Assessment of nanofiltration and reverse osmosis potentialities to recover metals, sulfuric acid, and recycled water from acid gold mining effluent

Bárbara C. Ricci, Carolina D. Ferreira, Larissa S. Marques, Sofia S. Martins and Miriam C. S. Amaral

ABSTRACT

This work assessed the potential of nanofiltration (NF) and reverse osmosis (RO) to treat acid streams contaminated with metals, such as effluent from the pressure oxidation process (POX) used in refractory gold ore processing. NF and RO were evaluated in terms of rejections of sulfuric acid and metals. Regarding NF, high sulfuric acid permeation (∼100%), was observed, while metals were retained with high efficiencies (∼90%), whereas RO led to high acid rejections (<88%) when conducted in pH values higher than 1. Thus, sequential use of NF and RO was proved to be a promising treatment for sulfuric acid solutions contaminated by metals, such as POX effluent. In this context, a purified acid stream could be recovered in NF permeate, which could be further concentrated in RO. Recovered acid stream could be reused in the gold ore processing or commercialized. A metal-enriched stream could be also recovered in NF retentate and transferred to a subsequent metal recovery stage. In addition, considering the high acid rejection obtained through the proposed system, RO permeate could be used as recycling water.

Key words | gold mining effluent, metal separation, nanofiltration, reverse osmosis, sulfuric acid recovery

INTRODUCTION

The pressure oxidation process (POX) is frequently employed in refractory gold ore processing. This pretreatment alters or destroys the sulfide matrix in which gold is occluded, thus leaving the gold ore accessible to cyanide leaching (Granato 1986; Gudyanga et al. 1999). Similarly to other gold ore processing stages, POX generates a large volume of liquid effluents which are characterized by substantial metal concentrations and high acidity. A neutralization process, using alkalinizing agents as quicklime or hydrated lime, is usually employed during the treatment of POX effluent. Although it is a simple method, its main disadvantage is the generation of large volumes of liquid effluents which are characterized by substantial metal concentrations and high acidity. A neutralization process, using alkalinizing agents as quicklime or hydrated lime, is usually employed during the treatment of POX effluent. Although it is a simple method, its main disadvantage is the generation of large volumes of precipitate (sludge) which contains significant heavy metal content. This sludge represents an environmental threat and must be properly disposed of, which increases costs related to final disposal (Soares & Borma 2002; Fu & Wang 2011). Therefore, the recovery of metals, sulfuric acid, and water from this effluent could reduce costs related to neutralization and aggregate value to this effluent.

Accordingly, membrane separation processes appear as a promising technology to be used in the treatment of POX effluent. In this context, the association of nanofiltration (NF) and reverse osmosis (RO) is of special interest, especially due to the continuous development of membranes which are chemically resistant to extreme pH conditions (Schäfer et al. 2005). Due to its particularities, NF offers a singular opportunity for the purification of acid streams contaminated with metals cations, such as POX effluent. This could be explained by the NF membrane isoelectric point (IEP). NF membranes usually exhibit an IEP between 3 and 6; thus, at low pH, the membrane is positively charged (Hagmeyer & Gimbel 1999; Schaep & Vandecasteele 2001). Consequently, in such conditions, NF membranes will strongly retain multivalent metal cations while allowing acid anions to permeate almost freely through the membrane (Schäfer et al. 2005). As a result, a high acid recovery in
NF permeate with a lower content of metal contaminants is obtained.

RO processes allow retentions of dissolved salts and organic low molar mass molecules above 99%. Therefore, it is frequently applied in the concentration of diluted solutions. Ahsan et al. (2014), for example, have reported the use of RO to concentrate acetic acid, and acid content in the concentrate increased more than 400% when compared to the feed solution (Ahsan et al. 2014).

Several studies have reported the use of NF and RO in the treatment of acid streams contaminated with metal cations (Gonzalez et al. 2002; Jakobs & Baumgarten 2002; Gonzalez et al. 2006; Tanninen et al. 2007; Qinying et al. 2013). Eriksson et al. (1996), for example, reported the application of NF in treatment of effluent from a copper smelting plant. The studied effluent was characterized by extreme acidity, i.e., 33% w/w of H2SO4, and high impurity presenting 25 g L−1 of dissolved solids. In the proposed treatment, a four-stage NF system was used in order to reach technical grade purity sulfuric acid. The overall retention of heavy metals was 99.9% for iron and zinc; 99% for copper and cadmium, and 50% of arsenic. The study was carried out in a pilot plant in which a DK membrane supplied by Osmonics was used. Although metals recovered in the retentate were not recycled, the cost associated with effluent neutralization and sludge production were significantly reduced (Eriksson et al. 1996).

