FINAL REPORT
DOE-UTAH-93ER14315

The Hydrophobic Character of Nonsulfide Mineral Surfaces as Influenced by Double-Bond Reactions of Adsorbed Unsaturated Collector Species

DOE Grant NO. DE-FG02-93ER14315
Separations and Analysis Program

Grant Period: July 1993 to December 2017

The Flotation Chemistry of Nonsulfide Minerals

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February 28, 2018

DOE Final Report

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1. ABSTRACT

The Final Report for Grant No. DE-FG02-93ER14315, on "The Flotation Chemistry of Nonsulfide Minerals," includes the following sections:

- Introduction
- Research Summary
- Graduate Student Education
- Research Recognition
- Conclusion

Significant achievements have been made in this Separations Program supported by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences of the U.S. Department of Energy. The flotation chemistry results have been published and classified into the following topics:

- Soluble Salt Minerals
- Collector Adsorption
- Wetting, Surface Forces, and Bubble Attachment
- Interfacial Water Structure
- Phyllosilicate Minerals

with a review of each topic given in the Research Summary.

The research results summarized herein have resulted in more than 225 publications, the education of 28 PhD graduate students, and impressive recognition with university, national, and international awards. It is evident that the flotation separation research program has been quite successful.

Key words: flotation separations; surface chemistry; mineral particles; soluble salt minerals; semi-soluble salt minerals; phyllosilicate minerals; oxide/hydroxide minerals; interfacial water structure; bubble attachment; hydrophobic surfaces; collector (surfactant) absorption; atomic force microscopy; vibrational spectroscopy (FTIR, SFVS); molecular dynamics simulations (MDS); surface forces; particle interaction

DOE FINAL REPORT

Grant No. DE-FG02-93ER14315

2. INTRODUCTION

2.1 Background

Particulate separations are of considerable significance in many areas of technology ranging from pharmaceutics and microelectronics, to mining and construction materials industries. In addition, particulate separation technology is of critical importance in the environmental area, for example, the development of advanced water treatment processes for the 21st century will rely on more efficient particulate separation techniques. In this regard it is most appropriate that the Separations Program supported by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences of the U.S. Department of Energy supports basic sciences research in the area of particulate separations. One such particulate separation process of special importance is froth flotation. Froth flotation is a physico-chemical process that is used to separate particles in an aqueous suspension via differences in hydrophobicity as established by the interaction of various reagents at the solid/water, solid/gas and water/gas interfaces. Surfactants, called collectors, are added to a suspension to selectively adsorb at the surface of specific particles, rendering these particles hydrophobic. Regulators are employed to promote collector adsorption at the desired surfaces, while preventing such reactions at other surfaces. When air is dispersed into the suspension, the bubbles generated attach to the hydrophobic particles. The resulting bubble/particle aggregates float to the suspension surface and are collected in a froth phase as a concentrate. Frothers are used to stabilize the froth and prevent the concentrate from collapsing back into the suspension of hydrophilic particles (tailings product). Clearly, particulate separation by froth flotation is an outstanding example of applied surface chemistry, and is used in the food, petroleum, pulp/paper, and mineral industries.

Flotation separation technology is now being developed to solve environmental problems including resource conservation, pollution prevention, and environmental remediation. Examples such as the separation of radionuclides from contaminated soils, the removal of dispersed oil from oily wastewater, recycling of plastics, recycling of wastepaper to produce a clean cellulose product, and clean coal production, demonstrate the utility and need for the development of improved flotation separation technology. The use of this technology is perhaps most significant in the mineral industry where, in the U. S. alone, over 500,000 tons/day of nonsulfide minerals are processed by flotation. In this regard, a research program has been in progress with DOE support from Grant DE-FGO2-93ER14315 to study the fundamental interfacial chemistry features in nonsulfide mineral flotation systems in order to increase our understanding of the interfacial chemistry for improved separation efficiencies and energy economy in mineral flotation processes involving collector (surfactant) adsorption phenomena. The need for research in this area was documented in a National Research Council (NRC) report *Evolutionary and Revolutionary Technologies for Mining*, commissioned by DOE and published by the National

Academy Press, Washington D.C. in 2001. More recently a report *Beyond the Molecular Frontier: Challenges for Chemistry and Chemical Engineering*, prepared under the auspices of the NRC Board on Chemical Sciences and Technology (BCST) underlined areas of huge potential benefit for society, some of which relate directly to the flotation chemistry of particle separations.

Flotation technology is of significant importance to the mineral industry, an industry which contributes substantially to our nation's economy. The estimated value of all nonfuel mineral materials processed in the United States during 2015 totaled $630 billion. As mentioned previously, particle separation by flotation is an important process that is used in many of the mineral industries. Understanding of the interfacial chemistry for the development of improved flotation separations is required for more effective production and utilization of our mineral resources, especially the critical minerals as identified in the 2017 USGS report, "Critical Mineral Resources of the United States – Economic and Environmental Geology and Prospects for Future Supply."

2.2 Research Need

The separation of minerals by froth flotation has frequently been investigated from a macroscopic perspective rather than through a detailed spectroscopic surface analysis. Most likely, this is due to a combination of two factors. First, mineral systems are often quite complex and vary considerably from one ore deposit to the next. Second, analytical techniques for detailed, in-situ, and real time observation of the solid/liquid interface have now been developed. The advent of these sophisticated experimental methods now allows for a more detailed investigation of the critical role that interfacial chemistry plays in separations by flotation. Understanding the interfacial chemistry will allow for the design of new procedures for improved flotation separation efficiency and reduced energy consumption. This lack of detailed knowledge concerning the surface chemistry of froth flotation systems is unfortunate considering the importance of flotation technology in many industries. Now, the availability of new analytical instruments such as the atomic force microscope and sum frequency generation spectrometers can provide crucial surface chemistry information regarding collector adsorption phenomena and the hydrophobic surface states. With such information, it is expected that improved, energy efficient flotation separations can be devised.

The critical need for understanding these phenomena is perhaps most evident by examining the number of recent meetings and proceedings dealing with surface chemistry and flotation separation technology, for example, the 7th International Flotation Conference, Cape Town, South Africa in November of 2015, with a subsequent conference in Cape Town, November of 2017, and the XXVIII International Mineral Processing Congress (IMPC 2016), Quebec City, Canada, September 2016. Further evidence of the importance of flotation technology and the need for the techniques being developed in this research program are clearly demonstrated by the Committee on Separation Science and Technology of the Board of Chemical Science and Technology of the Research Council, in their report, *Separation and Purification: Critical Needs and Opportunities*:

> To facilitate future progress a broad effort is needed to develop the underlying knowledge base for separations. Empirical understanding of separation processes needs to be reinforced by understanding at the molecular level, new separation processes must be devised and investigated, better integrated systems

need to be designed, and research personnel must be trained and stimulated to provide these breakthroughs.

Although progress has been made since this report, there is still much to be done. According to the C&EN report on the growth of separations technology, it is clear that there is a great potential to make significant contributions to flotation technology and separation science by a detailed study of relevant interfacial phenomena as has been the intent of this research program.

This separation research program has supported the need expressed by the 2017 USGS report, "Critical Mineral resources of the United States – Economic and Environmental Geology and Prospects for Future Supply," and the 20 December 2017 executive order by President Trump to increase the discovery, production, and domestic refining of critical minerals. In view of this recent executive order, the termination of "The Flotation Chemistry of Nonsulfide Minerals" research program by DOE is quite surprising.

Now our country is faced with a mineral resources challenge. It was reported in the journal *Science,* 17 December 2010, that the U.S. Department of Energy has recently held workshops to discuss policies and technological efforts to ensure supplies of rare earth minerals and other strategic minerals including research programs to support such technological development. As a result of these workshops, DOE issued the report "Critical Materials Strategy", December 2010, which describes the research agenda for critical materials including technology for processing and recovery of strategic minerals. Of course, improved flotation technology would help in securing strategic mineral production from domestic resources, including rare earth minerals for solar cells and hybrid cars, lithium resources for batteries and electric vehicles, and other strategic resources such as cobalt, indium, and tellurium. The U.S. National Research Council warned in 2008 of a possible shortage of critical minerals, as was also discussed in a report by the European Commission, citing concerns over access to many strategic minerals. In addition, a USGS report which provides an overview of domestic rare earth elements and possibilities for utilizing those resources is available at http://pubs.usgs.gov/sir/2010/5220. In this regard, our separations research program included the flotation chemistry of rare earth minerals in an effort to develop improved technology for the recovery of such strategic minerals from domestic resources.

The need for energy-efficient technologies such as flotation separations is evident from the "Mining Industry of the Future" program implemented by the Office of Industrial Technologies (OIT) of DOE. Such technologies cannot be developed without fundamental research support. The need for energy efficiency technologies is further documented in the literature and indicated in the report, *Federal Energy Research and Development for the Challenges of the Twenty First Century*, by the Energy Research & Development Panel of the President's Committee of Advisers on Science & Technology. Interfacial chemistry was identified as one of four major areas for future research, which offers tremendous opportunities for further advances in the field of separations. Certainly our research efforts on the fundamental interfacial chemistry of particulate separations by froth flotation need to be sustained.

2.3 Major Goals

The primary goal of this research program has been to provide a basis for improved flotation separation efficiency in nonsulfide mineral systems by establishing the fundamental features of collector (surfactant) adsorption reactions associated with the hydrophobic surface state and developing appropriate surface chemistry control strategies. In-situ FTIR internal

reflection spectroscopy (FTIR/IRS) and FTIR external reflection spectroscopy (FTIR/ERS) measurements, sum frequency vibrational spectroscopy (SFVS), molecular dynamics simulations (MDS), atomic force microscopy (AFM), nonequilibrium electrophoresis, photon-correlation spectroscopy, collector studies by analysis of Langmuir-Blodgett (LB) and self-assembled films, vacuum and bench scale flotation experiments, as well as bubble attachment time measurements and contact angle goniometry, have been used to accomplish this goal. These advanced experimental techniques, together with more traditional experimental methods, provide crucial information concerning the hydrophobic surface state for nonsulfide mineral flotation systems, particularly the flotation separation of critical mineral resources.

Specifically, the research program was designed to examine flotation phenomena such as interfacial water structure, surfactants at surfaces, and the hydrophobic surface state. All of these matters provide a fundamental foundation for an improved understanding of the surface chemistry of nonsulfide minerals, with the intent to impact flotation technology for separation and recovery of nonsulfide mineral particles.

Studies of water structure at the water/solid and water/adsorbed surfactant/solid interfaces are of great interest not only in particulate separations by flotation but also in a number of other scientific and technological areas including nanotechnology, biotechnology, medicine, and electrochemistry. Correlating the nature of the surface state (the extent of wetting by water) with the structure of interfacial water, has been, and continues to be, an important objective of our research program. How do we determine the structure of interfacial water, particularly in the water film between bubble and surface? How does the structure influence the hydrophobic surface state, so important in many areas of science and technology? In another aspect of this research program, we tried to improve the understanding of surfactant adsorption phenomena, the adsorption of macromolecules, and bubble attachment phenomena.

The flotation chemistry research used advanced diagnostic tools such as atomic force microscopy (AFM), molecular dynamics simulations (MDS), density functional theory (DFT) computations (Gaussian 9), and surface spectroscopy. Of course in most cases, the hydrophobic surface state is determined by the nature of surfactant adsorption. Important questions to be answered included the following: How are the wetting characteristics of surfaces altered by surfactant/macromolecule surface structures? How do intrinsic mineral surface properties such as hydrophobicity, charge density and roughness, as well as the surfactant chemistry, influence the surfactant surface structures? What happens to interfacial water and surfactant disposition in the water film during bubble contact and attachment? In addition to the new attention being given to the water film stability, flotation fundamentals for critical mineral resources, such as the rare earth mineral bastensite, might be considered.

Finally, in order to better understand flotation response, hydrophobic surface forces were being studied using the atomic force microscopy colloidal probe technique. Understanding the complicated nature of these attractive interactions between hydrophobic surfaces requires answering important questions: How do these forces depend on subtle properties of the surfaces, including surface roughness and heterogeneity? How are the forces altered by adsorption phenomena? What is the influence of solution chemistry, including amount and composition of gaseous species dissolved in water on the range and magnitude of hydrophobic surface forces?

How is the hydrophobic surface force altered at highly deformable surfaces such as the surface of a gas bubble?

Answers to the aforementioned questions will greatly enhance our understanding of the hydrophobic surface state and hence contribute significantly to the general development of flotation technology and to the flotation chemistry of nonsulfide minerals in particular.

Understanding the fundamental interfacial phenomena involved in the complex interactions of collector molecules adsorbed at nonsulfide mineral surfaces will not only allow for the development of more energy efficient flotation separations but also provide the basis for improved utilization of mineral and energy resources. In addition, it is important to note that the results from this research program have provided a fundamental basis for solving environmental problems, which involve particulate separations. These include resource conservation, pollution prevention, and pollution remediation. Interfacial chemistry has been identified as one of the major areas for future research, which offers tremendous opportunities for further advances in the field of separations. In this way our research program was designed to increase our understanding of the fundamental interfacial chemistry of particulate separations by froth flotation.

