 1. It consists of two sections made of poly(methyl methacrylate) resin leaving a effective membrane area ca. 5.07 cm^2 and a empty volume 25 ml. Two special-designed fine glass tubes of diameter 1 mm were connected to each section. One end of the tube was calibrated to detect the volume flow and the other is plugged to adjust the initial volume position of the tube. In experiments, one half of the half-cell is fully fed with the feed containing H_2SO_4 : 47 g/l, Ni^{2+} : 72 g/l (conforming to the later dynamic dialysis tests) and the other with deionized water. Due to the water osmosis, volume at the feed side is overflowed from the calibrated tube and thus water volume change with time can be recorded and plotted, and then the apparent water osmosis coefficients K_W is given by slope of volume–time curve divided by the active membrane area (m/h).

The apparatus for dynamic diffusion dialysis is of industrial scale. As shown in Fig. 2, it is separated by 49

Table 1
Properties of example membrane series developed in this paper^a

Cross-linking time (h)	Cross-linking degree ^b (100%)	Wet thickness (mm)	Water content (% g/g dry)	IEC (mmol/g dry)	Area resistance ($\Omega \text{ cm}^2$)
1	0.036	31.0	50.7	2.04	3.07
1.5	0.078	28.9	44.6	2.08	5.01
2	0.115	27.1	37.2	2.19	5.52
4	0.123	25.1	34.4	2.11	8.65
8	0.146	22.5	30.7	2.09	11.32
10	0.170	21.7	25.1	2.02	19.72
14	0.187	20.5	24.4	2.04	25.67
18	0.255	20.6	21.4	2.02	27.52
24	0.333	19.2	20.4	2.07	33.86

^a All the measurements were conducted at temperature of 25 ± 1 °C.

^b Cross-linking degree was calculated from the weight difference before and after cross-linking and expressed as the cross-linking unit ratio per PPO basic unit.

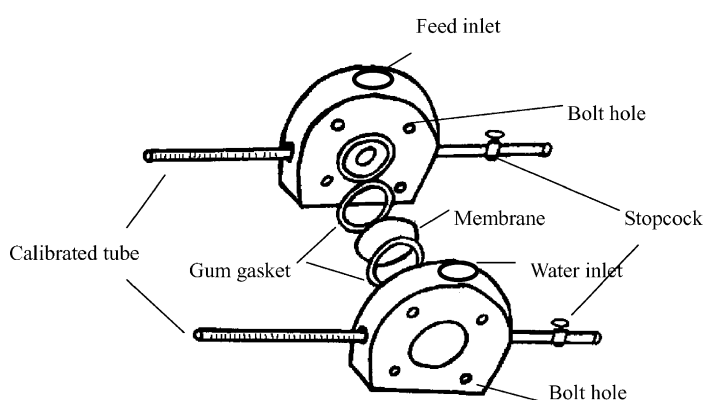


Fig. 1. Schematic diagram for the determination of apparent water osmosis coefficient.

sheets of anion exchange membranes into 25 dialysate cells and 25 diffusate cells through which the feed and stripping water pass respectively. The total membrane area is about 3 m^2 ($49 \times 0.21 \text{ m} \times 0.30 \text{ m}$) and the effective area for diffusional dialysis is about 2.32 m^2 . The margin of the apparatus between the cells is about 2 mm using plastic net

spacers and gum gaskets. These tests were conducted for measurements of acid recovery and nickel leakage ratio as well as the dialysis coefficient by determining the acid and nickel concentration at outlet waste stream C_{wi} ($i = \text{H, Ni}$) and those at the outlet-stripping stream C_{di} ($i = \text{H, Ni}$). Acid was determined by titration with a 0.1 M NaOH solution

