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Surface Tension Estimates for Droplet Formation in Slurries with Low Concentrations of Hydrophobic Particles, Polymer Flocculants or Surface-Active Contaminants

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June 2011



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Pacific Northwest National Laboratory
Richland, Washington 99352

Executive Summary

In support of the K Basin project, Pacific Northwest National Laboratory (PNNL) was requested to evaluate the appropriate surface tension value to use in models predicting the formation of droplets from spray leaks of K Basin slurries. The specific issue was whether it was more appropriate to use the surface tension of pure water in model predictions for all plausible spray leaks or to use a lower value. The surface tension of K Basin slurries is potentially affected not only by particles but by low concentrations of nonionic polyacrylamide flocculant and perhaps by contaminants with surfactant properties, which could decrease the surface tension below that of water. A lower surface tension value typically results in smaller droplets being formed with a larger fraction of droplets in the respirable size range, so using the higher surface tension value of pure water is not conservative and thus needs a strong technical basis.

The literature provides a number of studies of droplet formation from liquids, but there is very little information on droplet formation from materials that are representative of K Basin waste slurries. A limited literature search was completed to find data on the effect of polymers (flocculants), particles, and surfactants on the surface tension of aqueous mixtures. The literature was also reviewed to estimate the time scale for droplet formation and determine whether the dynamic surface tension of aqueous mixtures at a representative time scale is appropriate for use in spray leak models. When gas-liquid interfaces are formed rapidly in dilute aqueous mixtures, the interface typically behaves like pure water because the dilute surface-active components in the mixture do not have enough time to diffuse to and adsorb at the interface. Accordingly, for any dilute solute or particle in water, the surface tension of pure water will be the appropriate value to use if the formation of an interface (droplet) is sufficiently fast. An evaluation of the literature on droplet formation suggests that spray droplets are created on the time scale of ~ 0.001 s.

With respect to the effect of solid particles, the literature showed that particles can affect the equilibrium surface tension, depending on the particle wettability. In general, the surface tension of a fluid is reduced from its pure-fluid value when materials, such as surfactants, adsorb at the interface. With hydrophobic particles that attach to the interface, the reduction in surface tension is typically explained as being due to particle adsorption. Hydrophilic (water-wet) particles do not reduce the surface tension because they generally do not collect, or adsorb, at the interface. Hydrophobic (non-wetting) particles, however, have been found to reduce the equilibrium surface tension. In one study, surface tension values as low as 50 to 55 mN/m (as compared with 72 mN/m for pure water) were reported whether the particles were all colloidal sized (<0.5 μm) or predominantly larger (50 μm mean). In a second study, water slurries of two different polystyrene particles were investigated, each having a particle diameter of 10 μm , and the particles reduced the surface tension to as low as 30 mN/m. There is some evidence of reduced equilibrium surface tension in some coal-water slurries of particles with a 50 μm mean size; the coal particle might be hydrophobic, but the surface tension reduction might be due to surface-active materials rather than the particles.

The K Basin slurries are predominantly water-wet particles (metal oxides), but dirt, grit, and other particulates are present in significant quantity and may include small amounts of non-wetting minerals or materials, including GraFoil[®] fragments. The majority of these particles, with the exception of GraFoil[®], are expected to be hydrophilic in comparison to hydrophobic particles in the literature studies (coal, some have a high graphitic content, or polystyrene). The lower bound on the equilibrium surface tension of the K Basin slurries is considered to be 30 mN/m, which represents the extreme of only very hydrophobic particles and the interface at equilibrium.

In general, the formation of aerosol droplets involves the rapid creation of an interface and there may be too little time for particles or surface-active materials to adsorb at the interface and reduce the surface tension during the period of droplet formation. There are a number of studies in the literature reporting the dynamic surface tension of rapidly created interfaces. In one study, tests were conducted with coal-water slurries with interface formation on a time scale of 0.1 to 1 s and with high solids concentration (40 to 50 wt% solids). The results indicated that the apparent dynamic surface tension of concentrated aqueous slurries was equal to or greater than the equilibrium surface tension by up to 12 mN/m. The dynamic surface tension increased as the time scale decreased, so at a time scale of 0.001 s, the apparent dynamic surface tension of those concentrated slurries would probably have been higher than at the fastest test condition of 0.1 s. The term “apparent dynamic surface tension” is used because increased viscosity is known to increase the dynamic resistance when creating an interface and the high solids concentrations in the slurries probably increased the viscosity sufficiently to cause this effect. Overall, the dynamic surface tension of K Basin slurries under spray conditions is expected to be equal to the value of pure water.

It should be noted that in a previous study PNNL measured aerosol formation from high-velocity 9/16-in. diameter jets. The tests compared aerosol formation from water and kaolin slurries at identical jet conditions. The data showed that slurry and water jets produced similar amounts of droplet release. The aerosol droplets collected were approximately 10 μm and smaller; the average particle size of the kaolin was not reported but is probably a few microns. This result cannot be directly generalized to K Basin slurries nor does it directly address surface tension; still, it does confirm that slurry particles did not change droplet-type releases for this slurry and aerosol size.

The flocculant is unlikely to affect the surface tension. One article showed equilibrium surface tension data for 1000-ppm polyacrylamide (PAM) solutions for a range of temperatures. The surface tension was 95% or more of the value for pure water. In a second article, an aqueous solution of a somewhat similar material (a copolymer with 75% neutral PAM and 25% charged polyacrylamido-methylpropane sulfonate) was studied. The equilibrium surface tension was equal to that of pure water for concentrations up to 2000 ppm. The tested polymer was not pure PAM, but these data strongly suggest that 1000- to 2000-ppm quantities of polyacrylamide do not change the equilibrium surface tension of the solution from that of water. The flocculant concentration in the planned waste treatment process will be 1000 ppm (1 mg/mL) in the solution that is added to the slurry and the concentration will be closer to 1 ppm in the process slurry. At this concentration, the effect of the flocculant on surface tension should be negligible.

If surfactants were present in the waste as a result of unintended contamination, their concentration would be too low to affect the dynamic surface tension at a time scale of ~ 0.001 s. There is no evidence of significant quantities of surface-active species in the K Basin slurries, and any surfactant present would be a contaminant. In partial confirmation of these conclusions, no foaming was observed during sparged settling tests of KW slurry samples. The absence of foam suggests that neither particles nor surface-active species were present in a quantity sufficient to reduce the surface tension of the samples.

In conclusion, although the *equilibrium* surface tension of K Basin slurries might be below the surface tension of water, owing to the possible presence of hydrophobic particles or surface-active contaminants, the *dynamic* surface tension should be equal to the surface tension of pure water. For the K Basin slurries, the effects of surface-active properties of the materials in the slurry, either hydrophobic particles or surface-active contaminants, are expected to be weak. For droplet formation, which always

has rapid surface formation (0.001 s and faster), the effects of dynamic surface tension are such that the surface tension of water should always be appropriate for use when determining spray droplet size.

Acronyms and Abbreviations

AED	aerodynamic equivalent diameter
DOE	U.S. Department of Energy
CMC	critical micelle concentration
KE	K-East (Basin)
KW	K-West (Basin)
LABA	N-dodecyl-lactobionamide
MBP	maximum bubble pressure
PAM	polyacrylamide
PAMPS	polyacrylamido-methylpropane-sulfonate
PCB	polychlorinated biphenyl
PNNL	Pacific Northwest National Laboratory
PSD	particle size distribution
PSDD	particle size and density distribution
STP	Sludge Treatment Project

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1.0 Introduction

Radioactive sludge was generated in the K-East (KE) Basin and the K-West (KW) Basin fuel storage pools at the Hanford Site while irradiated uranium metal fuel elements from the N Reactor were being stored and packaged. The fuel has been removed from the K Basins, and currently both KE and KW sludges reside in the KW Basin in large underwater Engineered Containers or in settler tanks that were used during sludge processing. In the course of further processing, the sludge will be moved between containers, stored, treated, and packaged for eventual shipment to the Waste Isolation Pilot Plant. The safety analyses required for these operations will include, among others, analyses of hypothetical leak accidents that produce pressurized sprays.

The safety-related consequences of pressurized spray accidents depend on the quantity of respirable particles or droplets that is produced, the rate of production, and the extent to which atmospheric or other mixing dilutes the release. Thus, both the total release (or release rate) and its size distribution must be determined. A respirable particle is defined as one having an aerodynamic equivalent diameter (AED) of 10 μm , where the AED is defined as the diameter of a sphere of density 1 g/cc that has the same terminal velocity as the particle in question (DOE 1994). Since particles in this size range have terminal velocities determined by the laminar settling regime (the Stokes regime), the AED is equal to the physical diameter multiplied by the square root of the ratio of the particle density to the unit density (DOE 1994). As the particle density increases, the physical diameter corresponding to an AED of 10 μm decreases.