Significant scientific accomplishments have been made and include quantitative in-situ and ex-situ surface spectroscopy of adsorbed surfactants, hydrophobic surface force measurements and analysis, in-situ imaging of surfactant surface structures and molecular dynamics simulations. In addition detailed studies have revealed the many important fundamental issues associated with the surface chemistry of phyllosilicate minerals, particularly kaolinite. These clay minerals are frequently of concern in nonsulfide flotation systems, including phosphate, potash, and oil sand resources. Based on the scientific foundation established from our most recent research program, new collector chemistries and understanding for the flotation of rare earth minerals, specifically bastnaesite, are being established.

The minerals and associated industries are becoming increasingly dependent on innovative and cross-disciplinary approaches in order to meet the challenges of growing competition, remaining profitable, and meeting environmental standards. For example, knowledge and experience gained through fundamental and applied studies can resolve environmental problems or allow for increased production via increased resource recoveries which, in turn, can help satisfy environmental imperatives by minimizing and even preventing pollution. At the same time, through the rigors of education, a more knowledgeable student is prepared for employment by industry. The PI and his research team have certainly had successes in all of these areas. The experience and success gained with the implementation of this program have created numerous professional opportunities for a number of students, post docs and visiting researchers from all over the world who have worked with the PI on this program for many years.

Results will identify opportunities for applications in industry, including the consideration of flotation chemistry fundamentals for critical minerals, specifically the rare earth mineral bastnaesite, the only domestic rare earth production from Mountain Pass, CA, and to

continue to provide the foundation for improved, energy efficient particle separations by froth flotation.

Our research program has been in progress with DOE support from Grant DE-FG-02-93-ER14315 to study the fundamental interfacial chemistry features in nonsulfide mineral flotation separations in order to provide a basis for improved efficiencies and energy economy in the separation, recovery, and utilization of our mineral resources. The efficient separation of mineral particles by flotation is of significant importance in order to provide us with a supply of critical materials.

3. RESEARCH SUMMARY

Research contributions from the DOE Basic Energy Sciences Grant DE-FG02-9314315, "The Flotation Chemistry of Nonsulfide Minerals," are many, with more than 225 publications, and are summarized herein under the following topics:

- Soluble Salt Minerals
- Collector Adsorption
- Wetting, Surface Forces, and Bubble Attachment
- Interfacial Water Structure
- Phyllosilicate Minerals

A short summary regarding the results for each topic is given followed by a listing of the corresponding publications.

3.1 Soluble Salt Minerals

The surface chemistry of soluble salt flotation continues to be an important area of research and included the study of several soluble salt mineral resources, including potash, borax, and trona. Significant contributions to the scientific literature have been made. For the first time, the sign of the surface charge for soluble salt minerals, particularly the alkali halides in their saturated brines, has been experimentally established by nonequilibrium electrophoretic measurements, and explained based on the lattice ion hydration theory. Further, the flotation response with traditional collectors, alkyl amines and sodium dodecyl sulfate, has been explained based on the interfacial water structure of the associated brine. For example, in the case of alkali halides, the fact that flotation is possible with either the cationic alkyl amine or the anionic sodium dodecyl sulfate, if the alkali halide salt forms water structure-breaking brine, had not been understood previous to this research. In contrast, flotation of the alkali halide salt is not possible if the salt forms structure-making brine. Finally, the soluble salt research resulted in the development of a flotation strategy for the alternative processing of our trona resources in order to reject insoluble mineral components and make a high quality trona concentrate. Trona is a sodium sesquicarbonate dihydrate mineral which is typically converted to soda ash, an important item of commerce. Soluble salt flotation chemistry publications are as follows:

1. "Surface Charge of Alkali Halide Particles as Determined by Laser–Doppler Electrophoresis," J. D. Miller, M. R. Yalamanchili, and J. J. Kellar, Langmuir, 8, pp. 1464–1469 (1992).
2. "Adsorption of Collector Colloids in the Flotation of Alkali Halide Particles," M. R. Yalamanchili, J. J. Kellar, and J. D. Miller, International Journal of Mineral Processing, 39, pp. 137–153 (1993).
3. "Discussion–Flotation of Boron Minerals," M. R. Yalamanchili and J. D. Miller, Minerals and Metallurgical Processing, 11, pp. 121–123 (1993).
4. "Borax Flotation — A Discussion," M. R. Yalamanchili and J. D. Miller, Minerals and Metallurgical Processing, 11, pp. 121–122 (1994).

5. "Fundamental Aspects of Soluble Salt Flotation," J. D. Miller and M. R. Yalamanchili, Minerals Engineering, 7 (2/3), pp. 305–317 (1994).
6. "Interaction of Alkali Halide Particles in Their Saturated Brines and the Significance of Attractive Hydration Forces," M. R. Yalamanchili and J. D. Miller, in *Proceedings of the Engineering Foundation Conference on Dispersion and Aggregation: Fundamentals and Applications,* Palm Coast, Florida, March 15–20, 1992, Engineering Foundation, pp. 155–168 (1994).
7. "The Surface Charge of KCl as Influenced by Crystal Lattice Defects," M. R. Yalamanchili and J. D. Miller, Journal of Colloid and Interface Science, 163, pp. 137–144 (1994).
8. "The Influence of Oxygen Defect States on the Surface Charge of Alkali Halides," S. Veeramasuneni, M. R. Yalamanchili, and J. D. Miller, Journal of Colloid and Interface Science, 182, pp. 275–281 (1996).
9. "Amine Flotation of Soluble Sulfate Salts," M. Hancer, Y. Hu, M. C. Fuerstenau, and J. D. Miller, in *Proceedings of the XX International Mineral Processing Congress, Volume 3: Flotation and Other Physical–Chemical Processes*, Aachen, Germany, 21–26 September 1997, pp. 715–723 (1997).
10. "Electrokinetic Behavior of Fluoride Salts as Explained from Water Structure Considerations," Y. Hu, Y. Lu, S. Veeramasuneni, and J. D. Miller, Journal of Colloid and Interface Science, 190, pp. 224–231 (1997).
11. "Recent Contributions to the Analysis of Soluble Salt Flotation Systems," J. D. Miller, S. Veeramasuneni and M. R. Yalamanchili, International Journal of Mineral Processing, 51, pp. 111–123 (1997)
12. "The Surface Charge of Alkali Halides — Consideration of the Partial Hydration of Surface Lattice Ions," S. Veeramasuneni, Y. Hu, and J. D. Miller, Surface Science, 382, pp. 127–136 (1997).
13. "Effect of In-situ Ultrasonic Treatment on the Flotability of Slime Coated Colemanite," M. S. Celik, I. Elma, M. Hancer, and J. D. Miller, in *Proceedings of the 7th International Mineral Processing Symposium*, *Innovations in Mineral and Coal Processing*, Istanbul, Turkey, 15–17 September 1998, pp. 153–157 (1998).
14. "Electrokinetic Behavior of Selected Alkali and Alkaline Earth Fluoride Salts in Organic Solvents," Y. Hu, S. Veeramasuneni, and J. D. Miller, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 141, pp. 193–203 (1998).
15. "Interaction Forces in the Flotation of Colemanite as Measured by Atomic Force Microscopy," J. Nalaskowski, S. Veeramasuneni, and J. D. Miller, in *Proceedings of the 7th International Mineral Processing Symposium*, *Innovations in Mineral and Coal Processing*, Istanbul, Turkey, 15–17 September 1998, pp. 159–165 (1998).
16. "The Surface Charge of Alkali Halides in Their Saturated Solutions," J. D. Miller, and S. Veeramasuneni, in *Surfaces of Nanoparticles and Porous Materials,* Surfactant Science Series, J. A. Schwartz and C. Contescu, eds., Marcel Dekker, Inc., New York, 78, pp. 613–644 (1999).
17. "Electrokinetic Behavior of Borax in Saturated Solutions and its Role in Flotation," M. Muduroglu, M. S. Celik, M. Hancer, and J. D. Miller, in *Mineral Processing on the Verge of the 21st Century, Proceedings of the 8th International Mineral Processing Symposium*, Antalya, Turkey, 16–18 October 2000, G. Ozbayoglu, C. Hosten, M. U. Atalay, C. Hicyilmaz, and A. I. Arol, eds., Brookfield, CT, pp. 231–236 (2000).

18. "The Flotation Chemistry of Potassium Double Salts: Schoenite, Kainite, and Carnallite," M. Hancer and J. D. Miller, Minerals Engineering, 13 (14/15), pp. 1483–1493 (2000).
19. "Flotation Fundamentals of Soluble Salts," M. Hancer, J. D. Miller, U. Mart, M. S. Celik, in *Proceedings of the 9th Balkan Mineral Processing Congress – New Developments in Mineral Processing*, Istanbul, Turkey, 11–13 September 2001, G. Onal, S. Atak, A. Guney, M. S. Celik, and A. E. Yuce, eds., pp. 147–154 (2001).
20. "The Significance of Interfacial Water Structure in Soluble Salt Flotation Systems," M. Hancer, M. S. Celik, and J. D. Miller, Journal of Colloid and Interface Science, 235, pp. 150–161 (2001).
21. "Flotation Chemistry of Boron Minerals," M. S. Celik, M. Hancer, and J. D. Miller, in *Journal of Colloid and Interface Science, Proceedings of the 13th International Symposium on Surfactants in Solution (SIS–2000),* Gainesville, Florida, 11–16 June 2000, 256, pp. 121–131 (2002).
22. "Flotation of Sodium Carbonate and Sodium Bicarbonate Salts from their Saturated Brines," O. Ozcan and J. D. Miller, Minerals Engineering, 15 (8), pp. 577–584 (2002).
23. "The Effect of Thermal Stability on the Flotation Response of Sodium Carbonate Salts," O. Ozcan, M. S. Celik, Z. S. Nickolov, and J. D. Miller, Minerals Engineering, 16, pp. 353-358 (2003).
24. "FTIR Analysis of Water Structure and Its Significance in the Flotation of Sodium Carbonate and Sodium Bicarbonate Salts," Z. S. Nickolov, O. Ozcan, and J. D. Miller, Colloids and Surfaces A, 224 (1–3), pp. 231-239 (2003).
25. "Adsorption of Carbonate and Bicarbonate Salts at the Air-brine Interface," O. Ozdemir, S. I. Karakashev, A. V. Nguyen, and J. D. Miller, International Journal of Mineral Processing, 81, pp. 149-158 (2006).
26. "Evaluation of Reverse Flotation for the Trona Industry," A. Jain, O. Ozdemir, X. Wang, and J. D. Miller, in *Proceedings of the XXIII International Mineral Processing Congress*, Istanbul, Turkey, 3–8 September 2006, Volume 3, G. Onal, N. Acarkan, M. S. Celik, F. Arslan, G. Atesok, A. Guney, A. A. Sirkeci, A. E. Yuce, K. T. Perek, eds., Promed Advertising Agency, Istanbul, Turkey, pp. 1002–1005 (2006).
27. "Flotation Chemistry Considerations in the Development of Flotation Technology for the Trona Industry," O. Ozdemir, A. V. Nguyen, Z. S. Nickolov, M. S. Celik, and J. D. Miller, in *Proceedings of the XXIII International Mineral Processing Congress*, Istanbul, Turkey, 3–8 September 2006, Volume 2, G. Onal, N. Acarkan, M. S. Celik, F. Arslan, G. Atesok, A. Guney, A. A. Sirkeci, A. E. Yuce, K. T. Perek, eds., Promed Advertising Agency, Istanbul, Turkey, pp. 911-916 (2006).
28. "Structural and Dynamic Properties of Concentrated Alkali Halide Solutions: A Molecular Dynamics Simulation Study," H. Du, J. C. Rasaiah, and J. D. Miller, Journal of Physical Chemistry B, 111 (1), pp. 209–217 (2007).
29. "Water Structure and Its Influence on the Flotation of Carbonate and Bicarbonate Salts," O. Ozdemir, M. S. Celik, Z. S. Nickolov, and J. D. Miller, Journal of Colloid and Interface Science, 314 (2), pp. 545–551 (2007).
30. "Fundamental Aspects of Carbonate and Bicarbonate Salt Flotation," O. Ozdemir, C. Karaguzel, A. V. Nguyen, M. S. Celik, and J. D. Miller, in *Proceedings Chemeca 2008 Conference*, Newcastle, NSW, Australia, 28 September –1 October 2008 (2008).