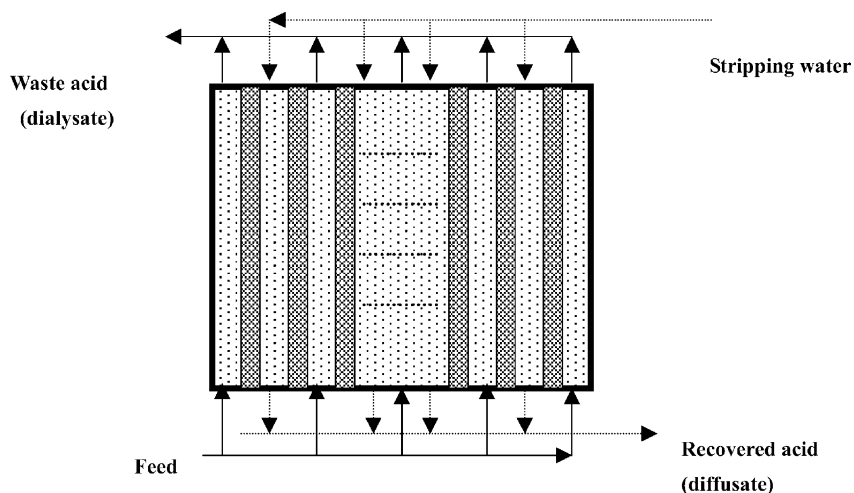


Fig. 2. Experimental apparatus for industrial dialysis.

using phenolphthalein as an indicator and Ni^{2+} was determined by titration with a 0.0225 EDTA standard solution using murexide as an indicator. Then the apparent dialysis coefficients U_i ($i = \text{H, Ni}$) is given by the amount of the respective component that is transported across the membrane per unit active membrane area, per unit time and per unit concentration difference of the component:

$$U_i = \frac{M_i}{A \Delta C_i} \quad (1)$$

where M_i is the amount of component transported acid in gram per liter and hour (g/lh), A the effective area in m^2 , and ΔC_i the log mean concentration difference of the component across the membrane in gram per liter (g/l) [4]:

$$\Delta C_i = \frac{C_{fi} - C_{di} - C_{wi}}{\ln(C_{fi} - C_{di})/C_{wi}} \quad (2)$$

and the selectivity S_{Ni}^{H} is given by the ratio of apparent dialysis coefficients:

$$S_{\text{Ni}}^{\text{H}} = \frac{U_{\text{H}}}{U_{\text{Ni}}} \quad (3)$$

The acid recovery ratio η_{H} , or nickel leakage ratio η_{Ni} can be calculated respectively from the following formula [4,5,10]:

$$\eta_i = \frac{C_{di} Q_d}{C_{fi} Q_f}, \quad i = \text{H, Ni} \quad (4)$$

where Q_d is the flow rate of recovered acid and Q_f the flow rate of the feed.

All the diffusional tests were conducted at ambient temperature about $20 \pm 1^\circ\text{C}$ and three repetitious analyses showed that the error was within 6%.

3. Results and discussions

3.1. Membrane properties and structures

As shown in our previous paper [11], the membranes were prepared from linear polymer following the procedures of bromination in both aryl and benzyl positions and then quaternary amination. In that case, the membrane properties

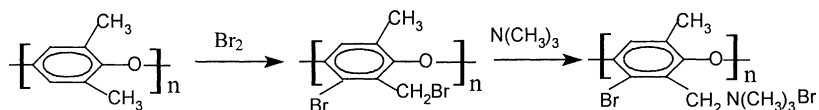
were controlled by bromination process: benzyl substitution enhanced the ion exchange capacity and water content, while the aryl substitution decreased the water content with ion exchange capacity approximately unchanged. As shown in Scheme 1, the advantage of this route for an anion exchange membrane is the avoiding of chloromethyl methyl ether, which is a carcinogen and potentially harmful substance and used in most chloromethylation processes.

In present case, membrane properties were adjusted by surface-cross-linking with ammonium aqueous solution using the benzyl-substituted base membrane. The possible cross-linking reaction was shown in Scheme 2.

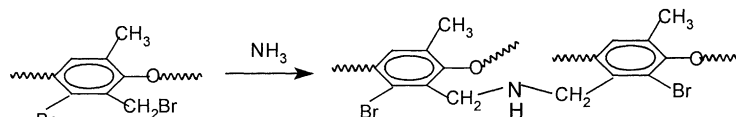
The cross-linking reaction was approved by the measured cross-linking degree as shown in Table 1. Obviously, with an increase in time, the cross-linking degree increase, correspondingly giving rise to an appreciable change in membrane properties: with an increase in cross-linking degree, the membrane moisture decreases rapidly and cause a corresponding increase in membrane area resistance. Since the cross-linking reaction was mainly constrained in the membrane surface (due to the hydrophobicity of the based membrane [13]), the exhaust of benzyl methyl groups in this process is much less than the its total quantity, and thus the resultant membrane IEC keeps approximately unchanged after quaternary amination, in which the functional groups were formed from benzyl methyl groups. It should be noted that though the cross-linking can be conducted with ethylenediamine (EDA) as described in another paper [12], cross-linking with ammonium aqueous solution provides a more cheap, fast and effective method, which mainly alters the membrane surface hydrophilicity without changing membrane regime structure and thus conform to the followed dialysis tests.

