A circular process for phosphoric acid plant wastewater facilitated by selective electrodialysis

Lior Monat, Wei Zhang, Alice Jarošíková, Hao Haung, Roy Bernstein[*] and Oded Nir[*]

Zuckerberg Institute for Water Research, The Jacob Blaustein Institutes for Desert Research, Ben-Gurion University of the Negev, Sede-Boqer Campus, 8499000, Israel

*Corresponding authors

Emails: odni@bgu.ac.il ; royber@bgu.ac.il

Corresponding author mailing address:

Dr. Oded Nir[*]: Zuckerberg Institute for Water Research, The Jacob Blaustein Institutes for Desert Research, Ben-Gurion University of the Negev, Sde Boqer Campus, Midreshet Ben-Gurion, Israel. Fax: +972-(0)8-656-3503, Tel: +972-(0)8-656-3540, e-mail: odni@bgu.ac.il.

Dr. Roy Bernstein[*]: Zuckerberg Institute for Water Research, The Jacob Blaustein Institutes for Desert Research, Ben-Gurion University of the Negev, Sde Boqer Campus, Midreshet Ben-Gurion, Israel. Tel: +972-(0)8-656-3534, e-mail: royber@bgu.ac.il.

Synopsis

An energy-efficient ion-selective membrane process can neutralize acidic industrial wastewater and recover valuable resources

TOC image

ABSTRACT

Phosphoric acid production generates large volumes of industrial wastewater that cannot be treated efficiently by existing processes because of its low pH and high precipitation potential. At present, the wastewater is generally stored in evaporation ponds that are prone to breaches, leakage, and flooding. We developed an alternative three-step process for the treatment of phosphoric acid wastewater including selective electrodialysis, reverse osmosis, and neutralization. Testing the process with synthetic wastewater yielded promising results. An exceptional Na/Ca selectivity (up to 18.3 was observed in low-pH electrodialysis, enabling the separation of concentrated H_2SO_4 without gypsum scaling. Sulfate removal from the electrodialysis diluate prevented scaling in the subsequent high-recovery (>90%) reverse osmosis step, generating high-quality water. A final reaction between the reverse osmosis concentrate and natural phosphate rock enabled P recovery and neutralization of remaining acidity. The electric-power requirement of the process was estimated to be 4.4 kWh per m^3 of wastewater, from which 0.78 m^3 of clean water, ~3 kg H_2SO_4, and ~2.5 kg P were recovered. Overall, lab-scale results indicate that this process would be a sustainable and techno-economically viable solution for the treatment of hazardous wastewater byproducts of the phosphoric acid industry.

Introduction

The phosphoric acid (PA) industry is essential for global food security, but it generates toxic and challenging wastewater (WW) of environmental concern. PA is the primary P source of the chemical fertilizer industry [1]. With an estimated 46 million tonnes (Mt) of global demand in 2019/20 and steady growth of P output, global PA fertilizer production is expected to reach ~52.5 Mt in 2025/26 [2]. PA is currently produced mainly by the "wet process" utilizing concentrated H_2SO_4 to dissolve phosphate ore comprising mainly hydroxy/fluor-apatite [3]. Large volumes of water are required to facilitate the dissolution reaction and other tasks such as slurry transport, washing, and hydraulic pressurization [4]. The resulting WW is a highly acidic (pH 1.5–2) mixed electrolyte solution comprising mainly phosphate, sulfate, fluoride, hydronium, sodium, calcium, and magnesium ions; organic matter may be also present depending on rock composition [5].

At present, WWs are usually stored in evaporation ponds [6], and this approach incurs the risk of environmental contamination owing to unexpected accidents such as pond leakage in response to rain-induced overflow (e.g., Florida, 2004 [7]), structural failures (e.g., Israel, 2017 [8]), or percolation to vital groundwater reserves. The acidity may be neutralized with lime or calcite [9–11], but the resulting high salinity still poses a risk. Substantial reduction of the volume of PA industry wastewater (PAIWW) would reduce the environmental risk, but reduction of the volumes involved is technologically challenging. The high WW mineral content confers a high chemical-scaling potential that prevents the use of single concentration methods such as reverse osmosis (RO), thermal distillation, or electrodialysis (ED). Furthermore, supersaturation with fluorite (CaF_2) and near-saturation with gypsum ($CaSO_4.2H_2O$) means that these minerals precipitate with further concentration. Novel processes beyond current practice are thus needed for the challenge of concentrating PAIWW [12]. In addition to volume reduction, the transition to circular and cleaner production in the chemical industry demands the recovery of resources from waste streams [13–19].

Studies on PAIWW treatment are scarce, despite its great volume and impact. The integration of neutralization and membrane processes for treating PAIWW has been of growing interest in recent years. Battistoni et al. [20,21] suggested that membrane filtration processes are the only treatment methods that are able to meet regulatory requirements, despite their complex multistage structure, operational problems (due to scaling), and high costs. In examining pre-treatment methods, they concluded that the optimal pre-treatment step involves the use of $Ca(OH)_2$ for neutralization and gypsum precipitation; in testing with additional nanofiltration and RO filtration steps in a pilot facility, the process achieved a limited quantity of permeate with increased treatment cost. Similarly, Al-Harahsheh et al.[4,22] applied selective neutralization–precipitation pre-treatement involving the addition of $Ca(OH)_2$ (as also reported by Gouider et al.[23]). Nevertheless, there remains a lack of highly circular processes that maximize resource recovery while minimizing environmental risk. Innovative integration and

modification of mature technologies may promote advanced treatment processes that are applicable to PAIWW and other industrial WWs, as described in this contribution.

Figure 1. Suggested three-step treatment process for phosphoric acid industry wastewater, comprising selective electrodialysis (ED), reverse osmosis (RO), and neutralization with phosphate rock. The normalized flow rate (with respect to feed flow rate, Q) and major dissolved components appear next to each process stream. The process recovers H_2SO_4, clean water, and P while reducing wastewater volume by 93%. The remaining brine is not acidic and can be reused as process water or further treated by evaporation.