31. "Molecular Features of the Air/Carbonate Solution Interface," H. Du, J. Liu, O. Ozdemir, A. V. Nguyen, J. D. Miller, Journal of Colloid and Interface Science, 318, pp. 271–277 (2008).
32. "Surface Chemistry Features in the Flotation of KCl," F. Q. Cheng, Y. N. Zhang, H. Du, J. Liu, J. Nalaskowski, and J. D. Miller, in *Proceedings XXIV International Mineral Processing Congress*, Beijing, China, 24–28 September 2008, W. Dianzuo, et al, eds., Science Press, Beijing, China (2008).
33. "Adsorption and Surface Tension Analysis of Concentrated Alkali Halide Brine Solutions," O. Ozdemir, S. I. Karakashev, A. V. Nguyen, and J. D. Miller, Minerals Engineering, 22 (3), pp. 263–271 (2009).
34. "Contact Angle and Bubble Attachment Studies in the Flotation of Trona and Other Soluble Carbonate Salts," O. Ozdemir, C. Karaguzel, A. V. Nguyen, M. S. Celik, and J. D. Miller, Minerals Engineering, 22, pp. 168–175 (2009).
35. "Evaluation of Flotation Technology for the Trona Industry," O. Ozdemir, A. Jain, V. Gupta, X. Wang, and J. D. Miller, Minerals Engineering, 23 (1), pp. 1–9 (2010).
36. "Significance of Ion Interactions in Flotation in Saline and Brine Solutions," O. Ozdemir, A. Nguyen, J. D. Miller, H. Du, and M. Celik, in *Proceedings, XXV International Mineral Processing Congress (IMPC) 2010*, Brisbane, Qld., Australia, 6–10 September 2010, pp. 2977–2987 (2010).
37. "Surface Chemistry Features in the Flotation of KCl," Q. Cao, H. Du, J. D. Miller, X. Wang, and F. Cheng, Minerals Engineering, 23 (5), pp. 365–373 (2010).
38. "Bubble Attachment Time and FTIR Analysis of Water Structure in the Flotation of Sylvite, Bischofite and Carnallite," Q. Cao, X. Wang, J. D. Miller, F. Cheng, and Y. Jiao, Minerals Engineering, 24 (2), pp. 108–114 (2011).
39. "Production of Trona Concentrates Using High-intensity Dry Magnetic Separation Followed by Flotation," O. Ozdemir, V. Gupta, J. D. Miller, M. Cinar, and M. S. Celik, Minerals & Metallurgical Processing, 28 (2), pp. 55–61 (2011).
40. "Understanding the Role of Ion Interactions in Soluble Salt Flotation with Alkylammonium and Alkylsulfate Collectors," O. Ozdemir, H. Du, S. I. Karakashev, A. V. Nguyen, M. S. Celik, and J. D. Miller, Advances in Colloid and Interface Science, 163 (1), pp. 1–22 (2011).
41. "FTIR Analysis of Water Structure and Its Influence on the Flotation of Arcanite (K_2SO_4) and Epsomite ($MgSO_4 \cdot 7H_2O$)," F. Cheng, Q. Cao, Y. Guan, H. Cheng, X. Wang, and J. D. Miller, International Journal of Mineral Processing, 122, pp. 36–42 (2013).
42. "Flotation Chemistry of Soluble Salt Minerals: from Ion Hydration to Colloid Adsorption," H. Du, O. Ozdemir, X. Wang, F. Cheng, M. S. Celik and J. D. Miller, Minerals & Metallurgical Processing, 31 (1), pp. 1–20 (2014).
43. "Potash Flotation Practice for Carnallite Resources in the Qinghai Province, PRC," X. Wang, J.D. Miller, F. Cheng, and H. Cheng, Minerals Engineering, 66–68, pp. 33–39 (2014).
44. "Some Physicochemical Aspects of Water-soluble Mineral Flotation," Z. Wu, X. Wang, H. Liu, H. Zhang, and J.D. Miller, Advances in Colloid and Interface Science, 235, pp. 190–200 (2016).

3.2 Collector Adsorption

Collector adsorption has been studied primarily for semi-soluble salt minerals, but, in addition, the organization of collector nano structures at the surface of hydrophilic and hydrophobic mineral surfaces has been an important contribution. Semi-soluble salt minerals are characterized by their ionic bonding and are distinguished from soluble salt minerals by their limited solubility in water. One group of semi-soluble salt minerals considered was the alkaline earth salt minerals including fluorite (CaF_2), calcite ($CaCO_3$), and apatite ($Ca_5F(PO_4)_3$) as well as celestite ($SrSO_4$) and barite ($BaSO_4$). Another group of semi-soluble salt minerals of importance is the rare earth semi-soluble salt minerals, which include bastnaesite ((Ce, La) CO3F), monazite ($CePO_4$), and xenotime (YPO_4).

Interfacial characteristics of the mineral/water interface for both alkaline earth and rare earth semi-soluble salt minerals, including the surface charge, wetting characteristics and collector adsorption, have been reviewed and discussed. Studies on the zeta potential and contact angles, as well as collector adsorption mechanisms, have been reported in the literature. These results have been complimented with recent results from our laboratory, as well as with results from MDS analysis. Finally, unique surface nano structures of collector molecules have been found using AFM.

Alkaline earth semi-soluble salt minerals

Collectors frequently used for the flotation and separation of these minerals include fatty acids, sulfonates, sulfoscuccinates, sulfates, and hydroxamates, together with modifying agents. Due to the preferential floatability of fluorite from apatite, calcite and other gangue minerals, sodium oleate is most widely used as a collector for fluorite flotation. At low equilibrium oleate concentrations ($< 1\times10^{-5}$ M), monolayer coverage of oleate at the fluorite surface is reached, and the adsorption density of oleate at the fluorite surface is two to four times higher than at the surface of calcite and apatite.

In general the oleate adsorption isotherms are characterized by at least two regions. At low equilibrium oleate concentrations ($<1\times10^{-5}$M), in the absence of calcium dioleate precipitation, the density of the calcium surface sites dictates the adsorption density in the plateau region for the endothermic chemisorption reaction. In the case of fluorite, the adsorption density plateau for adsorbed oleate is 6.5 to 6.8 μmole/m^2, such as would be expected for a close-packed monolayer. Taking into consideration the density of calcium sites, this corresponds to a calcium-to-carboxylate ratio of about 2:1, and suggests that bridging occurs between the carboxylate group and two calcium ions at the fluorite surface. Such coordination appears to explain the spectral features of the chemisorbed carboxylate group. On the other hand, the chemisorption "plateau" for calcite and apatite at low equilibrium oleate concentrations is significantly less, approximately 1 to 2 μmole/m^2. Clearly a close-packed monolayer is not achieved for calcite and apatite at low concentrations, which accounts for a diminished state of hydrophobicity under these circumstances when compared to fluorite. For example, it has been found that for a 1×10^{-5} M equilibrium oleate concentration, fluorite exhibits a contact angle of close to 90°, whereas bubble attachment at a calcite surface does not occur.

In summary, based on these adsorption densities, thermochemistry, and spectroscopic considerations, chemisorption predominates at low equilibrium concentrations (low adsorption densities) and precipitated calcium dioleate predominates at higher equilibrium concentrations. In the case of fluorite, a close-packed monolayer of oleate forms during the endothermic chemisorption reaction, creating a strong hydrophobic state at the fluorite surface. On the other hand, in the case of calcite and apatite, monolayer formation is incomplete during chemisorption in region one, and, at best, a weak hydrophobic state is created at these surfaces.

Rare earth semi-soluble salt minerals

For rare earth semi-soluble salts, the electrokinetic behavior has been reported. The PZCs of monazite and xenotime, were found that to have PZC values within the acidic pH range. However, for the fluorocarbonate rare earth mineral bastnaesite, the PZC is higher, about pH 8. The reason for this difference has been attributed to the different anion properties. Both the first and second pK_as of carbonic acid are larger than phosphoric acid. Thus, the carbonate lattice ion (CO_3^{2-}) of bastnaesite acts as the weaker acid and tends to adsorb hydrogen ions from solution to a greater extent than the phosphate lattice ion (PO_4^{3-}) of monazite and xenotime.

Contact angle measurements as well as MD simulations have been done at both bastnaesite and monazite surfaces. The results indicate that both surfaces are naturally hydrophilic. Comparison of MDS interfacial water analysis, including water density profile and residence time measurements, suggests that water molecules interact stronger with the monazite surface than with the bastnaesite surface.

For the flotation of rare earth semi-soluble salt minerals, hydroxamate has been identified as a promising collector, the adsorption of which involves a chemisorption reaction. In the case of bastnaesite, it appears that a chemisorbed monolayer forms at low hydroxamate concentrations. The ratio of hydroxamate adsorption density to cerium surface site density appears to be 2:1 for monolayer coverage, which suggests that one cerium ion at the bastnaesite surface is reacting with two hydroxamate molecules. At higher collector concentrations multilayer adsorption occurs due to a surface precipitation reaction. Finally, alkyl phosphates have been identified as potential collectors for bastnaesite, with excellent flotation at remarkably low levels of collector concentration. The chemisorption of alkyl phosphate occurs at low concentrations leading to monolayer formation and a hydrophobic surface state, as substantiated by contact angle measurements and MDS analysis of the surface state.

Surfactant Nanostructures at Mineral Surfaces

The molecular level of surfactant organization at water/mineral interfaces has been investigated with respect to the effect of the surface properties such as hydrophobicity, crystallinity, and surface charge density, and the effect of surfactant structural properties such as surfactant type, and headgroup size. "Soft contact" atomic force microscope imaging has been used to visualize the nanometer scale organization of surface micelle structures at selected surfaces.

At hydrophobic surfaces such as graphite and glassy carbon, the AFM images revealed self-assembled ordered arrays of remarkable surfactant structures (cationic, anionic, and nonionic surfactants), which were characterized to be hemimicelles. In contrast, full micelles were observed for the adsorption of surfactants oppositely charged to the charge of hydrophilic surfaces such as mica, silica, and alumina. The templating effect of the crystalline hydrophobic graphite surface superceded all other molecular contributions, leading to the formation of highly ordered hemicylindrical structures for a variety of surfactants, with dimensions in the range of 5-6 nm in diameter. In comparison, at the hydrophobic amorphous glassy carbon surface only hemispherical structures were formed, with similar diameters of 5-6 nm. At the hydrophilic surfaces, however, a variety of structures ranging from wormy cylinders to spheres with dimensions around 5-6 nm, were observed, both at the crystalline mica and amorphous silica and alumina surfaces.

The shape of the surface micelles at hydrophilic surfaces is greatly influenced by the surface charge density and the size of the headgroup. It has been demonstrated for the first time that the surface micelles at the graphite surface can be modulated either physically by introducing some defects at the surface, or chemically through the addition of a cosurfactant. These results have been used to help understand the physical chemistry of the flotation process, and, in addition, provide important fundamental information of interest in nanotechnology.

Collector adsorption publications are as follows:

1. "Analysis of the Adsorption Behaviour of Oleate on Some Synthetic Apatites," A. Yehia, J. D. Miller, and B. G. Ateya, Minerals Engineering, 6 (1), pp. 79–86 (1993).
2. "Modification and Surface Spectroscopy of Semi–Soluble Filler Materials for Polymer Matrix Composites," J. D. Miller, W.–H. Jang, J. J. Kellar, R. Wensel, and R. M. Winter, in *Proceedings of First International Conference on Processing Materials for Properties,* H. Henein and T. Oki, eds., TMS, Warrendale, Pennsylvania, pp. 517–520 (1993).
3. "Significance of Temperature Control in FT–NIR Spectrometers," C. A. Young, K. Knutson, and J. D. Miller, Applied Spectroscopy, 47 (1), pp. 7–11 (1993).
4. "Surface Phase Transitions of Adsorbed Collector Molecules as Revealed by In–Situ FT–IR/IRS Spectroscopy," J. J. Kellar, W. M. Cross, M. R. Yalamanchili, C. A. Young, and J. D. Miller, Minerals and Metallurgical Processing, 10 (2), pp. 75–80 (1993).
5. "Verification of the Internal Reflection Spectroscopy Adsorption Density Equation by Fourier Transform Infrared Spectroscopy Analysis of Transferred Langmuir–Blodgett Films," W. H. Jang and J. D. Miller, Langmuir, 9, pp. 3159–3165 (1993).
6. "The Effect of Sample and Incident Beam Areas on Quantitative Spectroscopy," M. L. Free and J. D. Miller, Applied Spectroscopy, 48(7), pp. 891–893 (1994).
7. "Quantitative Fourier Transform–Infrared Internal Reflection Spectroscopy (FTIR/IRS) for Adsorption Density Measurements," M. L. Free, W. H. Jang, and J. D. Miller, Colloids and Surfaces, A: Physicochemical and Engineering Aspects, 93 (Special issue — Surface Characterization of Adsorption and Interfacial Reactions), pp. 127–135 (1994).
8. "Comments on the Nature and Structure of Adsorption Layer on Apatite Contacted with Oleate Solution I. Adsorption and FTIR Reflection Studies," J. D. Miller, W. H. Jang, and J. J. Kellar, Langmuir, 11 (8), pp. 3275–3277 (1995).

