

Influence of Ion Accumulation on the Emulsion Stability and Performance of Semi-Synthetic Metalworking Fluids

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The metalworking industry is one of the largest in the United States. Although metalworking fluids (MWFs) are ubiquitous in manufacturing as coolants and lubricants, these emulsified fluids have a significant environmental impact over their life cycle. Accordingly, it has become necessary to better understand emulsion destabilization mechanisms that lead to MWF deterioration and disposal so that MWF formulations can be designed for increased longevity. This paper investigates the impact of pH and a wide range of hard water salts on MWF emulsion stability. While expected trends from the emulsion science literature are observed, it is shown that MWF destabilization can lead to an increase in the microbial load that the MWF can sustain while only slightly improving manufacturing performance as measured by the tapping torque test. Experimental observations also indicate that these trends are strongly correlated with increased emulsion particle size, regardless of whether increased particle size is achieved by aging, by reductions in pH, or by the addition of hard water salts. In MWF systems, these conditions typically result from the accumulation of divalent and trivalent cations over time due to hard water additions and exposure to metal workpieces and tools. While MWFs are formulated with EDTA to avoid emulsion destabilization due to cation accumulation, it is shown that EDTA can be ineffective or highly inefficient for this purpose due to direct interactions between EDTA and the MWF emulsifier system. Given the ineffectiveness of EDTA and commonly utilized MWF emulsifier systems to maintain stable emulsion size in the presence of high concentrations of hard water salts, a more effective and environmentally preferable technological change to the MWF formulation design is proposed and successfully demonstrated.

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Introduction

Metalworking fluids (MWFs) serve as coolants, lubricants, chip evacuators, and corrosion inhibitors in metal cutting operations. They improve machining performance by increasing tool life, improving surface finish and tolerances, reducing cutting forces, and reducing vibrations (1). MWF use is therefore central to state-of-the-art machining processes, with over 2 billion gal of MWF consumed in North America during 2000 (2). Klocke and Eisenblaetter have shown that MWF use accounts for approximately 7–17% of total manufacturing costs (3). These costs as well as the potential human health and environmental hazards associated with MWF use have provided an impetus to eliminate MWFs from manufacturing (4) or to reduce their use to the largest extent possible (5). While it has been found that MWF use can be reduced, or even eliminated in less severe machining operations, most machining applications still require MWFs for high productivity.

MWF use can create human health risks from exposure to toxic chemical constituents (e.g., biocides) or from microbial populations that can grow in MWF (6, 7). Similarly, MWF disposal has associated with it environmental risks arising from hazardous chemicals, oxygen depletion potential, and excess nutrients (8, 9). For these reasons, the United States Environmental Protection Agency (U.S. EPA) has become increasingly interested in the regulation of MWF disposal. In 2001, the U.S. EPA revised their proposed effluent limitation guidelines and standards for MWFs in the Metal Products and Machinery Rule (10). If enacted, the rule would regulate the disposal of MWFs supplementary to the Toxic Substances Control Act, the Clean Water Act, and the Resource Conservation and Recovery Act (11). Among other restrictions, the proposed regulations would limit the daily discharge concentration of oil and grease to 15 mg/L, which is approximately 2 orders of magnitude below the actual oil and grease concentrations typically found in MWFs. This legislation, if enacted, would provide further incentive to reduce the frequency of disposals through recycling (12, 13) and encourage reduction in the use of hazardous constituents in MWFs.

To achieve a reduction in disposal frequencies, it is necessary to extend MWF lifetimes without compromising performance levels. This requires a fundamental understanding of the pathways for MWF deterioration, which include (i) microbial growth leading to biometabolism of MWF ingredients (14); (ii) accumulation of dissolved salts causing emulsion destabilization (11); (iii) poor concentration control leading to performance failure (15); (iv) accumulation of submicron particles that facilitate microbial growth and increase the surface area for oxidation reactions (16); and (v) oil-phase partitioning and removal of lubricants leading to tool breakage (17).

Several of these deterioration pathways may be influenced by emulsion stability. However, fundamental research directed toward describing and quantifying the relationships between emulsion stability, MWF formulation characteristics, and machining performance has been minimal. In this investigation, the impact of the accumulation of dissolved salts on MWF emulsion stability is considered. Such an investigation is necessary since concentrations of hard water salts in MWFs can vary significantly under typical manufacturing conditions. These salts are introduced into the system through tap water as it is added to replenish water lost due to evaporation. While it is known that increased emulsion droplet size and destabilization of MWF can arise

TABLE 1. Compositions of Commercially Available Semi-Synthetic Metalworking Fluids (SS1 and SS2)^a

semi-synthetic 1 (SS1) ^b		semi-synthetic 2 (SS2) ^c	
component	molar concn in use	component	molar concn in use
water		water	
mineral oil (naphthenic)	1.9×10^{-2}	mineral oil (naphthenic)	1.1×10^{-2}
surfactant (sodium petroleum sulfonate)	6.6×10^{-3}	surfactant (sodium petroleum sulfonate)	6.0×10^{-3}
coupler	4.6×10^{-3}	coupler	1.4×10^{-2}
secondary emulsifier	3.0×10^{-2}	secondary emulsifier	1.5×10^{-2}
tall oil fatty acid	6.6×10^{-3}	tall oil fatty acid	8.5×10^{-3}
corrosion inhibitor	4.9×10^{-2}	corrosion inhibitor	1.1×10^{-2}
EDTA	2.6×10^{-4}	EDTA	2.6×10^{-4}

^a Molar concentrations shown at 5% dilution of concentrate and represent "in use" conditions. ^b pH 9.1; single mode particle size distribution; mean particle diameter, ≈ 20 nm. ^c pH 9.1; bimodal particle size distribution; mean particle diameter mode 1, ≈ 20 nm; mode 2, ≈ 100 nm.

due to the accumulation of hard water salts, a quantitative assessment of ion characteristics for their impact on emulsion droplet size, microbial growth potential, and machining performance has yet to be described in the literature. Moreover, the effectiveness of chelating agents added to MWFs to counteract the accumulation of hard water ions has also yet to be investigated.