The initial process that controls the release rate and the size distribution is that of spray generation. For a pressurized spray, the parameters that define the initial release are the density, viscosity, and surface tension of the fluid, the density of the gas into which the spray is released, the size of the leak orifice, and the driving pressure (DOE 1994, Epstein and Plys 2006). As the material's surface tension decreases, as its viscosity decreases, or as its density decreases, the droplet diameter decreases, and the respirable release rate increases. Of the three controlling fluid properties, the surface tension tends to have the greatest effect because of its relation to the energy required to generate a new droplet surface area.

The objective of this report is to evaluate the appropriate surface tension value to use in models for predicting the formation of droplets from spray leaks of K Basin slurries. The specific issue is whether it is more appropriate to use the surface tension of pure water (72 mN/m at 25°C; Dean 1979) in model predictions for all plausible spray leaks or to use a lower value. The surface tension of K Basin slurries is potentially affected by the presence of slurry particles and by low concentrations of a nonionic polyacrylamide flocculant and perhaps by contaminants with surfactant properties, which could decrease the surface tension below that of water. A lower surface tension value typically results in smaller droplets being formed with a larger fraction of droplets in the respirable size range, so using the higher surface tension value of pure water is not conservative and thus needs a strong technical basis.

In general, the surface tension of a fluid is reduced from its pure-fluid value when materials, such as surfactants, adsorb at the interface (Berg 2010). With slurries, hydrophobic particles can attach to the gas-liquid interface and also cause a reduction in surface tension where the mechanism is typically considered to be a result of particle adsorption (Brian and Chen 1987; Okubo 1995; Waghmare and Mitra 2010). Hydrophilic (water-wet) particles do not reduce the equilibrium surface tension because they generally do not collect, or adsorb, at the interface.

The materials that might hypothetically be released from K Basin accidents are all slurries, and in general, the effect of particles on spray releases is not well established. The DOE Handbook (DOE 1994) provides respirable release fractions for liquids, but does not define the effect of slurry particles. Epstein and Plys (2006) carried out an experimental study of sprays from circular and slit orifices, but their tests were of water only.

The release-related properties of K Basin sludge vary according to the sludge type, which is determined by the area in which it was generated and its subsequent processing (washing, straining, settling, filtering). K Basin sludge is composed of water and a variety of particulate materials from corroded fuel and other debris: metallic uranium as fragments (up to 0.635 cm) or finer particles, uranium oxyhydrates, fission and activation products, iron and aluminum hydroxides and oxides, concrete grit, sand and dirt, operational debris, fragments of GraFoil[®] (graphite gasket material), biological debris, polyacrylamide flocculant, and polychlorinated biphenyls (PCBs). The particle density, when averaged over all the solid phases present in a sludge type, ranges from 2.4 g/cc (dirt and sand), to 19 g/cc (uranium metal). The liquid content of the sludges is 70 to 75 vol%, and the liquid composition and density are very close to those of water. The pH of the liquid in K Basin sludges can be anywhere from 5 to 10, depending on the sludge type. Over all the K Basin sludge types, the maximum fraction of particles smaller than 10 μm is 63 wt%, and the minimum is 10 wt%. Johnson (2010a, 2010b) and Schmidt (2009), the sources for the above information, summarize the characterization studies of the sludge material.

While estimating the appropriate surface tension to use in spray leak models is the focus of this report, the rapid formation of aerosol droplets from spray leaks is a complex problem and the surface tension is only one of the important parameters. In addition, after the initial formation of aerosol droplets a number of subsequent processes can modify the size distribution from its initial value. The spray droplets may agglomerate as they travel, increasing the mean of the size distribution and possibly reducing the respirable fraction. Conversely, evaporation would reduce droplet sizes; the magnitude of size reduction depends in part on whether the released material contains particles or dissolved material, whose presence will prevent droplets from evaporating to zero size.

A literature search was performed to quantify the effects of both the slurry particles and the polyacrylamide flocculant chemical on surface tension or aerosol formation. The literature was also reviewed to estimate the time scale for droplet formation and determine whether the dynamic surface tension of aqueous mixtures at a representative time scale would be appropriate for use in spray leak models. When gas-liquid interfaces are formed rapidly in dilute aqueous mixtures, the surface tension in this dynamic situation approaches the value for pure water when the dilute components in the mixture do not have enough time to diffuse to and adsorb at the interface (Berg 2010). Accordingly, for any dilute solute (such as flocculant) or particle in water, the surface tension of pure water will be the appropriate value to use if the formation of an interface (droplet) is sufficiently fast.

Section 2.0 is a brief summary of tests that determined the release fractions from jets of kaolin slurry and water. Section 3.0 provides and applies information gained from a literature search on the effects on surface tension of particles, surface-active solutes (such as flocculant and surfactant), and rapid interface creation. Section 4.0 gives the summary and conclusions, and Section 5.0 contains the references.

2.0 Previous Release-Factor Tests

Some direct evidence related to the spray behavior of slurries is found in the results of experiments that were conducted to measure release fractions during certain tank retrieval processes (Bamberger and Glissmeyer 2004). The tests were performed in a geometrically scaled (one-fourth size) model of a 75-ft diameter, million-gallon waste storage tank. The tank was covered, and there was no forced ventilation in the tank during the tests.

Three retrieval processes were simulated:

- The jet from a 9/16-in. diameter horizontal nozzle transferring liquid or slurry from one side of the tank to the other. The discharging liquid was aimed at the opposite side of the tank from the nozzle and either impacted the tank wall or fell into a liquid or slurry pool at the bottom of the tank.
- Discharging liquid or slurry from the mouth of a vertically oriented 2-in. Sch. 40 pipe. The discharging material was in free fall from the mouth of the pipe near the top of the tank into a liquid or slurry pool at the bottom of the tank, a distance of 11.4 ft.
- A high-pressure fan jet of liquid striking a steel plate or simulated waste from a stand-off distance of a few inches.

Kaolin clay was used to represent the waste solids.

Air samples were collected to determine the solids release fraction at the tank top, which is the fraction of the solids in the jet that are released as aerosol through the tank vent. The fluorescent dye that was used as a liquid tracer was leached from the sample to determine the liquid fraction; this method was more sensitive than the solids collection method. The particle size distribution (PSD) of the sprayed material, measured near the tank top, was determined to be log-normally distributed with geometric mean diameters ranging from 3 to 8 μm , depending upon the process simulated.

The test conditions and results are summarized in Table 2.1. In common practice, release fractions are reported as bounding release fractions with single-digit accuracy, as shown in the last column of Table 2.1. Using this representation, the liquid-fraction release fractions for the top of the unventilated tank ranged from 9×10^{-7} to 8×10^{-5} , depending upon the process simulated.

For K Basin, the most pertinent test case is the transfer jet, a horizontal jet at jet Reynolds number $Re_j = \sim 2 \times 10^5$. For this case, directly comparing the releases from water and slurry shows that at the top of the tank, the release fractions for the liquid fraction are essentially equivalent: 3×10^{-6} for the water jet and 2×10^{-6} for the slurry jet.

These data for kaolin slurries suggest that slurries and water behave similarly, with respect to releases, under conditions in which droplets are generated. However, the properties of the solids (hydrophilicity and size distribution, among others) can have significant effects, so the results for a kaolin slurry do not completely answer the question of spray behavior for K Basin waste. Section 3.0 provides a more complete examination of the effect of solids.

