Revised manuscript submitted to *Hydrometallurgy*, July 2004

TEACHING AND LEARNING ENVIRONMENTAL HYDROMETALLURGY

Fiona M. Doyle
University of California
Department of Materials Science and Engineering
Hearst Mining Building # 1760
Berkeley, CA 94720-1760
fiona@socrates.berkeley.edu

ABSTRACT

Environmental hydrometallurgy can be considered to comprise two distinctly different areas: environmentally compliant hydrometallurgy, and hydrometallurgy for environmental compliance. The latter includes both hydrometallurgical waste treatment and hydrometallurgical processes that can replace existing ones with attendant environmental benefits. This approach may find application in many fields well beyond those in which hydrometallurgy is traditionally encountered. Teaching environmental hydrometallurgy is truly coupled with learning, because this field is very much in its infancy. Students need a foundational knowledge base, but must learn to use these tools to think creatively, outside of the box. Cognizance of developments in other fields is also essential. Some of the most useful unit processes and new developments are discussed, such as biohydrometallurgy, ion exchange and membrane processes. These are examined as case studies that can be used to teach students to make future developments.

ENVIRONMENTAL HYDROMETALLURGY

What is meant by the term "environmental hydrometallurgy"? This term means different things to different individuals, and it is important to have a working definition before considering teaching and learning the topic. As depicted in Figure 1, the two principal categories considered here are environmentally compliant hydrometallurgy and hydrometallurgy for environmental compliance.

Environmentally compliant hydrometallurgy refers to traditional hydrometallurgical processes (i.e., the production of metals and metal-bearing compounds using aqueous processing), but performed in such a way as to ensure little or no adverse impact on the environment. When hydrometallurgical processes started to increase in popularity in the 1960's, there was a common perception that hydrometallurgy *was* environmentally compliant. The comparatively low temperatures used (relative to pyrometallurgical processes) were sometimes equated to low energy demands, and the perceived lack of air emissions was oft cited as demonstration that hydrometallurgy processes did not create as much pollution as pyrometallurgical processes. This perception did not stand up to rigorous scrutiny. Metals are recovered from many hydrometallurgical processes by electrowinning, which is inherently energy intensive (Bartlett and Malmquist, 1984). The perceived lack of air emissions from hydrometallurgical processes did not consider operations in which feed was being roasted or calcined. Moreover, pyrometallurgical plants have significantly improved their air emissions, further limiting the claims of hydrometallurgy to environmental superiority. At the same time, many environmental problems have emerged with hydrometallurgical processes. These have included the generation of reactive wastes, such as jarosite and goethite wastes from the electrolytic zinc process, accidental exposure of birds and other species to toxic lixiviants, and even releases of lixiviants.

Environmentally compliant hydrometallurgy adopts the philosophy that there are many potential benefits to the environment, as a whole, from producing many of our raw materials hydrometallurgically, and that it would be myopic to dismiss these potential benefits because of past mistakes. Instead, the field works to address the problems while retaining all the attendant benefits.

A recurring issue in modifying existing hydrometallurgical processes to improve their environmental impact is the additional costs involved. Many mining operations have modest profits, to say the least. Under such circumstances, it is hard to justify incurring additional costs, for example, to lower the amount of waste generated by a particular process, produce a more stable waste, or recycle water. By-product recovery, for example, is rarely profitable, on the basis of the value of the recovered product. However, this is an unrealistically restrictive measure of economics. One must, instead, compare the cost of recovering by-products, less their market value, with the true cost of not recovering the by-products.