While previous literature in the environmental science and engineering community describe the behavior of anionic: nonionic surfactant mixtures (18–20), the role of electrostatic double layers in emulsion stability (21–24), and the impact of surfactant structure on precipitation by divalent cations typical of hard water (25), systematic studies of these effects in MWF formulation design is lacking. Such studies are needed to elucidate the causes of MWF instability under field conditions so that MWF formulations can be designed to be more resistant to deterioration under typical manufacturing system conditions. Toward this end, this paper investigates the impact of the accumulation of hard water ions on MWF emulsion stability, microbial resistance, and machining performance. A novel technological approach to achieving MWF stability in hard water is also proposed.

Experimental Materials and Methods

The experiments described in this paper were performed using two semi-synthetic (25) metalworking fluids (SS1 and SS2) that are commercially available and produced by different manufacturers. While there are chemical differences in the two formulations, they are both based on the same six key component types. Each fluid also features the use of ethylenediaminetetraacetic acid (EDTA), biocides, fungicides, and dyes as shown in Table 1. Both SS1 and SS2 are based on naphthenic mineral oil and use a binary surfactant system with sodium petroleum sulfonate as the primary anionic emulsifier and an alkanolamide based on diisopropanolamide as the secondary nonionic surfactant. Both fluids were received as concentrate from their respective manufacturers and were subject to the same handling and storage conditions.

Emulsion stability of the two semi-synthetic MWFs was tested by adding a variety of salts at 0, 100, 300, 500, 700, and 800 ppm as calcium carbonate (CaCO₃). Conversions (based on equivalent charge of the cation with respect to calcium) from ppm as CaCO₃ to molar concentrations for each cation are presented in Table 2. The salts were chosen to represent a wide range of anionic and cationic species and charges and included salts of aluminum (AlCl₃, AlSO₄), calcium (Ca(OH)₂, CaCl₂, CaSO₄), magnesium (MgCl₂, MgSO₄), potassium (KOH, KCl, K₂CO₃, K₂SO₄), and sodium (NaOH, NaCl, Na₂CO₃, Na₂SO₄). The appropriate amount of each salt for the desired level of hardness was added to a 25-mL sample of diluted fluid, vigorously shaken for 1 min, and allowed to equilibrate. After 48 h, the emulsion droplet size of the fluid (and in some cases the ζ -potential) was measured.

TABLE 2. Conversions Based on Normal Equivalence from ppm as Calcium Carbonate to Molar Concentration for Each Cation

ppm as CaCO ₃	mol of Na ⁺ , K ⁺ /L	mol of Ca ²⁺ , Mg ²⁺ /L	mol of Al ³⁺ /L
0	0	0	0
100	2.0×10^{-3}	1.0×10^{-3}	6.7×10^{-4}
300	6.0×10^{-3}	3.0×10^{-3}	2.0×10^{-3}
500	1.0×10^{-2}	5.0×10^{-3}	3.3×10^{-3}
700	1.4×10^{-2}	7.0×10^{-3}	4.7×10^{-3}
800	1.6×10^{-2}	8.0×10^{-3}	5.3×10^{-3}
1000	2.0×10^{-2}	1.0×10^{-2}	6.7×10^{-3}

Emulsion droplet size and ζ -potential were measured as indicators of emulsion stability. One of the most common techniques to determine particle size is photon correlation spectroscopy (PCS). PCS allows for the detection of subtle fluid particle motion changes, including indications of coalescence (26, 27). For this research, a Nicomp 370/DLS (Particle Sizing Systems, Santa Barbara, CA) particle sizing system was used, with its particle size estimation capability verified independently by a wide-angle laser light scattering apparatus similar to the one described by Lee et al. (28). PCS is useful to measure particle sizes over a range of 10–1000 nm. For particle sizes greater than 1000 nm, a Multisizer 3 (BeckmanCoulter, Fullerton, CA) was used. This instrument utilizes the well-known "Coulter Counter" method (29). To provide a better understanding of the mechanisms destabilizing the MWFs, ζ -potential was measured by electroacoustic spectroscopy using a ZetaProbe instrument (Colloidal Dynamics, Warwick, RI). ζ -potential values for the MWF emulsion particles after the addition of dissolved salts are reported normalized with respect to the measured MWF ζ -potential prior to the introduction of salts.

Machining performance was measured on the fluids using a MicroTap Mega G8 (Rochester Hills, MI) at a machining speed of 1000 rpm on 1018 cold rolled steel workpieces that were predrilled and prereamed with 240 M6 holes (Maras Tool, Schaumburg, IL) with titanium nitride-coated (TiN) and uncoated high-speed steel taps with 60° pitch and three straight flutes. MWF evaluations were carried out according to ASTM D 5619, the Standard for Comparing Metal Removal Fluids Using the Tapping Torque Test Machine (30), with several modifications made to account for the use of a MWF evaluation test bed that permits multiple evaluations on a single workpiece as proposed by Zimmerman et al. (31). MWF performance is reported as tapping torque efficiency (η), with higher efficiency indicating higher MWF performance.