The association of NF and RO in the treatment of a sulfuric acid rinse water stream generated by a copper rod refinery was reported by van der Merwe (1998). The treated effluent was characterized by high concentrations of sulfuric acid (2% m/m) and high copper (1.2 g L−1). The treatment was aimed at the segregation of all components originally present in the effluent, i.e., sulfuric acid, water and copper, in separate streams, so that they could be reused in the process. The proposed treatment included two RO stages (ROI and ROII) and NF. During the first RO stage (ROI), the acid was concentrated from 2 to 10%, while the copper concentration was raised from 1.2 to 8.1 g L−1. Permeate obtained in the first RO stage was fed to the second RO (ROI) in order to improve its degree of purity, thus allowing its use as recycled water in the process. In the sequence, the retentate generated in the ROI was fed to the NF stage. In this stage, sulfuric acid could be recovered in the permeate, while an enriched copper stream was obtained in the retentate. In the sequence, recovered acid was transferred to the acid picking stage, while the copper rich was transferred to an additional concentration stage.

The membrane separation process emerges as a promising technology to be used in the purification of acid streams, aiming at metals, water, and acid recovery. In this context, this study aimed to evaluate the potential of NF and RO processes to treat acid streams contaminated with metals, such as effluent from POX. Specifically, NF membrane MPF-34 (Koch Membrane Systems) was evaluated for its potential to separate sulfuric acid from nickel and cobalt sulfates, valuable metals present in POX effluent. The RO membrane TFC-HR (Koch Membrane Systems) was assessed for its ability to concentrate the sulfuric acid recovered through the NF process, and to recover water.

**METHODS**

**NF and RO membranes**

The flat sheet NF and RO membranes used in this study were supplied by Koch Membranes. Some characteristics of these membranes as provided by the supplier are shown in Table 1.

**Experimental set-up**

NF and RO experiments were performed in a bench-scale unit. The experimental apparatus comprised a feed tank; a centrifugal pump connected to a speed controller; a rotameter; a valve for pressure adjustment; a stainless steel

<table>
<thead>
<tr>
<th>Characteristics of NF and RO membranes</th>
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<tbody>
<tr>
<td><strong>Membrane type</strong></td>
</tr>
<tr>
<td>Membrane chemistry</td>
</tr>
<tr>
<td>Molecular weight cut-off (Da)</td>
</tr>
<tr>
<td>Operating pH</td>
</tr>
<tr>
<td>Maximum operating pressure (bar)</td>
</tr>
<tr>
<td>Maximum operating temperature (°C)</td>
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<tr>
<td>Glucose rejection (%)</td>
</tr>
<tr>
<td>NaCl rejection (%)</td>
</tr>
</tbody>
</table>

*Not specified.

1The test conditions specified by Koch were: RO water at 440 psi (30 bar), 86°F (30°C). Feed solution for rejection tests with 3% glucose or 5% NaCl.

2The test conditions specified by Koch were: 2,000 mg·L−1 NaCl solution at 225 psi (15.50 bar), 15% recovery, 77°F (25°C), and pH 7.5.
membrane module; a manometer; and a thermometer. A schematic diagram of the experimental set-up is illustrated in Figure 1.

The stainless steel membrane module used has a diameter \(2R\) of 9 cm, providing a filtration area equals 63.60 cm\(^2\). The radial inlet radius of the cell \(r_1\) is 64 mm and the internal channel height \(2h\) is 1 mm. Tested membranes were properly cut before being placed in the cell and a feed spacer was placed over the membrane to promote flow distribution.