3.2. Volumetric expansion factor

In diffusion dialysis, water osmosis is a key factor affecting the operation. Based on our preliminary tests, we found that the outlet stream volume was largely dependent on the membranes' properties. To label the extent of this volumetric change, volumetric expansion factor is used here, which is defined as the volumetric ratio of outlet waste volume to



Scheme 1. Typical structures of PPO, simultaneous substituted PPO and the un-cross-linked membrane.



Scheme 2. Typical cross-linking reaction with ammonium aqueous solution.

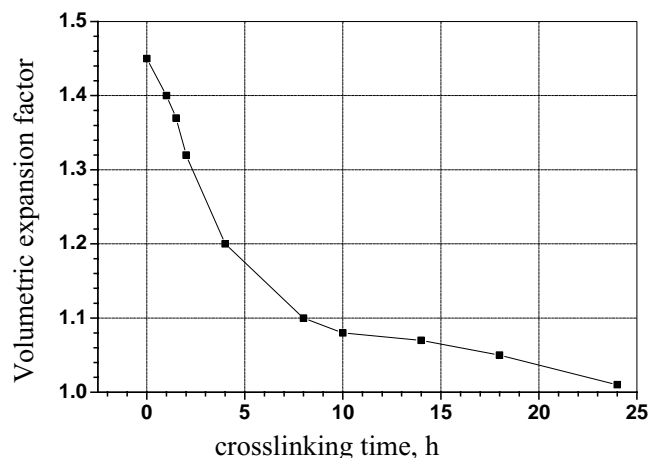


Fig. 3. Effect of amine-cross-linking time of membranes on volumetric ratio of waste to feed (volumetric expansion factor). Feed flow rate = 0.6 l/h, water to feed low ratio = 1.05.

the feed volume. As shown in Fig. 3, this volumetric expansion factor decreases with the cross-linking time of the membrane. Generally speaking, the volumetric change is a competition of two factors: here taking outlets waste stream as a example, one is the water osmosis from the stripping stream to the waste stream due to the osmosis pressure and the other is the water transport from the waste to the stripping due to the diffusion of hydrated ions (acid or salt). The relative magnitude of osmosis and diffusion will affect the volume of the two outlet streams: if the water osmosis is greater than its diffusion, it will result in an increase in waste volume and thus a corresponding increase in volumetric ratio and vice versa. In principle, the water transport is probably related with the ion transport and thus related the membrane characteristics such as water content and ion exchange capacity (IEC) in the membrane: the higher the water content and IEC of the membrane, the faster the transport of water hydrated ions and thus the larger water transport; while the water osmosis is not only dependent on feed concentration (osmosis pressure difference) but also dependent on membrane hydrophilicity: a larger concentration difference or a higher water content membrane permits a larger water osmosis flux. As shown in Table 1, though the IEC keeps approximately unchanged with cross-linking time, the water moisture is seriously affected by cross-linking time. With an increase in cross-linking degree, the membrane moisture decreases rapidly. This decrease can also be indirectly proved by the change trend of membrane's wet thickness and the membrane area resistance. The changes of these features cause corresponding changes in both acid and salt permeability rate as well as water osmosis rate. As shown in Fig. 4, compared with apparent acid and salt dialysis coefficient which are responsible for water transport from waste stream to stripping stream, apparent water osmosis coefficient is 4–5 times greater; while theoretically speaking the hydrated water molecules are 2–3 times than the transported species [14], therefore, the net result is that the volume of the outlet waste

