NANOSCIENCE IN AQUEOUS PROCESSING

K Osseo-Asare[1]

ABSTRACT

A search for the keyword *nano* reveals that it has not made a significant entry into the mineral processing research literature. In contrast, the terms *micelle, colloid, interface, and monolayer* are well established there. By considering nanoscience as colloid and interface science at the nanoscale, it is claimed that several previous and current investigations in the broad field of mineral processing fall under the umbrella of nanoscience. Several examples from hydrometallurgical processing systems (invisible gold and activated carbon in gold extraction; monolayers, reverse micelles, and microemulsions in solvent extraction; nanobiofilms and nanoparticles in biohydrometallurgy) are highlighted in support of this view.

Keywords: nanoparticles, nanobiofilms, monolayers, reverse micelles, microemulsions, invisible gold, carbon adsorption, solvent extraction, bioleaching

INTRODUCTION

In the period 1960-69 not a single paper appeared in the *Journal of Colloid and Interface Science*, a leading journal in the field, with 'nano' as a keyword. In the next decade (1970-79) there was only one paper. Two decades later (1990-99) the number had risen to 166 and considering the most recent decade (2000-09) with 1894 publications, it can be declared without ambiguity that there is now an explosion in nano-related papers. The relevant statistics, collected via Web of Science (using 'nano*' as the search word) are summarised in Table 1. In several fields related to the broad field of mineral processing, e.g., geoscience, environment, and energy, a similar 'nanonisation' seems to be occurring (Hochella, 2002a, b; Tratnyek and Johnson, 2006; Puurunen and Vasara, 2006; Zach *et al*, 2006). In this paper we consider the current state of nanoscience in the field of aqueous processing of metals. We explore some of the historical roots of nano-related research in hydrometallurgy, review some of the current trends, and discuss opportunities for further advancement of hydrometallurgical nanoscience.

The nanoscience and nanotechnology revolution is usually traced to Feynman's now-famous lecture, 'There is plenty of room at the bottom.' (Feynman, 1960; Shew, 2008; Sandhu, 2006). He began the talk by announcing:

> *I would like to describe a field, in which little has been done, but in which an enormous amount can be done in principle. This field is … like solid-state physics in the sense that it might tell us much of great interest about the strange phenomena that occur in complex situations. Furthermore, a point that is most important is that it would have an enormous number of technical applications.*

At the center of Feynman's vision was 'the problem of manipulating and controlling things on a small scale.' He raised the question: 'Why cannot we write the entire 24 volumes of the *Encyclopedia Britannica* on the head of a pin?' He then went on to imagine a future where it would be possible to synthesise chemicals and materials atom by atom:

> *But it is interesting that it would be, in principle, possible (I think) for a physicist to synthesize any chemical substance that the chemist writes down. Give the orders and the physicist synthesizes it. How? Put the atoms down where the chemist says, and so you make the substance. The problems of chemistry and biology can be greatly helped if our ability to see what we are doing, and to do things on an atomic level, is ultimately developed – a development which I think cannot be avoided.*

---

[1] Distinguished Professor, Department of Materials Science and Engineering, Department of Energy and Mineral Engineering, Penn State University, 208 Steidle Building, University Park PA 16802, USA. Email: ako1@psu.edu

TABLE 1
Nano-related papers in the *Journal of Colloid and Interface Science*.

Time Span	No. of Articles	Time Span	No. of Articles
1960-1969	0	2000-2001	99
1970-1979	1	2002-2003	188
1980-1989	2	2004-2005	360
1990-1999	166	2006-2007	560
2000-2009	1894	2008-2009	687

The word *nano*, however, appears nowhere in Feynman's lecture. The term *nanotechnology* first entered the scientific lexicon in 1974 through Taniguchi's paper, 'On the basic concept of 'nano-technology' ' (Taniguchi, 1974). The focus here was on 'the production technology to get the extra high accuracy and ultra fine dimensions, i.e., the preciseness and fineness of the order of 1 nm (nanometer), 10^{-9} m, in length.' Taniguchi (1974) further explained:

> *The name of 'Nano-technology' originates from this nanometer … 'Nano-technology' mainly consists of the processing of separation, consolidation and deformation of the materials by one atom or one molecule. Needless to say, the measurement and control techniques assure the preciseness and fineness of 1 nm play a very important role in this technology.*

Today, an important aspect of nanoscience is the science of nanomaterials. Materials in the nano domain are of interest because as the dimensions of a given material enter the nano scale (1-100 nm) the material experiences dramatic changes in many of its properties, such as electrical, optical, mechanical, and chemical (Buffat and Borel, 1976; Hochella, Jr. 2002a, b; Sandhu, 2006; Shew, 2008; Van Hove, 2006).