During tests, permeate flow rate was periodically monitored. Flux data were normalized to 20 °C using a correction factor calculated from the ratio of water viscosity at the permeation temperature and water viscosity at 20 °C as shown in Equation (1):

\[
J(20\, ^\circ C) = \frac{\mu(T)}{\mu(20\, ^\circ C)} J(T) \tag{1}
\]

where \(J(T)\) is the measured permeate flux at a given operation temperature, \(\mu(T)\) is the water dynamic viscosity at a given operation temperature, \(\mu(20\, ^\circ C)\) is the water dynamic viscosity at 20 °C and \(J(20\, ^\circ C)\) is the normalized flux at 20 °C.

Due to the concentration polarization phenomenon, the concentration of a particular solute \(i\) at the membrane surface is higher than that found in the bulk solution. Thus, the rejection data were interpreted in terms of real rejection, as shown in Equation (2):

\[
R_{r,i} = 1 - \frac{C_{p,i}}{C_{m,i}} \tag{2}
\]

Here, \(R_{r,i}\) and \(C_{m,i}\) are, respectively, the real rejection and concentration of solute \(i\) at the membrane surface.

The concentration of solute \(i\) at the membrane surface can be predicted by using the film model, given by Equation (3) (Mulder 1996):

\[
\frac{C_{m,i} - C_{p,i}}{C_{b,i} - C_{p,i}} = \exp \left( \frac{L}{R_i} \right) \tag{3}
\]

Here, \(C_{m,i}\), \(C_{p,i}\), and \(C_{b,i}\) are, respectively, the concentrations of solute \(i\) at the membrane surface, in the permeate, and in the bulk; \(J\) is the permeate flux; and \(k_i\) is the mass transfer coefficient of solute \(i\) in the test cell.

The mass transfer coefficient for solute \(i\) in a radial tangential flow filtration cell in laminar regime (Re < 1,800) may be obtained from the Sherwood number (Sh), according to Equation (4) (De & Bhattacharya 1997):

\[
Sh = \frac{k_i h}{D_i} = 1.05 \left( \frac{Re \cdot Sc}{R} \right)^{0.38} \tag{4}
\]

where \(h\) is half of the cell internal height; \(D_i\) is the diffusion coefficient of solute \(i\); \(Re\) is the Reynolds number; \(Sc\) is the Schmidt number; \(R\) is the filtration cell radius.

The Schmidt number is given by Equation (5):

\[
Sc = \frac{\nu}{D_i} \tag{5}
\]

Here, \(\nu\) is the kinematic viscosity of water at 20 °C.

The Reynolds number is given by Equation (6):

\[
Re = \frac{u_0 d_h}{\nu} \tag{6}
\]

Here, \(u_0\) is the average tangential velocity and \(d_h\) is the cell hydraulic diameter.
The average tangential velocity was determined by means of Equation (7) (Minnikanti et al. 1999):

\[ u_0 = \frac{Q}{4\pi hr_{imd}} \]  

Here, \( Q \) is the feed flow rate, \( h \) is half of the cell internal height, and \( r_{imd} \) is the logarithmic mean radius calculated from Equation (8) (Minnikanti et al. 1999):

\[ r_{imd} = \frac{R - r_1}{\ln\left(\frac{R}{r_1}\right)} \]

Here, \( R \) is the filtration cell radius and \( r_1 \) is the radial inlet radius of the cell.

The hydraulic diameter, \( d_h \), was estimated by means of Equation (9) (Minnikanti et al. 1999):

\[ d_h = 4h \]

The Reynolds number calculated for the operational conditions used in this study was 839. This value is lower than 1,800, thus, characterizing the flow as laminar.

Cleaning procedure

Prior to filtration tests, the NF and RO membranes were subjected to a cleaning procedure. This procedure consisted of ultrasonication with citric acid solution (pH 2.5), followed by ultrasonication with 0.1% NaOH solution, for 20 min each.

Assessment of NF performance on selective separation of sulfuric acid from nickel and cobalt sulfates

The performance of NF in the selective separation of sulfuric acid from metal salts was assessed by filtering a synthetic solution containing cobalt and nickel sulfates, and sulfuric acid. The synthetic solution consisted of 97 mg.L\(^{-1}\) of nickel and 17 mg.L\(^{-1}\) of cobalt. Solutions were prepared based on median value concentrations present in pressure oxidation effluent produced by a gold mining company located in the state of Minas Gerais, Brazil. In these tests, the effect of different pH values (0, 1, 2, 3 and 4) on the performance of the NF membrane was assessed. For all tests, pH adjustment was conducted with sulfuric acid.

