



Selective removal of halides from spent zinc sulfate electrolyte by diffusion dialysis



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ARTICLE INFO

Keywords:

Dechlorination
Zinc sulfate electrolyte
Diffusion dialysis
Permselectivity

ABSTRACT

Zinc metal is mainly produced by a hydrometallurgical process, in which zinc electrolyte is recirculated, and impurities especially halides are accumulated then, which have dreadful impacts on the process and product. Until now numerous efforts have been made to remove halides from the electrolyte, but none of them are fully satisfying, and it is still a big issue for the industry. As a conventional membrane technology, diffusion dialysis (DD) is originally designed to recover free acid from acid-salt mixture by concentration gradient. In this work, we proposed a novel process to selectively remove these halide impurities from the spent zinc electrolyte by DD directly. Significant Cl^- and F^- permselectivities over HSO_4^- are observed in this process. The removal efficiencies are as high as 50–70% and 30–42% for chloride and fluoride, respectively, while the zinc loss is less than 1%. The flow intensity in the current work is much higher than that in conventional DD, which reduces the overall cost immensely. The mechanism of this selective mass transfer is also studied intensively to understand influence of flow intensity, charge number and hydrated radii of ions on the permselectivity. The results here are not confined to provide a superior method to remove halide impurities for the zinc industry, but also extend new applications and deepen understandings for the well-established DD process in selective ion separation. This capability is very likely to become a new growth point and future direction for the DD process besides acid/alkali recovery.

1. Introduction

Approximately 80% of the total world production of metallic zinc comes from the hydrometallurgical roast–leach–electrowin process with zinc blend as typical starting materials [1]. The spent zinc electrolyte (also known as depletion or acidic electrolyte) after zinc electrowinning, mainly consisting of zinc sulfate and sulfuric acid, is used to leach the calcine and get neutral electrolyte for electrowinning again [1]. The biggest challenge of this route is the preparation of pure electrolyte, which ensures smoothing electrowinning, high-purity cathode zinc product and low energy consumption [1]. Most of the impurities, such as iron, cobalt, nickel, germanium, antimony, arsenic, chloride and fluoride, must be separated from the electrolyte circuit and maintained in low concentrations [1]. In conventional practices, it is difficult to get rid of the halides (typically chlorides and fluorides) from the solution circuit, and the main applied method is to remove them by roasting before the oxide leaching [1,2]. However, even after that they still build up in the electrolyte, because small amounts of halides

remain in the calcine. Halides are extremely harmful during the electrolysis. Specifically, chlorides corrode not only the stainless-steel equipment and pipes, but also the Ag–Pb anodes [2,3]. The uneven corrosion of anodes causes an increase in power consumption, besides the losses of expensive anode materials. What's more, the corrosion also aggravates the lead impurity in electrolyte and in zinc products, and then degrades the product qualities [3]. Fluorides cause zinc stick onto the aluminum cathode plate, which prevents the separation of zinc precipitate from the mother plate, and therefore this renders the electrolysis impossible [2].

Up to now, numerous efforts have been made to remove chlorides and fluorides from the hydrometallurgical circuit. (1) Halides can be removed as precipitations from neutral electrolyte before zinc electrolysis, such as AgCl [4], BOCl [5,6], Sn(OH)Cl [7] and CuCl [8–12] for chlorides and CaF_2 for fluorides, by dosage of appropriate chemicals. However, this approach is far from satisfying in practice. The AgCl , BOCl and Sn(OH)Cl methods have high efficiency in chlorides removal, but the operation cost is extremely high because of tedious recycling

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procedures as well as unavoidable material losses of expensive raw chemicals [4,7,13,14]. The economy is acceptable for CuCl precipitation method. However, the process is hard to handle because Cu^{2+} is likely to form instead of Cu^+ , which is easily soluble in water and therefore useless for chlorides removal at all [8]. In addition, metal zinc powder must be added to remove Cu^{2+} after the process, which increases the operational complexity and cost. (2) The chlorides can be oxidized and eliminated as Cl_2 gas from spent electrolyte (acidic electrolyte) by strong oxidants such as ozone [3,15] and PbO_2 [16]. Unfortunately, the utilization ratio of oxidants is normally low and the operation cost is high. In addition typically high concentration of Mn^{2+} ions (10–20 times higher than Cl^-) exist in the solution [3,15], which will consume much more oxidants and increase the operation cost further. (3) Ion exchange [17] and extraction [18,19] processes have also been employed for chlorides and fluorides removal from neutral electrolyte, but it suffers from low efficiency, high zinc loss and emission of huge amount of acidic waste water [17]. (4) A more reliable method to remove chlorides and fluorides from spent electrolyte is thermal evaporation [2], since HCl and HF is much more volatile than H_2SO_4 and sulfates. However, the cost is inappropriate because of superior corrosive-resistant equipment as well as high power consumption. Currently most of the zinc producers employ CuCl method for the chloride removal, although it has some unavoidable problems mentioned above. Meanwhile, regular partial discharge of the spent electrolyte is inescapable in order to eliminate the build-up of halides and make the whole electrolysis possible, even if it causes severe zinc loss and environmental issues.