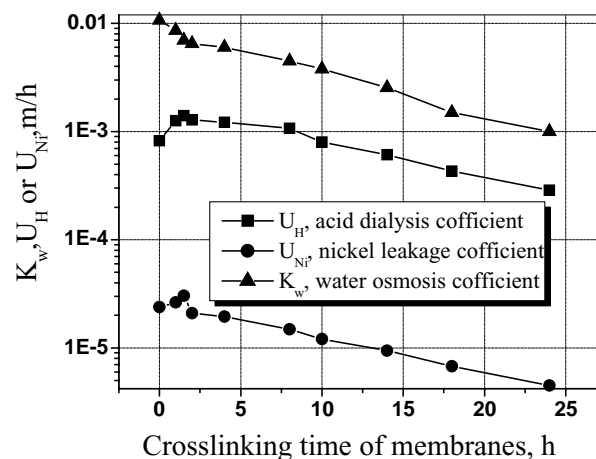


Fig. 4. Comparison of water osmosis of coefficient with components dialysis coefficient at various cross-linking time. Feed flow rate = 0.6 l/h, water to feed low ratio = 1.05.

stream is greater than that of stripping stream (i.e., the volumetric expansion factor is greater than unity at all cases). With an increase in cross-linking, the membranes become more compact and hydrophobic, so the absolute magnitude for apparent acid dialysis coefficient or water osmosis coefficient decreases several orders. This causes a decrease in absolute quantity of both water osmosis and water transport and thus the volumetric expansion factor then decreases with cross-linking time.

3.3. Acid recovery and nickel leakage

Further insight into the factors affecting the performance of these membranes can be seen in Fig. 5, where it demonstrates the acid recovery and nickel leakage as well as the selectivity against the membrane cross-linking time. It is noted in this figure that both the acid recovery and nickel leakage ratio increase with cross-linking time of membranes and reaches a maximum at 8 h of cross-linking time. Beyond this time, there is a rapid decrease in both acid recovery and nickel leakage. The first change trend is mainly due to the large osmosis of water to the waste stream (the volumetric expansion factor is relatively high as shown in Fig. 3) and the subsequently trend is due to the change in hydrophilicity and surface structure of membranes. As intensively discussed in our previous papers [9,15], an ion exchange membrane can be considered from the viewpoint of a three-phase membrane model where the membrane consists of hydrophobic polymer, an active exchange zone and an interstitial zone. A counter-ion transport occurs mainly through the active region where it moves by a hopping mechanism and while the co-ions leakage through the interstitial zone due to the minimal repulsive force. The portion of water in the membrane that is found in the solvation shells of the fixed ions and their counter-ions are not free to move within the membrane and will exert drag on ions moving through the membrane. Therefore, hydrated ions will require

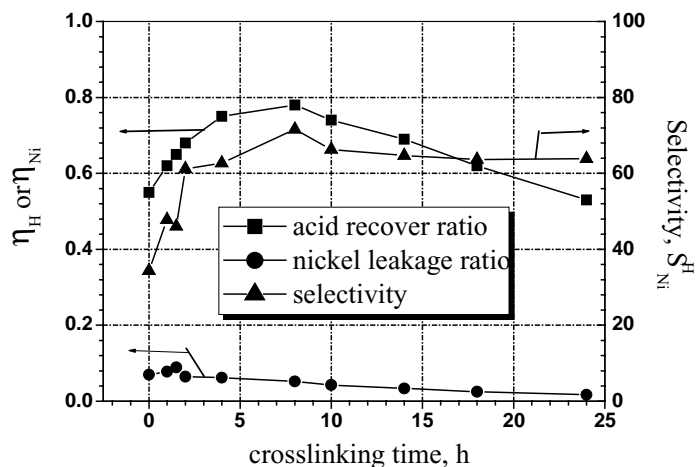


Fig. 5. Effect of cross-linking time of membrane on acid recovery ratio, nickel leakage ration as well as the selectivity. Feed flow rate = 0.6 l/h, water to feed low ratio = 1.05.

a certain volume of water within the membrane to permit migration through the membrane and thus the water content contained in the membrane will enhance the permeability of counter-ions. An decrease in water content due to an increase in cross-linking time will correspondingly give rise to a decrease in transport rate of counter-ions (sulfate ions here) and thus slow down the transport of co-ions (protons and nickel ions). Since proton shows small volume and little charge, and thus it has a strong competitive ability to nickel diffusion. As a result, the selectivity of proton to nickel ions roughly increase with cross-linking time until a constant is attained due to the co-ions transport limitations by water content of membranes at long cross-linking time.