9. "Molecular Orientation of Langmuir–Blodgett and Self–Assembled Monolayers of Stearate Species at a Fluorite Surface as Described by Linear Dichroism Theory," W. H. Jang and J. D. Miller, Journal of Physical Chemistry, 99, pp. 10272–10279 (1995).
10. "Wetting Characteristics and Stability of Langmuir–Blodgett Carboxylate Monolayers at the Surfaces of Calcite and Fluorite," W. H. Jang, J. Drelich, and J. D. Miller, Langmuir, 11, pp. 3491–3499 (1995).
11. "Adsorption of Model Collector Colloids at the Surface of Colemanite as Characterized by Optical and Atomic Force Microscopy," S. Veeramasuneni, M. R. Yalamanchili, J. D. Miller, and M. S. Celik, in *Proceedings of the VI International Mineral Processing Symposium: Changing Scopes in Mineral processing,* Kusadasi, Turkey, 24–26 September 1996, pp. 215–220 (1996).
12. "Formation and Wetting Characteristics of Adsorbed Layers of Unsaturated Carboxylic Acids at a Fluorite Surface," J. Drelich, A. A. Atia, M. R. Yalamanchili, and J. D. Miller, Journal of Colloid and Interface Science, 178, pp. 720–732 (1996).
13. "The Significance of Collector Colloid Adsorption Phenomena in the Fluorite/Oleate Flotation System as Revealed by FTIR/IRS and Solution Chemistry Analysis," M. L. Free and J. D. Miller, International Journal of Mineral Processing, 48, pp. 197–216 (1996).
14. "Examination of Adsorbed Oleate Layers at a Fluorite Surface by Contact Angle Measurements and FT–IR/IRS Spectroscopy," J. Drelich, W. H. Jang, and J. D. Miller, Langmuir, 13, pp. 1345–1351 (1997).
15. "Kinetics of 18–Carbon Carboxylate Adsorption at the Fluorite Surface," M. L. Free and J. D. Miller, Langmuir, 13, pp. 4377–4382 (1997).
16. "FTIR Internal Reflection Spectroscopy Studies on the Effect of pH on Adsorption of Oleate/Oleic Acid at the Surface of a TiO_2 Thin Film Deposited on a Ge Single Crystal," J. Drelich, Y. Lu, L. Chen, J. D. Miller, and S. Guruswamy, Applied Surface Science, 125, pp. 236–244 (1998).
17. "FT–IR Internal Reflection Spectroscopy Using Regular Polygonal Internal Reflection Elements," Y. Q. Lu, M. R. Yalamanchili, and J. D. Miller, Applied Spectroscopy, 52 (6), pp. 851–854 (1998).
18. "Oleate Adsorption at an Apatite Surface Studied by Ex–Situ FTIR Internal Reflection Spectroscopy," Y. Lu, J. Drelich, and J. D. Miller, Journal of Colloid and Interface Science, 202, pp. 462–476 (1998).
19. "Usefulness of Surfactants in Reducing Particle Adhesion and Their Effectiveness in Cleaning Silicon Wafers," S. Veeramasuneni, M. L. Free, and J. D. Miller, Journal of Adhesion Science and Technology, 12 (2), pp. 185–195 (1998).
20. "Improved Phosphate Flotation with Nonionic Polymers," Y. Lu, N. Liu, X. Wang, and J. D. Miller, *Proceedings of the Engineering Foundation Conference, Beneficiation of Phosphates: Advances in Research and Practice,* Palm Coast, Florida, 6–11 December 1998, P. Zhang, H. El–Shall, and R. Wiegel, eds., SME, Littleton, Colorado, pp. 3–19 (1999).
21. "In–Situ FT–IR/IRS and MLRS Examination of Adsorbed Oleate at Fluorite and Calcite Surfaces," C. A. Young and J. D. Miller, in *Analytical Technology in the Mineral Industries,* L. J. Cabri, C. H. Buckman, E. B. Milosavljevic, S. L. Chryssoulis, and R. A. Miller, eds., TMS, Warrendale, Pennsylvania, pp. 119–136 (1999).

22. "Internal Reflection Spectroscopy for FTIR Analysis of Carboxylate Adsorption by Semi–Soluble Salt Minerals," J. D. Miller and J. J. Kellar, in *Advances in Flotation Technology – A Symposium in Honor of M. C. Fuerstenau*, B. K. Parekh and J. D. Miller, eds., SME, Littleton, Colorado, pp. 45–58 (1999).
23. "Surface Chemistry of Flotation Phenomena as Revealed by FTIR/IRS," J. D. Miller, S. Veeramasuneni, and Y. Lu, in *Proceedings of the Engineering Foundation Conference, Development of Nonrenewable Resources, Challenges and Solutions,* Cairo, Egypt, 16–21 November 1997, pp. 31–42 (1999).
24. "Effect of Temperature on Oleate Adsorption at a Calcite Surface: An FT–NIR/IRS Study and Review," C. A. Young and J. D. Miller, IJMP, Special Edition, 58 (1–4), pp. 331–350 (2000).
25. "Conformation of Chemisorbed Oleate at a Calcite Surface," C. A. Young and J. D. Miller, Minerals and Metallurgical Processing, 18 (1), pp. 38–44 (2001).
26. "Bench Scale Flotation of Sedimentary Phosphate Rock with Hydroxamic Acid Collectors," J. D. Miller, X. Wang, and M. Li, in *Proceedings of the Engineering Foundation Conference, Beneficiation of Phosphates III: Fundamentals and Technology*, St. Pete Beach, Florida, 2–7 December 2001, P. Zhang, H. El-Shall, P. Somasundaran, and R. Stana, eds., SME, Littleton, Colorado, pp. 93-101 (2002).
27. "Carboxyl Stretching Vibrations of Spontaneously Adsorbed and LB Transferred Calcium Carboxylates as Determined by FTIR Internal Reflection Spectroscopy," Y. Lu and J. D. Miller, *Journal of Colloid and Interface Science, Proceedings of 13th International Symposium on Surfactants in Solution* (SIS–2000), Gainesville, Florida, 11–16 June 2000, 256, pp. 41–52 (2002).
28. "Fatty Acid Flotation of Calcareous Phosphate Rock Using Enzymes for a Selective Separation," A. Yehia, J. D. Miller, M. A. Abdel-Khalek, and M. Fadel, in *Proceedings of the Engineering Foundation Conference, Beneficiation of Phosphates III: Fundamentals and Technology*, St. Pete Beach, Florida, 2–7 December 2001, P. Zhang, H. El-Shall, P. Somasundaran, and R. Stana, eds., SME, Littleton, Colorado, pp. 221–227 (2002).
29. "Selective Flotation of Phosphate Minerals with Alcoholic Solutions of Alkyl Hydroxamic Acids," J. D. Miller, X. Wang, and M. Li, in *Proceedings of the Engineering Foundation Conference, Beneficiation of Phosphates III: Fundamentals and Technology*, St. Pete Beach, Florida, 2–7 December 2001, P. Zhang, H. El-Shall, P. Somasundaran, and R. Stana, eds., SME, Littleton, Colorado, pp. 13-20 (2002).
30. "Surface Properties of Fatty Amines as Revealed by Contact Angle, FTIR, and AFM Measurements," S. Wisniewska, J. Nalaskowski, and J. D. Miller, in *Contact Angle, Wettability, and Adhesion, Vol. 2, Proceedings of the 2nd International Symposium on Contact Angle, Wettability, and Adhesion,* Newark, New Jersey, 21–23 June 2000, K. L. Mittal, ed., VSP International Science Publishers, The Netherlands, pp. 109–124 (2002).
31. "Influence of Surfactants on Interaction Forces between Polyethylene Surfaces in a Hydrocarbon Solvent," R. Aranowski, J. Nalaskowski, J. Hupka, and J. D. Miller, in *Functional Fillers and Nanoscale Minerals*, J. J. Kellar, M. A. Herpfer, and B. M. Moudgil, eds., SME, Littleton, Colorado, pp. 139–150 (2003).
32. "Interaction Forces between a Calcium Dioleate Sphere and Calcite/Fluorite Surfaces and their Significance in Flotation," K. Fa, T. Jiang, J. Nalaskowski, and J. D. Miller, Langmuir, 19 (25), pp. 10523-10530 (2003).

33. "Interaction Forces between Silica Surfaces in Aqueous Solutions of Poly(Ethylene Oxide)s, V. K. Paruchuri, J. Nalaskowski, and J. D. Miller, in *Functional Fillers and Nanoscale Minerals*, J. J. Kellar, M. A. Herpfer, and B. M. Moudgil, eds., SME, Littleton, Colorado, pp. 151–164 (2003).
34. "Surfactant Adsorption Density Calculation from Fourier Transform Infrared External Reflection Spectroscopy (FTIR/ERS)," K. Fa and J. D. Miller, Journal of Chemical Physics, 119 (24), pp. 13068–13076 (2003).
35. "Liquid/Air Interfacial Structure of Alcohol-Octyl Hydroxamic Acid Mixtures: A Study by Sum-frequency Spectroscopy," Z. S. Nickolov, X. Wang, and J. D. Miller, Spectrochimica Acta Part A: Molecular & Biomolecular Spectroscopy, 60 (12), pp. 2711-2717 (2004).
36. "Optical and Spectroscopic Characteristics of Oleate Adsorption as Revealed by FTIR Analysis," K. Fa, T. Jiang, J. Nalaskowski and J. D. Miller, Langmuir, 20, pp. 5311-5321 (2004).
37. "Sodium Dodecyl Sulfate-Poly (amidoamine) (SDS_PAMAM) Interactions Studied by AFM Imaging, Conductivity, and Krafft Temperature Measurements," M. S. Bakshi, A. Kaura, J. D. Miller, and V. K. Paruchuri, Journal of Colloid and Interface Science, 278, pp. 472-477 (2004).
38. "Surface Micelles as Revealed by Soft Contact Atomic Force Microscopy Imaging," V. K. Paruchuri and J. D. Miller, in *Recent Research Developments in Surface & Colloids*, Research Signpost, Kerala, India, 1, pp. 205-216 (2004).
39. "Zeta Potentials of Self Assembled Surface Micelles of Ionic Surfactants Adsorbed at Hydrophobic Graphite Surfaces," V. K. Paruchuri, A. V. Nguyen, and J. D. Miller, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 250, pp. 519-526 (2004).
40. "Adsorption Density of Spherical Cetyltrimethylammonium Bromide (CTAB) Micelles at a Silica/Silicon Surface," V. K. Paruchuri, K. Fa, B. M. Moudgil, and J. D. Miller, Applied Spectroscopy, 59 (5), pp. 668-672 (2005).
41. "Interaction of Calcium Dioleate Collector Colloids with Calcite and Fluorite Surfaces as Revealed by AFM Force Measurements and Molecular Dynamics Simulation," K. Fa, A. V. Nguyen, and J. D. Miller in *Proceedings of Centenary of Flotation Symposium*, Brisbane, Australia, 6–9 June 2005, pp. 425–432 (2005).
42. "The Effect of Cosurfactants on Sodium Dodecyl Sulfate Micellar Structures at a Graphite Surface," V. K. Paruchuri, J. Nalaskowski, D. O. Shah, and J. D. Miller, Colloids and Surfaces A: Physicochemical Engineering Aspects, 272, pp. 157–163 (2006).
43. "Interaction of Calcium Dioleate Collector Colloids with Calcite and Fluorite Surfaces as Revealed by AFM Force Measurements and Molecular Dynamics Simulation," K. Fa, A. V. Nguyen, and J. D. Miller, International Journal of Mineral Processing, 81, pp. 166–177 (2006).
44. "Sum-Frequency Spectroscopy Analysis of Two-Component Langmuir Monolayers and the Associated Interfacial Water Structure," Z. S. Nickolov, D. W. Britt, and J. D. Miller, Journal Physical Chemistry B, 110, pp. 15506–15513 (2006).
45. "Adsorption States of Amphipatic Solutes at the Surface of Naturally Hydrophobic Minerals: A Molecular Dynamics Simulation Study," H. Du and J. D. Miller, Langmuir, 23, pp. 11587–11596 (2007).

46. "Surface Characterization and New Tools for Research," R. St. C. Smart, W. M. Skinner, A. R. Gerson, J. Mielczarski, S. Chryssoulis, A. R. Pratt, R. Lastra, G. A Hope, X. Wang, K. Fa, and J. D. Miller, in *Froth Flotation, A Century of Innovation*, M. C. Fuerstenau, G. Jameson, and R.-H. Yoon, eds., SME, Littleton, Colorado, pp. 283–337 (2007).
47. "Adsorption and Self-assembly of Octyl Hydroxamic Acid at a Fluorite Surface as Revealed by Sum-frequency Vibrational Spectroscopy," X. Wang, J. Liu, and J. D. Miller, Journal of Colloid and Interface Science, 325, pp. 398–403 (2008).
48. "Characteristics of Dextrin Adsorption by Elemental Sulfur," S. K. Brossard, H. Du, and J. D. Miller, Journal of Colloid and Interface Science, 317, pp. 18–25 (2008).
49. "Equilibrium Adsorption of Surfactants at the Gas-Liquid Interface," S. I. Karakashev, A. V. Nguyen, and J. D. Miller, in *Advances in Polymer Science, No. 218, Interfacial Processes and Molecular Aggregation of Surfactants*, R. Narayanan, vol. ed., Springer-Verlag, Berlin, Germany, pp. 25–55 (2008).
50. "Effect of Feed Characteristics on Flotation Performance of Phosphate Ores," H. El-Shall, R. Stana, G. Wang, M. Raslan, J. D. Miller, and P. Somasundaran, in *Beneficiation of Phosphates, Technology Advance and Adoption, Proceedings of Beneficiation of Phosphates V, ECI Conference 2008*, P. Zhang, K. Swager, L. L. Filho, and H. El-Shall, eds., SME, Littleton, Colorado, pp. 43–52 (2010).
51. "Liberation Limitations to Phosphate Flotation Recovery and Concentrate Grade as Revealed by 3-D X-ray Micro CT Analysis," J. D. Miller, C. L. Lin, and A. R. Videla, in *Beneficiation of Phosphates, Technology Advance and Adoption*, *Proceedings of Beneficiation of Phosphates V, ECI Conference 2008*, P. Zhang, K. Swager, L. L. Filho, and H. El-Shall, eds., SME, Littleton, Colorado, pp. 361–367 (2010).
52. "States of Adsorbed Dodecyl Amine and Water at a Silica Surface as Revealed by Vibrational Spectroscopy," X. Wang, J. Liu, H. Du, and J. D. Miller, Langmuir, 26 (5), pp. 3407–3414 (2010).
53. "Surface Chemistry Considerations in the Flotation of Rare-earth and Other Semisoluble Salt Minerals," X. Zhang, H. Du, X. Wang and J. D. Miller, Minerals & Metallurgical Processing, Special Rare-earth Minerals Issue, 30 (1), pp. 24–37 (2013).
54. "Surface Chemistry Aspects of Bastnaesite Flotation with Octyl Hydroxamate," X. Zhang, H. Du, X. Wang and J.D. Miller, International Journal of Mineral Processing, 133, pp. 29–38 (2014).
55. "Flotation Chemistry Features in Bastnaesite Flotation with Potassium Lauryl Phosphate," W. Liu, X. Wang, Z. Wang, and J.D. Miller, Minerals Engineering, 85, pp. 17–22 (2016).
56. "Flotation of Zinc Oxide Minerals with Potassium Lauryl Phosphate," X. Wang, J.D. Miller, Z. Wang, S. Jian, T. Song, and Y. Liang, in *IMPC 2016: XXVIII International Mineral Processing Congress Proceedings*, Canadian Institute of Mining, Metallurgy and Petroleum, 12 pp. (2016).
57. "Polysaccharide Depressants for the Reverse Flotation of Iron Ore," K. Shrimali and J.D. Miller, Transactions Indian Institute of Metals, 69 (1), pp. 83–95 (2016).
58. "The Surface Features of Lead Activation in Amyl Xanthate Flotation of Quartz," B. Liu, X. Wang, H. Du, J. Liu, S. Zheng, Y. Zhang, and J.D. Miller, International Journal of Mineral Processing, 151, pp. 33–39 (2016).
59. "Fundamental Issues on the Influence of Starch in Amine Adsorption by Quartz," K. Shrimali, X. Yin, X. Wang, and J.D. Miller, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 522, pp. 642–651 (2017).