In recent years, membrane processes have been rising for industrial applications, including the zinc electrolyte purification. Monovalent ions such as Cl^- and F^- are removed from divalent ZnSO_4 electrolyte by electrodialysis (ED), either with monovalent anion and monovalent cation permselective ion exchange membranes (IEMs) [20] or with common IEMs assisted by nanofiltration (NF) membranes [21]. However, these selective ED processes have not been widely accepted by the industry, mainly because of the high zinc loss as well as the expensive cost. On the one hand, in order to lower the power consumption of electrowinning, extremely high concentrated zinc electrolyte is utilized in the zinc industry, typically ~ 160 g/L Zn^{2+} and ~ 320 g/L for SO_4^{2-} ions. On the other hand, the permselectivities of monovalent IEMs [22] and monovalent-permeated NF membranes [23], usually decrease dramatically as the concentration of salt solution increases. Consequently, these membranes in ED processes are not able to provide sufficient selectivity. Therefore, developing a superior method is essential and urgent for the zinc industry. Diffusion dialysis (DD) is originally designed to recover free acid from waste acid by concentration gradient [24–26], the operation cost is low because it's spontaneous and consumes no external power at all [25]. Surprisingly, in the current work, it's found that halides impurities in the spent zinc electrolyte could be selectively removed by DD directly. The impurities are removed as HCl and HF along with small amounts of sulfuric acid, and significant Cl^- and F^- permselectivities are observed in the experiments with real spent electrolyte involved. The removal efficiencies are as high as 50–70% and 30–42% for chloride and fluoride, respectively, and the zinc loss is less than 1%. Different from traditional DD for sulfuric acid recovery, the ultimate purpose in this work is to remove Cl^- and F^- impurities with the least cost. The flow intensity is much higher (~ 5 times) here, which reduces the overall cost extremely. The results here not only provide a superior method to remove harmful halide impurities for the zinc industry, but also extend new applications and add original understandings for the well-established DD process in selective ion separation.

Table 1
Detailed specifications of TWDDA membranes.

Membrane	Wet thickness (μm)	IEC (meq/g dry membrane)	Water content	H^+ diffusion coefficient (m/h)	Separation factor $\text{H}^+/\text{Fe}^{2+}$
TWDDA standard	300–320	1.21	30.2%	$\geq 1.8 \times 10^{-3}$	≥ 15

2. Materials and methods

2.1. Materials

The anion exchange membrane (AEM, TWDDA standard) used in this work was obtained from Shandong Tianwei Membrane Technology Co., Ltd., China. The detailed specifications are listed in Table 1. Ion exchange capacity (IEC) and water content are measured in our lab, and all other data are provided by the membrane manufacturer. All chemicals used in this work were of analytical grade and obtained from Sinopharm Chemical Reagent Co., Ltd., China. Deionized water ($> 5\text{M}\Omega\text{ cm}$) was used during all tests. Real spent zinc electrolyte sample (50 L) was provided by a main zinc producers in south China. The sample was filtrated by $0.45\ \mu\text{m}$ membranes to remove all suspended solids before all tests.

2.2. Simulated DD tests

Various simulated feed solutions (marked in Fig. 1) were designed to evaluate the competitive permeation of Cl^- and SO_4^{2-} ions across the DD membrane. Batched DD tests were all carried out in a two-compartment cell [27] at room temperature ($25 \pm 0.5\ ^\circ\text{C}$). The same cell had been used to evaluate vanadium and proton permeability of membrane in our previous work [28]. The membrane was clamped between two cells, and the effective area was $12.0\ \text{cm}^2$. Initially the left feeding cell was filled with 50.0 mL of simulated feed solutions to mimic the spent zinc electrolyte, and the right recovering cell was filled with 50.0 mL of deionized water precisely. Solutions in both cells were circulated by a peristaltic pump at a flow of 10 mL/min instead of stirring. The DD tests lasted 2.0 h, and then solutions in both feeding and recovering cells were carefully collected and their volumes were measured. At last, the chemical compositions of both solutions were analyzed to evaluate the performance of the membrane.

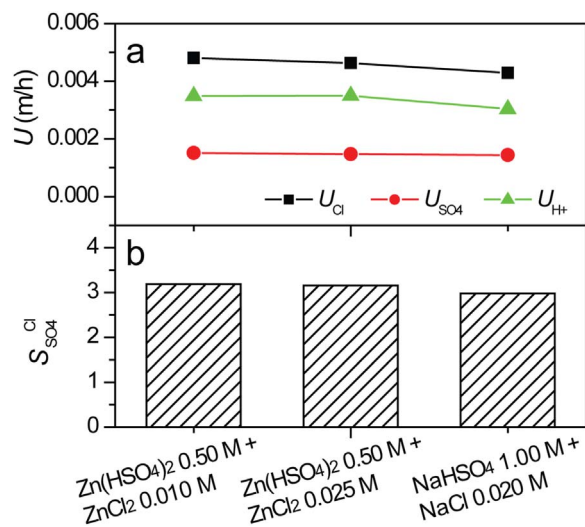


Fig. 1. (a) Dialysis coefficients of Cl^- , total SO_4^{2-} and total H^+ of TWDDA AEM in simulated feed solutions. (b) The corresponding separation factors of Cl^- over total SO_4^{2-} . Formulas of the simulated electrolytes are marked at the bottom.

2.3. Continuous DD tests with real spent electrolyte

A home-made DD dialyzer was used for halide impurities removal. The dialyzer was also equipped with home-made tortuous path flow spacer (260 mm length \times 130 mm width), and the scheme had been documented in our previous works [26,29]. In order to obtain higher flow velocities and better turbulence inside the dialyzer, the spacer thickness was reduced from 0.90 mm [26] to 0.70 mm in this work. The flow path geometry is 33 mm (width) \times 567 mm (length), with 187 cm² of effective area. The PP mesh net has a porosity of 72%, and projected shadow effective area of the spacer is 135 cm². The dialyzer consists of 3 hydraulic stages with a 170-cm flow path, which mimics the full-scale commercial DD dialyzer (~160 cm). There are 5 spacers each for both spent electrolyte and water streams in one stage. The stack was equipped with 27 anion exchange membranes (AEMs, TWDDA), 2 inter-stage PE sheets, and 30 turbulence accelerating spacers. The effective membrane area is 0.50 m² (187 cm² \times 27 pcs). The DD stack is operated in counter-current flow mode, and the electrolyte and water streams were delivered by a multi-channel metering pump (BT-100, from Baoding Longer Precision Pump Co., Ltd, China). All tests were conducted at 25 \pm 0.5 $^{\circ}$ C.