Here we describe a circular three-step process for the treatment of PAIWW. The first step involves ED with monovalent selective cation-exchange membranes, with this being followed by RO and precipitation (Figure 1). In the ED process, most divalent cations (e.g., Ca^{2+} and Mg^{2+}) remain in the diluate stream while the monovalent cations (e.g., H^+ and Na^+) migrate to the concentrate stream. This selective monovalent separation prevents scaling (mainly by gypsum, $CaSO_4.2H_2O$) in downstream RO processes. After the ED step, the diluate stream continues to RO filtration, while the ED concentrate comprising mainly H_2SO_4 is used for PA production. The low-SO_4^{2-} ED diluate is further treated high recovery RO, producing high-quality water while significantly concentrating the WW. In the final step, the RO concentrate is further neutralized with mined phosphate rock, enabling the recovery of process water. The overall process significantly reduces WW volumes and associated environmental risks, land footprints, and cost. The process also recovers clean water, H_2SO_4, and P, thus contributing to the economy and sustainability of the plant.

Here we describe our testing of the process with synthetic solutions based on PAIWW composition and discuss the process energy consumption and techno-economic feasibility.

Materials and methods

Materials

Experiments involved deionized water (0.1–20 $\mu S\ cm^{-1}$; TREION™, TREITEL Chemical Engineering Ltd, Israel); NaOH and HCl (J.T.Baker, Poland); H_2SO_4 (96%) and $Na_2HPO_4.H_2O$ (Carlo Erba, France); H_3PO_4 (85%, Biolab-chemicals, Israel); and anhydrous Na_2SO_4, $MgSO_4.7H_2O$, K_2SO_4, $CaCl_2.2H_2O$,

and NaF (Merck, Germany). Membranes, ED stack, and the ED 64004 cell were from PCCell GmbH, Germany. The properties of the ED membranes are listed in Table S1.

Selective cation-separation ED for acidic wastewater treatment

Figure 2. Schematic illustration of the ED experimental setup and membrane configuration. PC VK as cation-exchange membrane (CEM) and PC SA or PC Acid 100 as anion-exchange membrane (AEM) which construct the diluate compartment (depletion of ions) and concentrate compartment (concentrating the ions). All ED process streams (diluate, concentrate abd electrodes solution) are recycled to their respective chambers (batch mode).

All batch ED experiments with synthetic WW involved a BED 1–4 bench-scale laboratory electrodialyser (PCCell GmbH, Germany) connected to a DC power supply (HCS-3202, Manson). Two commercially available stacks were used with five cell pairs of monovalent selective cation-exchange membrane (MVS-CEM, PC VK), differing in their anion-exchange membranes (AEMs, PC SA or PC Acid 100), as shown in Table S1. The experimental setup and membrane configurations are depicted in Figure 2. In most experiments, the synthetic WW contained fluoride, so all equipment such as feed vessels and analytical instruments were polypropylene/polyethylene-based, as appropriate for handling fluoride solutions. The stack spacers were also replaced with polypropylene (1 mm thick) spacers. During the experiments, the current, voltage, and electrical conductivity (EC) were monitored using the inbuilt software of the ED system, and an external pH meter and thermometer (Orion Dual Star, Thermo Fisher Scientific, USA) were used for pH and temperature measurements. Concentrations of major cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) and total P, S, and Cl^- were determined by inductively coupled plasma–atomic emission spectroscopy (ICP–AES; SPECTRO ARCOS, SPECTRO Analytical Instruments GmbH, Germany). The Cl^- and F^- concentrations were determined by ion chromatography (IC; Dionex IonPac AS19 4 x 250 mm column, Thermo Fisher Scientific, USA).

Table 1: Average initial concentrations of diluate species in experiments 1–6 (low recovery) and 7–8 (high recovery).

Conc. ± SD (ppm)	Ca	K	Mg	Na	Tot P	SO₄	F	Cl
Exp. 1–3 pH ~1.5	144 ± 3	205 ± 6	221 ± 5	2658 ± 41	6219 ± 76	6070 ± 79	114 [a, b]	216 [a, b]
Exp. 4–6 pH ~2	70 ± 1	199 ± 3	206 ± 2	4840 ± 95	5874 ± 9	5954 ± 31	66 [a]	110 [a]
Exp. 7–8 pH ~1.5	134 ± 8	181 ± 8	189 ± 9	2266 ± 121	6061 ± 220	5570 ± 264	-	235 ± 9 [c]

[a]Approximately ±4% error in F and Cl concentrations. [b] F and Cl initial concentrations were not available in all experiments and are based on experiment 3 only. [c]Concentrations of all species were from ICP–AES analyses, including Cl (after verifying results by parallel IC analysis).

Three sets of experiments were undetaken. Experiments 1–3 and 4–6 were carried out using initial pH values of 1.5 and 2.0, respectively. Diluate and concentrate Solutions were prepared using the salts and acids specified above, totalling 1 L volumes (for 50% diluate recovery). In all of the experiments, 0.25 M Na_2SO_4 was used as an electrode-rinse solution. The initial concentrations are listed in Table 1. The third set of experiments (7–8) was undertaken with >80% higher recovery ratio (diluate to concentrate volume ratio) by circulating 2.2 L flouride-free solution in the diluate compartment and 0.4 L 10 mM H_2SO_4 in the concentrate compartment (Table 1). The applied voltages in all experiments were in the range of 4–30 V; flow rate and pressure ranges were 20–35 L h⁻¹ and 50–100 mbar, respectively (barring 360–390 mbar in experiment 1 and 300–360 mbar in experiments 7 and 8); the temperature was maintained at 25°C ± 1.5°C using an external chiller. Based on EC reduction, samples were collected according to desalination degree (0%–50%; experiments 2, 7, 8: 52%–55%). The experimental conditions are summarized in Table 2.

Table 2: Details of synthetic wastewater experiments. The electrode solution was 0.25 M Na_2SO_4 and the initial volume was 1 L in all compartments

Exp. No.	Membranes	pH	Applied Voltage (V)	Average Flow rate diluate/ concentrate (L h⁻¹)	Experimental Time (h)	Final volumes diluate/ concentrate (L)
1			12	30/20	24	0.93/1.09
2		1.5	18	30/35	24	0.92/1.10
3	PC SA,		30	30/35	12	0.97/1.05
4	PC VK		18	30/35	35	0.89/1.14
5		2.0	24	30/35	28	0.92/1.11
6			30	30/35	23	0.91/1.09
7	PC Acid 100,	1.5	4	30/30	7.2	2.13/0.45
8	PC VK		8	30/30	1.9	2.13/0.37

.