NANOSCIENCE IN MINERAL PROCESSING

In an effort to assess the state of nano-related research in aqueous processing in metallurgical systems a search was made via the Web of Science for the keyword *nano* in the journal *Hydrometallurgy*. According to the results compiled in Table 2 (after eliminating spurious candidates like $NaNO_3$), up to 2009 the keyword *nano* appears in the abstracts of only 16 papers. Noting that the journal was founded in 1975, it is clear that the language of *nano* has not made a significant entry into the hydrometallurgical literature—at least, as represented by this particular journal (Pesic, 2005; Mooiman *et al*, 2005). Using ScienceDirect (http://www.sciencedirect.com) the search was extended to include additional keywords and two other journals in the broad field of minerals processing, i.e., *International Journal of Mineral Processing* and *Minerals Engineering*. The results are presented in Table 3. It can be seen that none of the keywords *nanoparticle, nanosize, nanopores, nanoporous, nanoscience* and *nanotechnology* appears more than 10 times. In contrast, the keywords *micron, micelle, colloid, interface, and monolayer* appear numerous times (from 45 up to over 850).

The fact that in all three journals the incidence of *micron* far exceeds the *nano* terms at first gives the impression that minerals processing research, as a whole, has not embraced the nanodomain. It is suggested here, however, that if we view nanoscience as *colloid science in the nanodomain*, then the presence of terms like *micelle, colloid, interface, and monolayer* clearly shows that within the broad field of mineral processing there are research concerns that may properly be considered as falling within the field of nanoscience. A few examples of these nanoscience-related research issues are highlighted below in the areas of gold hydrometallurgy, solvent extraction, and biohydrometallurgy.

NANOSCIENCE AND AQUEOUS PROCESSING RESEARCH

Nanoparticles and nanostructures in gold hydrometallurgy

Invisible gold

In his lecture, Feynman reflected on 'the most central and fundamental problems of biology' of his time and concluded: 'It is very easy to answer many of these fundamental questions: you just look at the thing! … Unfortunately, the present microscope sees at a scale which is a bit too crude.' In the

TABLE 2

Nano-related papers in *Hydrometallurgy* journal.

Paper No.	Year	Authors	Paper Title	Ref.	Keywords/ Comments
1	2010	Wu *et al*	Lanthanum adsorption using iron oxide loaded calcium alginate beads	101, 76-83	'Nanoparticles'
2	2009	Zanjani *et al*	Factors affecting platinum extraction from used reforming catalysts in iodine solutions at temperatures up to 95 degrees C	97, 119-125	Pt was presented as dispersed nanoparticles in nanopores of spent catalyst
3	2009	Kim *et al*	Reductive acid leaching of spent zinc-carbon batteries and oxidative precipitation of Mn-Zn ferrite nanoparticles	96, 154-158	Mn-Zn ferrite product
4	2009	Zhang *et al*	Separation and preconcentration of trace indium(III) from environmental samples with nanometer-size titanium dioxide	95, 92-95	'Nanometer TiO_2'; application of nano-size adsorbent
5	2008	Creamer *et al*	A biogenic catalyst for hydrogenation, reduction and selective dehaloge-nation in non-aqueous solvents	94, 138-143	'Clusters'; Biosynthesis of Pd nano-particles
6	2008	Zammit *et al*	Evaluation of quantitative real-time polymerase chain reaction for enumeration of biomining microorganisms in culture	94, 185-189	Abstract mentions use of 'NanoDrop spectrophotometer'
7	2008	Holmes	Review of International Biohydro-metallurgy Symposium, Frankfurt, 2007	92, 69-72	Abstract mentions 'nano-biotechnology'
8	2008	Li *et al*	Preparation of synthetic rutile by hydrochloric acid leaching of mechanically activated Panzhihua ilmenite	91, 121-129	Abstract mentions adverse effect of 'nanosized primary particles' on solid/liquid separation
9	2008	Li and Demopoulos	Precipitation of nanosized titanium dioxide from aqueous titanium (IV) chloride solutions by neutralisation with MgO	90, 26-33	Keyword: 'TiO_2 nanoparticles'; Abstract mentions 'nanosized titanium dioxide'
10	2006	Gericke and Pinches	Biological synthesis of metal nanoparticles	83, 132-140	Keyword: 'Nanoparticles'; Abstract mentions 'nanoparticles' & 'nanosized materials'
11	2006	Loan *et al*	Defining the Paragoethite process for iron removal in zinc hydrometallurgy	81, 104-129	Keywords: 'Elelctron nano-difraction'; Abstract mentions 'nano-scale minerals'
12	2006	Konishi *et al*	Intracellular recovery of gold by microbial reduction of $AuCl_4^-$ ions using the anaerobic bacterium Shewanella algae	81, 24-29	Keywords: 'nanoparticles'; Abstract mentions 'gold nanoparticles'
13	2005	Richmond *et al*	Zinc sulfide as a solid phase additive for improving the processing characteristics of ferrihydrite residues	78, 172-179	Abstract mentions 'ZnS nanoparticles'
14	2005	Balaz *et al*	Mechanochemistry in hydrometallurgy of sulphide minerals	77, 9-17	Keywords: 'nano-crystal'; Abstract mentions 'ZnS nanoparticles'
15	2004	Huang *et al*	pH-controlled precipitation of cobalt and molybdenum from industrial waste effluents of a cobalt electrodeposition process	75, 77-90	Abstract mentions 'electrodeposition of nanocrystalline Co-based alloys'
16	2004	Konishi *et al*	A new synthesis route from spent sulfuric acid pickling solution to ferrite nanoparticles	74, 57-65	Keywords: nano-particle; Abstract mentions 'nickel ferrite particles' and 'magnetite particles'
17	1999	Gurmen	Acidic leaching of scheelite concentrate and production of hetero-poly-tungstate salt	51, 227-238	Abstract mentions 'nano-sized tungsten salt'