60. "Lauryl Phosphate Adsorption in the Flotation of Bastnasite, (Ce,La)FCO_3, W. Liu, X. Wang, H. Xu, and J.D. Miller, Journal of Colloid and Interface Science, 490, pp. 825–833 (2017).
61. "Physical Chemistry Considerations in the Selective Flotation of Bastnaesite with Lauryl Phosphate," W. Liu, X. Wang, H. Xu, and J.D. Miller, Minerals & Metallurgical Processing, 34(3), pp. 116–124 (2017).
62. "Specific Anion Effects on Adsorption and Packing of Octadecylamine Hydrochloride Molecules in the Air/Water Interface," E. Li, X. Wang, Z. Du, J.D. Miller, and F. Cheng, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 522, pp. 544–551 (2017).

3.3 Wetting, Surface Forces, and Bubble Attachment

With the availability and advances made in atomic force microscopy (AFM), considerable progress has been made with the in-situ measurement of surface forces to describe the wetting characteristics of mineral surfaces and of bubble/particle attachment phenomena. Such AFM studies coupled with molecular dynamics simulations (MDS) and sum frequency vibrational spectroscopy (SFVS) experiments have provided fundamental information important to the further development of flotation technology. Progress in our understanding of interfacial water structure and wetting phenomena has been reported for different mineral classes including sulfides, oxides/hydroxides, layered silicates (phyllosilicates), and salt-type minerals, both semi-soluble and soluble salts.

Atomic force microscopy has been used not only to describe charging of mineral surfaces, but also to describe the wetting characteristics of the surfaces using selected cantilevers with hydrophobic tips, such as a diamond-like-carbon tip. In this way, a hydrophobic mineral surface can be described by the magnitude of the attractive force at the PZC in the absence of electrostatic forces. Also, with AFM surface force measurements, we have the opportunity to interrogate the surfaces of small particles, such as nanometer clay particles, and from the polarity of such surfaces, describe their wetting characteristics.

Molecular dynamics simulations are being used in our flotation chemistry research not only to describe interfacial water features (extent of H-bonding, dipole orientation, exclusion zone thickness, residence time), but also to describe wetting phenomena both from sessile drop simulations and from bubble attachment simulations. In this way, wetting characteristics are examined and hydrophobic surfaces are distinguished from hydrophilic surfaces. Results from MDS contact angle simulations show that hydrophobic surfaces are characterized by the presence of a water exclusion zone, interfacial water dipoles parallel to the surface, a short residence time for interfacial water molecules (usually less than 10 ps), and incomplete wetting.

Water at a hydrophobic surface is distinguished in the SFVS spectrum by the strong band at approximately 3700 cm^{-1} corresponding to the free OH vibration, from water molecules that are not H-bonded. The water spectrum at the hydrophobic surface is similar to the SFVS spectrum for the air water interface. These results suggest the presence of a water void, or water

exclusion zone, at the hydrophobic surface, as supported by X-ray reflectivity measurements reported in the literature and which has been demonstrated for water at many different hydrophobic surfaces by molecular dynamics simulations (MDS). The MDS of water at the hydrophobic basal plane talc surface shows the thickness of the water exclusion zone to be about 3.5 angstroms, the same as that determined from X-ray reflectivity measurements. In contrast, the MD simulation of the hydrophilic talc edge surface shows that water bonds directly with the edge surface. Clearly the water exclusion zone is only present at the hydrophobic basal plane surface of talc. At the hydrophilic edge surface of talc, water is readily accommodated at surface sites and no exclusion zone is found.

Finally, extensive experimental results from AFM measurements and results from other experiments reveal the presence of a gas phase at hydrophobic surfaces. This gas phase is frequently observed as flattened nanobubbles. Therefore, it is evident that the hydrophobic surface state must include a water exclusion zone which may vary in thickness from less than 1 nanometer to 10s of nanometers, the size of nanobubbles. In this regard, the analysis of the attractive force between a bubble and a hydrophobic surface should take into account the presence of a void space (gas film) or water exclusion zone, extending to the dimensions even of nanobubbles.

By consideration of the water exclusion zone, the van der Waals force between a bubble and a hydrophobic surface is not repulsive as suggested in the literature. For example, even when the water exclusion zone is just 2 angstroms in thickness, an attractive van der Waals force is calculated and observed. It is clear that the critical factor which determines the magnitude and the range of this attractive van der Waals force is the dimension of the water exclusion zone or the size of the nanobubbles at the hydrophobic surface, both of which are influenced by surface roughness. The typical magnitude of the water exclusion zone thickness ranges from less than one nanometer for an atomically smooth surface, all the way to hundreds of nanometers for rough surfaces. As the thickness of the water exclusion zone increases to a thickness corresponding to the size of nanobubbles, the calculated attractive van der Waals force increases significantly, and this analysis of the attractive van der Waals force may help to explain the so-called “short range” and “long range” hydrophobic forces.

Wetting, surface forces, and bubble attachment publications are as follows:

1. “The Effect of Drop Size on Contact Angle over a Wide Range of Drop Volumes,” J. Drelich, J. D. Miller, and J. Hupka, Journal of Colloid and Interface Science, 155, pp. 379–385 (1993).
2. “Modification of the Cassie Equation,” J. Drelich and J. D. Miller, Langmuir, 9, pp. 619–621 (1993).
3. “The Effect of Solid Surface Heterogeneity and Roughness on the Contact Angle/Drop (Bubble) Size Relationship,” J. Drelich and J. D. Miller, Journal of Colloid and Interface Science, 164, pp. 252–259 (1994).
4. “Examination of Neumann's Equation-of–State for Interfacial Tensions,” J. Drelich and J. D. Miller, Journal of Colloid and Interface Science, 167, pp. 217–220 (1994).

5. "Wetting Characteristics of Liquid Drops at Heterogeneous Surfaces," J. Drelich, J. D. Miller, A. Kumar, and G. M. Whitesides, Colloids and Surfaces, A: Physicochemical and Engineering Aspects, 93 (Special Issue — Surface Characterization of Adsorption and Interfacial Reactions), pp. 1–13 (1994).
6. "A Critical Review of Wetting and Adhesion Phenomena in the Preparation of Polymer–Mineral Composites," J. Drelich and J. D. Miller, Minerals and Metallurgical Processing, 12 (4), pp. 197–204 (1995).
7. "Thermogravimetric/Mass Spectrometric (TG/MS) Characterization of Toner Particles from Photocopied Wastepaper and the Impact of These Features on Flotation Deinking," X. Nie and J. D. Miller, in *Tappi Proceedings, 1995 Pulping Conference, Book 1,* Chicago, Illinois, 1–5 October 1995, pp. 179–201 (1995).
8. "Contact Angles for Liquid Drops at a Model Heterogeneous Surface Consisting of Alternating and Parallel Hydrophobic/Hydrophilic Strips," J. Drelich, J. L. Wilbur, J. D. Miller, and G. M. Whitesides, Langmuir, 12 (7), pp. 1913–1922 (1996).
9. "The Effect of Drop (Bubble) Size on Advancing and Receding Contact Angles for Heterogeneous and Rough Solid Surfaces as Observed with Sessile–Drop and Captive–Bubble Techniques," J. Drelich, J. D. Miller, and R. J. Good, Journal of Colloid and Interface Science, 179, pp. 37–50 (1996).
10. "Effect of Roughness as Determined by Atomic Force Microscopy on the Wetting Properties of PTFE Thin Films," J. D. Miller, S. Veeramasuneni, J. Drelich, and M. R. Yalamanchili, Polymer Engineering and Science, 36 (14), pp. 1849–1855 (1996).
11. "Interaction Forces between Ink Particles, Cellulose Fibers and Mineral Fillers as Determined by AFM," M. A. D. Azevedo, M. R. Yalamanchili, J. Drelich, and J. D. Miller, in *Proceedings of the 19th Annual Meeting of the Adhesion Society*, Myrtle Beach, South Carolina, 18-21 February 1996, T. C. Ward, ed., pp. 513-515 (1996).
12. "Measurement of Interaction Forces between Silica and Alpha Alumina by Atomic Force Microscopy," S. Veeramasuneni, M. R. Yalamanchili, and J. D. Miller, Journal of Colloid and Interface Science, 184 (2), pp. 594–600 (1996).
13. "Wetting Characteristics of Newly Developed Water–Repellent Material," G. Yamauchi, J. D. Miller, H. Saito, K. Takai, T. Ueda, H. Takazawa, H. Yamamoto, and S. Nislhi, presented at the ACS Colloid and Surface Science Symposium, University of Utah, Salt Lake City, Utah, 11–14 June 1995, Colloids and Surfaces, A: Physicochemical and Engineering Aspects, 116, pp. 125–134 (1996).
14. "The Wetting Characteristics of PTFE Particulate Composites," G. Yamauchi, J. D. Miller, H. Saito, K. Takai, H. Takazawa, and T. Ueda, Materials Transactions, Japan Institute of Metals, 37 (4), pp. 721–728 (1996).
15. "Bubble Attachment Time Measurements at a Chalcopyrite Surface Using a High–Speed Video System," J. Drelich, J. D. Miller, J.–S. Li and R.–Y Wan, in *Proceedings of the XX International Mineral Processing Congress*, *Volume 3: Flotation and Other Physical–Chemical Processes*, Aachen, Germany, 21–26 September 1997, pp. 53–64 (1997).
16. "Hydrophobicity of Ion–Plated PTFE Coatings," S. Veeramasuneni, J. Drelich, J. D. Miller, and G. Yamauchi, Progress in Organic Coatings, 31, pp. 265–270 (1997).
17. "Interaction Forces at High Ionic Strengths — The Role of Polar Interfacial Interactions," S. Veeramasuneni, Y. Hu, M. R. Yalamanchili, and J. D. Miller, Journal of Colloid and Interface Science, 188, pp. 473–480 (1997).