Current efficiency and electric-power consumption in ED experiments

The specific electric-energy consumption (SEC, kWh per m^3) was calculated by Eq. (1):

$$SEC = \frac{\hat{I}Ut'}{1000V} \qquad (1)$$

where $\hat{I}$ is average current ($\hat{I} = \frac{1}{t}\int_0^t I(t)dt$) (amp), U is applied voltage, and t' is time (h).

RO experiments

RO experiments involved a cross-flow filtration system (Figure S1) including a CF042 filtration cell (Sterlitech, USA) and ESPA1 RO polyamide membrane (Hydranautics, USA) as described previously [24]. The experiments were undertaken at constant pressure (~60 bar) and temperature (25°C ± 2°C) with a 90 L h^{-1} feed flow rate (cross-flow velocity 0.28 m s^{-1}). Permeate flux was monitored by a flow meter (μ-FLOW, Bronkhorst, The Netherlands). Experiments were undertaken once with a closed-loop configuration where the permeate flux was returned to the feed, and once with an open-loop configuration where the permeate was collected, with the feed content changing with filtration time. In both cases, the membranes were first compacted for 24 h by filtering DDW at 60 bar and NaCl solutions of similar EC at 60 bar. Feed and permeate pH and EC were monitored frequently, and samples were collected every few hours for ICP–AES analysis. On completion of the experiments, the membranes were removed from the filtration cell, washed gently, and dried before analysis. The membrane surface (coated with Au) was imaged by scanning electron microscopy (SEM; Jeol JSM-IT200, Japan) and the surface was analyzed by SEM–energy-dispersive spectroscopy (SEM–EDS) and X-ray diffraction (XRD; Panalytical B.V., Almelo, The Netherlands) using a diffractometer with Cu Kα1 radiation (PANalytical Empyrean, The Netherlands).

Neutralization of acidic RO concentrate by phosphate rock

Batch leaching experiments involved different phosphate rock loadings in synthetic RO concentrate (0, 0.5, 1, 2, 6, or 9 g per 10 mL). The RO concentrate had a pH of 2.4, specific conductivity of 55 mS cm^{-1}, and contained 40.9 g L^{-1} P, 25.3 g L^{-1} Na, 3.18 g L^{-1} S, 2.50 g L^{-1} Mg, 2.37 g L^{-1} Cl, 1.78 g L^{-1} Ca, and 1.60 g L^{-1} K as made up from CaCl$_2$.2H$_2$O, K$_2$HPO$_4$, Na$_2$HPO$_4$.2H$_2$O, MgSO$_4$, MgCl$_2$.6H$_2$O, Ca(OH)$_2$, H$_3$PO$_4$ (85%), H$_2$SO$_4$ (96%), and ultrapure water (Millipore® Synergy® with UV, Germany). The grain size of natural phosphate rock was <500 μm (confirmed by sieving). The main mineral phases of the phosphate rock were calcite (CaCO$_3$), hydroxyapatite (Ca$_5$(PO$_4$)$_3$OH), and quartz (SiO$_2$), with major oxides CaO (58 wt.%), P$_2$O$_5$ (28 wt.%), Na$_2$O (0.4 wt.%), MgO (0.2 wt.%), and Fe$_2$O$_3$ (0.1 wt.%).

Leaching experimens were undertaken in duplicate in 50 mL conical polyethylene centrifuge tubes (GBO, Germany). Individual tubes (67 in total) were placed on a horizontal shaker (KOS-3333, MRC, UK) for different times (15 min to 48 h) at room temperature (22°C ± 2°C) before centrifugation at 3000 rpm (Sigma 4K15, Sigma Zentrifuges, Germany) and filtration of supernate with Millex® 0.22

μm syringe filters. pH and specific conductivity were measured by multimeters (Thermo Scientific, USA) immediately after collection. Elemental compositions of both solid and liquid samples, including procedural blanks, were determined by ICP–AES. Solid samples were pre-treated by digestion of 0.2 g sample in 10 mL 70 % HNO_3 at 175°C, based on US EPA method 3051A [25], using a microwave digestion system (ETHOS UP, Italy). Digestion efficiency was determined by processing of US National Institute of Standards and Technology (NIST) standard reference material (SRM) 694 (Western phosphate rock). The phase composition of ground rock was determined by XRD analysis.

Results and discussion

Monovalent-selective ED of synthetic acidic wastewater

To investigate the application of selective cation-separation ED to acidic WW from the wet sulfuric-acid process for PA production, sets of experiments at pH ~1.5 and ~2.0 and at 12–30 V applied voltage were undertaken, comparing the evolution of species concentrations and pH. In most experiments, desalination degree of 50% (i.e., recovery ratio = 2) was chosen as the endpoint (based on EC reduction). Several cation–cation selectivity values (defined in Eq S2) were calculated to indicate the separation achievable with ED (Table S2). Finally, concentration experiments were undertaken using a higher and more practical diluate recovery ratio (>80%) and the practicability of the process in view of its energy requirements was assessed.