In the present system, acid recovery ratio is not the decisive factor to be considered because the main aim of the operation is to decrease the acid concentration and recycle the waste to the initial leaching step so as to recover nickel and residual acid. The most important concern is the volumetric expansion factor and selectivity, a large volumetric expansion factor not only tends to increase the burden of recycling (pumping energy) but also dilute the useful components, further causing a decrease in selectivity and a loss of valuable metal nickel. So due to these considerations, the membrane with a 8 h cross-linking time seems to be most

suitable for this operation, which demonstrates the relatively small volumetric factor, relatively high acid recovery ratio (77%) and the highest selectivity as observed from Figs. 3 and 5. Therefore, the pilot runs results are discussed in the next section based on this membrane.

3.4. Pilot runs results

Series pilot runs were conducted with the mentioned dynamic diffusion dialyser and the membranes with 8 h cross-linking time. The tests included four different feed flow rates and four flow ratios of polished water to feed by using the industrial waste liquor as the feed compositions and the results were collected in Table 2. As can be seen, both the acid recovery ratio and nickel leakage ratio increase when the flow ratio of water to feed increases if flow rate of feed has kept fixed. This is mainly because that an increase in flow ratio means a corresponding increase in flow rate of water and thus the contacting time for a given volume of feed with water is elongated. In addition, a large water flow tends to decrease the concentration of recovered components and correspondingly increase the driven force for diffusion, which could also be tested from the dialysis data of acid and nickel as shown in Table 2. For the analogous reasons, an

Table 2
Pilot runs results under different operational conditions^a

Q_f (l/h)	Q_{water}/Q_f	Q_w/Q_f	η_H	η_{Ni}	U_H ($\times 10^{-3}$ m/h)	U_{Ni} ($\times 10^{-5}$ m/h)	S_{Ni}^H
0.6	0.96	0.98	0.73	0.042	0.71	1.12	63.40
0.6	1.05	1.1	0.78	0.052	1.07	1.49	71.55
0.6	1.15	1.12	0.82	0.053	1.17	1.53	76.41
0.6	1.23	1.13	0.86	0.056	1.33	1.63	82.13
0.6	1.1	1.1	0.79	0.055	1.02	1.58	64.64
0.9	1.1	1.08	0.75	0.046	1.17	1.94	60.46
1.2	1.1	1.04	0.72	0.040	1.27	2.20	57.66
1.8	1.1	1.02	0.66	0.034	1.42	2.75	51.59

^a Composition of the feed—H₂SO₄: 47 g/l, Ni²⁺: 72 g/l.