2.4. Analytical methods

Potentiometric titration (ZDJ-4B automatic titrator from INESA Scientific Instrument Co., Ltd, China) was utilized to analyze concentrations of ions in feed and sample solutions. The Cl⁻ concentrations were titrated with AgNO₃ standard solutions [26]. The total H⁺ concentrations (including free H⁺ and HSO₄⁻) were titrated with NaOH standard solutions [26]. Additionally, the total concentration of SO₄²⁻ (including SO₄²⁻, HSO₄⁻ and H₂SO₄) were titrated with Pb(NO₃)₂ standard solutions [30]. Fluoride ion selective electrode method was used to analyze the total F⁻ concentrations [31]. Concentrations of all metallic ions, including Zn²⁺, Mg²⁺, Mn²⁺, Na⁺ and K⁺, were all analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, PerkinElmer Optima 8000).

The overall dialysis coefficient U (m/h) of a given kind of ions is generally calculated by the following formula as in the literature [27,32]:

$$U = \frac{M}{At\Delta C_{avg}} = \frac{J}{A\Delta C_{avg}} \quad (1)$$

where M is the total amount of ions (mol) across the membrane, A is the effective area of membrane (m²), t is the time (h) for dialysis, J is the permeating flux (mol/h), and ΔC_{avg} is the logarithm average of concentration difference between the feeding and recovering chamber, which can be calculated as the following formula [27,32–34]:

$$\Delta C_{avg} = \frac{\Delta C_0 - \Delta C_t}{\ln [\Delta C_0 / \Delta C_t]} \quad (2)$$

where ΔC_0 and ΔC_t are the concentration difference before and after the DD operations. In batched simulated DD tests, Eq. (2) manifests to the following formula [27,33,34]:

$$\Delta C_{avg} = \frac{(C_f^0 - C_d^0) - (C_f - C_d)}{\ln [(C_f^0 - C_d^0) / (C_f - C_d)]} = \frac{C_f^0 - (C_f - C_d)}{\ln [C_f^0 / (C_f - C_d)]} \quad (3)$$

where C_f^0 and C_f are the ion concentrations (mol/m³) in the feeding chamber before and after the dialysis, C_d^0 (equals 0 when pure water is used as the initial recovering solution) and C_d are the ion concentrations (mol/m³) in the recovering chamber before and after the dialysis. Similarly, in continuous DD tests operated in counter-flow mode, ΔC_{avg} can be calculated as following [32]:

$$\Delta C_{avg} = \frac{(C_f^{in} - C_d^{out}) - (C_f^{out} - C_d^{in})}{\ln [(C_f^{in} - C_d^{out}) / (C_f^{out} - C_d^{in})]} = \frac{C_f^{in} - C_d^{out} - C_f^{out}}{\ln [(C_f^{in} - C_d^{out}) / C_f^{out}]} \quad (4)$$

where C_f^{in} and C_f^{out} are the ion concentrations (mol/m³) at the inlet and outlet of the feeding stream, C_d^{in} (equals 0 when pure water is used as the initial recovering stream) and C_d^{out} are the ion concentrations (mol/m³) at the inlet and outlet of the recovering stream. Separation factor S of one species A relative to another species B is defined as the ratio of dialysis coefficients of the two species [27]:

$$S_B^A = \frac{U_A}{U_B} \quad (5)$$

The recovery (favorable mass transfer) or leakage (unfavorable mass transfer) ratio of a species in continuous DD process is calculated by the formula as in our previous work [26] and other literature [32]:

$$\eta = \frac{C_d^{out} Q_d^{out}}{C_f^{in} Q_f^{in}} = \frac{C_d^{out} Q_d^{out}}{C_f^{out} Q_f^{out} + C_d^{out} Q_d^{out}} \quad (6)$$

where Q_f^{in} and Q_f^{out} are the flow (L/h) at the inlet and outlet of the feeding stream, Q_d^{in} and Q_d^{out} are the flow at the inlet and outlet of the recovering stream.

3. Results and discussion

3.1. Chemical compositions of spent zinc electrolyte

The detailed chemical compositions of real spent zinc electrolyte were obtained by ICP-OES and potentiometric titration which are listed in Table 2. The spent electrolyte is mainly composed of ZnSO₄, free H₂SO₄ and other impurities. Considering the dissociation equilibrium, H₂SO₄ exists as H⁺ and HSO₄⁻ in the electrolyte. Both of them are determined quantitatively in the final form of H⁺ by potentiometric titration, and therefore the result is described as total H⁺ concentration. The total H⁺ concentration is 1.63 M as H₂SO₄, indicating that 1.63 M Zn²⁺ (namely 106 g/L as Zn) had been electrodeposited as metallic zinc during electrowinning, which accords well with the zinc mass balance in the plant. The concentrations of Cl⁻, total F⁻ and Mn²⁺ are also similar to those in the literature [35].

3.2. Simulated DD tests

As shown in Table 2, in real spent electrolyte the total concentrations of SO₄²⁻ (3.8 M) and H⁺ (3.3 M) are nearly equal, so most sulfate ions are presented as HSO₄⁻ form. In some other literatures the Mg²⁺ concentration in spent electrolyte might be lower [35] and the concentrations of SO₄²⁻ and H⁺ would be closer. In order to evaluate the competitive permeations of Cl⁻ and HSO₄⁻ across AEM, various simulated feed solutions are designed and marked in Fig. 1. All of these solutions are composed of high concentrations of HSO₄⁻ and low concentrations of Cl⁻, which mimic the anion composition of real spent electrolyte. The total sulfate concentration in the simulated solution (1.0 M) is significantly lower than that in the real solution (3.8 M), because high ion concentration in feed solution causes severe water transport across the membrane and brings extra difficulty for the

Table 2
Detailed chemical compositions of real spent zinc electrolyte.