past this inability to 'just look at the thing' hampered research into the origins and processing of refractory gold ores which contain 'invisible' gold. However, recent improvements in high-resolution transmission electron microscopy (HRTEM) and the introduction of scanning probe microscopes (SPMs) such as the scanning tunneling microscope (STM), the atomic force microscope (AFM) or scanning force microscope (SFM) promise new advances (Buffat and Borel, 1976; Hochella, Jr. 2002a, b; Sandhu, 2006; Shews, 2008; Van Hove, 2006).

TABLE 3
Selected keywords in mineral processing journals.

Keyword	Hydrometallurgy	Int. J. Min. Proc.	Minerals Eng.
Nanoparticle	9	3	3
Nanosize	2	7	3
Nanopore	0	1	0
Nanoporous	2	1	0
Nanoscience	2	4	3
Nanotechnology	7	5	5
Micron	75	220	396
Micelle	45	61	57
Colloid	289	714	514
Interface	721	844	859
Monolayer	84	247	147

Using HRTEM and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) has permitted the previously invisible gold to be revealed as nanoparticles (~5-10 nm) (Palenik, et al, 2004). This finding has inspired new questions and new research. For example, in their STS investigation of gold nanoparticles deposited on the surface of arsenopyrite and pyrite, Mikhlin *et al* (2006, 2007) observed that the magnitude of the tunneling current decreased with decrease in the Au^o particle size. This effect is suggestive of the phenomenon of Coulomb blockage, whereby a new electron transfer event in a nanoparticle is inhibited by the electrostatic potential produced by the preceding electron transfer event (Chen, 2004). Mikhlin *et al* (2006, 2007) speculate that this effect may have important implications for the extraction of the *invisible* gold found in gold ores. Conventional wisdom is that gold associated with pyrite and arsenopyrite is refractory because it is entrapped in sulfide mineral grains and therefore not accessible to the cyanide lixiviant. Mikhlin *et al* (2006, 2007) raise the possibility that another pathway for the refractory nature of invisible gold may lie in the Coulomb-blockage-related slow electron transfer of even exposed nanogold surfaces.

Activated carbon

Since the 1980s activated carbon has established itself as an important adsorbent in the gold extraction industry, where it is used for recovery of the precious metal from aurocyanide ($Au(CN)_2^-$) solution (Marsden and House, 2006). The structure of this carbonaceous material consists of an assemblage of graphite crystallites linked by disordered regions of carbon hexagons. Its capacity as an adsorbent is the combined result of its unique physical and chemical properties. The chemical characteristics are determined largely by the functional oxygen groups on its surface and the π electrons of the aromatic rings in the graphene planes. The physical properties of most importance are the surface area and pore size distribution. Activated carbon is a nanostructured material. The graphite crystallites are of nanosize (~ 1 – 1.5 nm high and ~ 2 – 2.5 nm wide). The internal pores are classified into three groups on the basis of pore size, i.e., micropores (< 2 nm), mesopores or transitional pores (2 – 100 to 200 nm) and macropores (> 100 to 200 nm) (Marsden and House, 2006; Mattson and Mark, 1971; Bansal, *et al*, 1988).