18. "Wetting of Francolite and Quartz and Its Significance in the Flotation of Phosphate Rock," Y.Lu, J. Drelich, and J. D. Miller, Minerals Engineering, 10 (11), pp. 1219–1231 (1997).
19. "Interactions between Dissimilar Surfaces in High Ionic Strength Solutions as Determined by Atomic Force Microscopy," S. Veeramasuneni, M. R. Yalamanchili, and J. D. Miller, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 131, pp. 77–87 (1998).
20. "Use of Atomic Force Microscopy in Particle Science and Technology Research," M. R. Yalamanchili, S. Veeramasuneni, M. A. D. Azevedo, and J. D. Miller, Colloids and Surfaces, A: Physicochemical and Engineering Aspects, 133, pp. 77–88 (1998).
21. "AFM Measurements of Hydrophobic Forces between a Polyethylene Sphere and Silanated Silica Plates – The Significance of Surface Roughness," J. Nalaskowski, S. Veeramasuneni, J. Hupka, and J. D. Miller, presented at the International Symposium on Apparent and Microscopic Contact Angles, 216th American Chemical Society Meeting, Boston, Massachusetts, 23–27 August 1998, Special Issue of Journal of Adhesion Science and Technology, 13 (12), pp. 1519–1533 (1999).
22. "Influence of Surface Charge on Particle Dispersion/Aggregation as Determined by Atomic Force Microscopy," S. Veeramasuneni and J. D. Miller, in *Particles on Surfaces 5 & 6: Detection, Adhesion and Removal,* Dr. K. L. Mittal, ed., VSP International Science Publishers, The Netherlands, pp. 59–73 (1999).
23. "Influence of Dissolved Gas on the Interaction Forces between Hydrophobic Surfaces in Water — Atomic Force Microscopy Studies," J. Nalaskowski, J. Hupka, and J. D. Miller, in *Physicochemical Problems of Mineral Processing No. 33,* Proceedings of the XXXVI Symposium, Polanica–Zdroj, Poland, 6–9 September 1999, Z. Sadowski, ed., Technical University of Wroclaw, Poland, pp. 129–141 (1999).
24. "Interaction Forces between Polyethylene Surfaces in Water in the Presence of Cationic and Anionic Surfactants," J. Nalaskowski, J. Hupka, and J. D. Miller, in *Proceedings of the Engineering Conference, Analysis and Utilization of Oily Wastes (AUZO '99), Environmental Technology for Oil Pollution,* Jurata, Poland, 29 August–3 September 1999, J. Hupka and J. D. Miller, eds., 1, pp. 76–83 (1999).
25. "Toner Surface Roughness and Wettability," M. A. D. Azevedo, S. Veeramasuneni, and J. D. Miller, Progress in Paper Recycling, 8 (2), pp. 20–33 (1999).
26. "Limitation of the Young–Dupre Equation in the Analysis of Adhesion Forces Involving Surfactant Solutions," J. Drelich, E. Beach, A. Gosiewska, and J. D. Miller, Journal of Adhesion, Special Issue, 74, pp. 361–371 (2000).
27. "Spreading Kinetics for Low Viscosity n–Alkanes on a Water Surface as Recorded by the High–Speed Video System," J. Drelich and J. D. Miller, Annales Universitatis Mariae Curie–Sklodowska, 54/55, Section AA, Chemistry, pp. 105–115 (1999/2000).
28. "Contact Angle Relaxation for Ethoxylated Alcohol Solutions on Hydrophobic Surfaces," J. Drelich, R. Zahn, J. D. Miller, and J. K. Borchardt, in *Contact Angle, Wettability, and Adhesion, Vol. 2, Proceedings of the 2nd International Symposium on Contact Angle, Wettability, and Adhesion,* Newark, New Jersey, 21–23 June 2000, K. L. Mittal, ed., VSP International Science Publishers, The Netherlands, pp. 253–264 (2002).
29. "Study of Particle–Bubble Interaction Using Atomic Force Microscopy–Current Possibilities and Challenges," J. Nalaskowski, A. V. Nguyen, J. Hupka, and J. D. Miller, Physicochemical Problems of Mineral Processing, 36, pp. 253–272 (2002).

30. "Adhesion between Hydrocarbon Particles and Silica Surfaces with Different Degrees of Hydration as Determined by the AFM Colloidal Probe Technique," J. Nalaskowski, J. Drelich, J. Hupka, and J. D. Miller, Langmuir, 19 (13), pp. 5311-5317 (2003).
31. "Attraction between Hydrophobic Surfaces Studied by Atomic Force Microscopy," A. V. Nguyen, J. Nalaskowski, J. D. Miller, and H. J. Butt, in Douglas W. Fuerstenau Volume of International Journal of Mineral Processing, 72 (1–4), K. Han, T. W. Healy, and R. P. King, eds., Elsevier, The Netherlands, pp. 215–225 (2003).
32. "The Dynamic Nature of Contact Angles as Measured by Atomic Force Microscopy," A. V. Nguyen, J. Nalaskowski, and J. D. Miller, Journal of Colloid and Interface Science, Letter to the Editor, 262 (1), pp. 303–306 (2003).
33. "Hydrodynamic Interactions between Particles in Aggregation and Flotation," Y. Hu, G. Qiu, and J. D. Miller, International Journal of Mineral Processing, 70 (1-4), pp. 157-170 (2003).
34. "Investigations of Bubble–Particle Interactions," C. M. Phan, A. V. Nguyen, J. D. Miller, G. M. Evans, and G. J. Jameson, in Douglas W. Fuerstenau Volume of International Journal of Mineral Processing, 72 (1–4), K. Han, T. W. Healy, and R. P. King, eds., Elsevier, The Netherlands, pp. 239–254 (2003).
35. "A Study of Bubble-Particle Interaction Using Atomic Force Microscopy," A. V. Nguyen, J. Nalaskowski, and J. D. Miller, Minerals Engineering, 16, pp. 1173-1181 (2003).
36. "Bubble-Particle Interaction Measured by Atomic Force Microscopy," A. V. Nguyen, J. Nalaskowski, and J. D. Miller, APCChE 2002 Conference Special Volume of Journal of Chemical Engineering of Japan, 37 (2), pp. 231-237 (2004).
37. "Hydrodynamic Interaction between an Air Bubble and a Particle: Atomic Force Microscopy Measurements," A. V. Nguyen, G. M. Evans, J. Nalaskowski, and J. D. Miller, Experimental Thermal and Fluid Science, 28 (5), pp. 387–294 (2004).
38. "Atomic Force Microscopy Investigation of Interaction Forces between Polyethylene and Asphaltene Surfaces in Nonaqueous Systems," R. Aranowski, J. Nalaskowski, J. Hupka, and J. D. Miller, in *Functional Fillers and Nanoscale Minerals: New Markets/New Horizons*, J. J. Kellar, ed., SME, Littleton, Colorado, pp. 187–198 (2006).
39. "Particle-Particle Interaction," A. V. Nguyen, L. T. T. Tran, and J. D. Miller, in *Encyclopedia of Chemical Processing*, S. Lee, ed., Taylor & Francis, pp. 2017–2029 (2006).
40. "Air Bubble and Oil Droplet Interactions in Centrifugal Fields during Air-Sparged Hydrocyclone Flotation," M. Niewiadomski, A. V. Nguyen, J. Hupka, J. Nalaskowski, and J. D. Miller, International Journal of Environment and Pollution, Special Issue on Flotation in Wastewater Treatment, K. Matis, ed., 30 (2), pp. 313–331 (2007).
41. "Bubbles: Interaction with Solid Surfaces," A. V. Nguyen, J. Drelich, M. Colic, J. Nalaskowski, and J. D. Miller, in *Encyclopedia of Surface and Colloid Science* (2nd Edition), P. Somasundaran, ed., Marcel Dekker, Inc., New York, New York, pp. 1–29 (2007).
42. "Direct Measurement of Particle-bubble Interaction Forces Using Atomic Force Microscopy," S. Assemi, A. V. Nguyen, and J. D. Miller, International Journal of Mineral Processing, 89, pp. 65–70 (2008).
43. "Forces between Polyethylene Surfaces in Oxyethylene Dodecyl Ether Solutions as Influenced by the Number of Oxyethylene Groups," J. Nalaskowski, J. Drelich, and J. D. Miller, Langmuir, 24, pp. 1476–1483 (2008).

44. "Interaction Forces for Symmetric Hydrophilic and Hydrophobic Systems in Aqueous Isopropanol Solutions," L. Hupka, J. Nalaskowski, and J. D. Miller, Langmuir, 26 (4), pp. 2200–2208 (2010).
45. "Induction Time Measurements for Air Bubbles on Chalcopyrite, Bornite, and Gold in Seawater," J. Drelich and J.D. Miller, in *Water in Mineral Processing, Proceedings of the First International Water Symposium*, J.-Y. Hwang, J. Adams, D.R. Nagaraj, X. Sun, and Z. Xu, eds., 2012 SME Annual Meeting, Seattle, Washington, 19–22 February 2012, SME, Englewood, Colorado, pp. 73–85 (2012).
46. "Wetting of Selected Fluorite Surfaces by Water," X. Zhang, X. Wang, and J.D. Miller, Surface Innovations, 3 (SI1), pp. 39–48 (2015).
47. "MDS Analysis of Film Stability and Bubble Attachment at Selected Mineral Surfaces," J. Jin and J.D. Miller, in *IMPC 2016: XXVIII International Mineral Processing Congress Proceedings*, Canadian Institute of Mining, Metallurgy and Petroleum, 14 pp. (2016).
48. "Dodecyl Amine Adsorption at Different Interfaces during Bubble Attachment/Detachment at a Silica Surface," X. Wang and J.D. Miller, Physicochemical Problems of Mineral Processing, Special Issue Honoring Professor Kazimierz Malysa, 54 (1), pp. 81–88 (2018).
49. "Molecular Dynamics Simulations Study of Nano Bubble Attachment at Hydrophobic Surfaces," J. Jin, L.X. Dang, and J.D. Miller, Physicochemical Problems of Mineral Processing, Special Issue Honoring Professor Kazimierz Malysa, 54 (1), pp. 89–101 (2018).

3.4 Interfacial Water Structure

Interfacial water structure and the wetting of mineral surfaces are of fundamental importance in the area of flotation chemistry, as well as having importance in other areas of technology. Now, with advanced tools, the features of interfacial water structure and wetting phenomena at mineral surfaces can be considered in greater detail. These tools include atomic force microscopy (AFM), sum frequency vibrational spectroscopy (SFVS), and molecular dynamics simulations (MDS).

In the case of sum frequency vibrational spectroscopy, the surface spectra reveal information regarding the structure and the degree of coordination of water molecules at the mineral surface. In this way, the extent to which interfacial water molecules are hydrogen bonded to each other and at the surface can be described based on the frequencies observed for OH vibrations. The SFVS spectra for the hydrophilic surface state, a surface well wetted by water, reveal characteristic absorption peaks for water with complete tetrahedral coordination (ice-like water at ~3200 cm^{-1}) and with incomplete tetrahedral coordination (liquid-like water at 3400 cm^{-1}), but no peak for the free OH stretch (vapor-like water at 3600–3700 cm^{-1}). In contrast, the SFVS spectra for the hydrophobic surface state reveal a strong and distinct absorption at 3600–3700 cm^{-1} corresponding to the free OH stretching vibration which supports the notion of a water exclusion zone (~ 3 Å in thickness) at hydrophobic surfaces.

Finally, molecular dynamics simulations are being used in flotation chemistry not only to describe interfacial water features (extent of H-bonding, dipole orientation, exclusion zone

thickness, residence time), but also to describe wetting phenomena both from sessile drop simulations and from bubble attachment simulations. In this way, wetting characteristics are examined and hydrophobic surfaces are distinguished from hydrophilic surfaces. Results from MDS contact angle simulations show that hydrophobic surfaces are characterized by the presence of a water exclusion zone, interfacial water dipoles parallel to the surface, a short residence time for interfacial water molecules (usually less than 10 ps), and incomplete wetting.

Progress in our understanding of interfacial water structure and wetting phenomena is reported for different mineral classes including sulfides, oxides/hydroxides, layered silicates (phyllosilicates), and salt-type minerals, both semi-soluble and soluble salts.

Interfacial water structure is described by characteristic features including H-bonding, dipole orientation, exclusion zone thickness, and residence time. In contrast to polarized hydrophilic surfaces with oriented water dipoles, MDS analysis of water at hydrophobic surfaces reveals that these water molecules are not oriented; rather, the water dipoles are separated from, and parallel to, the surface. Sulfide mineral surfaces are found to be hydrophobic under anaerobic conditions and become hydrophilic upon oxidation and hydrolysis. The hydrophobic sulfide surface is characterized by a "water exclusion zone" of ~ 3 Å, water residence times of less than 10 ps, and reduced H- bonding. Oxide mineral surfaces have a modest hydrophobicity depending on how the surface is prepared. However, given sufficient time and an appropriate pH, surface hydroxylation occurs and the surfaces become hydrophilic. In the case of layered silicates, the silica face surface of the anisotropic clay minerals exhibits a hydrophobic character in the absence of isomorphous substitution in the silica tetrahedral layer, examples include pyrophyllite, talc, and kaolinite. Of course, the edge surfaces are well wetted by water. Salt-type minerals are generally well wetted by water, but some salt surfaces appear to have a lower level of polarity such as the (111) surface of fluorite (CaF_2) and the surfaces of structure breaking alkali halide salts such as sylvite (KCl).

Information on interfacial water structure helps to explain film rupture during bubble attachment in the flotation process, and results from such research have provided significant contributions to the flotation chemistry literature. For example, research published in Surface Innovations was recognized with the Surface Innovations Prize from the Institution of Civil Engineers for the best paper in the journal for the year 2015.

Interfacial water structure publications are as follows:

1. "Characterization of Interfacial Water at Hydrophilic and Hydrophobic Surfaces by In Situ FTIR/Internal Reflection Spectroscopy," M. R. Yalamanchili, A. Atia, J. Drelich, and J. D. Miller, in *Proceedings of the First UBC–McGill Bi–Annual International Symposium: Processing of Hydrophobic Minerals and Fine Coal,* Vancouver, B.C., Canada, 20–24 August 1995, pp. 3–16 (1995).
2. "Analysis of Interfacial Water at a Hydrophilic Silicon Surface by In–Situ FTIR/Internal Reflection Spectroscopy," M. R. Yalamanchili, A. Atia, and J. D. Miller, Langmuir, 12 (12), pp. 4176–4184 (1996).