Quantification of microbial concentration in MWFs was performed using a direct fluorescent counting technique. Prior to counting microbial population in the MWF systems, 100 mL of each MWF was autoclaved and adjusted to a pH between 9.0 and 9.1. The systems were then inoculated to achieve 10⁵ cells/mL with a microbial sample collected from the sump of a 30 000-gal MWF reservoir that had been in-

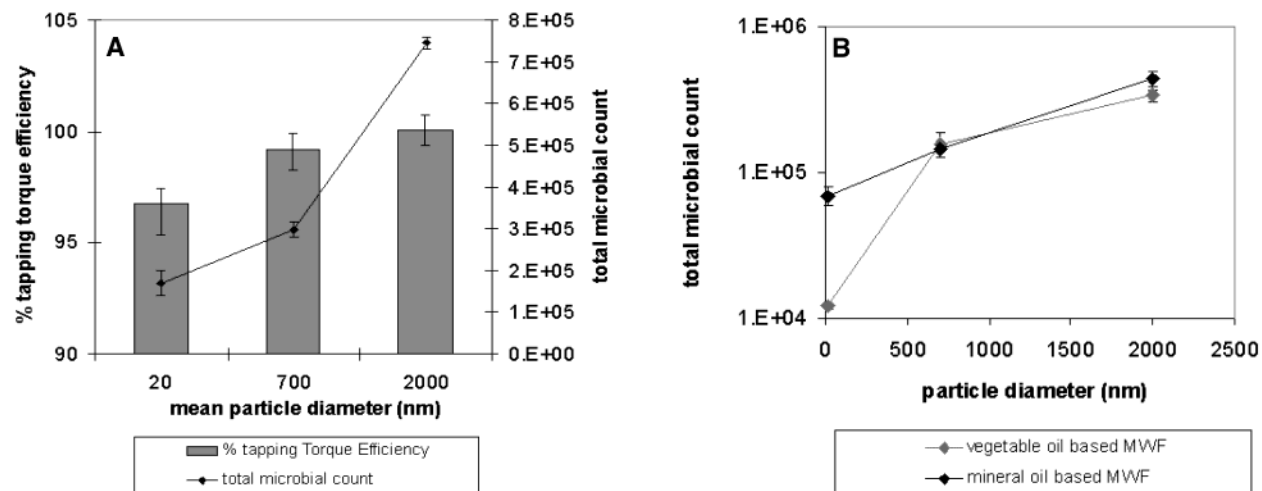


FIGURE 1. Observed microbial concentrations as a function of particle size for (A) petroleum-based MWF (with corresponding tapping torque data) and (B) vegetable and petroleum-based MWF (without tapping torque data). Microbial culture was isolated from an industrial facility, cultured over several generations, and incubated for 48 h. Particle size changes were induced by adding calcium. 95% confidence intervals are shown.

use for several months. The microcosms were incubated at 30 °C, and after 48 h, triplicate 1-mL samples were taken from each microcosm and centrifuged at 2100 rpm for 30 min. The supernatant was decanted, and the cell pellet was resuspended in pH 7.2 phosphate-buffered saline (PBS) to 1.5 mL. This procedure was repeated three times to achieve a recovery rate of 70%. After the final washing, the cell pellet was resuspended in PBS to 0.5 mL and stained using 0.5 mL of Acridine Orange at a concentration of 1 mg/mL. The stained cell suspension was then filtered through a 25 mm diameter, 0.22- μ m pore, prestained black polycarbonated filter (Osmomics, Inc., Minnetonka, MN) and transferred to prepared slides for counting by epifluorescent microscopy (Axioplane, Zeiss, Germany).

Impact of Dissolved Salt Addition on Bioresistance and Tapping Torque

The introduction of acids and hard water salts can impact semi-synthetic MWFs by increasing the droplet size of the emulsions. In turn, it is possible that the droplet size of the emulsion can significantly impact the bioresistance of MWF systems (32). For instance, Figure 1 illustrates the relationship between increasing emulsion droplet (or “particle”) diameter, tapping torque performance, and microbial load for both a petroleum- and a biobased semi-synthetic MWF formulation after the addition of calcium hydroxide. For the petroleum-based MWF (Figure 1A), a mean emulsion size shift from 20 to 2000 nm was observed and led to a slight, albeit statistically significant, improvement in machining performance as measured by tapping torque efficiency. Interestingly, the same emulsion particle size shift increased the total microbial load in the MWF by nearly 440%. Repeating the experiment for a biobased MWF (Figure 1B) led to similar results.

The results shown in Figure 1 are likely to be due to the physical size of the MWF emulsion rather than the addition of calcium. This is because similar results to Figure 1 were observed under conditions of low pH and MWF aging, as previously observed in the literature (11). Moreover, calcium is not typically a limiting nutrient in aqueous systems such as MWFs (33). The results shown in Figure 1 are also consistent with recent research efforts by Hamouda et al. (34) and Hamouda and Baker (35), which describe the effectiveness of anionic and nonionic nanoemulsions against *Bacillus* spores, enteric G-bacilli, yeasts, fungi, and viruses, suggesting that stable nanoemulsions have inherent antimicrobial properties.

These data enhance the notion that stability of nanoscale emulsion droplets is a key parameter in the design of MWFs for improved microbial resistance and improved MWF longevity, as microbial growth can lead to the release of acids that can in turn further increase particle size and accelerate the deterioration of MWFs. This acceleration results from the higher probability for coalescence and flocculation associated with larger droplets (36). Since coalescence and flocculation can in turn lead to increased microbial growth (e.g., Figure 1) and the release of acids that can further destabilize the MWF, the emulsion may completely break down into oil and water phases leading to premature MWF disposal. Higher microbial loads can also alter MWF performance by selectively metabolizing individual components (37), accelerating corrosion of tools and machined product (38), and creating masses of biofilm that can physically block MWF delivery lines (39). Given the potential health risks associated with microbial proliferation and the potential impact of microorganisms on MWF deterioration and performance, the small and short-term increase in machinability due to the addition of calcium salts is not likely worth the consequences of a concurrent and significant increase in microbial growth. This conclusion motivates investigations into MWF stability under hard water conditions and the design of alternative hard water stable MWF systems.