Ions	Concentrations	
	g/L	mol/L
Zn ²⁺	58.0	0.887
Mg ²⁺	27.6	1.137
Mn ²⁺	6.65	0.121
H ⁺ as H ₂ SO ₄	160.0	1.631
Na ⁺	2.15	9.35 \times 10 ⁻²
K ⁺	0.661	1.69 \times 10 ⁻²
SO ₄ ²⁻	366.8	3.82
Cl ⁻	0.540	1.52 \times 10 ⁻²
F ⁻	0.120	6.32 \times 10 ⁻³

volume measurement, which involves more errors. The simulated solution and deionized water were filled in the feeding cell and recovering cell during the simulated DD test, respectively. Dialysis coefficients of Cl^- , total SO_4^{2-} and total H^+ are calculated by Eqs. (1) and (3), and illustrated in Fig. 1a. It displays clearly that dialysis coefficients (including U_{Cl^-} , $U_{\text{SO}_4^{2-}}$ and U_{H^+}) of TWDDA AEM are very stable in the three simulated feed solutions. U_{Cl^-} , $U_{\text{SO}_4^{2-}}$ and U_{H^+} are about 4.6×10^{-3} , 1.5×10^{-3} and 3.5×10^{-3} m/h, respectively. Intriguingly, the value of U_{Cl^-} is much higher than $U_{\text{SO}_4^{2-}}$. According to Eq. (5), the corresponding separation factors of Cl^- relative to total SO_4^{2-} ($S_{\text{SO}_4^{2-}}^{\text{Cl}^-}$) are calculated in all three simulated solutions, which are up to 3.1, and presented in Fig. 1b.

3.3. New strategy for selective halides removal

In this electrolyte system, sulfate presents in the form of HSO_4^- . Generally, it is difficult to selectively separate anions for AEM, let alone the anions with the same charge number. Interestingly, the selective permeation of Cl^- relative to HSO_4^- is realistically observed in the simulated DD tests. As an ordinary AEM, TWDDA shows remarkable permselectivity to Cl^- over HSO_4^- . Based on this phenomenon, it is believed that the selective removal of Cl^- and other halide impurities from the acidic electrolyte by DD may be feasible. The process diagram for selective halide removal from zinc electrolyte circuit by DD is proposed and shown in Fig. 2. In this process, the main zinc electrolyte circuit is untouched, which involves minimal impact on the zinc hydrometallurgy. Part of the spent electrolyte circulates through the feeding cell of DD dialyzer, and another water stream passes through the recovering cell counter-currently. In the DD dialyzer, H^+ and anions (such as Cl^- , F^- and HSO_4^-) can permeate across the AEMs. Due to the Cl^- permselectivity over HSO_4^- , the Cl^- ions are enriched in the recovering stream and leave the hydrometallurgical circuit; meanwhile the loss rate of total SO_4^{2-} ions is restrained. Finally, in the feed stream the majority of halides are removed and a small fraction of sulfate is lost. In order to rebalance the sulfate amount, a concentrate H_2SO_4 makeup is necessary. Fortunately, in zinc hydrometallurgy process, concentrate H_2SO_4 is the main byproduct and the field price is very low. Therefore, the cost increase of the replenishment procedure is acceptable.

The main flaw of the new strategy is that only part of the halide impurities can be removed, however, it is not a big problem for the practical purposes. As the halide build-up is slow and small amounts of impurities are tolerable in the process, it is not necessary to remove all the impurities. For example, in the plant, which provided us spent electrolyte samples, the total electrolyte circulation is $4000 \text{ m}^3/\text{day}$, and the yield of metallic zinc is $400 \text{ t}/\text{day}$. Currently the plant chooses to discharge part of the spent electrolyte routinely ($100 \text{ m}^3/\text{day}$, namely 2.5% total electrolyte) to eliminate the chlorides build-up and keep the system running smoothly. The DD process shown in this paper

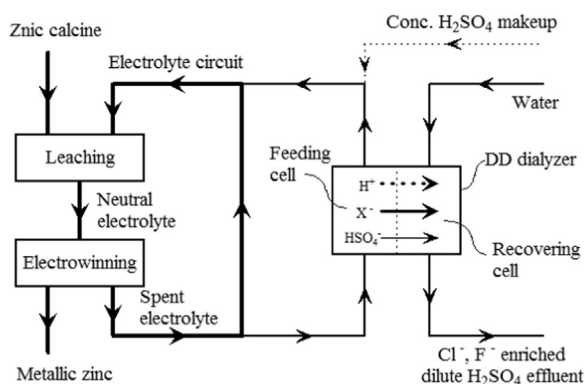


Fig. 2. Simplified process diagram for selective halides removal in zinc electrolyte circuit. X⁻ are halide ions such as Cl^- and F^- .

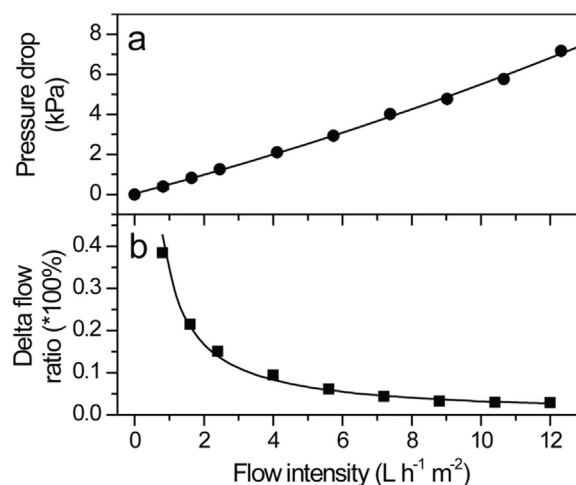


Fig. 3. (a) The pressure drops of the 3-stage DD dialyzer at different flow intensities. (b) The delta flow ratio of spent electrolyte and water streams at different flow intensities.

can meet the requirement and be a better alternative for halide removal in zinc hydrometallurgy.

3.4. Continuous DD results with real spent electrolyte

3.4.1. Pressure drop and water transfer in DD dialyzer

Since thin spacers (0.7 mm thickness), long flow path length (170 cm in total for 3 stages) and higher flow intensity were used in our continuous DD tests, the hydraulic characteristic of the dialyzer was investigated first. Usually, DD operates in a counter-current mode, which means that it is sensitive to pressures difference across membranes. The hydraulic pressure drops, at different flow intensities with pure water, were measured by digital differential pressure meter (GM510, Benetech) and plotted in Fig. 3a. The pressure drop is only 7 kPa at maximum flow intensity ($12 \text{ L h}^{-1} \text{ m}^{-2}$, corresponding flow velocity 1.48 cm/s in DD stack), which is acceptable because the burst strength of IEM is much higher (0.1–1 MPa). So our DD dialyzer is able to work at such high flow intensity.