The mechanism by which metal cyanide complexes adsorb on activated carbon is still not resolved, in spite of the publication of numerous papers on the subject (Ibrado and Fuerstenau, 1992; Jia *et al*, 1998; Jia and Thomas, 2004; Klauber, 1991; Adams and Fleming, 1989; Radovic *et al*, 2001). Many investigators consider the adsorption sites to be the oxygen functional groups located at the edges of the graphitic sheets. On the other hand others favor the planar surface of the graphitic sheets where it is considered that the aurocyanide complex interacts with delocalised π electrons. Given that micropores (pore size < 2 nm) contribute most of the total surface area of activated carbon, it is clear that future efforts to advance the science of this adsorbent in gold hydrometallurgy cannot afford to ignore the nanostructural nature of this material. Thus, while previously activated carbons were designated as microporous carbons, they can now be properly called nanoporous carbons. Thus, it may well be that some of the progress being made in the development of new nanocarbons (Inagaki and Radovic, 2002), such as fullerenes and carbon nanotubes, will have some relevance for activated-carbon-based technologies as well as the problem of refractory carbonaceous gold ores (Osseo-Asare *et al*, 1984; Ofori-Sarpong *et al*, 2010).

Monolayers, reverse micelles, and microemulsions in solvent extraction of metals

Monolayers, reverse micelles and extraction

Solvent extraction is an important purification and concentration unit process in hydrometallurgy (Cox and Flett, 1979; Flett, 1977). The molecular structure of a typical extractant used in hydrometallurgical solvent extraction consists of a polar (inorganic) functional group and a hydrocarbon (organic) radical. It is generally accepted that the hydrocarbon radicals ensure organic phase solubility of the extracted complex, whereas the polar groups serve as binding sites for metal complexation, as illustrated below for carboxylic acid (Eq. 1), phosphoric acid (Eq. 2) and amine (Eqs. 3 and 4) extractants:

$$\mathrm{RCOOH\ (org) + M^{+}\ (aq) = RCOOM\ (org) + H^{+}\ (aq)} \quad (1)$$

$$\mathrm{R_2POOH\ (org) + M^{+}\ (aq) = R_2POOM\ (org) + H^{+}\ (aq)} \quad (2)$$

$$\mathrm{R_3N\ (org) + H^{+}\ (aq) + A^{-}\ (aq) = R_3NH^{+}A^{-}\ (org)} \quad (3)$$

$$\mathrm{R_3NH^{+}A^{-}\ (org) + MA_2^{-}\ (aq) = R_3NH^{+}MA_2^{-}\ (org) + A^{-}\ (aq)} \quad (4)$$

The dual polar-nonpolar character of the extractants has additional consequences. Interfacial tension data show that extractant molecules are interfacially active at the oil/water interface and can adsorb to form monolayers (Flett, 1977; Cox and Flett, 1979; Osseo-Asare, 1984; Chaiko and Osseo-Asare, 1988a, b; Szymanowski, 2000; Cote, 2003). Extractants with ionizable functional groups can also impart a corresponding negative or positive charge to the oil/water interface, as demonstrated by electrophoretic mobility and surface potential measurements (Flett, 1977; Cox and Flett, 1979; Osseo-Asare, 1984). It is now well accepted that the metal extraction involves interfacial reactions and therefore in formulating rate mechanisms interfacial concentrations are the relevant quantities to consider.

As with classifical surfactants, some extractants as well as metal-extractant complexes can aggregate to form reverse micelles in nonpolar organic solvents. The polar regions of these aggregates can solubilise water molecules, forming water-in-oil (w/o) microemulsions. Dramatic changes in metal extraction selectivities and rates have been reported for several mixed extractant systems containing reverse micelles and microemulsions. These effects are attributable to significant changes in the concentrations and reactivities of the extractants in the resulting nano domains (Osseo-Asare and Keeney, 1980; Osseo-Asare, 1984; Paatero and Sjöblom, 1990; Cote, 2003).

Microemulsions and third phase formation

In certain solvent extraction systems, especially those that involve basic extractants (e.g., organophosphorus esters and amines), there is a tendency for the metal- and acid-containing organic phase to separate into two liquids. This phase splitting has an adverse effect on mixing efficiency and puts severe limitations on metal loadings. Using tri-n-butylphosphate (TBP) as a model extractant, Osseo-Asare (1990,1991) critically assessed the experimental evidence for the existence of molecular aggregates and identified these entities as nanometer-size reverse micelles containing solubilised water, and therefore microemulsions. It was postulated that, 'The solvent extraction third phase corresponds to the middle phase in a microemulsion fluid system' (Osseo-Asare, 1991; 2002). This initial proposal encouraged investigations into the structural characteristics of TBP-containing organic solvents susceptible to third phase formation. Using spectroscopic techniques sensitive to nano-scale structures, such as small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) the presence of extractant aggregates was confirmed in TBP and other extractant systems. Further, the scattering data were successfully rationalised in terms of an aggregation model in which the polar cores are under the influence of attractive van der Waals forces whereas organic tails of the extractant contribute steric interactions (Chiarizia *et al*, 2003, 2004; Erlinger, *et al*, 1999).