Table 2.1. Summary of Release Fraction Test Conditions and Results

Run Process	Fluid	Impact- ing ^(d)	Pressure Range		Nozzle Diameter	Test Flow Rate	Test Flow Rate Std. Dev.	Jet Reynolds Number ^(a)	Release Fraction Data from Fluorescent Tracer on Process Water and from Dry Solids (in parentheses)			Release Fraction at Scaled Tank Top to 1 Significant Figure	
			psig	in.					gpm	gpm	Tank Top		Tank Wall
Transfer Jet													
5	Liquid Discharge at 32 gpm (0.00202 m ³ /s)	Water	Floor	N.A.	N.A.	0.5625	32.2	5.7	1.95 × 10 ⁵	0.48 and 3.2 × 10 ⁻⁶	3.6 and 5.0 × 10 ⁻⁶	4.1 × 10 ⁻⁶	3 × 10 ⁻⁶
10	Slurry Discharge at 23 gpm (0.00145 m ³ /s)	Slurry	Floor	N.A.	N.A.	0.5625	23.3	2.3	1.41 × 10 ⁵	1.8, 2.1 and 2.1 × 10 ⁻⁶	2.5 and 2.7 × 10 ⁻⁶ (3.5 and 6.8 × 10 ⁻⁶)	1.6 × 10 ⁻⁵ (4.4 × 10 ⁻⁵)	2 × 10 ⁻⁶
Pipe Discharge													
2	Liquid Discharge at 35 gpm (0.0022 m ³ /s)	Water	Floor	N.A.	N.A.	2.067	34.8	7.1	5.73 × 10 ⁴	0.69, 0.80, and 0.93 × 10 ⁻⁶	0.55 and 1.2 × 10 ⁻⁶	2.2 × 10 ⁻⁶	0.9 × 10 ⁻⁶
11	Slurry Discharge at 43 gpm (0.00271 m ³ /s)	Slurry	Floor	N.A.	N.A.	2.067	43.1	19.4	7.11 × 10 ⁴	0.43, 1.5, and 1.7 × 10 ⁻⁶	2.1 and 2.4 × 10 ⁻⁶	2.1 × 10 ⁻⁶	2 × 10 ⁻⁶
12	Slurry Discharge at 125 gpm (0.00789 m ³ /s)	Slurry	Floor	N.A.	N.A.	2.067	124.7	2.5	2.05 × 10 ⁵	3.1, 3.7, and 4.1 × 10 ⁻⁶	5.0 × 10 ⁻⁶	4.5 × 10 ⁻⁶	4 × 10 ⁻⁶
Cutting Jet													
7	Jet ^(b) on steel at low pressure	Water	Steel	Low	340- 380	0.056	1.55	N.A.	9.41 × 10 ⁴	1.0 and 5.6 × 10 ⁻⁴	0.12 and 6.3 × 10 ⁻⁴	4.0 × 10 ⁻⁴	3000 × 10 ⁻⁶ (c)
8	Jet ^(b) on simulat at low pressure	Water	Kaolin Clay	Low	300	0.056	1.30	N.A.	7.89 × 10 ⁴	5.5 and 7.7 × 10 ⁻⁵	N.A.	1.4 × 10 ⁻⁴ (1.3 × 10 ⁻⁴)	80 × 10 ⁻⁶
9	Jet ^(b) on simulat at high pressure	Water	Kaolin Clay	High	1200	0.056	2.70	N.A.	1.66 × 10 ⁵	6.0, 6.0 and 8.1 × 10 ⁻⁵ (6.6, 6.6 and 7.9 × 10 ⁻⁵)	8.8 and 9.1 × 10 ⁻⁵ (3.9 and 3.9 × 10 ⁻⁵)	8.0 × 10 ⁻⁵	80 × 10 ⁻⁶

(a) Kinematic Viscosity of water at ~72 F, 0.00001 ft²/s; (b) Spraying Systems Company 1/4 MEG 2505, vendor supplied diameter of 0.056 in.; (c) based on average, not maximum;

(d) when impacting the floor, some pooling of water occurred during some tests and the impacting surface became liquid.

3.0 Results of Literature Search

The literature search covered (1) the effect of solid particles on equilibrium surface tension, (2) the effect of surface-active solutes on equilibrium surface tension, and (3) the role of rapid surface generation in causing the dynamic surface tension to be determined by the solvent (water) rather than by solutes and particles. These three topics and their application to K Basin sprays are discussed in Section 3.1, Section 3.2, and Section 3.3, respectively.

3.1 Effect of Solid Particles on Equilibrium Surface Tension

The presence of particles at an air-water interface can be expected to affect the overall surface tension of the interface. For colloidal particles, the effect is determined largely by the contact angle that the particle makes with the air-water interface (Binks 2002). Hydrophilic particle surfaces, such as those of metal oxides, have aqueous-side contact angles that are less than 90° , while hydrophobic particles have contact angles greater than 90° . It is plausible that certain minerals in the K Basin slurries may be hydrophobic and GraFoil[®] fragments that are known to be present in the K Basin waste (Johnson 2010a) may also behave as hydrophobic particles.

Okubo (1995) tested the effect of both hydrophilic and hydrophobic colloids on the equilibrium water-air surface tension. A Wilhelmy-type surface tensiometer (suspended plate) was used. Effects generally began to be measurable above 0.5 vol% solids in the bulk suspension. The air-water surface tension of suspensions of colloidal spheres of washed silica, a polar and therefore hydrophilic material, showed slight increases or decreases as solids concentrations increased. The largest particles tested, which were 0.1 to 0.2 μm in size, produced a decrease of 1 to 2 mN/m at concentrations of 10 vol% in the bulk. Both crystal-like and less-organized surface layers were observed. In the former, which were seen only for silica particles larger than about 0.05 μm , iridescence and glittering crystals were observed on the surface. In the latter, suspensions were observed to be turbid or milky. In general, the surface activity of silica (with particle sizes from 0.006 μm to 0.184 μm) was low for both types of surface layer. The surface tension of the suspension consistently remained within ± 2 mN/m of the value for deionized water.

The hydrophobic particles that Okubo tested (washed polystyrene) produced larger changes in equilibrium surface tension, all of which were decreases. At 10 vol% solids in the bulk suspension, polystyrene particles that had diameters between 0.05 and 0.11 μm reduced the surface tension by 15 to 25 mN/m, relative to the value for deionized water. However, smaller and larger particles (the largest tested was 0.46 μm) produced reductions of 10 mN/m or less. The surface tension decreases of more than 5 mN/m were consistently associated with the presence of crystal-like surface layers. In his discussion, the surface tension reduction is associated with the adsorption (excess concentration at the interface in comparison to the bulk) of the particles at the interface, and the hydrophobic particles had the largest adsorption. A crystal-like surface layer suggesting particle adsorption was not observed, and surface tension remained within 2 mN/m of the value for water, when low concentrations of NaCl (less than 10^{-4} M) were added.

Okubo argued that the crystal-like surface phase depended on the particles being large with respect to the diffusing ions, allowing electrical double layers to be formed. This explained the absence of

observations of crystal-like layers for particles less than 0.05 μm in size, under deionized conditions where the only ions present were the simple ions produced by dissociation of water. The reason for the effect of NaCl in preventing the crystal-like phase of polystyrene particles from forming was not discussed. The low surface activity of the silica particles was attributed, at least in part, to the tendency of hydrophilic particles to not attach to the air-water interface.

Waghmare and Mitra (2010) measured the effect of particle concentration on the surface tension of slurries made from diluting slurries of 10 μm polystyrene particles from two different manufacturers in deionized water. The authors did not comment on the presence or absence of any surfactants or dispersants with these particles, but absence of any discussion suggests that the surface tension reduction was only due to the particles. For one particle, the surface tension was reduced to as low as 30 mN/m, which is the lowest surface tension found in this literature survey; the reduction was only to 55 mN/m for the second particle.

Other studies were found that tested the effect on the equilibrium surface tension of particles that were too large to be considered colloidal. In one study (Stewart et al. 2007), a 2 wt% suspension of hydrated alumina, containing particles with a volumetric mean diameter of 61 μm , had an equilibrium surface tension equal to that of water. In another study, Kihm and Deignan (1995) studied coal-water slurries. The coal size distribution had a volumetric mean diameter of 55 μm , with the upper end of the distribution at 200 μm and the lower end not stated. At 50 wt% solids in the bulk slurry, the equilibrium slurry surface tension was the same as that of water at the same temperature. However, Andreussi et al. (1990) showed equilibrium surface tension data for six different types of coal-water slurries with a particle mass median diameter of $\sim 50 \mu\text{m}$. The range of equilibrium surface tensions was from 50 to 70 mN/m. Unfortunately, the solids concentrations in the six slurries are not given.

The hydrophobicity or hydrophilicity of coal (Kihm and Deignan 1995, Andreussi et al. 1990) and alumina (Stewart et al. 2007) were not discussed by those authors, but are relevant to the problem. Groszek and Partyka (1993) noted that a material can have both hydrophobic and hydrophilic surface sites, depending on the purity of the material and the way in which it was produced. The alumina they studied showed no signs of hydrophobicity, whereas the samples of coal they studied were 49% to 96% hydrophobic. The authors suggested that the hydrophilic sites on the coal surface might be mineral in nature and the hydrophobic sites graphitic, and that oxidizing treatments would be expected to increase hydrophilicity. Trasatti (1991) described metal oxides as generally having strongly hydrophilic surfaces with the caveat that thermal treatments, such as calcination, may make oxide surfaces hydrophobic by decreasing the hydrous nature of the oxide. CJ van Oss (2008) notes that grinding, even when carried out in a way that produces no measurable heating, considerably reduces the hydrophilicity of the surfaces of materials.

The limited information found in the literature that was discussed above indicates that particles can affect the equilibrium surface tension of the slurry, whether the size distribution is predominantly colloidal or whether it is larger. It seems likely that particles with hydrophobic surfaces are the source of the effect.

The materials present in K Basin sludges include uranium metal, whose surface is probably oxidized, uranium oxyhydrates, fission and activation products, iron and aluminum hydroxides and oxides, concrete grit, dirt, and sand. Many of these materials, particularly the U metal and the metal oxides, probably have

hydrous surfaces that would be hydrophilic, but it is possible that not all the solids in the sludges are hydrophilic. Soil and mineral components are present in the K Basin sludges. It is known that some clays and minerals, for example, hectorite, talc, and pyrophyllite, are hydrophobic, although others, such as kaolinite, silica, and mica, are hydrophilic (Table 2.5 of van Oss 2008).