Real spent electrolyte and pure water were pumped through the DD dialyzer at different flow intensities. After a steady state was achieved, the process parameters such as the inlet/outlet flows, detailed chemical compositions of all streams were analyzed and shown in Table S1 in Supporting information. At the beginning the set values of the inlet flow of water are equal to spent electrolyte. However, since the density and viscosity of the spent electrolyte are significantly greater than water, the inlet flow of the spent electrolyte becomes slightly lower. As shown in Table S1, at low flow intensity ($0.80 \text{ L h}^{-1} \text{ m}^{-2}$) the flows of the two liquids are almost the same. While at high intensity ($12.0 \text{ L h}^{-1} \text{ m}^{-2}$), the inlet flow of the spent electrolyte drops approximately 8%. The water transfer inside a DD dialyzer can be described as delta flow ratio, which is defined by the percentage of flow decrease in the recovering stream or the percentage of flow increase in the feeding stream [26]. According to the flow in Table S1, delta flow ratio can be readily calculated. Although the flow of spent electrolyte side is slightly lower at high intensity, delta flow ratios calculated respectively by the data of the feeding cell and recovering cell accord very well, which can be found in Fig. 3b and Table S1. This figure illustrates that at the low flow intensity, the water transfer in DD Dialyzer is extremely severe (38% at $0.8 \text{ L h}^{-1} \text{ m}^{-2}$), while along with the flow intensity rising the delta flow ratio drops sharply. For example, the delta flow ratio is less than 4% when the flow intensity is higher than $7.0 \text{ L h}^{-1} \text{ m}^{-2}$.

3.4.2. DD separation performance

The recovering ratio of total H^+ and leakage ratio of other ions can be calculated by Eq. (6) according to the chemical compositions and

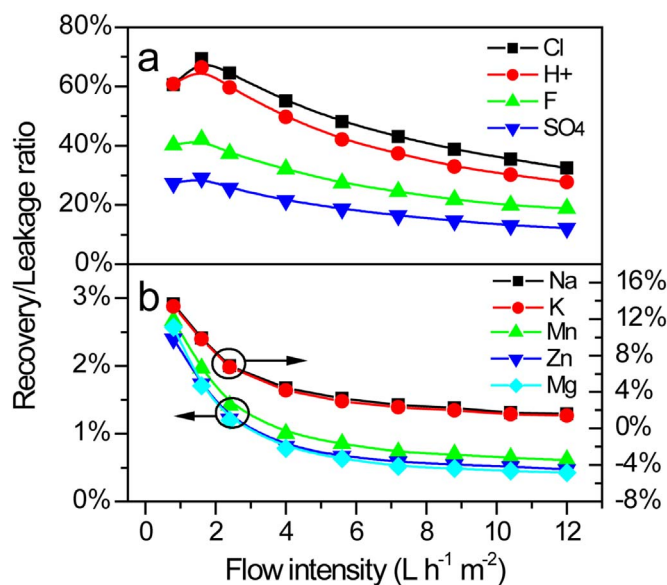


Fig. 4. (a) The recovery ratio of Cl⁻, total H⁺, total F⁻ and SO₄²⁻ ions; (b) The leakage ratio of metal ions including Na⁺, K⁺, Mn²⁺, Zn²⁺ and Mg²⁺ at different flow intensities.

flow rates of corresponding streams listed in Table S1, and the results are plotted in Fig. 4. The recovery ratio of H⁺ increases from 27.8% to 66.3% smoothly as the flow intensity decreases from 12.0 to 1.6 L h⁻¹ m⁻². However, it decreases slightly to 60.8% when the flow intensity reduces further to 0.8 L h⁻¹ m⁻², and this is due to large amount of water migrating across the membrane (delta flow ratio of 38% in Fig. 3b) from the recovering stream to the feeding stream and diluting the feed solution, which consequently diminishes the concentration gradient as well as the H⁺ transfer. The trends of leakage ratio for Cl⁻, total F⁻ and total SO₄²⁻ are very similar to that of H⁺, and they all have maximum values at flow intensity of 1.6 L h⁻¹ m⁻². At the same flow intensity, the leakage ratios of Cl⁻ and total F⁻ are significantly higher than that of total SO₄²⁻, which exhibits obvious permselectivity to chlorides and fluorides. This accords well with the results in simulated DD tests. The leakage ratios of metal cations (Na⁺, K⁺, Mn²⁺, Zn²⁺, Mg²⁺) monotonically increase as the flow intensity decreases from 12.0 to 0.8 L h⁻¹ m⁻² as shown in Fig. 4b, and the values are much lower than the data in Fig. 4a. Consequently, the concentrations are very limited in the recovering stream and the concentration gradient can be retained even after the feed stream is diluted by the water osmosis. That is the very reason why no inflection points are observed in these curves.

3.4.3. Anion permselectivity of membrane

The permeations of different anions (or different cations) across the membrane are not equivalent to each other, and it is termed permselectivity [22,32] between ions charged with the same sign. To some extent, the separation factor S in Eq. (5) does stand for permselectivity, and has been widely used in previous literature [27,33,34]. However, unlike batched tests, the dialysis coefficient U in Eq. (1) as well as separation factor S in Eq. (5) make little sense in continuously DD tests. First, the natural logarithm in Eqs. (3) or (4) will be not valid if C_d is equal or greater than C_f or C_f^0 . In simulated DD tests the mass transfer across membrane is usually insufficient, namely $C_f^0 \approx C_f > C_d$, in this situation both Eqs. (3) and (5) get reasonable and consistent results. However, in continuous DD tests (usually adopted in real practice) the recovery ratio of free acid (or leakage ratio of impurity ions, such as Cl⁻ in this study) is usually greater than 50%, which means $C_d > C_f$ and makes Eq. (3) invalid. Comparably, Eq. (4) can be used more extensively. However, in some cases the H⁺ concentration of recovered acid can even be higher than that of feed acid [26], namely $C_d > C_f^0$, which makes both Eqs. (3) and (4) invalid. Furthermore, the overall

dialysis coefficient U will be abnormally high and meaningless as the mass transfer across membrane becomes sufficient (when C_d increases to be close to C_f or C_f^0). The overall dialysis coefficient U of all ions are calculated by Eqs. (1) and (4) and listed in Table S2 in the supporting information. U_{Cl} , U_{SO4} and U_{H+} at high flow intensities correlate with those in simulated DD tests in Fig. 1a while dialysis coefficients at low flow intensities are either abnormally high or meaningless for total H⁺ and all anions.