Impact of Dissolved Salts and pH on Tapping Torque Measurement and Microemulsion Particle Size

To understand the impacts of dissolved salts on emulsion particle size and machining performance, varying amounts of Ca(OH)₂ were added to SS1 and SS2. While Figure 2 suggests that an increasing emulsion particle size is correlated with improved tapping torque efficiency in both SS1 and SS2, it is important to note that the concentration of calcium hydroxide, and therefore pH, was also increasing in each system. This raises the issue of whether improved tapping torque efficiency was due to the additional calcium, the increased pH, or the increasing emulsion particle size. To resolve the cause of the improved machining performance, the mean emulsion particle size of SS1 was increased to 100 and 500 nm in separate experiments using calcium salts, magnesium salts, and nitric acid. The results indicate that for a given emulsion particle size (100 or 500 nm) the tapping torque efficiencies are statistically identical (Figure 3). That is, the final particle size determines the machining perfor-

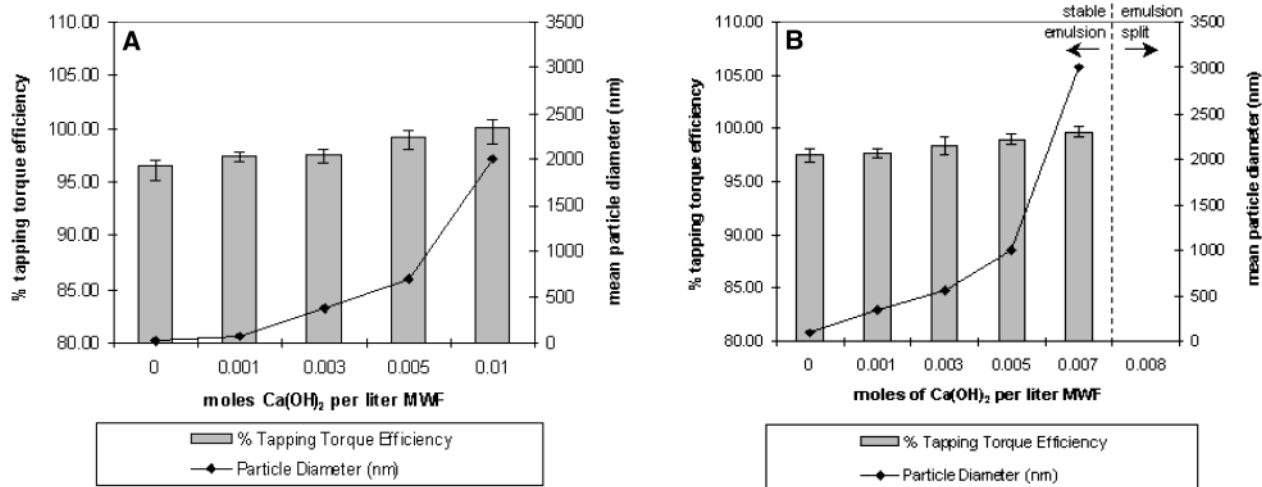


FIGURE 2. Percent tapping torque efficiency and mean particle diameter as a function of hard water concentration for (A) SS1 and (B) SS2. Tapping torque was evaluated using an M6 TiN-coated tool, a 1018 cold rolled steel workpiece, and a machining speed of 1000 rpm. 95% confidence intervals are shown.

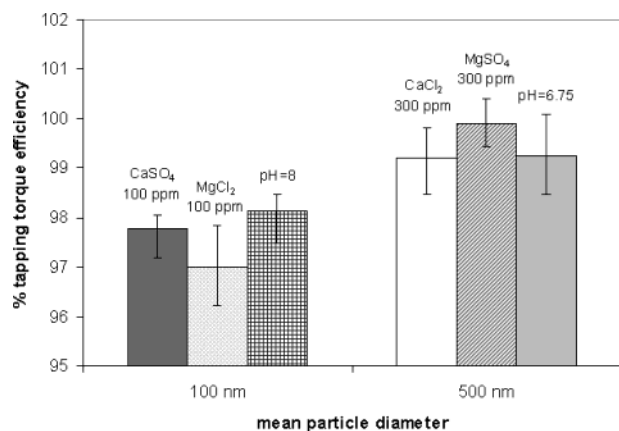


FIGURE 3. Percent tapping torque efficiency as a function of mean particle diameter where particle size of SS1 was adjusted by the treatment indicated.

mance of the MWF regardless of the cause of the particle size shift.

To evaluate the impacts of pH on emulsion particle size and machining performance, nitric acid was introduced to SS1 and SS2 in order to incrementally reduce the pH to 6.5. Size measurement results for SS1 and SS2 over this pH range indicate that emulsion particle size increases with decreasing pH. This is most likely the result of the hydrogen ions protonating the anionic emulsifier, which neutralizes electrostatic repulsive forces and increases the potential for emulsion droplets to collide (40–42). For instance, 70% of the emulsion droplets are no longer within their initial size range at pH 6.5. However, in the case of SS2, only 45% of the emulsion particles are outside the initial size range. This indicates that even small changes in MWF formulation can have a major impact on emulsion stability under acidic conditions. Although not shown, the emulsion completely separates below a pH of 5, making it especially important to maintain higher pH values regardless of the MWF formulation.

Similar to pH, changes in cation valence impact emulsion particle size and machining performance. To evaluate these impacts, a series of salts with cations ranging from plus one (sodium) to plus three (aluminum) were added to both SS1 and SS2 at various concentrations. The pH of each fluid was then adjusted to 9.0 prior to the measurement of particle

size and tapping torque efficiency. As shown in Figure 4A, the addition of sodium to SS1 and SS2 resulted in little change of the initial emulsion particle size. Figure 4B shows that when calcium was introduced to SS1 and SS2, there is a trend of increasing emulsion particle size with increasing calcium concentration. In fact, when 0.008 M calcium chloride was introduced to SS2, the MWF split into separate oil and water phases. Increasing aluminum concentration had the most significant impact on the increasing emulsion particle size, with both fluids split into oil and water phases after the addition of 0.005 M AlCl_3 as shown in Figure 4C. In fact, at 0.008 M calcium and 0.005 M aluminum chloride, white precipitate products begin to form, indicating that the onset of emulsion separation and the precipitation of hard water cations are related.

The precipitation observed in these systems is most likely the cation (calcium or aluminum) neutralizing the anionic surfactant, which causes the surfactant to precipitate out of solution. This is analogous to the observations of Rouse et al. (41), who reported the presence of precipitate as a heavy white flock in systems containing a model monosulfonate surfactant (C_{12} -sodium dodecylbenzenesulfonate) over the same calcium concentration range. Talens-Alession (42) also reported anionic surfactant precipitation resulting from electroneutralization by aluminum cations.

