


tonomous University. This research was supported by the National Science Foundation under grant number DMI-0001006.


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FIG. 1. Schematic of CUF Process

FIG. 2. Schematic of: (a) Emulsified Oil Droplet; (b) Oleate Molecule; and (c) Breaking of Metallic Soap Complexes by EDTA Addition

\[
\text{EDTA}^{4-} + \text{Mg}^{2+} \rightarrow \text{EDTA-Mg}^{2-}, \quad pK_{\text{EDTA-Mg}} = 8.64 \quad (2)
\]

where \(\equiv \text{OA}\) represents oil-bound oleic acid, and \(pK\) is the formation or stability constant (Dean 1979). The larger the formation constant, the more stable the complex. The formation constants for Al and Mg with oleic acid are not known. However, if \(pK_{\text{EDTA-Al}}\) and \(pK_{\text{EDTA-Mg}}\) are greater than \(pK_{\text{EDTA-AI}}\) and \(pK_{\text{EDTA-Mg}}\), then the metallic soap complex can be broken, and Al/Mg will reside in the aqueous phase as EDTA complexes. Because these reactions occur at the oil-water interface mass transfer phenomena will affect the overall process kinetics.

For a nonoil system, all aqueous-phase Al will be complexed by EDTA under the following conditions (Westall et al. 1976): (1) pH is greater than -2; (2) EDTA/Al molar ratio \(\geq 1\); and (3) only 1:1 EDTA-Al complexes are formed. For pHs less than -2, \(\text{H}^+\) successfully competes with the Al for the EDTA. For Mg, the EDTA-Mg complex becomes significant at pH -4 and all aqueous Mg is associated with EDTA at pHs greater than -6. For both Al and Mg, the formation of hydroxide solids is prevented at EDTA/metal molar ratios \(\geq 1\).

UF and CUF Process

UF is a pressure-driven membrane technique that uses porous membranes for the separation of material in the 1-nm to 10-\(\mu\)m size range or compounds with molecular weights in excess of 1,000 (Cheryan 1986). In all membrane processes, a solute boundary layer will form at the membrane surface due to convective mass transport, which is one reason why the permeate flux for a waste is lower than the clean water flux. The buildup of solute near the membrane surface is reduced by diffusion processes, and the solute boundary-layer thickness is reduced through hydraulic turbulence. In conventional tubular UF systems, the thickness of the solute boundary layer is reduced by recycling a large portion (-98%) of the feed back to the membrane unit, producing large liquid velocities near the membrane surface. In high-shear UF systems, the energy required to produce the “cleaning action” is applied directly to the membrane surface by rotating or vibrating the membrane. In this study, a HSRUF system equipped with a ceramic membrane was used to separate oil droplets from the aqueous phase. The reader is referred to Reed et al. (1997) and Viadero and Reed (1999) for a detailed description of the high-shear system.

MATERIALS AND METHODS

Two batches of MW fluid were received directly from a rolling mill operation in 55-gal. drums. The first batch was used for runs 1 and 2, and the second batch was used for runs 3 and 4. The MW fluid contained soil (\(\approx 5\%\) volume-to-volume ratio), oleic acid (an emulsifier), film strength additives, and antifoaming agents. Specific contents of the mixture cannot be disclosed for proprietary reasons. The first batch of MW fluid contained 212-mg/L Al (7.86 \(\times 10^{-3}\) M) and 14.8-mg/L Mg (6.1 \(\times 10^{-4}\) M). The second batch contained 230-mg/L
every 30 min for the first 5 h of a dosage interval and every hour thereafter and analyzed for Al within 2 h of sampling, and when the permeate Al concentration stabilized for a given EDTA concentration, the next EDTA dose was added; and (3) after final EDTA addition, the system was operated in batch-down mode until the CF reached 4X.