In Eq. (1), the concentration difference of a specific species across the membrane is assumed as the only driven force for the mass transfer. This theory has been developed in dialysis processes such as hemodialysis, in which porous semi-permeable membranes are used and neutral molecules such as urea and creatinine permeate through the membrane. While in diffusion dialysis the situation is different because the ions are charged. One more principle must be strictly obeyed in the membrane and solution: electric neutrality. It will accelerate the movement of ions if the counter-ions have higher diffusivity in the membrane [32]. For example, in some applications acid recovery will be facilitated and its concentration in the recovery stream can be higher than the feed ($C_d > C_f^0$) when co-existed anions have higher diffusivity [26], and this phenomena is also known as up-hill transfer in donnan dialysis [36]. So, neither the overall dialysis coefficients in Eq. (1) nor the separation factors in Eq. (5) are reasonable in continuous DD tests with sufficient mass transfer (at low flow intensities). In our opinion, the recovery/leakage ratio in Eq. (6) is a more practical indicator of the removal performance for a specific kind of ions in continuous DD processes. A high ratio species has priority to permeate across the membrane and vice versa. The relative ratio between leakage ratios of two ions can be a more reasonable and straightforward gauge for permselectivity in this study (virtually identical with definitions in previous literature [22,32]):

$$P_B^A = \frac{\eta_A}{\eta_B} \quad (7)$$

where P_B^A represents the permselectivity of ions A relative to ions B, η_A and η_B are the leakage/recovery ratio of A and B, respectively.

The permselectivity of halide impurities (Cl⁻ and total F⁻) versus total SO₄²⁻ at different flow intensities have been calculated and plotted in Fig. 5. Even though the permselectivity of Cl⁻ versus total sulfate decreases from about 2.70 to 2.21 as the flow intensity decreases from 12.0 to 0.8 L h⁻¹ m⁻², all permselectivity are still significantly higher than 1.0, which means that Cl⁻ ions are more favorable than sulfates to permeate through AEMs in this process. The leakage ratios of both Cl⁻ and total SO₄²⁻ ions are low at high flow intensities and the concentration gradients for both species are retained. But as the flow intensities decrease, the leakage ratios increase and concentration gradients decrease for both. During this period Cl⁻ ions dominate in permeation

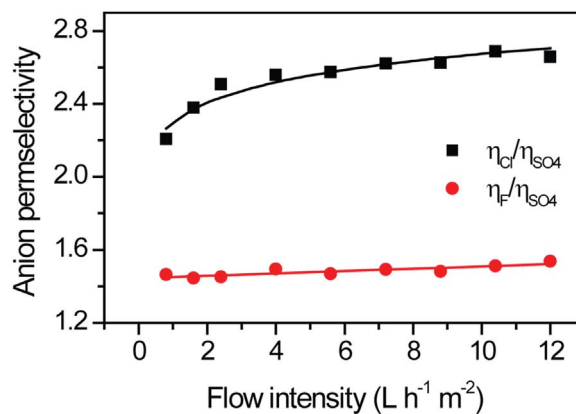


Fig. 5. Anion permselectivity (Cl⁻ and total F⁻) versus total SO₄²⁻ at different flow intensities. The permselectivity is presented as the ratio of leakage ratio of the two kinds of anions.

through the membrane, so the concentration gradient of Cl^- ions decreases rapidly, which conversely causes a slow-down in the Cl^- transfer and then a decrease of permselectivity, as shown in Fig. 5. The permselectivity of total F^- versus total sulfate is also significantly higher than 1.0, which means F^- outperforms sulfate in the transfer, too. While compared with Cl^- (2.21–2.70), the permselectivity of total F^- (1.44–1.56) is relatively lower and it is probably caused by the partial dissociation of HF in acidic aqueous solutions. The mobility of H^+ in the membrane is high, which will accelerate the transport of anion impurities such as free Cl^- and F^- ions. During this process, part of the fluorides present as non-charged HF molecules, so the acceleration is not as strong as Cl^- ions. In the current work, nearly all sulfates exist as HSO_4^- ions in the spent zinc electrolyte, and the permselectivity of halide impurities is not caused by the charge number differences, since all halide and HSO_4^- ions have the same electric charge number. However, HSO_4^- ions have larger hydrated radii than Cl^- ions in aqueous solutions due to their superior affinity with H_2O molecules, which may hinder their permeation across the AEM. That is probably the origin of this interesting permselectivity in this work. Since TWDDA is an ordinary commercial AEM for DD applications, other DD AEMs (such as ASTOM AFX/AFN) may exhibit similar permselectivity. In conventional DD process, the prime goal is to recover as much free acid as possible from the feed stream, and the recovery ratio of free acid is usually $> 85\%$ [26]. In that situation, the flow intensity is quite low, which would diminish the anion permselectivity (as shown in Fig. 5). Therefore, based on the current discussion, it is not difficult to understand why permselectivity is observed less in conventional DD process.