Such precipitates further destabilize emulsion droplets by acting as a nucleus for particle coalescence. Surfactant losses arising from precipitation in turn decrease the amount of surfactant available to “pack” around the oil droplet and stabilize the emulsion. Due to these positive feedback mechanisms, it can be expected that MWFs stabilized by monosulfonate surfactants are vulnerable to the presence of calcium and aluminum cations. As such, a renewed effort at MWF design focused on the maintenance of electrostatic repulsion when using anionic surfactants under hard water conditions should be considered an important design criterion, balanced by the need for emulsion splitting at end-of-life for oil recovery and recycling.

To further understand the impact of specific ions and ion charge on the emulsion stability and tapping torque efficiency of semi-synthetic MWFs, five representative cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and Al^{3+}) and four representative anions (OH^- , Cl^- , SO_4^{2-} , and CO_3^{2-}) were added as various salt combinations. Each salt was added to SS1 and SS2 at an equivalent concentration of 500 ppm as CaCO_3 . A clear trend of increasing emulsion particle size is observed with increasing

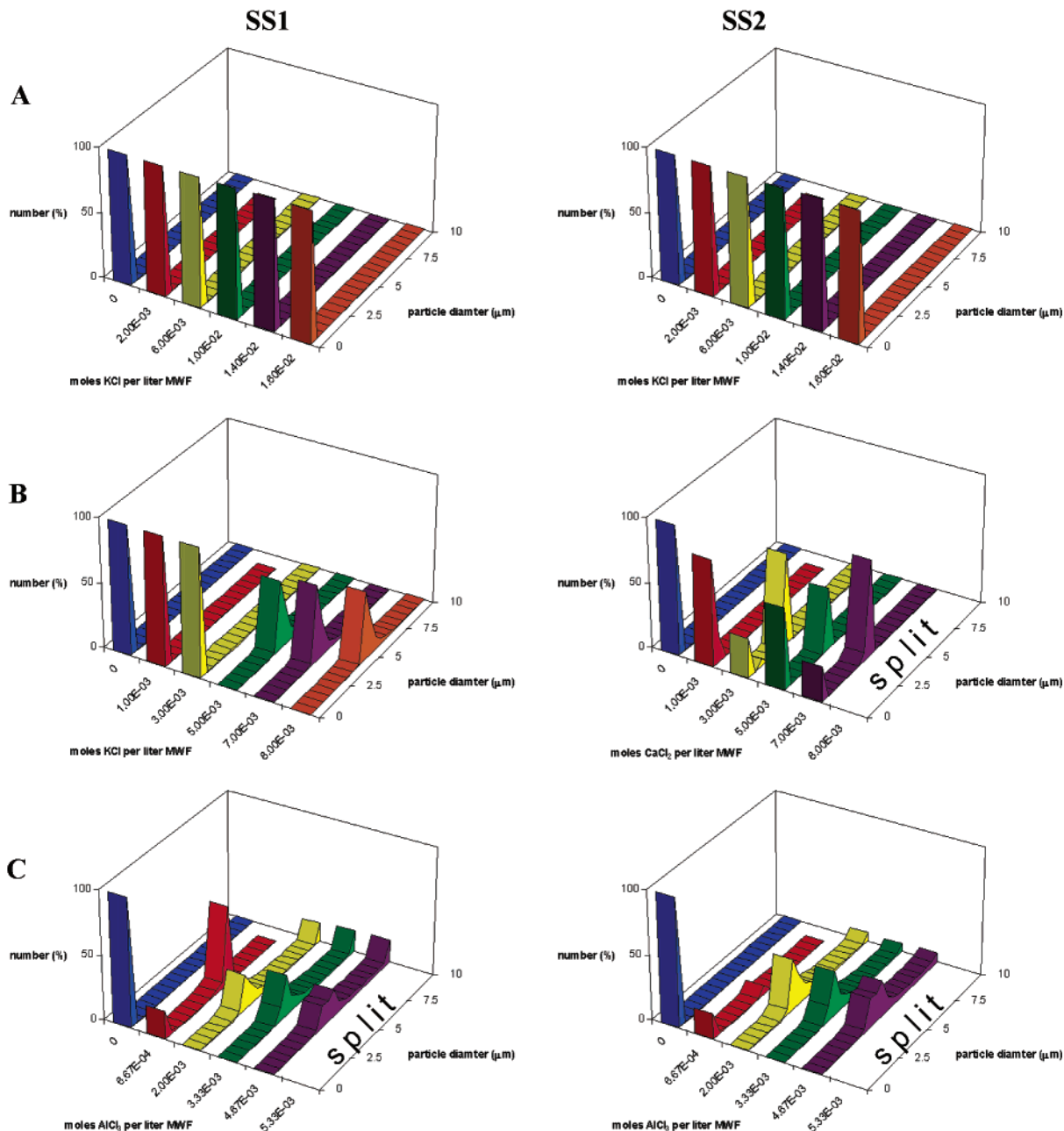


FIGURE 4. Particle size of SS1 and SS2 as a function of molar chloride salt concentration where the cation was added as (A) sodium (Na^+), (B) calcium (Ca^{2+}), and (C) aluminum (Al^{3+}).

cation charge from +1 (sodium, potassium) to +2 (calcium, magnesium) to +3 (aluminum). The results hold for both SS1 and SS2. In contrast, the salt counterion (anion) has little effect on the resulting particle size or the machinability of the fluid. These conclusions are clearly illustrated by the correlation statistics for SS1 and SS2 calculated in Table 3. The correlation results indicate that the mean emulsion particle diameter is highly correlated to the cation charge and much less so to the anion charge. The trend in Table 3 is expected whether the emulsion particle size is increasing due to interference with electrostatic stabilizing forces or due to increased precipitation or due to both mechanisms. This is because more highly charged cations result in greater disruption to electrostatic double layers and are also more likely to react to form insoluble precipitates (42).