Johnson (2010b) presents concentrations and mass-based particle size and density distributions (PSDDs) for the settled solids in three sludge types: KE Engineered Container Sludge, KW Engineered Container Sludge, and Settler Tank Sludge. (These will be referred to as “KE,” “KW,” and “settler” for brevity.) Part of this information is shown in Table 3.1, which is taken from the design basis information in Table 2-2 and Table 2-5 of Johnson (2010b). Those sources said that submicron particles made up zero percent of the non-uranium, non-uranium-oxide solids (hereafter abbreviated to “non-U” solids). However, the minimum concentration usually measurable by PSD measurement instruments is 0.5 vol%, so these zero values probably represent some concentration that is less than 0.5 vol%.

Table 3.1. Particle Concentration, Size, and Density Information for Settled Solids in K Basin Sludges

Property	KE	KW	Settler
Wt% solid phase in settled solids	48%	53%	72%
Wt% of non-U material in the solid phase	81.0%	61.3%	12%
Wt% of <5 μm size in the non-U solid	14%	14%	36%
Wt% of <1 μm size in the non-U solid	0 ^(a)	0 ^(a)	15%
Wt% of <5 μm size in the uranium metal plus uranium oxide	30%	30%	32%
Wt% of <1 μm size in the uranium metal plus uranium oxide	17%	17%	15%

(a) The minimum concentration usually measurable by PSD measurement instruments is 0.5 vol%; these zero values represent some smaller concentration.

Consider the possible effect of the submicron solids alone, assuming that only the submicron non-U solids could be partly or wholly hydrophobic material. Based on the size, density, and concentration data given by Johnson (2010b, Tables 2-2, 2-5), the settled solids in the K Basin sludges contain at most 4.7 vol% of submicron non-U solids. This maximum value is for settler sludge.

For comparison, concentrations of about 0.5 vol% hydrophobic particles (sizes 0.05 to 0.11 μm) reduced the equilibrium surface tension of deionized water from 72 mN/m to 65 mN/m, and 3 vol% of the same particles reduced it to 45 to 50 mN/m (Figures 2 and 4, Okubo 1995). Therefore, it is possible that the settled solids in K Basin sludge contain enough hydrophobic particles in the ~0.1-μm size range to reduce the equilibrium surface tension to ~50 mN/m. As mentioned above in this section, Waghmare and Mitra (2010) reported surface tension values as low as 30 mN/m for slurries of 10 μm polystyrene particles, so 30 mN/m is still the lowest literature value for the role of hydrophobic particles.

When the hydrophobic colloidal particles were polystyrene, their effect on equilibrium surface tension was found to be considerably less when small concentrations of ions were present (Okubo 1995). When a low (1.67×10^{-5} M) concentration of NaCl (0.6 μg/mL Cl) was present, a 3 vol% concentration of

hydrophobic solids decreased the equilibrium surface tension to 65 mN/m (Figure 2 of Okubo 1995), a decrease of only 10%. Tables 4-26a, 4.26b, and 4.26c of Schmidt (2009) provide measured concentrations of chloride, fluoride, nitrate, nitrite, phosphate, sulfate, bromide, and hydroxide in a number of K Basin sludges and sludge liquids. The sludge streams that were listed all contained at least one ion whose molar concentration was in the same range as the NaCl in the tests performed by Okubo (1995):

- KW Canister Sludge: 2×10^{-7} M Cl (minimum), 2×10^{-5} M SO_4^{2-} (mean)
- KW Canister Sludge Supernatant: 2×10^{-5} M SO_4^{2-} (mean)
- KE Canister Sludge: 1×10^{-5} M Cl (minimum), 3×10^{-5} M SO_4^{2-} (mean), 1×10^{-5} M H^+
- KE Canister Decant Water: 8×10^{-5} M Cl (minimum), 1×10^{-3} M NO_3^- (mean)
- KE Floor and Pit Sludge: 5×10^{-7} M Cl (minimum), 8×10^{-6} M NO_3^- (mean), 5×10^{-5} M SO_4^{2-} (mean).

However, the tendency of small concentrations of ions to reduce the effect of hydrophobic particles is not reliable. The coal-water slurries studied by Andreussi et al. (1990) probably did not contain pure deionized water, but their equilibrium surface tension measurements were as low as 50 mN/m.

The effect of the solids on surface tension may be decreased by dilution. The concentrations of hydrophobic solids are likely to be less than the values that were given above for settled solids simply because the K Basin sludges consist not only of settled solids but also of excess (supernatant) liquid. The fraction of supernatant liquid that is present to dilute the solids in a hypothetical spray accident will depend on the type of processing or handling that the sludge is postulated to be undergoing at the time of the spray accident. One plausible range of dilution is that used in the settling tests (Johnson 2010b) where solids concentrations of 0.5 wt%, 2.5 wt%, 5 wt%, and 10 wt% were tested. For comparison, the settled solids are 50 to 70 wt% solids. The corresponding volume concentrations were ~0.1 vol% to ~3 vol%, depending on which type of sludge was tested.

To the extent that the settling-test concentrations represent process conditions, they indicate that the concentration of hydrophobic solids of all sizes in the total slurry is likely to be low, potentially 2 to 3 vol% for KE and KW sludge and less than 0.5 vol% for settler sludge. For hydrophobic colloidal polystyrene particles in this concentration range, Okubo (1995) reported equilibrium surface tension values reduced to 50 to 65 mN/m and Waghmare and Mitra (2010) reported a reduction to 30 mN/m. The soils and minerals that are present in sludge are unlikely to be as hydrophobic as polystyrene, though the GraFoil[®] might have hydrophobicity similar to polystyrene's. Based on the information found in the literature, the equilibrium surface tension of the K Basin slurries could be as low as 30 mN/m if the effect of the particles is the only effect considered. As discussed in Section 3.3, with the rapid interface formation that occurs during droplet formation, it is unlikely that hydrophobic particles could diffuse to and adsorb at the interface and lower the surface tension during the time period of aerosol droplet formation.

3.2 Effect of Surface-Active Solutes on Equilibrium Surface Tension

The most significant surface-active solutes that are likely to be present in K Basin waste are flocculants and cleaning materials (surfactants such as detergents, which would be contaminants rather than intended constituents and present only in low concentrations).

The flocculant Clarifloc® N-3300P,¹ which is a nonionic, water-soluble, high-molecular-weight polyacrylamide, will be used in processing. The concentration of Clarifloc N-3300P will be between 1000 ppm (the aqueous solution injected into the slurry transfer line) and less than 1 ppm [the concentration at which it has been found effective in the slurry (Dhaliwal 2011)].

The surface tension of a solution of 1000 ppm PAM is approximately equal to that of water, as shown in Table 3.2, which contains data extracted from Tables 1 and 2 of Hai et al. (1998).

Table 3.2. Surface Tension (mN/m) of Solution Against Air (from Hai et al. 1998)

Temperature	Surface Tension (mN/m)	
	1000 ppm PAM in water	1000 ppm PAM in 0.1 M NaOH
25°C	69.0	68.9
35°C	68.4	68.0
45°C	67.0	66.6

Information about the effects of higher concentrations of flocculant was obtained from Asnacios et al. (1996). In this study, the copolymer tested was 75% neutral PAM and 25% charged polyacrylamido-methylpropane-sulfonate (PAMPS). Figure 2 of Asnacios et al. shows the effect of the polymer on the air-water surface tension compared to that of the surfactant-free solution. There was no effect at concentrations less than 2000 ppm, which is consistent with Hai et al. (1998). At 4000 ppm, the surface tension was reduced to 67 mN/m. The reference did not show data for higher concentrations of PAM/PAMPS. Although the solute tested by Asnacios et al. was not pure PAM, their data indicate that the decrease in equilibrium surface tension caused by the K Basin flocculant would be low at concentrations of less than 2000 ppm.

Surfactants (for example, detergents) are contaminants that can potentially be present in K Basin sludges and that could have a significant effect on the surface tension of K Basin slurries (Berg 2010). Characterization results have not included concentration measurements or estimates of surface-active solutes, but there is no indication that surface-active species are present. As discussed in Section 3.3, with the rapid interface formation that occurs during aerosol droplet formation, it is unlikely that surface-active species could diffuse to and adsorb at the interface and lower the surface tension during the time period of droplet formation.

3.3 Dynamic Surface Tension

Whenever a fresh air-liquid surface is formed, surface-active components cannot affect the surface tension of the new interface until they have been transported from the subsurface bulk liquid to the interface and then adsorbed (Eastoe and Dalton 2000; Berg 2010). This requires finite time. Therefore,

¹ Clarifloc is a trademark of SNF/Polydyne, Riceboro, Georgia.

the dynamic, rather than equilibrium, surface tension is the controlling parameter for droplet formation (Chung and Wasan, 1988). As a result, for sufficiently fast interface formation or sufficiently low surfactant concentration, the surface tension of water can be appropriate for use when determining droplet formation size. Therefore, the time scale of droplet formation must be evaluated to determine the applicability of assuming fast interface formation in hypothetical K Basin sprays.