Membranes were stabilized with deionized water at a pressure of 10 bar, prior to filtration tests and after the cleaning procedure. Then, 4,000 mL of the solution at pH 4 was transferred to the feed tank. Permeation was performed under constant pressure of 10 bar and at a temperature range of 20±2 °C for 1 hour with return of permeate and retentate to the feed tank. After 1 hour, 80 mL of permeate was collected in order to determine metal concentration and acidity. During filtration, permeate flux was monitored every 10 minutes.

After filtration of pH 4 solution, the filtration system was cleaned with deionized water. After that, 1 L of a pH 3 solution was used to rinse the unit. In the sequence, the solution was drained and 4,000 mL of the solution (pH 3) was transferred to the feed tank. The permeation procedure for this solution was the same as the one described earlier for the former one (pH 4). Then, the procedure described for solutions with pH 4 and 3 was repeated for all of the other solutions (pH 0, 1 and 2).

Assessment of RO performance in sulfuric acid retention

The efficiency of RO to retain sulfuric acid was assessed by using a synthetic solution containing only acid. The effect of pH on RO performance was evaluated. Assessed pH values were 0.78, 1, 2, 3 and 4. For all tests, pH adjustment was performed with sulfuric acid (98% solution). The experimental procedure used was the same as described in the previous section.

Analytical methods

Metal concentrations were analyzed by an atomic absorption spectrophotometer (supplied by CBC Scientific Equipment). Sample acidity was determined by titration with NaOH solution. Sample pH was determined by a Qualxtron QX 1500 pH meter.

Sulfate concentration in each sample was calculated by means of charge balance as shown in Equation (10):

\[ C_{SO_4^{2-}} = \frac{1}{2} x (C_{H^+} + 2C_{Cu^{2+}} + 2C_{Co^{2+}} + 2C_{Ni^{2+}}) \]

where \( C_{SO_4^{2-}} \), \( C_{H^+} \), \( C_{Cu^{2+}} \), \( C_{Co^{2+}} \) and \( C_{Ni^{2+}} \) are, respectively, the molar concentrations of sulfate, hydrogen, copper, cobalt and nickel.

RESULTS

Assessment of NF performance on selective separation of sulfuric acid from nickel and cobalt sulfates

Considering the evaluated pH range, a maximum permeate flux was observed at pH 5, as shown in Figure 2. Other
published studies have reported the detection of maximum permeate flux for a given pH range.

Childress & Elimelech (2000), for example, evaluated the pH effect on permeate flux for NF-55 aromatic polyamide membrane. The pH range assessed varied from 3 to 9 and 0.01 mol.L\(^{-1}\) NaCl was used as solution. The authors observed that the permeate flux was approximately constant for all of the tested pH values, except for pH 5 in which a peak was verified. As discussed by these authors, one hypothesis for the observed phenomenon would be that the IEP of this membrane corresponded to pH 5. Thus, when pH is lower than 5, amino groups on the selective layer would be protonated, whereas for higher pH values, carboxylic groups would be deprotonated. In both cases, the electrostatic repulsion between the charged groups results in a reduction of the membrane pores, thus leading to nearly constant flux. However, at IEP, in which there is no effective charge, there is no reduction in pore size due to electrostatic repulsion, so that an increase in the permeate flux is observed.

Ahmad & Ooi (2010) evaluated the pH effect on permeate flux for a polyamide membrane synthesized in laboratory. Tests were performed in pH ranging from 1 to 6 and copper sulfate solutions of 0.5, 1 and 5 mM were used. When filtering a 0.5 mM solution of copper sulfate, the authors observed a permeate flux peak at pH 4.5. However, by increasing the solution concentration to 5.0 mM, they observed a peak shift to pH 3.5. Thus, the authors proposed that the membrane IEP was situated between 3.5 and 4.5 and that it was dependent on the concentration of the feed solution.

Based on the relationship observed between permeate flux and IEP, it is proposed that the IEP of membrane MPF-34 is close to 3 for experimental conditions employed in this present study. This hypothesis is in accordance with other studies which have reported MPF-34 IEP at pH 4.5 (Dalwani et al. 2011). The difference between the IEP values may be related to the different operating conditions used in each test. Thus, for pH values higher than 3, MPF-34 is negatively charged, while for lower pH values it is positively charged.