Low-recovery (50%) ED experiments

The effect of operating parameters on the ion-separation capability of ion-exchange membranes was assessed in low-recovery (50%) ED experiments with synthetic PAIWW. A high degree of separation was observed for both anions and cations throughout the applied voltage range (Figure 3). The P/SO_4– time plot (Figure 3A) for diluates in experiments 3, 4, and 6 (pH 1.5–2; 18–30 V) indicates the excellent separation of total P, which was mostly retained, and SO_4^{2-} (with 80%–90% transport at the endpoint). The selectivity of total P over SO_4^{2-} was estimated to be 0.1–0.17 (Table S2). Only minor changes in diluate F(I) concentration were observed. Cation transport through the CEM (Figure 3B) was dominated by H^+ transport, with excellent separation between monovalent and divalent cations (experiment 2; pH ~1.5; 18 V). Diluate Ca^{2+} and Mg^{2+} concentrations were almost constant (increasing slightly toward the end of the experiment, likely owing to H_2O osmosis toward the concentrate). In contrast, H^+, (Fig. 3C) K^+, and Na^+ concentrations decreased markedly (Figure 3B). The Na^+–cation selectivities were in the range of 4.3–18.3 for Na^+ over Ca^{2+}, 4.6–42.1 over Mg^{2+}, and 0.69–1.72 over K^+ (Table S2 for specific selectivity values. Increases in applied voltage promoted ion transport by increasing the current, with no significant effect on ion selectivity (Figure 3A). Overall, the results indicate that H^+ and SO_4^{2-} are the primary solutes transferred from the diluate to the concentrate stream, enabling two practical

objectives: (1) neutralization of the acidic diluate by >70%; and (2) recovery and recycling of H_2SO_4 without the risk of $CaSO_4$ scaling in the concentrate (owing to negligible Ca^{2+} transfer).

Figure 3: Results of low-recovery ED experiments. Transport of (A) major anions in experiments 3, 4, and 6 (pH 1.5, 30 V; pH 2.0, 18 V; and pH 2.0, 30 V, respectively) and (B) cations in experiment 2 (pH 1.5, 18 V) as a function of time in the diluate compartment. Error bars represent the standard deviation of ion concentrations (n = 3). (C) pH evolution over time in the diluate and concentrate compartments in experiments 2 and 4. (D) Changes in diluate and concentrate EC and current density as a function of time (experiment 2).

The initial feed pH in the diluate (1.5–2.0) did not affect cation separation (Figure 3B) but did affect anion separation (Figure 3A) through acid–base equilibria. Electro-driven P transport was greater with the higher initial feed pH (2.0) due to the decreased proportion of non-ionized H_3PO_4 species (43% at pH 2.0 and 76% at pH 1.5, as calculated with the PHREEQC [26] sit.dat database [27]). Similarly, F(I) transport was negligible due to the pH-dependent species distribution, which dictated a high proportion

of uncharged HF (90% at pH 2.0 and 97% at pH 1.5, as calculated with the PHREEQC phreeqc.dat database). In contrast, sulfate species (HSO_4^-, SO_4^{2-}) were completely ionized in the tested pH range and thus carried most of the current through the AEM. Acid–base equilibria at pH values typical of PAIWW thus enabled the effective separation of sulfate from phosphate and fluoride.

For both initial pH values, the pH of the diluate increased as the ED process progressed, while the pH of the concentrate first decreased then increased (Figure 3C). The increase in diluate pH was due to the

dominant H^+ transport; toward the end of the experiment, the rate of increase in pH was lower as H^+ ions were depleted. The initial decrease in concentrate pH was due to the predominant transport of strongly acidic sulfate species, supporting a high H^+ concentration. The following increase in pH was due to the uptake of H^+ by $H_2PO_4^-$ as the transport of such weakly acidic species became more significant. For practical purposes, the increase in diluate pH leads to the neutralization of most environmentally hazardous acidity in the PIWAA.

Although the ion-separation results of the low-recovery ED experiments (Figure 3) were encouraging, the presence of F(I) reduced the practicability of the process. High F(I) concentrations at low pH require the use of special-grade polymers and safety measures, which complicate procedures and raise the cost of membrane separation. Here we used 1 mm PP-based fluoride-resistant spacers in the ED stack, resulting in high single-cell specific electrical resistance (858–1419 $\Omega \cdot cm^2$). This high resistance was evident with low current densities (e.g., ~31 A m^{-2} in experiment 2; Figure 3D) and long durations (~25 h to reach ~50% diluate EC reduction; Figure 3D). Most critically, the SEC was impracticably high at 39–91 kWh m^{-3} for 80% SO_4^{2-} removal in the low-recovery experiments. The limitations caused by F(I) and the high SEC prompted a modification of the stack and operational approach in high-recovery ED experiments, as follows.

High-recovery ED experiments

Building on the results of the low-recovery experiments, high-recovery (~80%, achieved by adjusting diluate and concentrate volumes) ED experiments (7 and 8; Figure 4) were undertaken. A commercial AEM specifically designed to facilitate high SO_4^{2-} flux under acidic conditions (PC Acid 100, PCCell) was used with the same monovalent-selective CEM. To avoid F(I)-related limitations, fluoride-free solution was used to simulate PIWAA pre-treated for F(I) removal. Previous studies [28] and current industrial practice indicate effective F(I) removal in PIWWA treatment by, for example, adsorption on silicate-bearing materials. Omitting F(I) allowed the use of a standard 0.45 mm spacer rather than the special-grade 1 mm spacer. To minimize P transport, the feed pH was lowered to 1.5, with (note that F(I) removal was shown to reduce PIWAA pH, [28] thus no acid addition is required). Under these conditions and with the modified stack, the current density (Figure 4D) was higher than that achieved in the low-recovery experiments (Figure 3D), despite the higher voltage of the latter (18 V vs. 4 V).

Accordingly, an approximately 10-fold reduction in SEC (3.9–9.6 kWh m^{-3}, Figure S4) was achieved in the high-recovery experiments without compromising ion selectivity (Figure S3).

Figure 4: High-recovery ED experiment 7 (pH 1.5; 4 V). Transport of (A) major anions and (B) cations in the concentrate compartment over time. Error bars represent the standard deviation of ion concentrations (analytical replicates; n = 3). (C) pH evolution for the diluate and concentrate compartments as a function of time. (D) Changes in diluate and concentrate EC and current density with time. The results of experiment 8 (pH 1.5; 8 V) are shown in Figure S2. Ion-separation results were very similar for the two voltages, whereas current efficiency and electricity consumption differed

(Figure S4).