It is difficult to assess the *true* cost of not recovering by-products. Certainly one can obtain estimates for the construction of relevant waste management facilities, and attendant operating costs, or for the minimum acceptable level of treatment and management of any associated sludges or precipitates. However, there have been numerous instances where wastes that were managed with best available technology at the time of generation, in full compliance with all applicable regulations, have subsequently been cited for non-compliance with later regulations. Acid mine drainage has frequently developed after the closure of mining and processing operations, and mobilized heavy metals from waste-rock, tailings and residues, but there are other examples. The cost of liability for the responsible party, such as the mining company or its successors, can be substantial in these instances. Assuming that environmental regulations are likely to become more stringent in the future, and that developing countries are likely to take aggressive steps to protect their environments, it is not unreasonable to assume that some of the wastes now being generated and disposed of in full compliance of all applicable regulations will, at some future date, become non-compliant, and require extensive expenditure. The true cost of not minimizing the waste volume or potential toxicity through recovering by-products must include these possible future liabilities. In the absence of a crystal ball, a realistic approach to estimating possible future costs would be to examine some previous case histories, and estimate the cost of taking similar remedial action. This exercise makes the economics of more aggressive strategies for waste minimization and by-product recovery look much more attractive.

Hydrometallurgy for environmental compliance covers hydrometallurgical processes used to assist in complying with waste discharge and management regulations, along with processes that lower the overall environmental impact of a particular process. In this case the core process may be far removed from the conventional realm of hydrometallurgy. Two significant areas within the overall category of hydrometallurgy for environmental compliance are the hydrometallurgical treatment of wastes and alternative, hydrometallurgical processes.

Although both of these approaches can be used in the commercial scale production of bulk mineral products and metals, they have much broader potential application. Hydrometallurgical processes are now usefully being applied to the treatment of obsolete electronic components (Gibson *et al.*, 2003; Koyoma *et al.*, 2003; Pilone and Kelsall, 2003), spent catalysts, and reactive process residues, to recovering metals from effluents generated in many manufacturing activities (Huang and Alfantazi, 2003), including the manufacture of integrated circuits and printed circuit boards (Ding *et al.*, 2003; Ewing *et al*., 2003), and to recycling water itself (Brown, et al. 2003). What would be recognized as hydrometallurgical processes, or variations thereof, to practitioners in this field are already supplanting more traditional manufacturing processes, because of numerous inherent advantages. Examples include the adoption of electro- and electroless-deposition methods for depositing copper metallization on integrated circuits (Braun, 1999; Lingk and Gross, 1998), and efforts to replace organic solvents with aqueous-surfactant systems. At the more experimental level, there is serious discussion of adopting “soft solution processing” (Yoshimura *et al.*, 2000) in a number of different areas, often driven by considerations of environmental acceptability and low energy intensity, but also by considerations of feasibility for scale up for commercial production, and the flexibility offered by biomimetic approaches. In these non-traditional fields, the terms “aqueous processing” or “solution processing” are more widely used than “hydrometallurgy”, but it is well to remember that the field of hydrometallurgy offers a rich bank of expertise to serve as a foundation in these emerging areas.

The foregoing comments should make it clear that environmental hydrometallurgy is *not* a clearly, or even loosely defined body of knowledge that can be presented as an independent course, or an identifiable topic within a course. Instead, environmental hydrometallurgy is probably best considered to be a way of thinking about *all* hydrometallurgy or solution processing, identifying how to accomplish a given goal in as environmentally acceptable manner as possible.

TEACHING AND LEARNING

No-one who has ever taught is likely to disagree with the assertion that teaching is always coupled with learning. At the most superficial level, there is much truth in the adage that one never really understands a subject until one teaches it. Teachers seriously committed to education must be able to assess how a student is viewing the material, and explain it in those terms. It may be necessary to cover the same ground in several different ways before the proverbial *eureka* moment, when the student finally understands. One cannot possibly explain a topic from so many different perspectives unless one truly understands it.