The potential K Basin sprays, or jets, can be characterized by three distinct flow regimes: dripping, jetting, and wind-induced, which are highlighted in Figure 3.1 (Hoeve et al. 2010). The dominant parameters involved with jet breakup are the Weber number ($We = \rho_l r v^2 / \sigma$) and the Ohnesorge number ($Oh = \mu / \sqrt{\rho_l r \sigma} = We / \sqrt{Re}$) where ρ_l is the jet liquid density, r is the jet radius (or characteristic length scale), v is the jet velocity, σ is the surface tension, μ is the jet liquid dynamic viscosity, and Re is the jet Reynolds number. The Weber number relates the jet inertial and surface tension forces. The Ohnesorge number is the ratio of liquid viscous to inertial and surface tension forces.

The dripping jet regime is characterized by slow emission of a liquid from a nozzle. The jetting regime, or Rayleigh breakup, is formed from an instability associated with the tendency of surface tension to minimize surface energy (i.e., area). Further increases in the liquid velocity result in the wind-induced regime, in which the aerodynamic pressure of the surrounding fluid (i.e., air) can no longer be neglected. A critical gas Weber number ($We_g = \rho_g / \rho_l We$, where ρ_g is the gas density), of around 0.2 defines the transition into the wind-induced regime. At high We_g the aerodynamic effects accelerate jet breakup and decrease the downstream distance between the jet orifice and the point at which droplets pinch off.

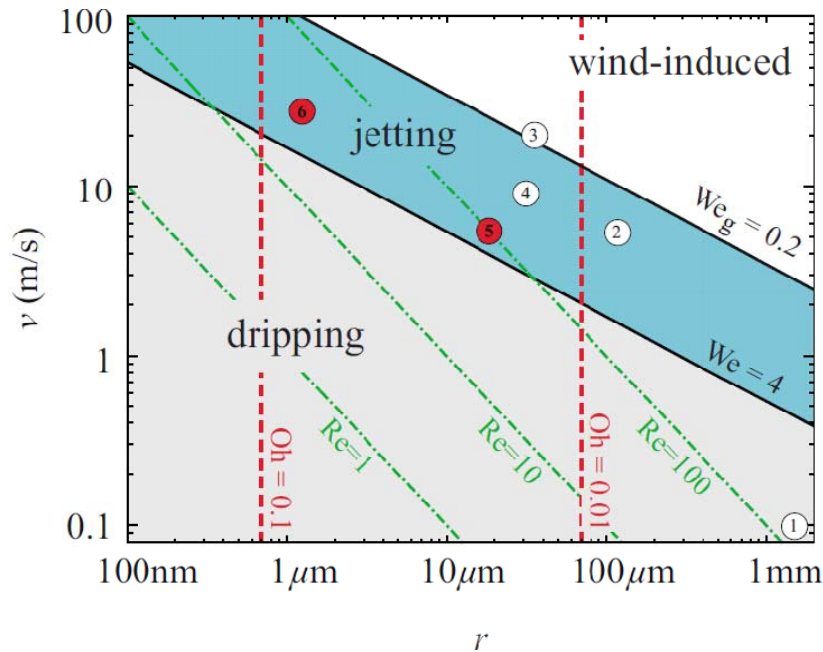


Figure 3.1. Classification of Droplet Formation Regimes for a Liquid Discharging an Orifice of Radius r with a Liquid Velocity v ; taken from Hoeve et al. (2010). The three formation regimes are dripping, jetting, and wind-induced; they are dependent on the Reynolds ($\rho_l v r / \mu$), Weber, and Ohnesorge numbers.

The formation of droplets resulting from the jetting regimes is categorized as primary and secondary breakup. The primary droplet is formed in accordance with each jetting regime and is dominated by

surface tension. The primary droplet size will be controlled by the jet diameter and surface tension alone. Further breakup of droplets is associated with secondary breakup, where other forces act to overcome the surface tension forces, depending on the jetting regime. In the wind-induced regime, secondary droplet breakup occurs (as shown in Figure 3.2) where two dominant breakup mechanisms occur: bag and stripping breakup. These are associated with low and high gas Weber number, respectively. The primary and secondary breakup of droplets is shown in Figure 3.3, where (a) and (b) show primary droplet sizes on the order of the jet diameter. The secondary bag and stripping breakup mechanisms are shown in (c) and (d), where larger droplets are broken up into many smaller droplets.

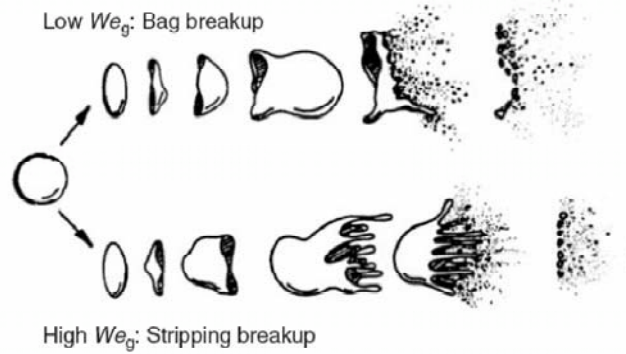


Figure 3.2. Secondary Droplet Breakup; Taken from Rahman (2011)

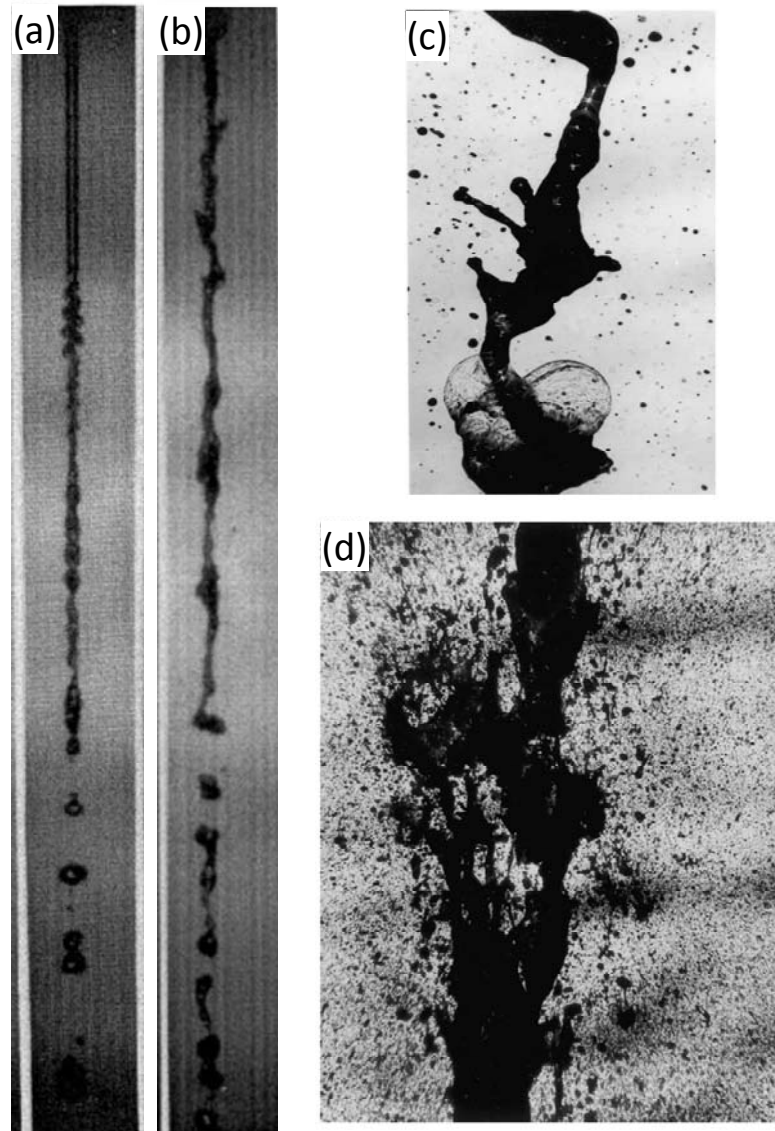


Figure 3.3. Primary and Secondary Droplet Breakup (adapted from Sallam et al. 2002) Where (a) and (b) Indicate Primary Breakup with $We = 235$ and 1670 , Respectively. Bag and stripping breakup are shown in (c) and (d), where $We = 33,100$ and $271,000$, respectively (note $We_g = \rho_g / \rho_l We$).

For sufficiently small Oh numbers, the liquid viscosity can be neglected and the resulting time scale of primary droplet formation is defined by the capillary time scale given by

$$\tau_c = \sqrt{\frac{\rho_l r^3}{\sigma}} \quad (3.1)$$

which is only valid for primary droplet formation and becomes a conservative (longest time scale) estimate for increasing We in the wind-induced regime. Gas pressure forces will break up primary droplets on an aerodynamic time scale given by

$$\tau_i = \frac{d}{u} \sqrt{\frac{\rho_l}{\rho_g}} \quad (3.2)$$

where d is the droplet size and u is the mean jet velocity (Gelfand, 1996). The capillary time scale has no dependence on the jet velocity, whereas the aerodynamic time scale is not a function of the surface tension.