Nanobiofilms and nanoparticles in biohydrometallurgy

Nanobiofilms

Biohydrometallurgy is now a well-established branch of hydrometallurgy, with many important commercial applications, such as bioleaching of copper sulfides and biooxidation of refractory gold ores (Brierley and Brierley, 2001; Rawlings, 2004; Brierley, 2008). The bacterial-mineral interactions that drive these industrial applications are also responsible for the environmental problems of acid-mine and acid-rock drainage (Evangelou and Zhang, 1995; Johnson and Hallberg, 2005). The commercial successes of biohydrometallurgy and the related environmental challenges have stimulated considerable research into the underlying physicochemical processes (Holmes, 2008; Donati *et al*, 2009). It is now generally accepted that the biooxidation of a metal sulfide (e.g., pyrite, FeS_2) by a microorganism such as Acidithiobacillus ferrooxidans in acidic solution occurs via an indirect mechanism whereby the active lixiviants, ferric ions, are regenerated by bio-mediated oxidation of ferrous ions. The complete mechanistic details of this indirect microbial process are still waiting to be unraveled (Rohwerder *et al*, 2003).

Current understanding is that mineral decomposition is promoted by the attachment of bacteria to the mineral surface. Further, the bacteria are typically covered by an organic film, the extracellular polymeric substance (EPS), which constitutes a reaction zone of nanometer dimensions (Kinzler *et al*, 2003; Rohwerder *et al*, 2003). High resolution electron microscopy and atomic force microscopy reveal the thickness of this layer to be in the range of 10-100 nm (Rodriguez-Leiva and H. Tributsch, 1988; Sand *et al*, 1995; Rohwerder *et al*, 2003; Rojas-Chapana and Tributsch, 2004; Taylor and Lower, 2008; Florian *et al*, 2010). Reflecting on the role of the EPS, Sand *et al* (1995) stated: 'we have no idea about the actual concentrations of protons, ferrous/ferric and/or other cations, and sulfur compounds in the reaction space between the bacterium and the sulfide surface.' This knowledge gap remains a major research challenge today, as demonstrated by this more recent comment by Harneit *et al* (2006): 'Up to now the conditions within this reaction space, e.g. pH, redox potential, or ion concentrations are unknown.' Much of the recent progress has come from adoption of the concepts and tools of nanoscience (Rodriguez-Leiva and H. Tributsch, 1988; Sand *et al*, 1995; Rojas-Chapana and Tributsch, 2004; Taylor and Lower, 2008; Mangold *et al*, 2008; Florian *et al*, 2010).

Nanoparticles

Inorganic nanoparticles are produced during bioleaching of metal sulfides. An HRTEM investigation by Rojas *et al* (1995) revealed the formation of nanosize sulfur particles (4-70 nm) during bioleaching of pyrite by Acidithiobacillus ferrooxidans. These nanoparticles serve as an energy source for bacteria cells not in direct contact with the metal sulfide surface. In a TEM and high resolution SEM study of Leptospirillum ferrooxidans cells following bacterial leaching of pyrite, Rojas-Chapana and Tributsch (2004) observed nanosize pyrite particles (5-50 nm) in the EPS. The presence of these nanoparticles was attributed to the extremely corrosive reaction environment; it was suggested that the highly concentrated ferric ions in the EPS produced locally high electrode potentials, which resulted in an electrochemical comminution effect. More research is needed to better understand the processes that lead to the formation and subsequent consumption of these nanoparticles in the bio-reaction environment.

It has long been known that the interactions of microorganisms with minerals in the geo-environment can produce secondary minerals, a process that is termed 'biomineralisation' (Southam and Beveridge, 1992; Lloyd *et al*, 2008). Borrowing from this terminology, the nanosulfur and nanopyrite particles discussed above may be viewed as products of hydrometallurgical biomineralisation. In response to the growing technological interest in nanoparticles, research in biomineralisation is being extended to the microbial-mediated synthesis of such materials (Lloyd *et al*, 2008). The materials produced thus far with this designed biomineralisation include nanosize metal oxides, silicates, carbonates, phosphates, sulfides, and selenates, as well as zero-valent metals, e.g., Au, Ag, Pd, and Pt (Lloyd *et al*, 2008). Attempts are also being made to link metal recovery with production of functional materials (Deplanche *et al*, 2008). The progress to date suggests that it is worth exploring opportunities for wedding bioleaching to biomineralisation.

CONCLUSION

It was noted in the Introduction that Feynman, the 'founder' of nanoscience and nanotechnology did not use the word *nano* in his famous lecture (Feynman, 1960). This illustrates the important truth that reality precedes terminology. Thus, likewise, leading researchers in mineral processing were advancing nanoscience long before *nano* terminology emerged (Fuerstenau, 1956). Feynman surmised that 'The problems of chemistry and biology can be greatly helped if our ability to see what we are doing, and to do things on an atomic level, is ultimately developed.' There is no question that the recent introduction of various nanoscale-sensitive microscopies and spectroscopies has led to major advances in our understanding (particularly the structural aspects) of hydrometallurgical reaction systems. Computational and molecular modeling tools (not discussed here) have also contributed immensely to our ability to make nanoscale rationalisations of hydrometallurgically relevant processes (Ladeira *et al*, 2001; Kubicki *et al*, 2007). More secrets hidden within the nanodomains of various hydrometallurgical systems are waiting to be unlocked with creative applications of these new characterisation and molecular modeling tools.