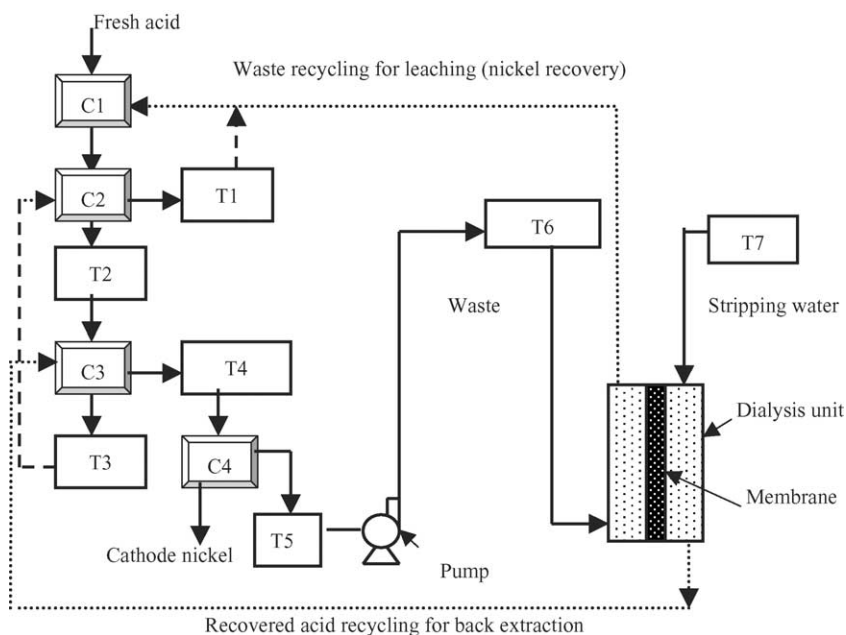


Fig. 6. The schematic flow sheet of simultaneous recovery of nickel and acid sulfate from nickel hydrometallurgy industries using diffusion dialysis. T1: raffinate aqueous tank; T2: extraction organic phase tank (nickel-rich phase); T3: regenerated organic phase tank; T4: nickel aqueous phase collection tank; T5: spent electrolysis waste liquor tank; T6: spent waste liquor head tank; T7: stripping water head tank; C1: leaching cell; C2: extraction cell; C3: back-extraction cell; C4: electrolysis cell.

increase in feed flow rate with constant flow ratio reduces the contact time for a specifically defined volume of feed and thus the acid recovery ratio and the nickel leakage ratio decrease. However, due to slowly decrease in concentration of feed, dialysis coefficients for both acid and nickel increase.

It has been noted that for all runs the volumetric expansion factor was controlled within 1.15 by using membrane of cross-linking time 8 h. As mentioned above, it is of crucial importance to control this factor in practical applications. In addition, processing ability and nickel leakage should also be considered if the acid recovery ratio is guaranteed. With these considerations and referring the results in Table 2, the practical operations can be optimized as: flow speed of feed = 1.2–1.8, flow ratio of water to feed = 1.05–1.1, cross-linking time \geq 8 h. At these optimum conditions, the volumetric factor can be controlled within 1.1, nickel leakage is less than 4% and the acid recover ratio can attain as high as 66–72%. The residual 28–34% acid in the waste can satisfy with the request of acidity in initial leaching process at the same time 96% nickel can be recycled by recycling the waste to leaching process as shown in Fig. 6. The recovered 66–72% acid can be recycled to the back-extraction stage by supplementation of some fresh acid.

Due to lack of original technology details, the process economics estimation has not been included in this discussion. However, as discussed above, an incorporation of a diffusional dialyser into nickel electrolysis industries demonstrates many advantages:

(1) Originally, the waste acid was directly neutralized with NaOH, the new technology consume no base.

- (2) The recovered acid can be recycled to the back-extraction step by addition of some new concentrated acid, saving acid in this step.
- (3) The waste can be recycled to the initial leaching stage by adjusting the acid concentration, valuable metal nickel and the residual acid are recovered.
- (4) The whole technology discards no waste (zero discarding), possessing significant environmental benefits apart from the attractive economical benefits. The only supplement is a diffusional dialyser which is very simple in operation and energy saving (the only energy needed is pumping the waste) and can run automatically without any maintenance.

4. Conclusions

Continued to our previous recovery of acid sulfate from titanium white pigment waste liquor and mixed acid from titanium leaching liquor, this paper reports the results of acid sulfate from electrolysis waste solution with relatively low acid concentration. The main difference of this system from the investigated ones is the deletion of acid from the waste feed and then recycling it to recover both acid and the valuable metal nickel. To satisfy with this new request, the membrane is surface-cross-linked with aqueous ammonium to control the volumetric expansion factor caused by the water osmosis. The results showed that the best membrane for the operation is the membrane cross-linked at least 8 h.

Pilot diffusional runs were conducted with this cross-linking membrane at various feed flow rate and flow rate ratio. The operational conditions were optimized with comprehensive considerations of volumetric expansion factor, processing ability, acid recovery ratio as well as the lost of nickel and the more recommendable conditions are as: flow speed of feed = 1.2–1.8 l/h, flow ratio of water to feed = 1.05–1.1, cross-linking time \geq 8 h. At these optimum conditions, the volumetric expansion factor can be controlled within 1.1, nickel leakage is less than 4% and the acid recover ratio can attain as high as 66–72%. The residual 28–34% acid in the waste can be recycled to initial leaching process. Therefore, the whole technology presents no discarding, possessing significant environmental benefits apart from the economical benefits.

Possibility of such dialyser application to practical nickel production is discussed. By incorporating a diffusional dialyser into nickel electrolysis line, the diffusate stream can be recycled to the back-extraction step and the waste stream (dialysate stream) recycled to the initial leaching stage to simultaneously recover acid and valuable metal nickel.

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