3.4.4. Competitive permeation of co-existent cations

The leakage ratios of all metal cations, such as Na^+ , K^+ , Zn^{2+} , Mg^{2+} and Mn^{2+} , are much lower than the recovery ratio of total H^+ ions (shown in Fig. 4). Namely, the AEMs in this study are far more selective to H^+ , which is expected in a DD process. All of these metal cations in spent zinc electrolyte are well rejected, and it is essential to retain the valuable metal resource, especially zinc. At different flow intensities the leakage ratio of metal cations with the same charge number are almost exactly the same, such as Na^+ and K^+ , as well as Mn^{2+} , Zn^{2+} and Mg^{2+} . The leakage ratios of mono-valent cations (Na^+ and K^+) are significantly higher than those of divalent cations (Zn^{2+} , Mg^{2+} and Mn^{2+}). The leakage ratio of Na^+ and K^+ is nearly identical at all flow intensities, which increase from 1.5% to 13.5% as the flow intensity decreases from 12.0 to $0.8 \text{ L h}^{-1} \text{ m}^{-2}$. The leakage ratio of divalent cations is also similar at all flow intensities, which increase from 0.5% to 2.5% as the flow intensity decreases from 12.0 to $0.8 \text{ L h}^{-1} \text{ m}^{-2}$. The permselectivity of mono-valent metal ions versus divalent metal ions is straightforward and makes sense. Mono-valent cations not only have smaller hydrated ion radii, but also feel lower electric repulsion from the positive charged AEM matrix. Both of the two effects make them much easier to leak through the membrane. As a result, part of the mono-valent cations (1.5–13%) can be selectively removed in this process, which is favored to improve the electrolyte quality.

3.5. Cost analysis

The cost of halides removal in this study mainly consists of capital cost, chemical cost and the disposal cost of effluent. The total dechlorination capacity needed in the plant can be estimated by the chlorine mass balance. As previously described, the total electrolyte circulation is $4000 \text{ m}^3/\text{day}$, and part of the spent electrolyte ($100 \text{ m}^3/\text{day}$) has to be discharged to eliminate the chlorides build-up. The normal concentration of Cl^- is 540 mg/L (listed in Table 2) in electrolyte, so the expected total dechlorination requirement is $54,000 \text{ g/day}$ for the plant. Furthermore, the dechlorination capacity of the lab-scale DD dialyzer is determined by the product of leakage ratio of Cl^- ions and the inlet flow of the spent electrolyte. The scale-up factor, as well as the

total membrane area and the total capital cost needed in a full-scale system, can be calculated from these requirements and capacity data. Detailed procedure to determine the capital cost is provided in Table S3 in Supporting information. The long-term stability of DD membranes (especially for TWDDA) is well-proven in industrial applications such as H_2SO_4 , HCl and HF reclamations from various acid-salt mixtures. A reasonable long life-span (5-year for typical acid recovery) of the DD system is expected in this work. Concentrated H_2SO_4 is needed as makeup to balance the sulfate in electrolyte circuit as previously mentioned, and its amount can be calculated from the concentration and the flow of dilute H_2SO_4 effluent (the recovery acid stream in DD process). Zinc plants generate lots of SO_2 gas during the roasting process, which is utilized as raw material for H_2SO_4 byproduct. Therefore the internal price of H_2SO_4 is much lower than that in commercial markets, which makes the current process more economically efficient. The chemical cost of H_2SO_4 makeup at different flow intensities is also calculated by procedure in Table S3. Meanwhile, the DD dialyzer consumes pure water and converts it to dilute H_2SO_4 enriched with halide impurities, and extra costs are needed for the pure water and the disposal of dilute acid. Fortunately, zinc plants use water in gas scrubbers to cool and remove HCl impurity from the roasting fumes, and also generate contaminated acid (5–10% H_2SO_4 with $\sim 3000 \text{ mg/L Cl}^-$). The dilute H_2SO_4 effluent ($\sim 300 \text{ mg/L Cl}^-$) in this new process is much less polluted than the contaminated acid, which can be used in gas scrubbers instead of water. Namely, this water can be used in the DD process firstly as a receiving stream, and then used again in a gas scrubber. So, disposal cost of the DD effluent is low in this study, which is estimated at $\$1.0/\text{m}^3$ (cost to compensate the extra operations, also available in Table S3).

The detailed calculation procedures of the process parameters and costs are all listed in Table S3 in the Supporting information, and the corresponding results are plotted in Fig. 6. Volumetric expansion of a feed stream is a common issue in the DD process and it may result in the whole hydrometallurgical process not being sustained. Because the overall ion strength in the feed stream is usually higher than that in the recovering stream, water molecules always permeate from recovering cells (water side) to feeding cells by osmosis. Furthermore, H_2SO_4 makeup involves extra volume expansion. The amount of water transfer in DD dialyzer and concentrated H_2SO_4 makeup can both be calculated by the process data, which have been well recorded in Table S3 of supporting information. The total volume expansion in a full plant at different flow intensities are calculated and plotted in Fig. 6a, which is low ($< 20 \text{ m}^3/\text{day}$) at high flow intensities ($\geq 4.0 \text{ L h}^{-1} \text{ m}^{-2}$) and increases rapidly as the flow intensity decreases to $0.8 \text{ L h}^{-1} \text{ m}^{-2}$

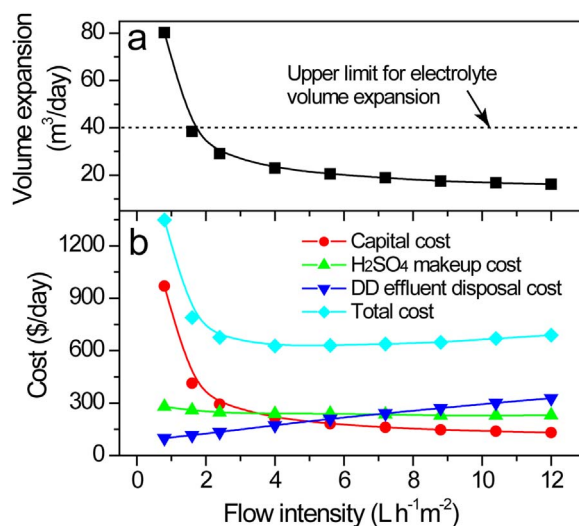


Fig. 6. (a) Total volume expansion of zinc electrolyte, and (b) Cost estimations at different flow intensities in full-scale plant.