REFERENCES

Adams, M D and Fleming, C A, 1989. The mechanism of adsorption of aurocyanide onto activated carbon, *Metall Trans* B, 20B:315-325.

Bansal, R C, Donnet J B and Stoeckli, F, 1988. *Active Carbon* (Marcel Dekker, New York).

Brierley, J A and Brierley, C L, 2001. Present and future commercial applications of biohydrometallurgy, *Hydrometallurgy*, 59:233–239.

Brierley, J A, 2008. A perspective on developments in biohydrometallurgy, *Hydrometallurgy*, 94: 2–7.

Buffat, P and Borel, J P, 1976. Size effect on the melting temperature of gold, *Physical Review A*, 13: 2287–2298.

Chaiko, D J and Osseo-Asare, K, 1988a. Desorption of benzophenone oxime monolayers at the air/water interface, *J. Colloid Interface Sci.*, 121:13-21.

Chaiko, D J and Osseo-Asare, K, 1988b. Monolayer behavior of hydroxyoxime extractants, *Sep Sci Techno*l, 23:1423-1434.

Chen, S, 2004. Chemical manipulations of nanoscale electron transfers, *Journal of Electroanalytical Chemistry*, 574:153–165.

Chiarizia, R, Jensen, M P, Borkowski, M, Ferraro, J R, Thiyagarajan, P and Littrell, K C, 2003. Third phase formation revisited: the U (VI), – HNO_3, TBP, n-dodecane system, *Solv Extr Ion Exch*, 21:1-27.

Chiarizia, R, Jensen, M P, Borkowski, M, Thiyagarajan, P and Littrell, K C, 2004. Interpretation of third phase formation in the Th (IV) – HNO_3, TBP-n-Octane system with Baxter's 'sticky spheres' model, *Solv Extr Ion Exch*, 22:325-351.

Cote, G, 2003. The supramolecular speciation: a key for improved understanding and modeling of chemical reactivity in complex systems, *Radiochimica Acta*, 91:639-643.

Cox, M and Flett, D S, 1979. The significance of surface activity in solvent extraction reagents, in *Proceedings International Solvent Extraction Conference*. *ISEC 77* (eds: B H Lucas, G M Ritcey and H W Smith) pp 63-72 Canadian Institute of Mining and Metallurgy: Montreal).

Deplanche, K and Macaskie, L E, 2008. Biorecovery of gold by Escherichia coli and Desulfovibrio desulfuricans, *Biotechnology and Bioengineering*, 99:1055-1064.

Donati, E R, Viera, M R, Tavani, E L, Giaveno, M A, Lavalle, T L, Chiacchiarini, P A (eds), 2009. *Biohydrometallurgy: a meeting point between microbial ecology, metal recovery processes and environmental remediation (IBS 2009)* (Trans Tech Publications: Stafa-Zurich, Switzerland).

Erlinger, C, Belloni, L, Zemb, Th, and Madic, C, 1999. attractive interactions between reverse aggregates and phase separation in concentrated malonamide extractant solutions, *Langmuir* 15:2290-2300.

Evangelou V P and Zhang Y L, 1995. A review – pyrite oxidation mechanisms and acid-mine drainage prevention, *Critical Reviews in Environmental Science and Technology*, 25: 141-199.

Feynman, R, 1960. There's plenty of room at the bottom, *Engineering and Science*, 23:22-36.

Flett, D S, 1977. Chemical kinetics and mechanisms in solvent extraction of copper chelates, *Acc Chem Res*, 10:99-104.

Florian, B, Noël, N and Sand, W, 2010. Visualization of initial attachment of bioleaching bacteria using combined atomic force and epifluorescence microscopy, *Minerals Engineering*, 23: 532–535.

Fuerstenau, D W, 1956. Streaming potential studies on quartz in solutions of aminium acetates in relation to the formation of hemimicelles at the quartz-solution interface, *J Phys Chem*, 60: 981-985.

Harneit, K, Goksel, A, Kock, D, Klock, J-H, Gehrke, T, and Sand, W, 2006. Adhesion to metal sulfide surfaces by cells of Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans and Leptospirillum ferrooxidans, *Hydrometallurgy*, 83:245-254.

Hochella Jr, M F, 2002a. Nanoscience and technology: the next revolution in the earth sciences, *Earth Planet Sci Lett*, 203:593-605.