At a deeper level, teaching and learning are coupled in the way that many students teach their teachers as much or more than they learn. Much of what the teacher learns, for example a deeper insight into the human condition, or an update on popular culture, has nothing to do with the instructional matter. However, there are often moments when alert teachers are prompted by questions from students to consider a different perspective on problems with which they are grappling, or even consider a whole new avenue of inquiry in research. It is useful to recall that the word "education" comes from the Latin *e-*, out, and *ducere*, to lead. One cannot educate, or lead out, students without accompanying them on their journey, and there is much learning by both parties in this journey.

EDUCATION IN ENVIRONMENTAL HYDROMETALURGY

The very nature of environmental hydrometallurgy makes it challenging, but exciting to teach. Effective teachers must acknowledge to the students at the outset that they are also learning. The coupling between teaching and learning is probably stronger in the field of environmental hydrometallurgy than in many more established fields precisely because one is trying to teach a way of thinking rather than a prescribed package of facts, and this way of thinking continues to evolve. In many instances, one is teaching and learning to do things that are currently unknown. Consequently, routine exercises in problem solving, or class discussions, may narrow down the field of possible approaches, and focus effort. Occasionally real solutions to hitherto unsolved problems emerge.

Course Content

At the outset, a teacher must decide what material will be taught and (hopefully) learned in a course. Even though environmental hydrometallurgy can be considered to be a way of thinking about *all* hydrometallurgy or solution processing, as discussed in more detail below, factual information is certainly needed to provide the theoretical foundation for new approaches and processes. The student should also be made aware of the existence of relevant other fields in which fruitful solutions may be found. More subtly, the student should grasp that although the solution to a particular problem may not be currently lying in another field, waiting to be stumbled upon, the trajectory of developments in some fields make them likely candidates for relevant *future* developments. Finally, the student must be encouraged to think creatively "out of the box", but critically, and develop the confidence to do so.

Curriculum Structure

Having determined what factual information is to be conveyed, and thought processes nurtured, the instructor must decide how to structure the curriculum, and what pedagogical approach, or approaches, to adopt. These can have a profound effect on what the student takes from the course.

Table 1 compares two different curriculum structures. The conventional, principles-based curriculum structure presents factual information in a systematically structured manner. For an introductory hydrometallurgy course, this is likely to cover reaction stoichiometry, mass balances, thermodynamics of aqueous-solid systems, reaction kinetics, and engineering principles relevant to hydrometallurgical processes, including some economic analysis. Advanced courses would assume mastery of the first two topics, and tackle the remaining topics at a higher level. One could expect pertinent examples to be introduced to illustrate the principles throughout the course. However, case studies cannot easily be tackled comprehensively until all of the principles have been covered, at which point the case study can be "dissected" to see what principles are involved. Not only can it sometimes be difficult to identify all of the principles involved using this approach, but it does not provide experience with developing solutions to new problems.

An alternative curriculum structure starts with applications, or case studies, and identifies what factual information is needed to tackle this application. With judicious selection of case studies, the instructor can lead students to a wide range of appropriate principles, *because they see the need to master these principles.* Although it can be more difficult to ensure comprehensive coverage of principles following this approach, and those principles are unlikely to be introduced in an order that corresponds to that in standard text books, this approach has the huge benefit of leading the student through the steps of building up the process. For an evolving field such as environmental hydrometallurgy, this is more likely to equip the student to tackle new problems in the future. In addition, because of the general public awareness and widespread media coverage of environmental issues, case studies are rather easy to come by, and can be selected to draw upon current events or developments. This approach is more likely to capture the attention of students and generate enthusiasm. The astute instructor can then instill a deeper and more rigorous understanding of the technical issues involved.