The excellent ion separation was retained in the high-recovery experiments, as reflected in the diluate and concentrate compositions (Figure 4). Diluate solute concentrations (Figure S3) were similar to those of the low-recovery experiments. The high SO$_4^{2-}$ flux relative to that of P and the high monovalent cation selectivity were maintained, as reflected in the evolution of the concentrate stream composition (Figure 4A, B). A marked increase in SO$_4^{2-}$ concentration of up to ~20 g L^{-1} is evident in Figure 4A, with only a moderate rise in P content of up to ~4 g L^{-1} and a low ~0.6 g L^{-1} Cl$^-$ concentration (also low in the diluate). Na$^+$ and K$^+$ concentrations increased monotonically in the concentrate, while Ca^{2+} and Mg^{2+} concentrations remained at <11 mg L^{-1} (Figure 4B) and the pH (Figure 4C) increased from 1.5 to 1.9. This pH increase was slightly lower than that recorded in the low-recovery experiments

(Figure 3C; pH 1.5 to 2.1) due to a higher concentration gradient of H^+ across the CEM at higher recoveries, reducing the net H^+ flux. The concentrate pH (Figure 4C) reached a lower level (<1) because of the accumulation of H_2SO_4. Ion concentrations in the concentrate stream were somewhat reduced by water transfer from the diluate, with the diluate/concentrate volume ratio decreasing from 5.5 at the beginning to 4.7 at the end of the experiment. However, ion-separation performances in the high-recovery experiments enabled attainment of the treatment goals, with diluate neutralization and H_2SO_4 recovery while avoiding $CaSO_4$ scaling.

Overall, these lab-scale results demonstrate the potential efficacy of ion-selective ED as an upstream process in the treatment of PAIWW (Figure 1), with further downstream processing as follows.

RO membrane desalination of the ED diluate

Concentration of the diluate is desirable for the recovery of clean water and P, but the precipitation of minerals, especially those containing Ca, may hinder the process. The final ED diluate had a pH of ~2 and high concentrations of P (~5.25 g L^{-1}), Na^+ (~1.9 g L^{-1}), and SO_4^{2-} (~0.72 g L^{-1}), with lower concentrations of Mg^{2+} (~0.2 g L^{-1}), Ca^{2+}, K^+ (both ~0.13 g L^{-1}), and Cl^- (~0.08 g L^{-1}; Table S3 and Figure 3A, B). To assess mineral precipitation during concentration of the diluate, PHREEQC software (sit.dat database) was used to simulate the gradual concentration of the diluate through the removal of aliquots of H_2O. Even after removing 95.5% of the water (i.e., a 22-fold concentration), the saturation indices (defined as the log of the ion activity product over the solubility constant) of all possible solid phases were negative, suggesting no scaling risk. Ca–P and Mg–P minerals were undersaturated due to the low pH, and gypsum was nearest saturation with a saturation index of −0.09 (Supplementary Information). This simulation thus suggest that a high permeate recovery ratio can be attained by RO without scaling, owing to the removal of most sulfate species by the upstream ED.

Figure 5: Representative RO filtration experiment, with feed solution simulating a recovery ratio of ~88%. (A) Permeate flux and EC rejection (Eq. S3) over 72 h in a constant-recovery experiment. (B) Permeate flux and EC as a function of filtration volume of permeate with increasing recovery. Flux was corrected for osmotic pressure changes. (C) Feed and permeate composition (average concentrations) over 72 h in a constant-recovery experiment. Error bars represent standard deviation. (D) Element rejection as a function of filtration volume of the permeate in an increasing-recovery experiment.

Laboratory-scale filtration experiments were undertaken with synthetic water simulating a concentrated ED diluate to investigate the feasibility of the RO step. Two types of experiment were undertaken [24]: (1) a constant-recovery experiment where both concentrate and permeate streams were circulated back to the feed tank, maintaining a constant feed composition; and (2) an increasing-recovery experiment where only the feed stream was recirculated to the feed tank and the permeate was collected in a different tank, thus concentrating the feed. In both cases, the initial feed solution simulated a concentrate stream obtained by applying RO to the ED diluate with an ~88% recovery ratio (with concentration factors of initally ~8.3 and up to ~12.5 in the increased-recovery mode). To avoid gypsum supersaturation due to concentration polarization or fluctuations in solution composition and temperature, the maximal experimental recovery ratio was set to 92%, which is lower than the 95.5% threshold reached in the PHRREQC geochemical simulation. The feed solution was adjusted to pH > 2, the limit for polyamide membrane operation [29]. Scaling risk was assessed by running the experiments

at constant pressure for several days while monitoring their performance and analyzing the membrane surface after filtration.

Filtration results indicate that the ED diluate can be treated with high-recovery RO without scaling. The permeate flux was initially relatively constant during 72 h of filtration for both the constant-recovery (Figure 5A) and increased-recovery (Figure 5B) experiments, indicating no significant scaling. Ion rejection was stable, as indicated by minor changes in permeate EC (Figure 4A) and ion composition (Figure 5C), further indicating absence of mineral fouling, which may affect ion rejection by increasing concentration polarization [30], with constant rejection further indicating the absence of mineral fouling. Mineral precipitation was not detected on membrane surfaces after either experiment. SEM images of the membrane surface (Figure S5) revealed no distinct mineral crystals in either experiment. Elemental analysis of the membrane surface by SEM–EDS and XRD also revealed no crystals. Overall, the theoretical and empirical results thus establish the practicability of a high-recovery (up to 92%) RO step with no antiscalant addition, enabled by sulfate removal in the ED step.

The high-recovery RO treatment produced permeate of excellent quality in both the constant and increasing recovery experiments. The EC was reduced by ~97%, and the removal rate of all individual ions was >95%. The permeate pH (~3.4) was was higher than that of the feed (pH~2.5, likely due to the high rejection of acidic species (mainly H_3PO_4 and HSO_4^-). An industrial RO spiral-wound element may provide even higher salt rejection at lower energy with higher recovery than the spacer-less flow cell used here. Because of its high quality, the permeate produced by RO could replace freshwater in many plant processes.

Neutralization of the RO concentrate with phosphate rock

Figure 6: Results of the 48-h batch neutralization experiment. (A–D) changes in pH and elemental content of RO concentrate during neutralization compared with original values (red line); (E) changes in the phosphate rock composition after neutralization (9 g per 10 mL); (F) XRD spectra indicating phase changes in the phosphate rock after neutralization (9 g per 10 mL). Neutralization experiments were duplicated.