**Runs 3 and 4**

In runs 3 and 4, a single EDTA concentration (0.05 M) was used. Following EDTA addition, the system was operated in recycle mode with frequent permeate sampling. After the permeate Al concentration had reached a constant value, the system was operated in batch-down mode. The concentrated MW fluid was rinsed by bringing the contents of the feed tank back to the original volume using DI water, operating in recycle mode (for mixing purposes), and then operating in batch-down mode (to remove the rinse water as permeate). The rinsing procedure was repeated twice. Sampling was conducted in a manner similar to runs 1 and 2 except for the following: (1) Mg was not measured in runs 1 and 2 because it was demonstrated that Mg contributed relatively little to the production of metallic soaps; (2) permeate and concentrate conductivity were monitored frequently; and (3) mass of Al in the permeate and in the final UF concentrate was determined so that an Al mass balance could be conducted.

**RESULTS AND DISCUSSION**

**Run 1**

In Fig. 3, permeate Al and Mg concentrations versus time are presented for run 1. Prior to the addition of EDTA, the permeate Mg and Al concentrations were 1.5 mg/L and <0.1 mg/L, respectively. At an EDTA concentration of 10^{-4} M, the permeate Mg concentration doubled, but there was little
change in the Al concentration. Similar behavior was observed for $5 \times 10^{-4}$ M and $10^{-3}$ M EDTA concentrations. Not until the EDTA concentration was increased to $5 \times 10^{-3}$ M was there a significant amount of Al released from the oil phase. The initial Al and Mg concentrations in the MW fluid were 212 mg/L (7.86 $\times 10^{-3}$ M) and 14.8 mg/L (6.1 $\times 10^{-4}$ M), respectively. The amount of Mg complexed at $5 \times 10^{-3}$ M EDTA was approximately 10 mg/L (4.1 $\times 10^{-4}$ M) leaving $4.6 \times 10^{-3}$ M of EDTA available for Al complexation. Assuming the EDTA-Al complex was 1:1 and the remaining EDTA is 100% efficient in sequestering Al, [Al],, should equal $4.6 \times 10^{-3}$ [M] EDTA available for EDTA [Al] use in runs 2. As in run 1, prior to the addition of EDTA, the permeate Al concentration was negligible, and the Mg-oleic acid complex should be easier to break. Following the first EDTA addition ($10^{-3}$ M), the aqueous-phase Mg increased immediately but then declined as the Al concentration increased from $\approx 0.1$ mg/L to about 8 mg/L. This phenomenon was more apparent at $5 \times 10^{-3}$ M EDTA. The Al-EDTA chelation efficiency for run 2 at CF = 1 x was similar to that in run 1. The percentages of the total Al (Mg) residing in the aqueous phase at $5 \times 10^{-3}$ M and $10^{-2}$ M EDTA were 39% (77%) and 46% (81%), respectively. Given the small increases in aqueous-phase Al and Mg concentrations when the EDTA concentration was increased from $5 \times 10^{-3}$ M to $10^{-2}$ M, an EDTA concentration of $5 \times 10^{-3}$ M was chosen for use in runs 3 and 4.

Permeate Al and Mg concentrations increased with CF with the vast majority of total Al/Mg removal occurring as the CF was increased from 1 x to 3 X (Table 1). Actual Al and Mg mass removal efficiencies, based on the mass of Al and Mg in the permeate collected as the CF was increased from 1 X to 5X, were 49% for Al and 86% for Mg. These values were much higher than the removal efficiencies predicted using permeate Al and Mg concentrations observed during operation in recycle mode (37 and 64% for Al and Mg, respectively). Either additional Al/Mg was released as the oil content was increased or oil droplets containing Al/Mg passed through the membrane into the permeate. The latter explanation is unlikely given that the permeate turbidity and O/G did not increase substantially during batchdown. It is more likely that during batchdown the oil droplets coalesced into larger droplets that required less

**TABLE 1.** Percentages of Total Mass of Al and Mg Removed during Batchdown

<table>
<thead>
<tr>
<th>CF change (1)</th>
<th>Percent of Total Al or Mg Present</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al (%)</td>
</tr>
<tr>
<td>1x $\rightarrow$ 2x</td>
<td>61</td>
</tr>
<tr>
<td>2x $\rightarrow$ 3x</td>
<td>23</td>
</tr>
<tr>
<td>3x $\rightarrow$ 4x</td>
<td>12</td>
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<td>4x $\rightarrow$ 5x</td>
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emulsifier (oleic acid) to maintain emulsion stability. The formation of larger oil droplets caused the oil-bound Al and Mg to be released more easily.