It is observed in Table 3 that the tapping torque efficiency increases with cation concentration regardless of which cation causes the particle size shift. Moreover, tapping torque

TABLE 3. Calculated Correlation between Cation Charge, Anion Charge, Mean Particle Diameter, and % Tapping Torque Efficiency

	cation charge	anion charge	mean particle diameter	% tapping torque efficiency
cation charge	1.00			
anion charge	-0.21	1.00		
mean particle diameter	0.95	-0.23	1.00	
% tapping torque efficiency	0.84	-0.38	0.79	1.00

efficiency correlates poorly with anion concentration and ionic strength changes caused by anions. This suggests that corrosion, typically associated with anion concentration and penetration of surface films, is not likely playing a significant role in the enhanced tapping torque efficiency observed as ionic strength is increased.

TABLE 4. Normalized ζ -Potential Measurements as a Function of Ion Concentration and Mean Particle Diameter for SS1 and SS2

cation	MWF	ppm	mean particle diameter (μm)	normalized ζ -potential
potassium (+1)	SS2	0		1
	SS2	100		0.83
	SS2	300		0.74
	SS1	500	0.01	0.74
	SS2	500	0.08	0.72
calcium (+2)	SS2	700		0.69
	SS2	100		0.80
	SS2	300		0.58
	SS1	500	3.9	0.60
	SS2	500	3.5	0.41
aluminum (+3)	SS2	100		0.65
	SS2	300		0.23
	SS1	500	6.2	0.38
	SS2	500	5.9	0.04

To quantify the extent to which cations are disrupting the emulsion stabilizing forces, the ζ -potentials of SS1 and SS2 were measured over a range of cation concentrations and charges. Three salts (NaCl , CaCl_2 , and AlCl_3) were introduced into SS1 and SS2 at 500 ppm as CaCO_3 . As shown in Table 4, the normalized ζ -potential approaches zero and the emulsion particle size increases with increasing cation charge. This demonstrates that trivalent cations are more disruptive to the electrostatic repulsive forces than divalent and monovalent cations. This was expected and is also consistent with past research observations on cutting oil emulsion stability, which indicated that sodium had little or no effect on the ζ -potential while calcium and magnesium had a significant effect on ζ -potential over the same concentration range (43). It was also found in ref 43 that aluminum, a +3 cation, had the strongest effect on the electrostatic double layer, yielding a very small or zero ζ -potential value even at low concentrations.

Influence of EDTA-Based Chelation on Hard Water Stability of MWFs

It is interesting to note that cation interference with electrostatic repulsive forces occurs despite the presence of a chelating agent (EDTA). In both SS1 and SS2, the sodium salt of EDTA was included in the concentrate at a concentration of 2.5×10^{-4} M. This EDTA complex would ordinarily bind with calcium on a 1:1 molar basis, and at calcium concentrations below the EDTA concentration, there would not be any impact on emulsion stability. However, since emulsion stability was strongly affected, even by low concentrations of calcium ion in the MWF, it is clear that EDTA or the calcium ions in the system were unavailable in MWF to complex. For instance, it was observed that when calcium (as CaCl_2) and EDTA were added at an equal molar concentration (0.003 M) to SS1, the emulsion particle size distribution tended to broaden and shift to a larger mean value. This behavior indicated that not all of the EDTA in the system was available for complexation.

To further explore the effectiveness of EDTA in MWFs, formulations based on SS1 were produced with a range of EDTA concentrations from 0.0005 to 0.01 M. Several methods were utilized to add EDTA and salt (as 300 ppm CaCO_3) to the system. EDTA was added directly to the concentrate (Figure 5A), to the dilution water (Figure 5B), and to the final MWF as a complex with various salts (Figure 5C). As the EDTA concentration was increased in the concentrate (Figure 5A), the emulsion particle size distribution of the formulations shifted toward that of the unaltered MWF. However, even at an EDTA molar concentration three times greater than that of CaCl_2 , the emulsion particle size distribution was not

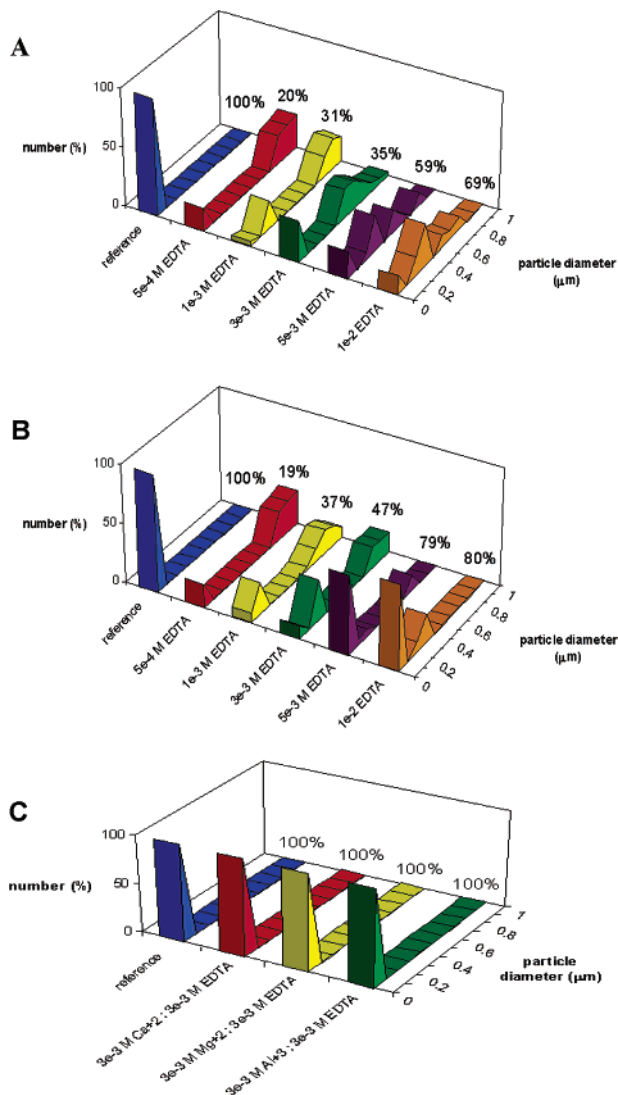


FIGURE 5. Particle size distribution of SS1 with 0.003 M calcium (as calcium chloride) added to the diluted MWF system as a function of EDTA concentration: (A) EDTA added to MWF concentrate with calcium dissolved in dilution water, (B) EDTA added to diluted MWF with calcium dissolved in dilution water, (C) a combined EDTA and calcium solution added to dilution water prior to diluting MWF. Reference particle size is that of the MWF without addition of calcium chloride. Percentages indicate the percentage of particles present in the original size range.