Although the RO concentrate stream comprises only ~7% of the PAIWW volume, it remains an environmental risk because of its composition (Table 3) and requires further treatment. Although the concentrate (pH ~2.4) may be slightly less acidic than the PIAWW (pH ~2.1), it is more hazardous because of the stronger buffering capacity induced by the higher phosphate concentration (~43 g L^{-1}). However, the high phosphate concentration and its predominance over other ions increase the viability of recovering P from the RO concentrate stream (relative to the original PIAWW). A treatment strategy that achieves both acid neutralization and P recovery is thus required.

Reaction of the acidic RO concentrate with phosphate rock at a high solid/liquid ratio effectively neutralized the solution and upgraded the rock by decreasing its Ca/P mass ratio. An extensive series of batch leaching experiments with different solid/liquid ratios and leaching times was undetaken using fine-grained natural phosphate rock obtained from a local mine and a synthesized RO concentrate solution. The solution pH increased soon after mixing with the rock for all five solid fractions tested (Figure 6A). This increase in pH was more marked with higher solid fractions at all neutralization times. The pH changed little with contact time for the lower solid loadings (0.5–2 g_{rock} mL^{-1}) but gradually increased with higher solid loadings. The P concentrations (Figure 6B) mirrored the trend in pH: at lower solid loadings, the concentration did not change significantly with contact time but decreased with increasing contact time with higher solid loadings. Different trends were recorded for dissolved Ca (Figure 6C). After 15 min, the Ca concentration increased with low solid loadings but decreased with higher loadings. The Ca concentration then fluctuated with contact time, but with no significant changes at all but two data points (A decrease at 24 h and 48 h for the 2 g L^{-1} solid loading. The Mg concentrations (Figure 6D) changed only with higher loadings, decreasing significantly after 24 h. Analysis of the rock composition before and after neutralization (Figure 6E) with the 9 g_{rock} mL^{-1} loading indicated an increase in the P/Ca mass ratio relative to the natural rock.

The compositions of the solution and rock provide a clear indication of the geochemical processes involved in the reaction between natural phosphate rock and synthetic RO concentrate. Initially, $CaCO_3$ minerals dissolved rapidly with visible CO_2 bubbling, leading to a rapid pH increase (Figure 6A) and an increase in Ca concentration with low solid loadings. This was supported by XRD analysis of the rock before and after leaching (Figure 6F), with a marked decrease in calcite diffraction peak areas. With high solid loadings (6 or 9 g_{rock} mL^{-1}), calcite dissolution triggered precipitation of Ca–P and Mg–P minerals, as indicated by compositional changes in both solution and rock and further supported by

XRD analyses that exposed new Ca–P (brushite, $CaHPO_4.2H_2O$) and Mg–P (newberyite, $Mg(PO_3OH).3H_2O$) phases after neutralization (Figure 6F). Amorphous precipitates and phase transformations may also have occurred but had no significant effect on the practical outcome. A positive-feedback loop may explain the progression of the reaction over 48 h, with precipitation of phosphate minerals causing decreases in pH and Ca concentration, driving further calcite dissolution that again increased pH and Ca and promoted phosphate precipitation. The relative stability of the solution composition over time with low solid loadings (0.5–2 g_{rock} mL^{-1}) suggests that the lower amount of dissolved calcite was insufficient to trigger significant precipitation of phosphate minerals. A high loading with ground rock thus maximizes acid neutralization and P recovery through calcite dissolution and phosphate mineral precipitation.

Resource recovery and energy requirements

The energy requirement for the hybrid ED–RO system for treatment of PAIWW was found to be within a practicable range. The SEC was calculated for both steps with respect to the RO permeate volume (Figure 1). The optimal ED results (experiment 7) with 82% sulfate reduction requiring 3.3 kWh m^{-3} ED diluate (Figure S4) equate to 3.6 kWh m^{-3} RO permeate. The SEC for the RO step is calculated by Eq. (3) [31]:

$$SEC = \frac{\frac{P_{in}[bar]}{36\left[bar \cdot m_{feed}^3 / kWh\right]} \cdot \frac{1}{R\left[m_{permeate}^3 / m_{feed}^3\right]}}{\eta_{pump}} \tag{3}$$

where P_{in} is RO feed pressure, R is recovery ratio, and η_{pump} is pump efficiency. The applied pressure and maximum recovery ratio in the RO experiments were 60 bar and 92%, respectively, or 2.0 kWh m^{-3} RO permeate (assuming 91% combined efficiency for motor and high-pressure pump). Summing the SEC for the ED and RO steps indicates a total power consumption of 5.6 kWh m^{-3}, which is lower than that reported previously for near-zero liquid-discharge desalination of brackish water (9.48 kWh m^{-3}) [32].

Recovered resources may offset the energy cost. Normalization of SEC with respect to PIAWW results in 4.4 kWh m^{-3}. For every m^3 of PIWAA, the process recovers 0.78 m^3 of clean water, ~3 kg H_2SO_4, and ~2.5 kg P based on Table 3, showcasing solution compositions for best-scenario experimental results. In optimized industrial ED and RO processes, the SEC and associated economic and environmental costs would likely decrease. This preliminary empirical energy analysis suggests that the proposed ED–RO scheme is a cost-effective and sustainable solution for PAIWW treatment.

Table 3: Average solution compositions of all process streams representing the best separation and energy-use performances obtained experimentally for each step, including ED (4–8 V experiments at

pH ~1.5 and recovery ratio ~80%), RO (with recovery ratio of 92%), and neutralization (rock/liquid loading 9 g per 10 mL). Errors represent standard deviations (when n>2) or range (when n=2).