The pH effect on NF performance in selective separation of sulfuric acid from nickel and cobalt sulfates was assessed in terms of rejection of Co\(^{2+}\), Ni\(^{2+}\), H\(^+\) and SO\(_4^{2-}\) species (Table 2).

<table>
<thead>
<tr>
<th>pH</th>
<th>Co(^{2+}) rejection (%)</th>
<th>Ni(^{2+}) rejection (%)</th>
<th>H(^+) rejection (%)</th>
<th>SO(_4^{2-}) rejection (%)</th>
<th>SO(_4^{2-}) speciation (%)</th>
<th>HSO(_4^{-}) speciation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>89.8</td>
<td>89.8</td>
<td>3.7</td>
<td>3.9</td>
<td>1.0</td>
<td>98.9</td>
</tr>
<tr>
<td>1</td>
<td>89.7</td>
<td>91.1</td>
<td>-2.3</td>
<td>-0.7</td>
<td>9.2</td>
<td>90.7</td>
</tr>
<tr>
<td>2</td>
<td>89.7</td>
<td>94.9</td>
<td>23.2</td>
<td>38.6</td>
<td>50.5</td>
<td>49.5</td>
</tr>
<tr>
<td>3</td>
<td>93.5</td>
<td>96.1</td>
<td>35.4</td>
<td>82.7</td>
<td>91.1</td>
<td>8.9</td>
</tr>
<tr>
<td>4</td>
<td>93.7</td>
<td>96.0</td>
<td>24.1</td>
<td>93.8</td>
<td>99.0</td>
<td>0.9</td>
</tr>
</tbody>
</table>
For pH values lower than IEP (pH < 3) the membrane is positively charged so that the rejection is determined by cations (co-ions) present in solution. Due to higher charge density, Co$^{2+}$ and Ni$^{2+}$ cations were strongly repelled by the membrane, which resulted in a higher rejection coefficient of these species. On the other hand, H$^+$ ions have lowest charge density and so they were transported through the membrane, keeping the permeate electroneutrality (Gibbs–Donnan equilibrium), and resulting in a lower rejection of this.

The decrease of the pH from the IEP caused a reduction in sulfate rejection which might be associated with changes in speciation of the sulfuric acid in such conditions. At pH 3, for example, nearly 10% of the sulfuric acid is in the form of bisulfate anion (HSO$_4^-$), while for pH 0 that fraction raises to 99%. Thus, the profile of sulfate rejection indicated that the acid is weakly retained by the membrane in the form of the bisulfate anion. Tanninen et al. (2007) also studied the pH effect on selective separation of copper sulfate from sulfuric acid and they found a sulfate rejection profile very similar to the one found in this study.

Above the IEP (pH > 3), the NF membrane is negatively charged so that the rejection is determined by the anions present in the solution. The main anion found above the IEP is sulfate, which is strongly repelled by the membrane, resulting in high sulfate rejection coefficients. Sulfate high rejection caused increased retention of counter-ions Co$^{2+}$ and Ni$^{2+}$ so that system electroneutrality is re-established according to Gibbs–Donnan equilibrium theory.

Therefore, for pH values lower than 3, lower rejections of bisulfate anion (HSO$_4^-$) and proton (H$^+$) are responsible for the sulfuric acid transportation to NF permeate. Besides that, high rejection of metal cations (~90%) associated with low acid rejection resulted in high acid recovery in permeate with low content of contaminants. Thus, NF demonstrated its potential for acid recovery (permeate) and for production of a metal enriched stream (retentate) from POX effluent.

### Assessment of RO performance in sulfuric acid rejection

As shown in the Figure 3, when operating in constant pressure ($\Delta P - \Delta \pi$), pH reduction decreased permeate flux and acid rejection coefficient. An even sharp decrease of such parameters was observed when operating in pH 0.78, for which the rejection coefficient was reduced to 67%, and permeate flux to 3.22 L.h$^{-1}$.m$^{-2}$.

The sharp flux decrease observed for pH 0.78 was caused by the increase of the feed osmotic pressure ($\Delta \pi$) which reduced the effective applied pressure ($\Delta P - \Delta \pi$). On the other hand, the decrease in the acid rejection ratio may be better understood from the standpoint of the solution-diffusion model.