Except for a few samples between 29 and 32 h, permeate turbidity was generally <1 (NTU) and O/G < 200 mg/L, demonstrating the effectiveness of the ceramic membrane in rejecting oil droplets. The pH of the permeate and concentrate increased because the EDTA stock solution pH (made from Na₂EDTA) was 11.9. Increasing the pH should not affect the chelation of aqueous-phase Al and Mg because Al and Mg are theoretically fully complexed with EDTA between pH = 7-9. However, pH could affect the relationship between oleic acid and Al/Mg as well as the chemistry of the oil droplet. The permeate flux increased from 195 to 250 gal./ft²-day when the EDTA concentration was increased from 10⁻³ M to 5 × 10⁻³ M. Additional increases in EDTA concentration had little effect on the permeate flux. An increase in flux with conductivity (ionic strength) has been reported for the microfiltration of a domestic wastewater (Al-Malack and Anderson 1996) and for fuel and crude oil contaminated waters (Tansel et al. 1995). Al-Malack and Anderson (1996) reported an increase in flux with increasing salt concentration until an optimum dose was reached above which no improvement in flux was observed. During batchdown, permeate flux decreased with increasing CF (i.e., increasing concentrate oil content). These results were consistent with earlier work on the same MW fluid (Reed et al. 1997, 1998). As the oil concentration was increased, the solute boundary-layer thickness increased due to (1) more oil being transported to the membrane surface via convection; (2) decreased back-diffusion of oil from the membrane surface because of a smaller oil concentration gradient between the membrane surface and bulk solution; and (3) less turbulence.
at the membrane surface due to an increase in viscosity (Reynolds number $\sim 1/\mu$).

**Runs 3 and 4**

In Fig. 5, permeate Al concentration, permeate and concentrate conductivity, and flux and CF versus time are presented for run 3. Results for run 4 were similar and will not be presented. Following the $5 \times 10^{-3}$ M EDTA addition, the permeate Al concentration increased over a 5-h period from near zero to 90 mg/L, and then remained fairly steady for the remainder of the CF = 1X portion of the experiment. First- and second-order kinetic models ($r = k[Al]$ and $r = k[Al]^2$) were applied to the data in this 5-period, but neither model adequately described the increase in Al with time. The following multistep process may be occurring:

- Step I-EDTA transport from the bulk aqueous solution to the stagnant liquid layer surrounding the oil droplet
- Step II-Diffusion of the EDTA through the stagnant liquid layer
- Step III-Reaction of the oleic acid-Al and oleic acid-Mg complexes with EDTA
- Step IV-Diffusion of EDTA-Al and EDTA-Mg complexes through the stagnant liquid layer
- Step V-Transport of EDTA-Al and EDTA-Mg complexes to the bulk solution

The bulk solution hydrodynamic conditions in the experimental system were turbulent as the MW fluid and EDTA were well mixed in a number of locations: (1) In the centrifugal pump that provided recirculation between the membrane chamber and feed tank; (2) within the high-shear membrane chamber; and (3) within the feed tank itself where a pneumatic mixer was located. The Reynolds number in the high-shear membrane chamber and feed tank; (2) within the high-shear membrane chamber; and (3) within the feed tank itself where a pneumatic mixer was located. The Reynolds number in the high-shear membrane chamber can be estimated by (Murkes and Carlsson 1988)

$$R = \frac{\omega r^2}{\mu}$$  \hspace{1cm} (7)