Hochella Jr, MF 2002b. There's plenty of room at the bottom: Nanoscience in geochemistry, *Geochim Casmochim, Acta*. 65:735-743.

Holmes, D S, 2008. Review of International Biohydrometallurgy Symposium, Frankfurt, 2007, *Hydrometallurgy*, 92: 69-72.

Ibrado, A S and Fuerstenau, D W, 1992. Effect of the structure of carbon adsorbents on the adsorption of gold cyanide, *Hydrometallurgy* 30:243-256.

Inagaki, M and Radovic, L R, 2002. 'Nanocarbons,' *Carbon* 40:2263–2284.

Jia, Y F, Steele, C J, Hayward, I P and Thomas, K M, 1998. Mechanism of adsorption of gold and silver species on activated carbons, *Carbon* 36:1299-1308.

Jia, Y and Thomas, K M, 2004. Observation of the adsorption of $K^+ Au(CN)_2^-$ ion pairs on the surface of nanoporous carbon by XANES, *J Phys Chem B*, 108:17124-17128.

Johnson, D B and Hallberg, K B, 2005. Acid mine drainage remediation options: a review, *Science of the Total Environment*, 338: 3–14.

Kinzler, K, Gehrke, T, Telegdi, J and Sand, W, 2003. Bioleaching—a result of interfacial processes caused by extracellular polymeric substances (EPS), *Hydrometallurgy*, 71:83–88.

Klauber, C, 1991. X-ray photoelectron spectroscopy study of the adsorption mechanism of aurocyanide onto activated carbon, *Langmuir*, 7:2153-2159.

Kubicki, J D, Kwon, K D, Paul, K W and Sparks, D L, 2007. Surface complex structures modelled with quantum chemical calculations: carbonate, phosphate, sulphate, arsenate and arsenite, *European Journal of Soil Science*, 58: 932–944.

Ladeira, A C Q, Ciminelli, V S T, Duarte, H A, Alves, M C M and Ramos, A Y, 2001. Mechanism of anion retention from EXAFS and density functional calculations: arsenic (V) adsorbed on gibbsite, *Geochimica et Cosmochimica Acta*, 65:1211–1217.

Lloyd, J R, Pearce, C I, Coker, V S, Pattrick, R A D, Van Der Laan, G, Cutting, R, Vaughan, D J, Paterson-Beedle, M, Mikheenko, I P, Yong, P and Macaskie, L E, 2008. Biomineralization: linking the fossil record to the production of high value functional materials, *Geobiology*, 6:285–297.

Mangold, S, Laxander, M, Harneit, K, Rohwerder, T, Claus, G and Sand, W, 2008. Visualization of Acidithiobacillus ferrooxidans biofilms on pyrite by atomic force and epifluorescence microscopy under various experimental conditions, *Hydrometallurgy*, 94:127-132.

Marsden, J O and House, C I, 2006. *The Chemistry of Gold Extraction*, 2nd ed (Littleton: Society of Mining, Metallurgy and Exploration).

Mattson, J S and Mark, H B, 1971. *Activated Carbon: Surface Chemistry and Adsorption from Solution*, (Marcel Dekker: New York).

Mikhlin, Y L, Romanchenko, A S and Asanov I P, 2006. Oxidation of arsenopyrite and deposition of gold on the oxidized surfaces: A scanning probe microscopy, tunneling spectroscopy and XPS study, *Geochimica et Cosmochimica Acta* 70:4874–4888.

Mikhlin, Y L and Romanchenko, A S, 2007. Gold deposition on pyrite and the common sulfide minerals: an STM/STS and SR-XPS study of surface reactions and Au nanoparticles, *Geochimica et Cosmochimica Acta*, 71: 5985–6001.

Mooiman, M B, Sole, K C and Kinneberg, D J, 2005. Challenging the traditional hydrometallurgy curriculum – an industry perspective, *Hydrometallurgy*, 79:80-88.

Ofori-Sarpong, G, Tien, M and Osseo-Asare, K 2010. Mycohydrometallurgy: coal model for potential reduction of preg-robbing capacity of carbonaceous gold ores using the fungus, Phanerochaete chrysosporium, *Hydrometallurgy,* 102:66-72.

Osseo-Asare, K and Keeney, M E, 1980. Aspects of the interfacial chemistry of nickel extraction with LIX63-HDNNS mixtures, *Metal Trans. B*, 11B:63-67.

Osseo-Asare, K, 1984. Interfacial phenomena in hydrometallurgical liquid-liquid extraction systems', in *Hydrometallurgical Process Fundamentals* (ed: R G Bautista), pp. 357-405 (Plenum: New York).