According to this model, solute flux is proportional to its concentration gradient across the membrane, as expressed by Equation (11) (Baker 2004):

$$J_j = B(C_{j0} - C_{jl})$$

(11)

where $J_j$, $B$, $C_{j0}$ and $C_{jl}$ are, respectively, flux, permeability, feed and permeate concentration of solute $j$.

Thus, acid concentration increase in feed solution also increased the driving force for its transport across the membrane, resulting in a reduction of its rejection.
Furthermore, the concentration of the solute in the permeate \( C_{jl} \) may be related to solvent and solute flux, as according to Equation (12):

\[
C_{jl} = \frac{J_j}{J_i} \times \rho_i
\]

(12)

where \( \rho_i \) and \( J_i \) are, respectively, density and flux of solvent \( i \).

The solvent flux \( J_i \) is proportional to effective pressure applied \( (\Delta P - \Delta \pi) \), according to Equation (13):

\[
J_i = L_p (\Delta P - \Delta \pi)
\]

(13)

where \( L_p \) is solvent permeability.

Thus, the reduction of effective pressure caused by the increase in the feed osmotic pressure causes solvent flux reduction (Equation (13)), and increases the acid concentration in the permeate (Equation (12)), consequently decreasing acid rejection. Therefore, considering the experimental conditions adopted in this study, it was observed that, for pH values ranging from 1 to 4, acid rejection was above 88%. Therefore, in such conditions, RO may be used for concentration of acid recovered through NF. Meanwhile, due to the high acid rejection, RO permeate could be used as recycling water. For pH values lower than 1, membrane efficiency should be assessed for pressures above 10 bar in order to mitigate the effect of decreasing effective pressure on the acid selectivity. Values above 10 bar were not evaluated in this study due to pressure limitation in the system employed in this study.

Considering that maximum operating pressure of the TFC-HR membrane is 40 bar, maximum acid concentration to be obtained in RO retentate was estimated, so that the retentate osmotic pressure did not exceed 50% of maximum operating pressure (20 bar). As shown in Figure 4, a sulfuric acid solution of 40 g·L\(^{-1}\) (pH 0.38) has an osmotic pressure equivalent to 20 bar. Thus, the TFC-HR membrane could be used to concentrate sulfuric acid solutions up to this value. The POX effluent has an average pH of 1.30, which corresponds to a sulfuric acid concentration of approximately 4.2 g·L\(^{-1}\). NF permeate obtained from POX effluent presents the same acid concentration of raw effluent, since, for these conditions, NF acid rejection is approximately zero. Therefore, if a recovery rate of 80% was used in RO for NF permeate, the acid concentration in retentate would be at most 21 g·L\(^{-1}\), considering 100% rejection. Thus, RO could be used for concentrating the acid recovered in the NF from the POX effluent, if pressures higher than 10 bar were applied.

**CONCLUSION**

The NF performance on selective separation of sulfuric acid from nickel and cobalt sulfates was assessed. For pH values lower than 3, the lower rejections of bisulfate anion \( (\text{HSO}_4^-) \) and proton \( (\text{H}^+) \) were responsible for the sulfuric acid transportation to NF permeate. Besides that, high rejection of metal cations (~90%) associated with low acid rejection resulted in high acid recovery in permeate and low content of contaminants.

Regarding RO performance for sulfuric acid rejection, it was observed that, for pH values higher than 1, acid rejections were high (<88%). Thus, RO may be used to concentrate the acid recovered in NF permeate. Considering high acid rejection, RO permeate has potential to be used as recycling water. For operation in pH values lower than 1, it is recommended that the membrane efficiency is assessed.
for pressures above 10 bar in order to mitigate the effect of effective pressure decrease on acid selectivity.

Therefore, the sequential use of NF and RO has proved to be a promising treatment for sulfuric acid solutions contaminated by metals, such as POX effluent. A purified acid stream could be recovered in NF permeate, which could be further concentrated in RO. This acid stream may be reused in the ore processing or commercialized. A metal-enriched stream could be also recovered in NF retentate, and may be transferred to a subsequent metal recovery stage. In addition, considering the high acid rejection obtained in this study, the RO permeate could be used as recycling water.

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