where $\omega$ = membrane rotational speed (rad/s); $r$ = membrane disk radius (m); and $\mu$ = absolute viscosity (kg/m-s). At 1,750 (183 rad/s) and 5% oil, $R$ was $> 1.8 \times 10^6$ (Viadero 1997), which is much $>2.5 \times 10^5$, the cutoff between laminar and turbulent flow (Ketola and McGrew 1968; Murkes and Carlsson 1988). Thus, it is unlikely that Steps I and V were rate limiting. Typically, reaction kinetics are not considered to be rate-limiting. However, little is known about the reaction between the metallic soaps and EDTA. As a side experiment, virgin MW fluid was contacted with Al to determine if a synthetically contaminated MW fluid could be developed. After several weeks of mixing, there was little change in the aqueous-phase Al concentration. In the full-scale MW process, it takes between 6 and 8 weeks before there is a buildup of metallic soaps. Thus, Step III as well as Steps II or IV may be rate-limiting. Complicating the transport of EDTA to the oil droplet and the transport of EDTA-Al and EDTA-Mg complexes away from the oil droplet are the presence of negative charges on the oil droplet, EDTA (-4), EDTA-Al (-1), and EDTA-Mg (-2) complexes. The rapid increase in bulk aqueous-phase Mg concentration compared with Al could be due to Steps III and IV being faster for Mg-the more negative EDTA-Mg^-2 complex may move away from the negatively charged oil droplet faster than the EDTA-Al^-1 complex due to differences in electrostatic repulsive forces.

During the first batchdown (CF = 1X to 3X) the permeate Al increased from 90 to 127 mg/L and 30% of the Al was removed. Subsequent DI water rinses removed little additional Al (4.7% for rinse 1 and 4.3% for rinse 2). The total Al removal efficiency was 39% for run 3. The effectiveness of the rinse in removing ions from the aqueous phase is demonstrated by the decrease in permeate and concentrate conductivity. When the system was brought back to its original volume following the first batchdown, the concentrate conductivity was similar to the original value. This is important because the ash content of the MW fluid (defined by the MW industry as the residual remaining after heating at 770°C) would be unacceptable high, due to Na$_2$EDTA addition, unless the MW fluid was rinsed. During the first batchdown in run 4 (CF = 1X to 4.2X), 38% of the Al was removed from the system. In subsequent rinses, Al removal efficiencies for rinses 1 and 2 were 7.8 and 3.0%, respectively. The total Al removal efficiency for run 4 was 49% and was higher than that observed in run 3.
because a higher CF was reached (4.2X compared with 3X in run 3). Al mass balances, conducted at the end of the runs, produced errors of 2.8% for run 3 and 6.2% for run 4.

After the system was brought back to its original volume (CF = 1X), the flux took over 10 h to reach its prebatchdown level indicating that the solute boundary layer was somewhat stable. Similar behavior was observed during the second rinse. Stability of the solute boundary layer with changes in rotational speed were reported for an actual MW fluid (Reed et al 1997) and for a virgin MW fluid (Viadero 1997).

CONCLUSIONS

For the MW fluid investigated in this study, batch-life is controlled primarily by the concentration of complexes of anionic oil emulsifiers (e.g., oleic acid) and Al/Mg (known as metallic soaps). Metallic soaps increase the lubricating ability of the MW fluid, but eventually the MW fluid becomes too slippery, and the rolling process is adversely affected because of unwanted slippage between the workpiece and the rolling mill. EDTA, a strong metal chelator, was added to a MW fluid containing metallic soaps with the goal of transferring Al/Mg from the oil phase to the aqueous phase. The aqueous-phase EDTA-Al/Mg complexes and oil droplets were then separated using a UF membrane process. The following conclusions are drawn:

- The CUF process was effective in removing oil-bound Al and Mg (metallic soaps). Removal efficiencies for Al (39-49%) and Mg (67 and 86%) were highest at 5 X 10^{-3} M EDTA. Because metallic soaps, up to a certain concentration, impart valuable lubrication properties, higher Al/Mg removal efficiencies may not be required.
- Concentrating the MW fluid following EDTA addition increased Al and Mg removal efficiencies. The beneficial effect was minimal after a CF of 3X was reached, and the membrane separation portion of the CUF process can end at this level of concentration.
- Rinsing the concentrated MW fluid with DI water reduced the conductivity/ash content substantially but had a less significant impact on Al and Mg removal.
- Oil-bound Al release into the aqueous phase was slow.

First- and second-order aqueous-phase kinetics did not adequately describe the data; thus, a multistep, two-phase conceptual model was proposed.

The UF system (0.11-μm ceramic membrane) was effective in separating the oil droplets from the aqueous phase. Permeate turbidity was generally <1 NTU, and the O/G content was always <200 mg/L. The separation step does not appear to be the limiting factor in the effectiveness of the CUF process.

APPENDIX. REFERENCES