For the formation of aerosol droplets, the aerodynamic time scale is appropriate for estimating the time scale of interface formation, rather than the capillary time scale that is associated with primary droplet formation. Equation 3.2 shows that the aerodynamic time scale becomes longer for larger length scales d and small jet velocities given by u . Accordingly, the most conservative sprays for giving slow interface formation would be low-velocity, large-diameter sprays. However, these sprays do not generate as much aerosol droplets as higher-velocity, smaller-diameter sprays. Crowe (2010) gives a methodology for analyzing spray leaks for the sludge treatment project (STP) and also provides a sensitivity analysis for the effect of breach width. For spray releases, the analysis shows that the largest amount of aerosol comes from the smallest breaches (see Tables 7-1 and 7-2 of Crowe 2010). Interestingly, as the breach size becomes smaller, the leak flow decreases but the fraction of the flow that becomes aerosol droplets increases even more than the reduction in flow. Crowe (2011) analyzes spray release for a series of STP scenarios, and reports the specific breach sizes and jet velocities that result in the largest aerosol releases for each scenario (see Table 5-6 of Crowe 2011). The parameters for these specific scenarios can be used to estimate the aerodynamic time scale.

Table 3.3 shows the aerodynamic time scales for the spray leak scenarios analyzed by Crowe (2011). The time scales are of order 0.001 s, and vary from 0.0005 s to 0.0014 s. For comparative purposes, Figure 3 of Simpkins (1971) shows photographs of bag and stripping droplet breakup that occurs over 690 μ s, an approximate time scale of 0.0007 s. Overall, all K Basin spray leaks that would result in small aerosol droplet formation would occur in the wind-induced regime and, therefore, a 0.001-s time scale would represent a conservative, approximate estimate for all expected flow conditions. Therefore, the time scale for evaluating the dynamic surface tension is 0.001 s or faster.

Table 3.3. Aerodynamic Time Scale Estimates

Spray Release Scenario ^(a)	Breach Width (mm)	Leak Velocity (m/s)	Liquid Density (kg/m ³)	Aerodynamic Time Scale ^(b) (s)
Retrieval and Transfer	0.6	40.6	1375	0.0005
Decant	0.98	27.3	1015	0.0010
Back-flush	0.67	33	1045	0.0006
Overfill Recover	1.06	26.2	1375	0.0014

(a) Data and scenarios from Table 5-6 of Crowe (2011)
(b) Gas density assumed to be air at 1.20 kg/m³

The effect of any particle or surfactant molecule on dynamic surface tension and droplet generation in spray conditions will depend strongly on whether it can diffuse toward the interface in a time scale of 0.001s or less. That, in turn, will depend on the diffusivity and bulk concentration of the particle or molecule. The behavior of dynamic surface tension may be different for a bulk concentration below the critical micelle concentration (CMC) than for a higher concentration. (The CMC is the bulk concentration above which the equilibrium surface tension is approximately constant at its minimum value as the concentration is increased). When surfactants are intentionally added to a process stream, the design concentration is typically at or above the CMC.

Kao et al. (1992), Fainerman and Miller (1995), Fainerman et al. (1994), Kjellin et al. (2003) and Moorkanikkara and Blankschtein (2009) provide evidence that for high bubble frequency (i.e., fast interface formation) and dilute concentrations of surfactants, the dynamic surface tension approaches that of water, but does not in all cases. Figure 3.4 shows the effects of bubble frequency and surfactant concentration for N-dodecyl-lactate-bionamide (LABA) surfactant. The effective surface lifetime, which is the *x* axis in Figure 3.4, corresponds to the bubble formation time scale measured using the maximum-bubble-pressure approach. At sufficiently high concentration (above the CMC), the surfactant could reduce the dynamic surface tension even at a time scale of 0.001 s or less.

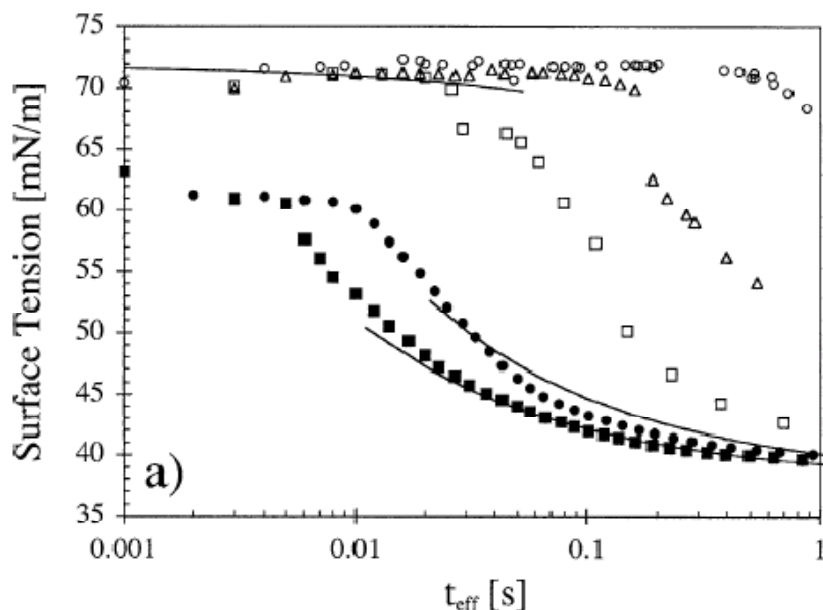


Figure 3.4. Dynamic Surface Tension versus Effective Surface Lifetime, Taken from Kjellin et al. (2003). The lines are theoretical calculations. Data shown for LABA surfactant, $c = 0.2$ mM (\circ), 0.4 mM (Δ), 0.8 mM (\square), 1.5 mM (\bullet), and 2.7 mM (\blacksquare). For comparison, the critical micelle concentration of LABA is 0.35 mM.

Fainerman et al. (1994) and Fainerman and Miller (1995) studied polyethylene glycol octylphenyl ethers: Triton[®] X-45, -100, -165, and -405, where the higher numbers represent higher polymerization and higher molecular weight. The tests were carried out at concentrations up to the CMC. For the lower-molecular-weight surfactants, Triton X-45 and X-100, the dynamic surface tension at 0.001 s was that of water when the surfactant was at its CMC. Some decrease in surface tension appeared for concentrations at or below the CMC of the heavier Triton surfactants. Similar behavior was seen in dynamic surface tension tests of N-dodecyl lactobionamide, C_{12} -maltose ester, and tetra(ethylene oxide) dodecyl amide (Kjellin et al. 2003). The dynamic surface tension at 0.001 s was that of water when these surfactants were at or below their CMCs. In particular, Fainerman and Miller (1995) provide effective surface age temporal resolution in the sub-millisecond range, further confirming the dynamic surface tension of water is approached at low concentrations.

Aytouna et al. (2010) studied five non-ionic surfactants at bulk concentrations above and below the CMCs of the surfactants. At concentrations above the CMC, two of the surfactants (“fast” surfactants) could diffuse to the surface and decrease the dynamic surface tension to nearly the equilibrium value within about 0.001 s, whereas others (“slow”) required 20 times as long to produce the same effect. The fast surfactants were a terpene mixture and a polyethylene glycol octylphenyl ether (Triton X-100, molecular weight 624) whereas the slow surfactants were a lecithin mixture, a trisiloxane (molecular weight 646), and a nonyl phenol ethylene oxide (molecular weight 603). At sub-CMC concentrations that were selected to give an equilibrium surface tension of 40 mN/m, the “fast” and “slow” surfactants both behaved like water at a time scale less than ~ 0.002 s (Figure 7 of Aytouna et al. 2010). Although the surfactants were present at high enough concentrations to significantly decrease the equilibrium surface tension, they had no effect on the dynamic surface tension at the 0.001 -s time scale.

Only a trace level of surfactant is expected in the K Basin liquid. Characterization results have not included concentration measurements or estimates of surface-active solutes, but there is no indication that surface-active species are present, and any surfactant present would be a contaminant rather than an intended constituent. In addition, particles would be likely to adsorb much of whatever surfactant did enter the slurry. Therefore, surfactant contamination is not expected to produce a measurable decrease in the dynamic surface tension of K Basin slurry. With the rapid interface formation that occurs during droplet formation, it is unlikely that trace levels of surface-active species could diffuse to and adsorb at the interface and lower the surface tension during the time period of droplet breakup.

The effect of particles on the dynamic surface tension is more complex. For comparison, one of the “fast” surfactants studied by Aytouna et al. (2010) was described as having an effective molecular size of 0.004 μm , which was considered to be consistent with its diffusion rate. This provides some context to assess the relative mobility of particles. Based on their relative size and density, even colloidal particles are very unlikely to behave like fast surfactants, which are capable of moving to the interface in 0.001 s or less; the indications are that they may not behave like slow surfactants, either.