Osseo-Asare, K, Afenya, P M, and Abotsi, G M K, 1984. Carbonaceous matter in gold ores: isolation, characterization and adsorption behavior in aurocyanide solution, in *Precious Metals - Mining, Extraction and Processing,* (eds: V Kudryk, D A Corrigan and W W Liang) pp 125-44 (TSM-AIME: Warrendale, PA).

Osseo-Asare, K, 1990. Volume changes and distribution of HCl and H_2O in the tri-n-butyl phosphate-H_2O-HCl liquid-liquid system: a reversed micellar phenomenological model, *Colloids and Surfaces*, 50:373-392.

Osseo-Asare, K, 1991. Aggregation, reversed micelles, and microemulsions in liquid-liquid extraction: the tri-n-butyl phosphate-diluent-water-electrolyte system, *Adv. Colloid Interface Sci*, 37:123-173.

Osseo-Asare, K, 2002. Microemulsions and third phase formation, in *Proceed. International Solvent Extraction Conference, ISEC 2002*, (eds: K C Sole, P M Cole, and D J Robinson), pp 118-124 (South African Institute of Mining and Metallurgy: Johannesburg).

Paatero, E and Sjöblom, J, 1990. Phase behavior in metal extraction systems, *Hydrometallurgy*, 25:231-256.

Palenik, C S, Utsunomiya, S, Reich, M, Kesler, S E, Wang, L and Ewing, R C, 2004. 'Invisible' gold revealed: Direct imaging of gold nanoparticles in a Carlin-type deposit, *American Mineralogist*, 89:1359–1366.

Pesic, B, 2005. Teaching and learning adaptive hydrometallurgy-nanohydrometallurgy, *J Min Metall,* 41B: 17-32.

Puurunen, K and Vasara, P, 2007. Opportunities for utilizing nanotechnology in reaching near-zero emissions in the paper industry, *J Cleaner Production*, 15: 1287-1294.

Radovic, L R, Moreno-Castilla, C and Rivera-Utrilla, J, 2001. Carbon materials as adsorbents in aqueous solutions, *Chemistry and Physics of Carbon* (ed: L R Radovic), 27:227-405.

Rawlings, D E, 2004. Microbially assisted dissolution of minerals and its use in the mining industry, *Pure Appl Chem*, 76:847–859.

Rodriguez-Leiva, M and Tributsch, H, 1988. Morphology of bacterial leaching patterns by Thiobacillus ferrooxidans on synthetic pyrite, *Arch Microbiol*, 149:401-405.

Rohwerder, T, Gehrke, T, Kinzler, K and Sand, W, 2003. Bioleaching review part A: progress in bioleaching: fundamentals and mechanisms of bacterial metal sulfide oxidation, *Appl Microbiol Biotechnol,* 63: 239-248.

Rojas, J, Giersig, M and Tributsch, H, 1995. Sulfur colloids as temporary energy reservoirs for Thiobacillus ferrooxidans during pyrite oxidation, *Arch Microbiol*, 163:352-356.

Rojas-Chapana, J A and Helmut Tributsch, H, 2004. Interfacial activity and leaching patterns of Leptospirillum ferrooxidans on pyrite, *FEMS Microbiology Ecology*, 47:19-29.

Sand, W, Gerke, T, Hallmann, R and Schippers, A, 1995. Sulfur chemistry, biofilm, and the (in)direct attack mechanism - a critical evaluation of bacterial leaching, *Appl Microbiol Biotechnol,* 43:961-966.

Sandhu, A, 2006. Who invented nano?, *Nature Nanotechnology*,1:87.

Shew, A, 2008. Nanotech's history. An interesting, interdisciplinary, ideological split, *Bull Sci Technol Soc*, 28:390-399.

Southam, G and Beveridge, T J, 1992. Enumeration of Thiobacilli within pH-neutral and acidic mine tailings and their role in the development of secondary mineral soil, Applied and Environmental Microbiology, 1904-1912.

Szymanowski, J, 2000. Kinetics and interfacial phenomena, *Solv Extr Ion Exch*, 18:729-751.

Taniguchi, N, 1974. On the basic concept of 'nano-technology,' in *Proceedings of the International Conference on Production Engineering*, pp *18-23* (Japan Society of Precision Engineering*:* Tokyo).

Taylor, E S and Lower, S K, 2008. Thickness and surface density of extracellular polymers on Acidithiobacillus ferrooxidans, *Applied and Environmental Microbiology*, 74:309–311.

Tratnyek, P G and Johnson, R L, 2006. Nanotechnology for environmental cleanup, *Nanotoday*, 1(2): 44-48.

Van Hove, M A, 2006. From surface science to nanotechnology, *Catalysis Today*, 113:133-140.

Zach, M, Hogglund, C, Chakarov, D and Kasemo, B, 2006. Nanoscience and nanotechnology for advanced energy systems, *Current Opinion Solid State Mater Sci*, 10:132-143.