3. "Hydrophobicity and Elemental Composition of Laser–Printed Toner Films," J. Drelich, M. A. D. Azevedo, J. D. Miller, and P. Dryden, Progress in Paper Recycling, 5 (4), pp. 31–38 (1996).
4. "Water at Interfaces—Some Recent Experimental Results from Surface Spectroscopy," J. D. Miller, M. R. Yalamanchili and S. Veeramasuneni, in *Proceedings of the International Conference on Analysis and Utilization of Oily Wastes* (AUZO '96), Gdansk, Poland, 8–12 September 1996, pp. 413–420 (1996).
5. "Further Consideration of the Spectral Characteristics of Interfacial Water at Hydrophobic Surfaces," M. Hancer, M. S. Celik, and J. D. Miller, in *Proceedings of the 7th International Mineral Processing Symposium*, *Innovations in Mineral and Coal Processing*, Istanbul, Turkey, 15–17 September 1998, pp. 105–111 (1998).
6. "In–Situ Detection of Butane Gas at a Hydrophobic Silicon Surface," J. D. Miller, Y. Hu, S. Veeramasuneni, and Y. Lu, Colloids and Surfaces A: Physicochemical and Engineering Aspects (Special issue – Surface Characterization of Adsorption and Interfacial Reactions II), 154 (1 & 2), pp. 137–147 (1999).
7. "Anomalous Dispersion Effects in the IR–ATR Spectroscopy of Water," M. Hancer, R. P. Sperline, and J. D. Miller, Applied Spectroscopy, 54 (1), pp. 138–143 (2000).
8. "Hydrophobic Surface State," J. D. Miller, in *Encyclopedia of Separation Science,* Academic Press, London, UK, pp. 1537–1541 (2000).
9. "The Significance of Interfacial Water Structure in Colloidal Systems – Dynamic Aspects," M. Colic and J. D. Miller, in *Interfacial Dynamics,* Surfactant Science Series, N. Kallay, ed., Marcel Dekker, New York, vol. 88, pp. 35–82 (2000).
10. "FTIR–ATR Studies of Water Structure in Reverse Micelles during the Synthesis of Oxalate Precursor Nanoparticles," Z. S. Nickolov, V. Paruchuri, D. O. Shah and J. D. Miller, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 232 (1), pp. 93-99 (2004).
11. "Hydrophobic Attraction as Revealed by AFM Force Measurements and Molecular Dynamics Simulation," K. Fa, A. V. Nguyen, and J. D. Miller, Journal of Physical Chemistry B, 109 (27), pp. 13112–13118 (2005).
12. "Water Structure in Aqueous Solutions of Alkali Halide Salts: FTIR Spectroscopy of the OD Stretching Band," Z. S. Nickolov and J. D. Miller, Journal of Colloid and Interface Science, 287, pp. 572–580 (2005).
13. "Interfacial Water Structure and Surface Charge of Selected Alkali Chloride Salt Crystals in Saturated Solutions: A Molecular Dynamics Modeling Study," H. Du and J. D. Miller, Journal of Physical Chemistry C, 111, pp. 10013–10022 (2007).
14. "Molecular Features of Water Films Created with Bubbles at Hydrophilic and Hydrophobic Surfaces," X. Wang, X. Yin, J. Nalaskowski, H. Du, and J. D. Miller, in *Proceedings, XXVI International Mineral Processing Congress (IMPC 2012)*, New Delhi, India, 24–28 September 2012, pp. 5819–5828 (2012).
15. "Molecular Features of Water Films Created with Bubbles at Silica Surfaces," X. Wang, X. Yin, J. Nalaskowski, H. Du, and J.D. Miller, Surface Innovations, 3 (SI1), pp. 20–26 (2015).
16. "The Nature of Graphene Surfaces as Determined from the Wettability Studies of Basal and Edge Planes," D. Bhattacharyya, T. Depci, S. Assemi, K. Prisbrey, and J.D. Miller, ECS Transactions, 66 (14), pp. 45–56 (2015).

17. "Interfacial Water Structure and the Wetting of Mineral Surfaces," J.D. Miller, X. Wang, J. Jin, and K. Shrimali, International Journal of Mineral Processing, 156, pp. 62-68 (2016).
18. "The Surface State of Hematite and Its Wetting Characteristics," K. Shrimali, J. Jin, B. Vaziri Hassas, X. Wang, and J.D. Miller, Journal of Colloid and Interface Science, 477, pp. 16–24 (2016).

3.5 Phyllosilicate Minerals

Clays are phyllosilicate minerals which are composed of two types of atomic sheets, namely a silica tetrahedral sheet and an alumina or magnesia octahedral sheet. Depending on the ratio of silica and alumina/magnesia sheets, phyllosilicates can be classified as bilayer phyllosilicates (1:1 type) or trilayer phyllosilicates (2:1 type). Phyllosilicate minerals, or clay minerals, are among the most important and useful industrial minerals because they have wide-ranging applications. For example, they are widely used in paper, ceramics, cosmetic products, catalysts, rubber, and polymer composites. In other situations, clay minerals (for example kaolinite, pyrophyllite, illite, and montmorillinite), are also a nuisance when present as gangue minerals in flotation separations and during the thickening of plant tailings. The flotation difficulties caused by clay minerals exist in industries such as oil sands, potash, phosphate, bauxite, rare earth resources, and metal sulfide ores such as copper, nickel, and PGM ores.

The surface charge and wettability for both trilayer silicate and bilayer silicate minerals have been established. Recent experimental advances have allowed for the surface chemistry analysis of anisotropic layered silicate minerals. Now it is possible to examine face surfaces and edge surfaces with regard to surface charge and wettability based on surface force measurements using atomic force microscopy (AFM). Such measurements have been done even for kaolinite particles 500 nm in size following appropriate procedures to order these particles for subsequent AFM interrogation. In addition to AFM surface force analysis, the wettability of layered silicates has been examined by molecular dynamics simulations and the hydrophobic state of certain silica tetrahedral surfaces (face surfaces) is evident based on the analysis of interfacial water structure.

A multi-scale investigation of polymer induced kaolinite flocs has been reported for the first time using high resolution X-ray micro tomography (HRXMT) and cryo-SEM procedures to determine not only floc structure, but also the water content of individual kaolinite flocs, as well as the microstructure of primary kaolinite nanoparticles. The procedure developed can be extended to water content and size distribution analysis of flocs formed from industrial flotation tailings at different conditions. This now enables us to study the effect of different parameters on the water entrapped in individual flocs as well as on the size distribution of the floc population. Both size and water content of flocs are crucial in determining the settling and self-weight consolidation of polymer induced clay flocs.

The use of cryo-SEM for visualization of floc microstructure and polymer chain organization has revealed the stabilization of primary kaolinite nanoparticles in the web

formed by polymer chains. The morphology of the polymer chains as well as the interaction between the primary nanoparticles and polymer chains is a key aspect of understanding floc growth and stability.

Phyllosilicate mineral publications are as follows:

1. "The Anomalous Behavior of Kaolinite Flotation with Dodecyl Amine Collector as Explained from Crystal Structure Considerations," Y. Hu, W. Sun, H. Jiang, J. D. Miller and K. Fa, International Journal of Mineral Processing, 76, pp. 163–172 (2005).
2. "The Anisotropic Character of Talc Surfaces as Revealed by Streaming Potential Measurements, Atomic Force Microscopy, and Molecular Dynamics Simulations," J. Nalaskowski, B. Abdul, H. Du, and J. D. Miller, in *Interfacial Phenomena in Fine Particle Technology, Proceedings of the Sixth UBC-McGill-UA International Symposium*, Montreal, Quebec, Canada, 1–4 October 2006, Z. Xu and Q. Liu, eds., Canadian Institute of Mining, Metallurgy and Petroleum, Montreal, Quebec, Canada, pp. 71–85 (2006).
3. "Anisotropic Character of Talc Surfaces as Revealed by Streaming Potential Measurements, Atomic Force Microscopy, Molecular Dynamics Simulations and Contact Angle Measurements," J. Nalaskowski, B. Abdul, H. Du, and J. D. Miller, Canadian Metallurgical Quarterly, 46 (3), pp. 227–236 (2007).
4. "A Molecular Dynamics Simulation Study of Water Structure and Adsorption States at Talc Surfaces," H. Du and J. D. Miller, International Journal of Mineral Processing, R. Peter King Special Issue, 84, pp. 172–184 (2007).
5. "Surface Characteristics of Kaolinite and Other Selected Two Layer Silicate Minerals," J. D. Miller, J. Nalaskowski, B. Abdul, and H. Du, The Canadian Journal of Chemical Engineering, Special Issue Honoring Professor Jacob Masliyah, 85 (5), pp. 617–624 (2007).
6. "Crystal Lattice Imaging of the Silica and Alumina Faces of Kaolinite Using Atomic Force Microscopy," V. Gupta, M. A. Hampton, A. V. Nguyen, and J. D. Miller, Journal of Colloid and Interface Science, 352 (1), pp. 75–80 (2010).
7. "Further Analysis of the Rheological Behavior of Kaolinite Suspensions," V. Gupta, J. D. Miller, and A. V. Nguyen, in *Proceedings, 49th Annual Conference of Metallurgists (COM 2010)*, M. Pawlick, ed., 3-6 October 2010, Vancouver, B.C. Canada, pp. 159–168 (2010).
8. "Recent Developments in the Beneficiation of Chinese Bauxite," Q. Zhao, J. D. Miller, and X. Wang, Mineral Processing and Extractive Metallurgy Review, 31 (2), pp. 111–119 (2010).
9. "Surface Force Measurements at the Basal Planes of Ordered Kaolinite Particles," V. Gupta and J. D. Miller, Journal of Colloid and Interface Science, 344 (2), pp. 362–371 (2010).
10. "Particle Interactions in Kaolinite Suspensions and Corresponding Aggregate Structures," V. Gupta, M. A. Hampton, J. R. Stokes, A. V. Nguyen, and J. D. Miller, Journal of Colloid and Interface Science, 359 (1), pp. 95–103 (2011).
11. "Flotation of a Brazilian Bauxite Ore," S. Marino, X. Wang, C. L. Lin, and J. D. Miller, in *Separation Technologies for Minerals, Coal, and Earth Resources*, C. A. Young and G. H. Luttrell, eds., SME, Englewood, Colorado, pp. 471–477 (2012).

12. "Particle Aggregation and Sedimentation Characteristics of Kaolinite Suspensions as Explained by Surface Charge Considerations," J. D. Miller and V. Gupta, in *Water in Mineral Processing, Proceedings of the First International Water Symposium*, J.-Y. Hwang, J. Adams, D. R. Nagaraj, X. Sun, and Z. Xu, eds., 2012 SME Annual Meeting, Seattle, Washington, 19–22 February 2012, SME, Englewood, Colorado, pp. 261–278 (2012).
13. "Surface Charge and Wetting Characteristics of Layered Silicate Minerals," X. Yin, V. Gupta, H. Du, X. Wang, and J. D. Miller, Advances in Colloid and Interface Science, 179–182, pp. 43–50 (2012).
14. "Surface Chemistry of Layered Silicate Minerals," J. D. Miller, V. Gupta, X. Wang, X. Yin, H. Du, and J. Wang, in *Separation Technologies for Minerals, Coal, and Earth Resources*, C. A. Young and G. H. Luttrell, eds., SME, Englewood, Colorado, pp. 289–298 (2012).
15. "Wettability of Kaolinite Basal Planes Based on Surface Force Measurements Using Atomic Force Microscopy," X. Yin and J. D. Miller, Minerals & Metallurgical Processing, Special Industrial Minerals Issue, 29 (1), pp. 13–19 (2012).
16. "Anisotropic Surface Charging of Chlorite Surfaces," X. Yin, L. Yan, J. Liu, Z. Xu, and J. D. Miller, Clays and Clay Minerals, 61 (2), pp. 152–164 (2013).
17. "Influence of Ionic Strength on the Surface Charge and Interaction of Layered Silicate Particles," J. Liu, J.D. Miller, X. Yin, V. Gupta, and X. Wang, Journal of Colloid and Interface Science, 432, pp. 270–277 (2014).
18. "Surface Force Measurements at Kaolinite Edge Surfaces Using Atomic Force Microscopy," J. Liu, L. Sandaklie-Nikolova, X. Wang, and J. D. Miller, Journal of Colloid and Interface Science, 420, pp. 35–40 (2014).
19. "Effect of Surface Charge and Elemental Composition on the Swelling and Delamination of Montmorillonite Nanoclays Using Sedimentation Field-Flow Fractionation and Mass Spectroscopy," S. Assemi, S. Sharma, S. Tadjiki, K. Prisbrey, J. Ranville, and J.D. Miller, Clays and Clay Minerals, 63 (6), pp. 457–468 (2015).
20. "Significance of Particle Aggregation in the Reverse Flotation of Kaolinite from Bauxite Ore," J. Liu, X. Wang, C.L. Lin, and J.D. Miller, Minerals Engineering, 78, pp. 58–65 (2015).
21. "The Surface and Colloid Chemistry of Layered Silicate Minerals," J.D. Miller and J. Liu, in *Beneficiation of Phosphates, Comprehensive Extraction, Technology Innovations, Advanced Reagents*, P. Zhang, J. D. Miller, E. Wingate, and L.L. Filho, eds., SME, Englewood, Colorado, pp. 139–146 (2016).
22. "Multi-scale Features Including Water Content of Polymer Induced Kaolinite Floc Structures," S. Sharma, C.L. Lin, and J.D. Miller, Minerals Engineering, 101, pp. 20–29 (2017).
23. "Simulated Permeability of Flocculated Kaolinite Sediments from X-ray Tomographic Images," J. Dong, C.L. Lin, and J.D. Miller, Minerals & Metallurgical Processing, 35 (1), pp. 13–18 (2018).