Stream ⸻ Element ± * (ppm)	PIAWW	ED diluate / RO Feed	ED concentrate	RO permeate	RO concentrate	RO concentrate after neutralization
pH	1.49 ± 0.01	1.97 ± 0.06	0.98 ± 0.02	2.97 ± 0.15	2.42 ± 0.05	6.41 ± 0.01
Ca^{2+}	134 ± 8	131.5 ± 3.9	< 11	4.8 ± 3.8	1512 ± 36	93 ± 4
K^+	181 ± 8	136.4 ± 7.7	86.6 ± 4.3	38 ± 25	1164 ± 234	1487 ± 10
Mg^{2+}	189 ± 9	194.2 ± 2.8	< 11	7.8 ± 5.6	2097 ± 36	217 ± 5
Na^+	2266 ± 121	1870 ± 44	4626 ± 402	635 ± 361	20805 ± 225	24461 ± 250
Total P	6061 ± 220	5253 ± 94	4026 ± 110	449 ± 328	36600 ± 2100	14070 ± 200
SO_4^{2-}	5570 ± 264	718.5 ± 6.6	19462 ± 445	67 ± 49	8166 ± 121	12736 ± 105
Cl^-	235 ± 9	82.4 ± 17.1	652 ± 25	502 ± 215	2373 ± 117	2545 ± 50

Summary and conclusions

A new circular treatment concept integrating selective ED, RO, and neutralization for treating PA-industry wastewater is introduced. The process reduces wastewater volume by >90% and neutralizes acidity while recovering clean water, H_2SO_4, and P, as enabled by the remarkable ion-separation performance in the low-pH ED step. Although pH-dependent PO_4–SO_4 separation can be directly related to acid–base chemistry, the high monovalent–divalent cation selectivity at low pH warrants further study.

The applied voltage in the ED step did not affect ion-separation performance but did influence electric power consumption. The removal of F(I) before the ED step is essential for achieving practicable power consumption. The RO results indicate that SO_4-deprived ED diluate could be concentrated by >10 fold (recovery ratio 90%), with no evidence of membrane scaling. The RO permeate had a low salt content, enabling unlimited water reuse in the industrial process, thus improving sustainability and economics. Furthermore, as the RO concentrate comprises mainly phosphoric acid (>40 g P L^{-1}) it can be recovered by different methods. Reaction of synthetic RO concentrate with natural phosphate rock results in higher P/Ca ratio in the rock and a neutralized concentrate. The results highlight the potential of the new process as an economically viable pathway toward more sustainable PA production. Processes targeting other acidic wastewaters may benefit from the high monovalent permselectivity at low pH.

Acknowledgments

Supporting Information

Properties of the commercial membranes in the ED stack, details of current efficiency and selectivity calculations, the evolution of ED process parameters in the high-recovery experiments including ion transport, pH, EC, and current density variation with time in the diluate compartment, and SEC values are described in the Supporting Information.

Properties of the cross-flow filtration system and feed composition for the RO system, including PHREEQC simulations and related calculations to correct for concentration polarization, SEM imaging, SEM–EDS, and XRD results are also described in the Supporting Information.

References

(1)   Geeson, M. B.; Cummins, C. C. Phosphoric Acid as a Precursor to Chemicals Traditionally Synthesized from White Phosphorus. *Science (80-.).* **2018**, *359* (6382), 1383–1385. https://doi.org/10.1126/science.aar6620.

(2)   Market Intelligence Service. Public Summary: Medium-Term Fertilizer Outlook 2021-2025 https://www.fertilizer.org/public/resources/publication_detail.aspx?SEQN=6177&PUBKEY=29353BFE-6AEF-4C6C-8DBC-A360A645F491 (accessed May 11, 2022).

(3)   Becker, P. *Phosphates and Phosphoric Acid: Raw Materials, Technology, and Economics of the Wet Process. Second Edition, Revised and Expanded.*; Marcel Dekker, Inc.: New York, 1989; Vol. 6.

(4)   Al-Harahsheh, M.; Batiha, M.; Kraishan, S.; Al-Zoubi, H. Precipitation Treatment of Effluent Acidic Wastewater from Phosphate-Containing Fertilizer Industry: Characterization of Solid and Liquid Products. *Sep. Purif. Technol.* **2014**, *123*, 190–199. https://doi.org/10.1016/J.SEPPUR.2013.12.027.

(5)   Nawghare, P.; Rao, N. N.; Bejankiwar, R.; Szyprkowicz, L.; Kaul, S. N. TREATMENT OF PHOSPHORIC ACID PLANT WASTEWATER USING FENTON'S REAGENT AND COAGULANTS. *J. Environ. Sci. Heal. Part A* **2001**, *36* (10), 2011–2026. https://doi.org/10.1081/ESE-100107444.

(6)   Albustami, S. F.; Hilakosa, S. W. FSA Neutralization with Calcium Compounds. *Procedia Eng.* **2014**, *83*, 286–290. https://doi.org/10.1016/J.PROENG.2014.09.007.

(7)   IAEA. Radiation Protection and Management of NORM Residues in the Phosphate Industry https://www-pub.iaea.org/MTCD/Publications/PDF/Pub1582_web.pdf (accessed May 25, 2022).

(8)   Becker, N.; Gross, Y.; Lavee, D. Cost–Benefit Analysis of Restoring an Ephemeral Desert Stream after an Ecological Accident. *Water Policy* **2020**, *22* (3), 328–347. https://doi.org/10.2166/wp.2020.014.

(9)   Astley, V. V.; Michalski, D. H. Process for Treating Pond Water. US7560031, 2009.

(10)   Zibrida, J. F. Treatment of Phosphate-Containing Wastewater. US4698163, 1987.

(11)   Weston, C. W.; Murray, M. A. Process for Treating Pond Water. US5112499, 1992.

(12)   Nelson, N. G.; Cuchiara, M. L.; Hendren, C. O.; Jones, J. L.; Marshall, A.-M. Hazardous Spills at Retired Fertilizer Manufacturing Plants Will Continue to Occur in the Absence of Scientific Innovation and Regulatory Enforcement. *Environ. Sci. Technol.* **2021**, *55* (24), 16267–16269. https://doi.org/10.1021/acs.est.1c05311.

(13)   Bunani, S.; Yoshizuka, K.; Nishihama, S.; Arda, M.; Kabay, N. Application of Bipolar Membrane Electrodialysis (BMED) for Simultaneous Separation and Recovery of Boron and Lithium from Aqueous Solutions. *Desalination* **2017**, *424* (September), 37–44.

https://doi.org/10.1016/j.desal.2017.09.029.

(14)   Martin, N.; Ya, V.; Leewiboonsilp, N.; Choo, K.-H.; Noophan, P. (Lek); Li, C.-W.
          Electrochemical Crystallization for Phosphate Recovery from an Electronic Industry
          Wastewater Effluent Using Sacrificial Iron Anodes. *J. Clean. Prod.* **2020**, *276*, 124234.
          https://doi.org/10.1016/j.jclepro.2020.124234.