identical to that of the unaltered MWF, with only 69% of the particles present in the initial size range at 0.01 M EDTA. Consequently, the addition of EDTA to the MWF concentrate is not effectively achieving hard water stability since the majority of the EDTA or metal ion is unavailable to complex. This is consistent with the recent findings of Nishimi and Miller (44), who found that when a dilute aqueous solution of the sodium salt of EDTA was placed in contact with an oil phase containing a calcium sulfonate surfactant salt, the EDTA sodium complex diffused into the oil phase. It is likely that, in the MWFs investigated here, the sodium ions from the sodium petroleum sulfonate surfactant salt are similarly complexing with EDTA and diffusing into the oil phase. The diffusion of the sodium-EDTA complexes into the oil phase provides a logical explanation for the lack of availability of EDTA to provide stoichiometric protection against the impact of hard water on MWF emulsion stability.

As the EDTA concentration in the dilution water was increased (Figure 5B), a higher percentage of emulsion

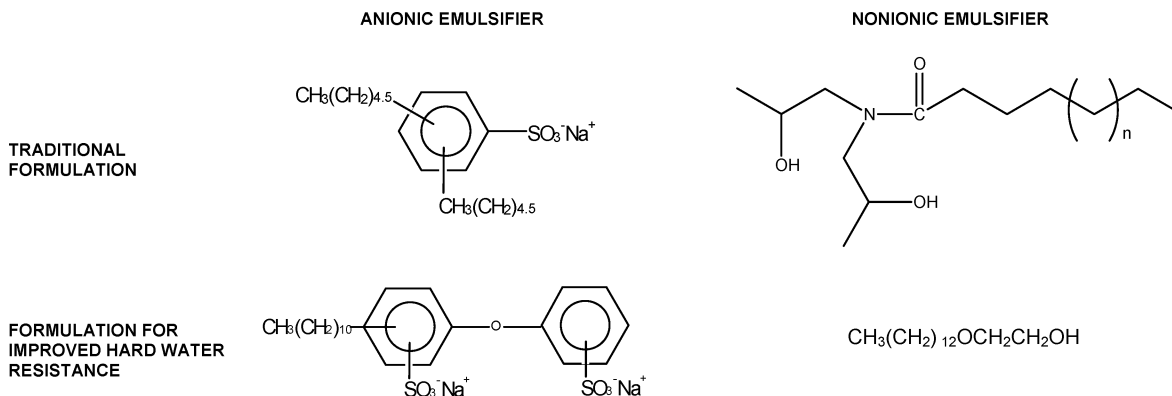


FIGURE 6. Chemical structures of emulsifier system components for traditional semi-synthetic metalworking fluid formulations and a new formulation for improved hard water resistance. The traditional emulsifier system is composed of a primary anionic emulsifier (sodium petroleum sulfonate) and a secondary nonionic surfactant (a fatty amide based on diisopropanolamide). The anionic emulsifier and nonionic surfactant in formulation for improved hard water resistance is a alkyldiphenyl oxide disulfonate and a linear alcohol ethoxylate, respectively.

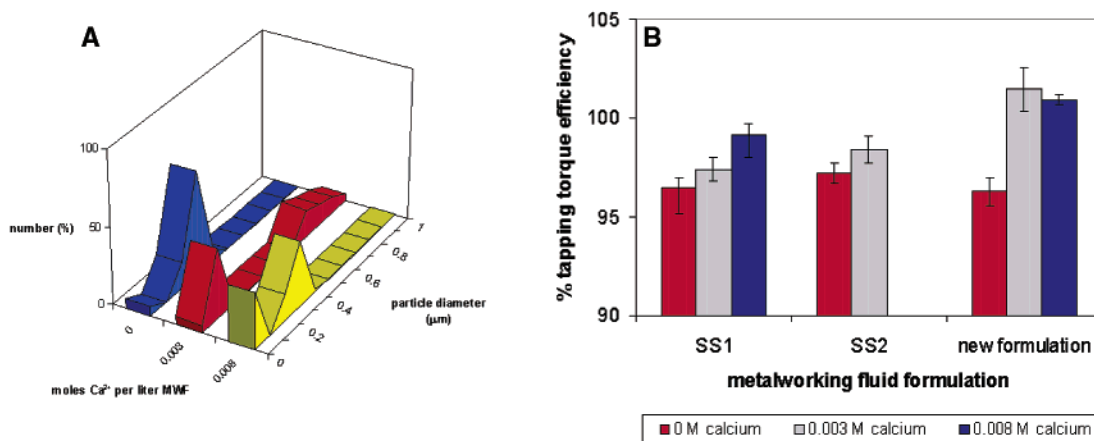


FIGURE 7. (A) Particle size distribution and (B) % tapping torque efficiency at 0.003 and 0.008 M calcium (introduced as calcium chloride) for a metalworking fluid formulation based on SS1 with substitutions for the emulsifier system (anionic and nonionic surfactant). Tapping torque data were not reported for SS2 at 0.008 M calcium due to phase separation and emulsion destabilization.

particles were measured in the initial particle size range as compared with EDTA addition to the concentrate as described above. After the addition of a 0.01 M concentration of EDTA to the dilution water, 80% of the emulsion particles remained in their initial size range. However, when EDTA and CaCl_2 were both introduced into the dilution water prior to addition to the MWF concentrate (Figure 5C), there was no effect on the particle size (as expected). Therefore, it is evident that EDTA preferentially forms calcium complexes over sodium in the water phase before the oil is introduced. This experiment was repeated with MgCl_2 and AlCl_3 , and the same behavior was observed regardless of the cation species (i.e., calcium, magnesium, aluminum) as shown in Figure 5C. This indicates that the concentration of EDTA in the concentrate is sufficient to prevent emulsion destabilization by cation introduction *if all of the EDTA and metal ion were available to complex*. At the same time, it is evident that when EDTA is in the concentrate, or even in the dilution water prior to mixing with the concentrate, it is not able to effectively complex with cations in the presence of MWF concentrate due to its partitioning to the oil phase. The unavailability of EDTA significantly reduces the ability of MWFs to resist emulsion destabilization due to addition of hard water salts.