4. GRADUATE STUDENT EDUCATION

Grant No. DE-FG02-93ER14315 was used to support the following graduate students who successfully defended their theses and received advanced degrees from the University of Utah (28 PhD degrees and 5 MS degrees).

Jaroslaw Drelich (PhD, 1993)
Madhava Rao Yalamanchili (PhD, 1993)
Michael L. Free (PhD, 1994)
Woo-Hyuk Jang (PhD, 1994)
Courtney A. Young (PhD, 1995)
Srinivas Veeramasuneni (PhD, 1997)
Yongqiang Lu (PhD, 1998)
William M. Cross (PhD, 1999)
Jakub Nalaskowski (PhD, 1999, Technical University of Gdansk (TUG), Poland)
Maria A.D. Azevedo (PhD, 2000)
Mehmet Hancer (PhD, 2000)
Ewelina Mutkowska (MS, 2001)
Minhua Li (MS, 2002)
Keqing Fa (PhD, 2004)
Xuming Wang (PhD, 2004)
Sylwia Wisniewska (PhD, 2005)
Marcin Michal Niewiadomski (PhD, 2006)
Hao Du (PhD, 2007)
Orhan Ozdemir (PhD, 2008)
Lukasz Hupka (PhD, 2008)
Vamsi Paruchuri (PhD, 2009)
Vishal Gupta (PhD, 2011)
Sandro Marino (MS, 2012)
Xihui Yin (PhD, 2012)
Xia Zhang (PhD, 2014)
Jing Liu (PhD, 2015)
Sugandha Sharma (MS, 2016)
Jiaqi Jin (PhD, 2016)
Behzad Vaziri Hassas (MS, 2017)
Vu Truong (PhD, 2017)
Kaustubh Shrimali (PhD, 2017)
Weiping Liu (PhD candidate)
Venkata Veeren Babu Atluri (PhD candidate)

5. RESEARCH RECOGNITION

Recognition of research supported by DOE Grant No. DE-FG02-93ER14315 has been significant for the PI, research staff and graduate students.

5.1 J.D. MILLER, PI and Distinguished Professor, Metallurgical Engineering, University of Utah – J.D. Miller, PI for the Nonsulfide Flotation Chemistry Grant No. DE-FG02-93ER14315, has received considerable recognition as a result, in part, from the support provided by the Basic Energy Science grant. See following list of awards:

- M. Gaudin Award, SME, Reno, Nevada, February 1993.
- **National Academy of Engineering, Washington, D.C., 1993.**
- Distinguished Achievement Medal — Colorado School of Mines, May 1994.
- Centennial Fellow of the College of Earth & Mineral Sciences, Penn State University, September 1996.
- AIME Mineral Industry Education Award — presented at the 126th AIME Annual Banquet, Denver, Colorado, February 1997.
- Faculty Fellow, University of Utah, 1999.
- Best Paper Award for Fundamental Research, "Interaction Forces between Toner Surfaces," M. A. D. Azevedo and J. D. Miller, 2000 TAPPI Recycling Symposium, Washington, DC, 5–8 March 2000.
- College of Mines and Earth Sciences, University of Utah, Outstanding Teaching Award, 2000.
- Stefanko Best Paper Award for, "Flue Gas Treatment for SO_2 Removal with Air-Sparged Hydrocyclone Technology," J. D. Miller, R. Bokotko and J. Hupka, Coal and Energy Division, Society of Mining, Metallurgy, and Exploration, SME Annual Meeting, Cincinnati, Ohio, February 2003.
- Frank Aplan Award, AIME, SME — for his outstanding and prolific contributions in research and education in mineral processing, surface chemistry and hydrometallurgy, AIME Annual Meeting, Denver, Colorado, October 2003.
- Sigel Lecturer, Chemical Engineering Department, Michigan Technological University, 2003
- Symposium and Proceedings Honoring Jan D. Miller, "Innovations in Natural Resource Processing," 2005 SME Annual Meeting, 28 February–2 March 2005, C. A. Young, J. J. Kellar, M. L. Free, J. Drelich, and R. P. King, eds., SME, Littleton, Colorado, 2005.
- Za Zaslugi Dla (Special Meritorious Recognition) Medal, Gdansk University of Technology, Gdansk, Poland, June 2005.
- Taggart Best Paper Award for "Three Dimensional Analysis of Particulates in Mineral Processing Systems by Cone Beam X-ray Microtomography," J. D. Miller and C. L. Lin, MPD/SME, 2005.
- Utah Governor's Medal Award for Science & Technology, 2006.
- **Honorary Doctorate Degree, University of Pretoria, Pretoria, South Africa, April 2007.**

- Honorary Professor Appointment, Central South University, Changsha, P.R. China, September 2007.
- Lindsay Lecture, Chemical Engineering Department, Texas A&M University, 2007.
- Certificate of Merit Award for "Trithiocarbonates for the Flotation of PGM Sulphides," C. F. Vos, J. C. Davidtz, and J. D. Miller, Mine Managers Association, Republic of South Africa, 2007.
- Distinguished Professor of Metallurgical Engineering, University of Utah, 2008.
- 2008 Old Timers Club Faculty Award, Old Timers Club/National Mining Association Coal Show, Las Vegas, Nevada, 22–24 September 2008.
- Grand Prix Award, Industrial Technology, Science and Innovation Fair TECHNICON, for mobile cyclonic reactor, J. Hupka, R. Aranowski, A. Dargacz, and J. D. Miller, Gdansk, Poland, 23 October 2008.
- John & Virginia Towers Distinguished Lecture, Materials Science and Engineering Department, Michigan Technological University, 2009.
- **Honorary Doctorate Degree, Doctor Honoris Causa, Gdansk University of Technology, Gdansk, Poland, May 2010.**
- Most Prolific Inventor Award, Technology Commercialization Award, University of Utah, January 2011.
- Honorary Professor, Institute for Process Engineering, Chinese Academy of Sciences, Beijing, China, March 2011.
- Honorary Professor, Kunming University of Science and Technology, Kunming, Yunnan, China, March 2011.
- Honorary Professor, Qinghai University, School of Chemical Engineering, Qinghai Province, Xining, China, July 2012.
- Milton E. Wadsworth 2012 Award, SME, MPD – for outstanding contributions to the fundamental theory and technology of hydrometallurgy, presented at the SME Annual Meeting, Denver, Colorado, February 2013.
- **National Academy of Inventors 2014 NAI Fellow** – for demonstrating a highly prolific spirit of innovation in creating or facilitating outstanding inventions that have made a tangible impact on quality of life, economic development, and the welfare of society. Induction at the 4th Annual Conference of the National Academy of Inventors, Pasadena, California, 2015.
- **Rosenblatt Prize for Excellence**, University of Utah's most prestigious award presented annually to a faculty member who displays excellence in teaching, research and administrative efforts, 2015.
- Surface Innovations Prize – Institution of Civil Engineers, recognition for best paper in journal – "Molecular Features of Water Films Created with Bubbles at Silica Surfaces," X. Wang, X. Yin, J. Nalaskowski, H. Du, and J.D. Miller, 2016.
- Taggart Best Paper Award for "Opportunities for Plant-site 3D Coarse Particle Characterization with Automated High-Speed X-ray Tomography," J. D. Miller and C. L. Lin, MPD/SME, 2016.
- Faculty Recognition Award, U of U Career Services Office for contributions to students' career development and exploration, 2017.
- Foreign Experts Friendship Award, Yunnan Foreign Experts Administration, Kunming, Yunnan, China, 2017.

5.2 XUMING WANG, RESEARCH PROFESSOR, Metallurgical Engineering, University of Utah – Xuming Wang obtained his graduate degrees from the University of Utah (MS in 1999 and PhD in 2004). Prior to returning to the University of Utah and his current position as Research Professor, Xuming worked for USG Research Center as a senior researcher and was responsible for the development of water and mold resistant gypsum wallboard. From 1984 to 1994 Xuming was employed by the Research Institute of Chemical Mineral Resources in P.R. China where he was responsible for much of the development of new phosphate processing technology in China.

- Surface Innovations Prize – Institution of Civil Engineers, recognition for best paper in journal – "Molecular Features of Water Films Created with Bubbles at Silica Surfaces," X. Wang, X. Yin, J. Nalaskowski, H. Du, and J.D. Miller, 2016.
- Selected as SME 2013-2014 Henry Krumb Lecturer.
- China National Science and Technology Achievement Award, Second Place on "Flotation Chemistry of Sillimanite Flotation in Alkaline Solution," 1994.

5.3 GRADUATE STUDENT RECOGNITION, Metallurgical Engineering, University of Utah – Over 30 graduate students have been supported from Grant No. DE-FG02-93ER14315 and successfully completed their thesis research and defended their theses. Based on their thesis research, a number of these students have received national awards, including the Best Paper Competition Award – Graduate Division (SME), the Garr Cutler Energy Award (U of U), R.W. Raymond Memorial Award (AIME), Outstanding Student for Best Paper Award (Beneficiation of Phosphates Conference), Rong Yu Wan PhD Dissertation Award (SME), and IPMI Awards. In addition, a number of the student researchers have been recognized with the Departmental Teaching Assistant Award, and one student received the College Teaching Assistant Award. At least twelve of these graduates/postdocs now hold tenured university faculty positions. Several have important administrative responsibilities – Department Chair, Dean, Vice President, etc.

- Michael L. Free (PhD, 1994) – College Teaching Assistant Award, 1993/94.
- Woo-Hyuk Jang (PhD, 1994) – Best Paper Competition, Graduate Student Division, 1st Place (SME).
- Courtney A. Young (PhD, 1995) – Garr Cutler Energy Award, University Competition; Best Paper Competition, Graduate Student Division, 2nd Place (TMS).
- Srinivas Veeramasuneni (PhD, 1997) – Best Paper Contest, Graduate Student Division, 1st Place (SME), 1997; Mineral Resources Student Prize Paper, 2nd Place (MMSA), 1997; Rossiter W. Raymond Memorial Award for Best Paper (AIME), 1999.
- Jakub Nalaskowski (PhD, TUG, Poland, 1999) – Graduated with Distinction, Special Recognition by the Faculty at the Technical University of Gdansk (TUG), 1999.
- Maria A.D. Azevedo (PhD, 2000) – Departmental Teaching Assistant Award, 1996/97; Best Paper Award, TAPPI Recycling Symposium, 2000.
- Mehmet Hancer (PhD, 2000) – Graduate Seminar Award, Dept. of Metallurgical Engineering, 1998/99.

- Ewelina Mutkowska (MS, 2001) – Environmental Engineering, 3rd Place, Masters Category, 2000 Annual Conference Student Program, Air & Waste Management Association, 2000.
- Sandro Marino (MS, 2012) – Outstanding Student Award for Best Paper, Beneficiation of Phosphates VI Conference, 2011.
- Jing Liu (PhD, 2015) – Departmental Teaching Assistant Award, 2011/12; Outstanding PhD Student Award, Dept. of Metallurgical Engineering, 2014, Rong Yu Wan PhD Dissertation Award for Outstanding Dissertation Research (SME), 2015.
- Sugandha Sharma (MS, 2016) – Outstanding MS Student Award, Dept. of Metallurgical Engineering, 2016.
- Jiaqi Jin (PhD, 2016) – Outstanding Student Award, IPMI, 2014; Student Presentation Award, Colorado MPD, 65th Annual Conference (SME), 2015.
- Behzad Vaziri Hassas (PhD, 2017) – Outstanding Student Award, Republic Metals, IPMI, 2017.
- Kaustubh Shrimali (PhD, 2017) – 1st Place, SME, MPD Graduate Student Poster Contest, SME Annual Meeting, 2017; 1st Place, SME Graduate Student Research Poster Contest, SME Annual Meeting, 2017; Outstanding PhD Student Award, Dept. of Metallurgical Engineering, 2017.

6. CONCLUSIONS

Significant contributions have been made to the chemistry of flotation separations in many areas, including, soluble salt minerals; collector adsorption; wetting, surface forces, and bubble attachment; interfacial water structure; and phyllosilicate minerals. The research results summarized herein have resulted in more than 225 publications, the education of 28 PhD graduate students, and impressive recognition with university, national, and international awards. It is evident that the flotation separation research program has been quite successful.

Unfortunately, the flotation chemistry research for mineral particle separation has been terminated even though the renewal proposal received an excellent review with recommended funding, and the need for continued support of minerals separation remains, as recognized by 1) the recent 2017 USGS report, "Critical Mineral resources of the United States – Economic and Environmental Geology and Prospects for Future Supply," and by 2) the 20 December 2017 executive order by President Trump to increase the discovery, production, and domestic refining of critical minerals. In view of our research accomplishments, the excellent review of the renewal proposal, and the expressed need for attention to the production of critical minerals, termination of "The Flotation Chemistry of Nonsulfide Minerals" research program by DOE is not appropriate, and continued support should be reconsidered.