(73.4 m³/day). The total zinc electrolyte circulation is 4000 m³/day in the plant, and the volume shrinks ~1% (namely 40 m³/day) in the electrowinning process because of water evaporation. So, the maximum volume expansion is 40 m³/day in the whole process, which is also marked in Fig. 6a. It's clear that this restraint is fulfilled when the flow intensity is higher than 1.6 L h⁻¹ m⁻².

The cost of H₂SO₄ makeup remains stable, and only a slight decrease is observed in Fig. 6b, which corresponds well with the anion permselectivity data. As shown in Fig. 5, the permselectivity of Cl⁻ versus total SO₄²⁻ increases slightly, while the total dechlorination requirement of the plant is constant (54,000 g/day), so the loss of sulfate and then the cost of H₂SO₄ makeup decrease slightly. Moreover, the dechlorination capacity of a specific area of membrane (mg h⁻¹ m⁻²) increases as the flow intensity increases, which means less membrane will be used in the stack, so the capital cost decreases rapidly (shown in Fig. 6b). As the flow intensity increases, the concentration of Cl⁻ in effluent decreases and more DD effluent is needed to get rid of the Cl⁻ impurities. Consequently, the effluent disposal cost increases accordingly. The total cost varies non-monotonically with the flow intensities, which decreases rapidly from 0.8 to 4.0 L h⁻¹ m⁻², and then increases slightly from 4.0 to 12.0 L h⁻¹ m⁻². The optimal flow intensity is 4.0 L h⁻¹ m⁻² in this study, and the total cost is 626.3 \$/day. In this scenario, 179.5 m³/day of spent zinc electrolyte is purified by DD, and 55.1% of Cl⁻ ions are removed from the electrolyte. The normalized cost is 3.49 \$/m³ for the spent electrolyte, which is much more cost-effective than current available purification methods.

3.6. Influence of chlorides concentration and coexisting cations

The influence of chlorides concentration on the purification performance is investigated in both simulated and real spent electrolyte solutions. As shown in Fig. 1, when the Cl⁻ concentration increases from 10.0 mM (mmol/L) to 25.0 mM in simulated electrolyte, the overall dialysis coefficients of both Cl⁻ and total SO₄²⁻ are virtually kept unchanged. This is because Cl⁻ ions only take a very small portion in all anions, and the overall mass transfer characteristics are almost the same. The amounts of Cl⁻ ions permeate across the membrane are positively correlated with the concentration difference of Cl⁻ between two sides, while the removal efficiency (leakage ratio) remains stable. A zinc electrolyte with higher Cl⁻ ions (2000 mg/L), obtained by adding NaCl solid into the real spent electrolyte, has also been purified by the continuous DD dialyzer in the lab at the optimal flow intensity. The test results further reveal that the leakage/recovery ratios of all ions are unchanged. To sum up, the dechlorination capacity of a DD dialyzer will increase proportionally as the Cl⁻ concentration in zinc electrolyte increases, and the purification cost will decrease relevantly because a smaller membrane area is needed for the plant. Other metal cations such as Mg²⁺, Mn²⁺, Na⁺ and K⁺ usually exist in zinc electrolyte. Also as shown in Fig. 1, after Na⁺ ions substitute all Zn²⁺ in the electrolyte, the dialysis coefficients of Cl⁻ and SO₄²⁻ are still stable, which means that the metal cations have minor impacts on the DD process. In other words, these cation impurities do no harm to the purification in this study.

3.7. Perspective of DD process

In recent years DD has become one of the best available technologies for the reclamation of free acid from acid-salt mixtures [25,26]. However, it faces big challenges for further popularity mainly in the economical aspect. Most of the widely used inorganic acids, such as HCl and H₂SO₄, are extremely low in prices, because they are by-products of other chemical manufacturing processes and the global supply is significantly higher than the demand. Therefore, it is hard to be profitable for DD to treat these acids. However, as demonstrated in this work, DD has the potential to separate different anions or cations in

highly concentrated and complicated solutions, which has still not been achieved by other competitive processes until now. Further efforts are needed to enhance this permselectivity by developing superior membrane materials and proposing novel process architectures. This capability would certainly enhance growth and lead future research for the well-established DD process.

4. Conclusions

In this work, a novel purification process is proposed to remove halide impurities from the spent zinc electrolyte by a conventional DD process. The findings show that the halide impurities such as Cl⁻ and F⁻ are more likely to permeate across the AEMs than sulfate (mainly HSO₄⁻). The overall dialysis coefficient of Cl⁻ is 3.1 times that of sulfate in simulated tests, and the leakage ratio of Cl⁻ is about 2.21–2.70 times that of sulfate in continuous DD tests. Eventually, with this process, halide impurities can be selectively removed from the zinc electrolyte. The only price to be paid is the loss of some H₂SO₄, which is the very by-product of the plant. The removal efficiency is not affected by the Cl⁻ concentration or the existence of other metal cations besides Zn²⁺. At the optimal flow intensity (4.0 L h⁻¹ m⁻²) 55.1% of the Cl⁻ ions can be removed, and only 21.5% of sulfates are lost. The normalized purification cost is only 3.49 \$/m³ for the spent electrolyte (55.1% Cl⁻ removal), which is more cost-effective than current CuCl methods. The results presented here not only provide an excellent method for eliminating the harmful halide impurities in the zinc industry, but also outline new applications and improve the understanding of the well-established DD process in the field of selective ion separation.

Acknowledgements

The authors are grateful for financial support by the National Natural Science Foundation of China (21673159 and 21203139) as well as the Xinmiao Talent Planning Foundation of China (2016R426057).

Appendix A. Supporting information

Supplementary tables as Excel worksheets, including detailed process parameters during the continuous DD tests (Table S1), dialysis coefficients in continuous DD tests (Table S2), and detailed procedure for the cost estimation (Table S3). Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.memsci.2017.05.009>.

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