Kihm and Deignan (1995) collected dynamic surface tension data for coal-water slurry at two different loadings (40 wt% and 50 wt% coal) with a maximum-bubble-pressure (MBP) method. The effects of five different surfactants on the slurry surface tension were measured for surfactant concentrations of 0.1 to 5 wt%. The surfactants were non-ionic alkylphenol ethoxylate (NP-100), branched dodecylbenzene sulfonic acid, linear dodecylbenzene sulfonic acid, a sodium salt of a branched alkylbenzene sulfonic acid, and a sodium salt of sulfonated fatty acid. The measurements of dynamic surface tension were carried out at bubble frequencies of 1 to 10 s^{-1} , so the droplet time scale was between 0.1 and 1 s.

The dynamic surface tension of coal-water slurry with no surfactant was 71 to 76 mN/m at 40 wt% coal and 80 to 84 mN/m at 50 wt% coal at a time scale of 0.1 s. Kihm and Deignan suggested that the measured dynamic surface tension of the slurry was higher than that of water partly because of the high viscosity of the slurry (high viscosity fluids are known to give an apparent surface tension that is higher than the true value) and partly because of the larger interface produced by coal particles at the surface. The combined effects of coal particles and surfactant are shown in Figure 3.5. As indicated by the equilibrium (static) and dynamic curves for coal-water slurry and water, when the surfactant concentration is greater than about 1000 ppm, the surfactant produces considerably reduced equilibrium surface tension. The dynamic surface tension of the slurry mixture decreased as the bubble frequency was decreased from 10 s^{-1} to the static condition.

When the concentration of surfactant (any of the five surfactants) was less than 0.2 wt%, the dynamic surface tension of the 50 wt% slurry was greater than that of water for a time scale of 0.1 s (bubble frequency of 10 s^{-1}). The concentration limit probably depended in part on the extent to which the particular surfactant was adsorbed onto the coal; the limit might be different for a different solid or surfactant. Apparently, at this effective concentration of surfactant, this rate of surface expansion, and this solids concentration, the surfactant was blocked from migrating to the surface rapidly enough to produce the lowering of surface tension that would normally be typical of the surfactant.

The results of the two coal-water slurry studies indicate that although these slurries may include hydrophobic particles, at high solids concentration the apparent dynamic surface tension at a time scale of 0.1 s can be higher than that of water. The term “apparent dynamic surface tension” is used because high

solids concentrations are thought to produce the appearance of increased surface tension partly by increasing the viscosity and partly because the particles at the surface increase the amount of air-liquid interface. Decreasing the solids concentration from 50 wt% to 40 wt% caused the apparent dynamic surface tension to decrease to near that of water. Unfortunately, the studies do not provide any definite information on solids concentrations of less than 40 wt% or on time scales shorter than 0.1 s. Regardless, the implication of the trend with decreasing time scale is that, at the spray generation time scale of 0.001 s, any K Basin slurry should have a dynamic surface tension equal to that of water.

One qualitative way to judge whether a slurry contains surfactants or hydrophilic particles is to observe the froth that is formed when the slurry is sparged with gas. A froth that is more stable than what is observed in clean water indicates the presence of surfactants or hydrophobic particles while the absence of any noticeable froth suggests, but does not prove, that these materials are likely absent. As an example, foaming was observed in a solution of sodium dodecyl sulfate that was at a concentration of 10^{-3} M, about one-eighth of the CMC (Djuve et al. 2001). At this concentration, the equilibrium surface tension was 68 to 69 mN/m, only slightly reduced from the surface tension of water (72 mN/m). The dynamic surface tension would have been even closer to the value for water. This example with a surfactant shows that froth formation can be very sensitive to concentrations of surfactants that are still too low to reduce the equilibrium surface tension. Because froth stability can be an indicator for the presence of surfactants or hydrophobic particles, examples of previous laboratory experiments were sought in which K Basin slurries were sparged. In one example, a sample of KW slurry (KW230 settler sludge) was sparged “vigorously” with nitrogen during settling tests.² This particular waste slurry contains GraFoil fragments (Johnson 2010a), which might be one of the most hydrophobic particles in the waste slurries. No foaming or froth formation was observed during this test. This result suggests that there were no surfactants or hydrophobic particles capable of reducing the surface tension of this particular K Basin slurry.

Recall that the KW sludge had a high concentration of non-U solids (Table 3.1), which were suspect of being hydrophobic and of potentially causing decreases in surface tension. The absence of foaming of KW slurry samples is reasonable evidence that any hydrophobic solids or surfactant contamination that might be present did not have a significant effect on the dynamic surface tension.

² E-mail from JM Billing (PNNL) to CH Delegard (PNNL), April 13, 2011, 05:59 AM, “RE: K Basin Waters Surface Tension.”

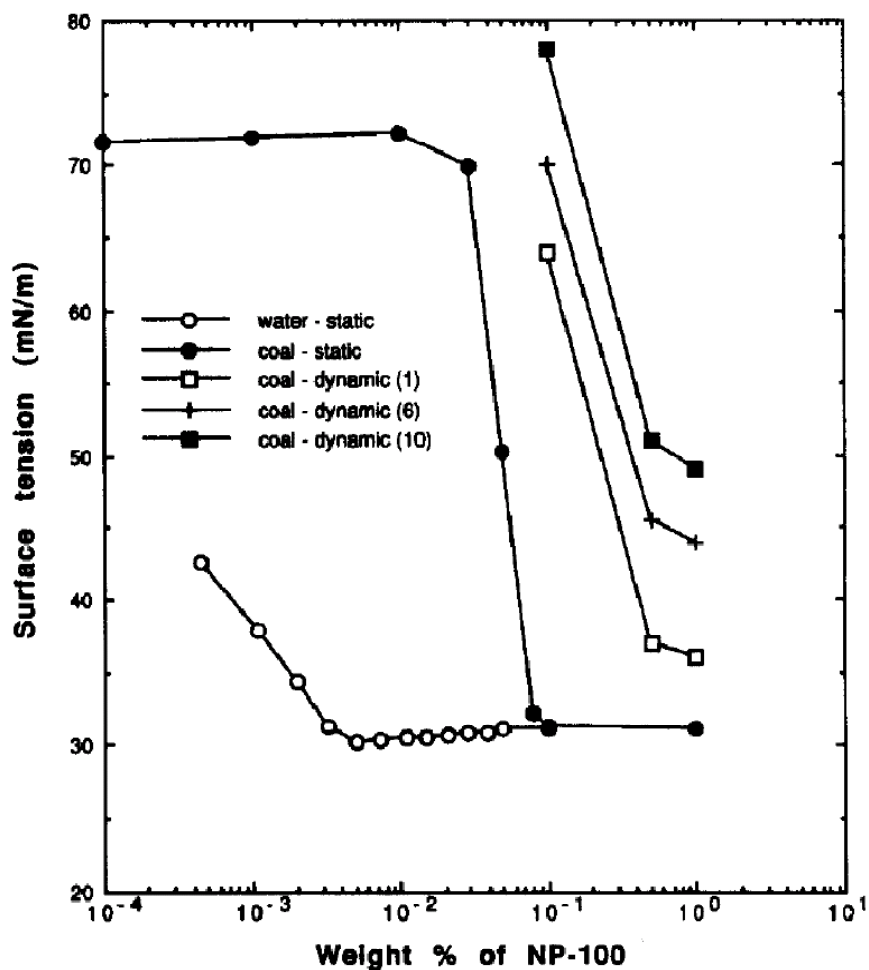


Figure 3.5. Equilibrium and Dynamic Surface Tension of 50-wt% Coal-Water Slurry with NP-100 Surfactant; Taken from Kihm and Deignan (1995). Numbers in parentheses indicate bubble frequency, s⁻¹.

4.0 Summary and Conclusions

A literature search was conducted to determine the effect of solid particles and of surface-active solutes on equilibrium surface tension and the role of rapid surface generation in causing the dynamic surface tension to be determined by the solvent (water) rather than by solutes and particles.

Characterization data for the K Basin sludges were also considered. The conclusions were these:

- The characteristic time scale for spray droplet formation was approximately 0.001 s or faster from both calculated time scales and experimental observations of droplet breakup at high Weber number.
- Hydrophobic particles, whether colloidal or larger, could reduce the equilibrium surface tension of an aqueous slurry from the surface tension of water, 72 mN/m, to 30 mN/m. However, K Basin slurry particles were not expected to be as hydrophobic as the particles in the literature studies. A fraction of K Basin solids is dirt, sand, or concrete grit, whereas the literature particles were coal or polystyrene. It seems reasonable to estimate the equilibrium surface tension of the K Basin slurries as between 30 mN/m and the surface tension of water, 72 mN/m, if the effect of the particles is the only effect considered. Nonetheless, the effect of particles on the dynamic surface tension at a time scale of ~ 0.001 s would be negligible because particles would be slow to diffuse to and adsorb at a newly-created surface on this time scale.
- The Clarifloc N-3300P flocculant would not affect the equilibrium surface tension at the concentrations used.
- If surfactant were present in the sludge liquid as a result of unintended contamination, its concentration would be too low to affect the dynamic surface tension at a time scale of ~ 0.001 s. The surfactant concentration would have to be fairly significant to have an effect on the dynamic surface tension. There is no evidence of significant quantities of surface-active species in the K Basin slurries, and any surfactant present would be a contaminant rather than an intended constituent. In partial confirmation of these conclusions, no foaming was observed during sparged settling tests of KW slurry samples. The absence of foam suggests that neither particles nor surface-active species were present in a quantity sufficient to reduce the surface tension of the samples.