Pedagogical Approach

The pedagogical approach adopted by an instructor can also have a significant effect on the enjoyment of students taking a course, as well as on their mastery and retention of material. Table 2 compares some different approaches suitable for classroom teaching in the sciences and engineering. The most conventional of these is lecturing, supplemented with examples, either in class, discussion sections or homework. Examinations test the mastery of the subject material. This widely accepted approach may be extremely effective at conveying factual information, for some students. Unfortunately, most of the time the student is passive, which can lead to boredom, or loss of attention. Furthermore, this approach implicitly establishes the instructor as an authority on the subject matter. There are compelling advantages in training students to view themselves as authorities, particularly for evolving subjects such as environmental hydrometallurgy. Assigning individual research topics, which are developed as papers, then presented to the entire class, can achieve this, to some extent, especially if these presentations are made at appropriate points throughout the course, rather than at the end. However, in my experience, team research topics and presentations are even more effective. In addition to training students to acquire information for themselves, team topics can be inherently more fun, and foster team work, which is becoming ever more essential in the workplace. The interdisciplinary nature of environmental hydrometallurgy makes it particularly important that students learn to work in groups of individuals with complementary backgrounds.

CASE STUDIES FOR AN APPLICATIONS-ORIENTED COURSE IN ENVIRONMENTAL HYDROMETALLURGY

An instructor who decides upon a principles-oriented course in environmental hydrometallurgy will be able to draw upon classical sources used in the instruction of hydrometallurgy, chemical engineering and related fields. The remainder of this paper is devoted to the less orthodox, applications-oriented approach. A few case studies that *could* be used in a course on environmental hydrometallurgy are examined, in the context of what principles they might illustrate. The objective here is not to provide a comprehensive guide for covering environmental hydrometallurgy, but rather to prompt the reader to start thinking about this *approach*, with the expectation that this will stimulate more ideas aligned to the reader's own interests.

Biohydrometallurgy

The broad field of biohydrometallurgy offers numerous case studies that might usefully be adopted as a mechanism for teaching fundamental concepts in environmental hydrometallurgy (Brierley and Brierley, 1993). The relative novelty of many of the processes, in conjunction with the potential of biological processing to be more benign than conventional approaches, is likely to intrigue many students. Table 3a suggests some case studies, covering both environmentally compliant hydrometallurgy and hydrometallurgy for environmental compliance. These encompass current practice, such as the oxidation of refractory gold ores (van Aswegen, 1993) and the biodegradation of toxins (Thompson, 1992), as well as processes that have been explored at the experimental level, but have not yet been adopted widely in commercial practice, such as the bioleaching of lateritic and bauxitic materials with heterotrophic bacteria (Andreev and Pol'kin, 1981; Bosecker, 1986; Groudev, 1987; McKenzie *et al.*, 1987; Natarajan *et al.*, 1997; Sukla and Panchanadikar, 1993), or the use of heterotrophs to upgrade industrial minerals (Friedrich *et al.*, 1991; Groudeva and Groudev, 1995; Turova *et al.,* 1996). The use of biological processes for removing trace metals from effluents and other solutions (McNew *et al.*, 1992; Nordwick *et al.*, 2003; Wahlquist *et al.*, 2003), and to replace solvents and etchants that are becoming increasingly problematic are additional areas where adaptation of hydrometallurgical processes could have a huge influence in a larger societal context.

Table 3b suggests a few of the principles that might be introduced in the context of rigorously examining biohydrometallurgical processing. The instructor is likely, for example, to want to include some rudimentary microbiology, particularly as this pertains to processing, such as what conditions are needed by different microorganisms, and how these can be provided during processing. The distinction between autotrophic and heterotrophic organisms is particularly crucial for process design and economic analysis. Biohydrometallurgy also offers an interesting approach to teaching chemical thermodynamics. Qualitative descriptors, such as “aerobic” and “anaerobic” could be probed to lead to the quantitative concept of electrode potential, and Nernst behavior. Armed with the tools to describe chemical environments quantitatively, the concepts of equilibrium and driving force for a reaction could be introduced, to identify whether processes are favorable or not. Numerous kinetic principles could be covered in the context of biohydrometallurgy. These might include macroscopic modeling of the overall rates of biologically mediated processes, and the effect of chemical parameters on these, examination of rate controlling processes in biological systems, with a view to optimizing these, or presentation of biologically mediated processes as examples of catalysis. The complexity of biohydrometallurgical processes make them particularly fertile ground for teaching systems analysis. It is essential that students considering environmental issues, either in the context of modifying existing hydrometallurgical processing practices or in the context of applying hydrometallurgy in other areas, are equipped to analyze the overall economic impact of a proposed action. As discussed earlier, this might entail making predictive estimates about the economic impact of future regulations and policies. Another area that might be explored while considering a biohydrometallurgical process is how to determine the overall environmental impact of a given process. Considerations such as the environmental impact of transporting raw materials to a processing site, and the environmental impact of generating energy needed for the process, should be included in such a treatment.