(15)   Lu, H.; Wang, Y.; Wang, J. Recovery of Ni2+ and Pure Water from Electroplating Rinse
          Wastewater by an Integrated Two-Stage Electrodeionization Process. *J. Clean. Prod.* **2015**, *92*,
          257–266. https://doi.org/10.1016/j.jclepro.2014.12.056.

(16)   Kim, J.; Yoon, S.; Choi, M.; Min, K. J.; Park, K. Y.; Chon, K.; Bae, S. Metal Ion Recovery
          from Electrodialysis-Concentrated Plating Wastewater via Pilot-Scale Sequential
          Electrowinning/Chemical Precipitation. *J. Clean. Prod.* **2022**, *330*, 129879.
          https://doi.org/10.1016/j.jclepro.2021.129879.

(17)   Mohdee, V.; Ramakul, P.; Phatanasri, S.; Pancharoen, U. A Numerical and Experimental
          Investigation on the Selective Separation of Pd (II) from Wastewater Using Aliquat 336 via
          Hollow Fiber Supported Liquid Membrane. *J. Environ. Chem. Eng.* **2020**, *8* (5), 104234.
          https://doi.org/10.1016/j.jece.2020.104234.

(18)   Kim, D. I.; Gwak, G.; Dorji, P.; He, D.; Phuntsho, S.; Hong, S.; Shon, H. Palladium Recovery
          through Membrane Capacitive Deionization from Metal Plating Wastewater. *ACS Sustain.
          Chem. Eng.* **2018**, *6* (2), 1692–1701. https://doi.org/10.1021/acssuschemeng.7b02923.

(19)   Jin, H.; Zhang, J.; Wang, D.; Jing, Q.; Chen, Y.; Wang, C. Facile and Efficient Recovery of
          Lithium from Spent LiFePO 4 Batteries via Air Oxidation–Water Leaching at Room
          Temperature. *Green Chem.* **2022**, *24* (1), 152–162. https://doi.org/10.1039/D1GC03333F.

(20)   Battistoni, P.; Carniani, E.; Fratesi, V.; Balboni, P.; Tornabuoni, P. Chemical−Physical
          Pretreatment of Phosphogypsum Leachate. *Ind. Eng. Chem. Res.* **2006**, *45* (9), 3237–3242.
          https://doi.org/10.1021/ie051252h.

(21)   Battistoni, P.; Carniani, E.; Fatone, F.; Balboni, P.; Tornabuoni, P. Phosphogypsum Leachate:
          Treatment Feasibility in a Membrane Plant. *Ind. Eng. Chem. Res.* **2006**, *45* (19), 6504–6511.
          https://doi.org/10.1021/ie060041p.

(22)   Al-Harahsheh, M.; Hussain, Y. A.; Al-Zoubi, H.; Batiha, M.; Hammouri, E. Hybrid
          Precipitation-Nanofiltration Treatment of Effluent Pond Water from Phosphoric Acid Industry.
          Desalination **2017**, *406*, 88–97. https://doi.org/10.1016/J.DESAL.2016.06.014.

(23)   Gouider, M.; Feki, M.; Sayadi, S. Separative Recovery with Lime of Phosphate and Fluoride
          from an Acidic Effluent Containing H3PO4, HF and/or H2SiF6. *J. Hazard. Mater.* **2009**, *170*
          (2–3), 962–968. https://doi.org/10.1016/J.JHAZMAT.2009.05.067.

(24)   Kaganovich, M.; Zhang, W.; Freger, V.; Bernstein, R. Effect of the Membrane Exclusion
          Mechanism on Phosphate Scaling during Synthetic Effluent Desalination. *Water Res.* **2019**,
          161, 381–391. https://doi.org/10.1016/j.watres.2019.06.013.

(25)   EPA. Method 3051A (SW-846): Microwave Assisted Acid Digestion of Sediments, Sludges, and Oils. Washington DC, U.S. 2007.

(26)   Parkhurst, D. L.; Appelo, C. A. J. *Description of Input and Examples for PHREEQC Version 3: A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations*; Reston, VA, 2013. https://doi.org/10.3133/tm6A43.

(27)   ThermoChimie (Consortium Andra - Ondraf/Niras - RWM) https://www.thermochimie-tdb.com/ (accessed May 25, 2022).

(28)   Epshtein, A.; Nir, O.; Monat, L.; Gendel, Y. Treatment of Acidic Wastewater via Fluoride Ions Removal by SiO2 Particles Followed by Phosphate Ions Recovery Using Flow-Electrode Capacitive Deionization. *Chem. Eng. J.* **2020**, *400*, 125892. https://doi.org/10.1016/j.cej.2020.125892.

(29)   Amaral, M. C. S.; Grossi, L. B.; Ramos, R. L.; Ricci, B. C.; Andrade, L. H. Integrated UF–NF–RO Route for Gold Mining Effluent Treatment: From Bench-Scale to Pilot-Scale. *Desalination* **2018**, *440*, 111–121. https://doi.org/10.1016/j.desal.2018.02.030.

(30)   Nnebuo, C. S.; Hambsch, D.; Nir, O. Elucidating Morphological Effects in Membrane Mineral Fouling Using Real-Time Particle Imaging and Impedance Spectroscopy. *Environ. Sci. Water Res. Technol.* **2022**. https://doi.org/10.1039/D2EW00155A.

(31)   Ophek, L.; Birnhack, L.; Nir, O.; Binshtein, E.; Lahav, O. Reducing the Specific Energy Consumption of 1st-Pass SWRO by Application of High-Flux Membranes Fed with High-PH, Decarbonated Seawater. *Water Res.* **2015**, *85*, 185–192. https://doi.org/10.1016/j.watres.2015.08.027.

(32)   Panagopoulos, A. Energetic, Economic and Environmental Assessment of Zero Liquid Discharge (ZLD) Brackish Water and Seawater Desalination Systems. *Energy Convers. Manag.* **2021**, *235*, 113957. https://doi.org/10.1016/j.enconman.2021.113957.