In conclusion, although the *equilibrium* surface tension of K Basin slurries might be below the surface tension of water, owing to the possible presence of hydrophobic particles or surface-active contaminants, the *dynamic* surface tension should be equal to the surface tension of pure water. For the K Basin slurries, the effects of surface-active properties of the materials in the slurry, either hydrophobic particles or surface-active contaminants, are expected to be weak. For droplet formation, which always has rapid surface formation (0.001 s and faster), the effects of dynamic surface tension are such that the surface tension of water should always be appropriate for use when determining spray droplet size.

5.0 References

- Andreussi P, L Tognotti, M Graziadio, and G De Michele. 1990. "Atomization of Coal-Water Fuels by a Pneumatic Nozzle: Characteristics of the Spray." *Aerosol Sci. and Tech.* 13:35–46.
- Asnacios A, D Langevin, and J-F Argillier. 1996. "Complexation of Cationic Surfactant and Anionic Polymer at the Air-Water Interface." *Macromolecules* 29:7412–7417.
- Aytouna M, D Bartolo, G Wegdam, D Bonn, and S Rafai. 2010. "Impact dynamics of surfactant laden drops: dynamic surface tension effects." *Exp. Fluids* 48:49–57.
- Bamberger JA and JA Glissmeyer. 2004. *Release Fraction Evaluation*. PNNL-14545, Pacific Northwest National Laboratory, Richland, Washington.
- Berg JC. 2010. *An Introduction to Interfaces and Colloids: The Bridge to Nanoscience*. World Scientific Publishing Co., Hackensack, New Jersey.
- Binks BP. 2002. "Particles as Surfactants—Similarities and Differences." *Curr. Opinion in Coll. and Interface Sci.* 7:21–41.
- Brian BW and JC Chen. 1987. "Surface tension of solid-liquid slurries." *AIChE J* 33(2):316-318.
- Chung SI and DT Wasan. 1988. "Dynamic stability of liquid-liquid dispersions containing polymeric suspension stabilizers." *Colloids and Surfaces* 29:323-336.
- Crowe RD. 2010. *Sludge Treatment Project (STP) Methodology for Spray Leak Scenarios*. PRC-STP-00292, Rev 0. CH2MHill Plateau Remediation Company, Richland, Washington.
- Crowe RD. 2011. *Sludge Treatment Project – Engineered Container Retrieval and Transfer System Draft Preliminary Design Accident Analysis*. PRC-STP-CN-N-00401, Rev 1. CH2MHill Plateau Remediation Company, Richland, Washington.
- Dean JA. 1979. *Lange's Handbook of Chemistry*. 12th Edition, McGraw-Hill, New York.
- Dhaliwal T. 2011. *Sludge Treatment Project Engineered Container Retrieval and Transfer System Flocculant System Status Report*. PRC-STP-00226, Rev. 1, CH2MHill Plateau Remediation Company, Richland, Washington.
- Djuve J, RJ Pugh, and J Sjoblom. 2001. "Foaming and dynamic surface tension of aqueous polymer/surfactants solutions 1: ethyl(hydroxyethyl) cellulose and sodium dodecyl sulphate." *Colloids and Surfaces* 186:189-202.
- DOE—U.S. Department of Energy. 1994. *DOE Handbook, Airborne Release Fractions/Rates and Respirable Fractions for Nonreactor Nuclear Facilities, Volume I - Analysis of Experimental Data*. DOE-HDBK-3010-94, Washington DC.
- Eastoe J and JS Dalton. 2000. "Dynamic surface tension and adsorption mechanisms of surfactants at the air-water interface." *Adv. Colloid & Interface Sci.* 85:103–144.

Epstein M and MG Phys. 2006. *Measured drop size distributions with cold sprays emanating from small leak openings*. FAI/06-55, Fauske & Associates, LLC., Burr Ridge, Illinois.

Fainerman VB, R Miller, and P Joos. 1994. "The measurement of dynamic surface tension by the maximum bubble pressure method." *Colloid and Polymer Science* 272:731–739.

Fainerman VB and R Miller. 1995. "Dynamic Surface Tension Measurements in the Sub-millisecond Range." *J. Colloid and Interface Sci.* 175:118-121.

Gelfand BE. 1996. "Droplet Breakup Phenomena in Flows with Velocity Lag." *Prog. Energy Combust. Sc.* 22:201-265.

Groszek AJ and S Partyka. 1993. "Measurements of Hydrophobic and Hydrophilic Surface Sites by Flow Calorimetry." *Langmuir* 9:2721–2725.

Hai M, B Han, H Yan, and Q Han. 1998. "Vapor Pressure of Aqueous Solutions of Polyacrylamide + Sodium Dodecyl Sulfate with and without NaOH." *J. Chem. Eng. Data* 43:1056–1058.

Hoeve WV, S Gekle, JH Snoeijer, M Versluis, MP Brenner and D Lohse. 2010. "Breakup of diminutive Rayleigh jets." *Phys. of Fluids* 22:11.

Johnson ME. 2010a. *Preliminary STP Container and Settler Sludge Process System Description and Material Balance*. HNF-41051, Rev. 6, CH2MHILL Plateau Remediation Company, Richland, Washington.

Johnson ME. 2010b. *Screening Evaluation of Characterization Data for Engineered Container SCSCON-220, -240, -250, and -260*. PRC-STP-00212, Rev 0, CH2MHILL Plateau Remediation Company, Richland, Washington.

Kao RL, DA Edwards, DT Wasan, and E Chen. 1992. "Measurement of Interfacial Dilatational Viscosity at High Rates of Interface Expansion Using the Maximum Bubble Pressure Method. I. Gas-Liquid Surface." *J. Colloid and Interface Sci.* 148: 247-256.

Kihm KD and P Deignan. 1995. "Dynamic surface tension of coal-water slurry fuels." *Fuel* 74(2):295-300.

Kjellin UR, J Reimer, and P Hannsson. 2003. "An investigation of dynamic surface tension, critical micelle concentration, and aggregation number of three nonionic surfactants using NMR, time-resolved fluorescence quenching, and maximum bubble pressure tensiometry." *J. Colloid & Interface Sci.* 262:506–515.

Moorkanikkara SN and D Blankshtein. 2009. "New Methodology to Determine Equilibrium Surfactant Adsorption Properties from Experimental Dynamic Surface Tension Data." *Langmuir.* 25: 6191-6202.

Okubo T. 1995. "Surface Tension of Structured Colloidal Suspensions." *J. Colloid & Interface Sci.* 171:55–62.

Rahman MA. 2011. "*Scaling of effervescent atomization and industrial two-phase flow.*" PhD Thesis, University of Alberta, Calgary, Alberta, Canada.

Sallam KA, Z Dai, and GM Faeth. 2002. "Liquid breakup at the surface of turbulent round liquid jets in still gases." *Inter. J. Multiphase Flow*. 28:427–449.

Schmidt AJ. 2009. *Spent Nuclear Fuel Project Technical Databook, Vol. 2, Sludge*. HNF-SD-SNF-TI-015, Rev 14B, Volume 2, Fluor Hanford, Richland, Washington.

Simpkins PG. 1971. "Non-linear response of deforming drops." *Nature: Physical Science*. 233:31–33.

Stewart CW, LA Mahoney, CE Guzman-Leong, JM Alzheimer, ST Arm, JA Bailey, MG Butcher, SK Cooley, EC Golovich, DE Hurley, LK Jagoda, CD Johnson, WR Park, LD Reid, RW Slauch, HD Smith, Y Su, BE Wells, C Wend, and ST Yokuda. 2007. *Results of Large-Scale Testing on Effects of Anti-Foam Agent on Gas Retention and Release*. PNNL-17170 (WTP-RPT-156) Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.

Trasatti S. 1991. "Physical Electrochemistry of Ceramic Oxides." *Electrochimica Acta* 36:225-241.

van Oss CJ. 2008. *The Properties of Water and Their Role in Colloidal and Biological Systems*. Academic Press, Amsterdam, The Netherlands.

Waghmare PR and SK Mitra. 2010. "Contact Angle Hysteresis of Microbead Suspensions." *Langmuir* 26(22):17082-17089.

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