MWF Surfactant Selection for Improved Hard Water Stability

As the preceding sections have shown, the addition of divalent and trivalent salts to the MWF system has a significant impact on emulsion particle size. A shift toward larger emulsion

droplet size leads to a decrease in bioresistance as well as the potential for emulsion separation, with only a subtle improvement in tapping torque efficiency. These outcomes can lead to premature fluid disposal and significant environmental and economic costs. While the use of deionized water in MWF systems could potentially avoid these impacts, there are significant resource, energy, and economic costs associated with this strategy. Furthermore, this strategy can fail in-use due to membrane fouling (32), leaving the MWF system susceptible to emulsion destabilization by hard water cation introduction. Consequently, it is imperative to develop MWF formulations that are inherently hard water stable. This would reduce expenditures on maintenance and move MWF formulations toward a more sustainable design (45–47). Ideally, an inherently hard water resistant MWF would be formulated with components that are more environmentally friendly and less energy consuming than those currently in use.

To assess the feasibility of producing MWFs with improved hard water stability, a new formulation was developed using the identical molar concentrations of ingredients as found in SS1 (Table 1). However, the traditional surfactants were replaced with surfactants that have a higher potential for stability in hard water. Based on the correlation of decreasing ζ -potential with increasing emulsion particle size, it was reasoned that increasing the electrostatic repulsive forces in the surfactant system would provide better emulsion stability under hard water conditions. Although anionic surfactants are utilized in MWFs to provide emulsion stability through

electrostatic repulsive forces, the results presented above indicate that the traditional anionic surfactant, sodium petroleum sulfonate (SPS), is not effective in this regard. Accordingly, SPS was replaced with an alkyldiphenyl oxide disulfonate (Dowfax 3B2, Dow Chemical Company, Midland, MI) (Figure 6A) that was found previously to provide better protection against surfactant precipitation by calcium (25). Whereas SPS has a single anionic headgroup per tail group, Dowfax 3B2 is twin-headed, providing two negatively charged headgroups per tail group. This provides increased electrostatic repulsion and potentially greater hard water resistance for the same molar concentration of anionic surfactant. The nonionic emulsifier, a fatty amide based on diisoproponal amine (DiIPA), was also replaced with a biobased linear ethoxylate alcohol (Tomadol 23-1, Tomah Products Inc., Milton, WI) (Figure 6B).

These surfactants were used at the same molar concentration ratio as SPS:DiIPA, and the concentrate was similarly diluted to 5% in deionized water. The initial emulsion particle size distribution of this formulation was similar to that of SS1. While there was a slight increase in emulsion particle size when 0.003 M calcium as CaCl₂ was introduced to this formulation, at 0.008 M calcium as CaCl₂ the emulsion particle size shifted back into the initial particle size range (Figure 7A). This decreasing emulsion particle size at high calcium concentrations appears to be the consequence of the existence of soluble anionic surfactant-cation complexes at high cation concentrations as reported by Talens-Alesson (42), Tezak et al. (48), and Fisher and Oakenfull (49). These data suggest that it is feasible to design inherently hard water resistant MWF formulations. Furthermore, the improved hard water resistant design is competitive with traditional semi-synthetic MWF formulations in machining performance as measured by the tapping torque test (Figure 7B).

Toxicity data also suggest that the surfactants in the new formulation are less toxic than the surfactants in traditional MWF formulations. For instance, toxicity evaluation of the anionic surfactants for the fathead minnow (*Pimephales promelas*) yielded an LC₅₀ of 0.4 mg/L after 48 h for SPS (50) and an LC₅₀ of 14.1 mg/L after 48 h for Dowfax 3B2 (51). Toxicity evaluation based on oral exposure of a rat indicated that DiIPA has an LD₅₀ of 2.7 g/kg bodyweight (52) while Tomadol 23-1 has an LD₅₀ of 2 g/kg bodyweight based on results for similar linear alcohol ethoxylates (53). In addition, recalling that these formulations contained no EDTA, these formulations based on twin-headed anionic emulsifiers demonstrate a potential for reduced mobilization of metals from manufacturing into environmental aqueous systems (e.g., cobalt-EDTA complexes released from manufacturing are not easily removed by traditional waste treatment operations). The formulations developed here also demonstrate the possibility of designing MWFs using fewer components as well as components that are renewable and more environmentally benign.

Environmental Relevance

Emulsion particle size has been linked in this research to increased microbial growth and a series of physicochemical changes that lead to premature MWF failure. Given the ineffectiveness of EDTA and SPS to maintain stable emulsion size in the presence of hard water salts, a more effective and environmentally preferable technological change to MWF was proposed and evaluated. Specifically, it was found that substituting a twin-headed anionic emulsifier for the typical anionic emulsifier resulted in a MWF formulation design that was inherently more resistant to destabilization by hard water than traditional formulations that include SPS and EDTA. Further investigations of biobased and more inherently stable MWF compositions have the potential to significantly reduce the environmental impact of machining operations.

Greater longevity can also lead to a reduction of MWF system costs that comprise 7–17% of manufacturing costs (3), while simultaneously reducing the energy and material requirements for MWF manufacture and the environmental impact of disposal.

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