Table 3c presents some fields and industries in which reside knowledge and expertise relevant to biohydrometallurgy. Biological processes have long been used on large scales in sanitary engineering, and in winemaking and brewing. More recently, fermentation has become an established method for producing bulk commodities such as citric acid (Crueger and Crueger, 1984; Grewal and Kalra, 1995). A brief mention of how the understanding of the microbiological mechanisms at play in these processes has been used to optimize processing would illustrate the value of "borrowing" expertise from other fields. Brief discussion of reactor designs, process control strategies and consideration of raw material supply would be similarly useful.

Conventional Leaching

By far the largest current application of biohydrometallurgy is for oxidation of gold ores in which the gold is locked in a matrix, such as pyrite, that must be degraded before conventional leaching with cyanide. Cyanide leaching, along with other leaching processes, also provides numerous opportunities for teaching the principles of environmental hydrometallurgy.

Table 4a lists a few projects on conventional leaching that might be adopted to explore pertinent principles. The leaching of gold ores provides an interesting case study in which students can be taught to obtain and analyze factual information. Cyanide leaching provokes such an intense emotional response in many quarters that one way to introduce the topic might be to get students to search the internet, then have an impromptu class discussion on their findings. The outcry against cyanide leaching is not consistent with global demands for gold (I did once have a student who opted for wooden rings for him and his fiancée when they married, so as not to be responsible for any cyanide utilization, but such conviction is rare). Student teams might then research alternative methods, such as mercury amalgamation, halogen/halide systems (Ferron *et al.*, 2003), thiocyanate (Wan *et al.*, 2003) and thiosulfate (Dai *et al.*, 2003). This would invite exploration of some of the principles identified in Table 4b. Comparison of the mechanisms and driving forces for gold leaching with different lixiviants would demonstrate relative efficacies. Such studies would also be relevant to applications where organic solvents are being replaced with more benign aqueous solutions for cleaning in manufacturing operations. Mass balances and an analysis of side reactions would provide crucial input for rigorous comparison of the economics of using different lixiviants. Further consideration of the process economics would demonstrate the need for good kinetic models (Dixon, 2003). Gold leaching may also provides extensive case histories that might be used to examine regulatory issues, and their impact on engineering decisions.

For applications of leaching for environmental compliance, such as soil washing (York and Aamodt, 1990) and steam injection, students need a strong grounding in the principles and modeling of fluid flow in soils, permeable and fractured geological media (Bartlett, 1992). They also need an understanding of procedures used to sample groundwater and soils, and interpret monitoring data. Although these aspects are not generally covered in classical hydrometallurgy courses, they are of increasing importance, particularly with larger heap or *in situ* operations, such as those used for oxidized copper ores. Knowledge of the design, construction and maintenance of impoundment linings and other flow barriers is increasingly important.

As noted in Table 4c, other fields may also provide information that is pertinent to conventional leaching efforts. Geochemical models such as EQ3/6 (Wolery. 1992) and PHREEQC (Parkhurst and Appelo, 2001) might be used more widely than they have been. A better understanding of the processes of ore-body formation and weathering processes would also provide insight into how to better emulate natural processes in leaching, which is, I believe, key to improving the environmental acceptability of hydrometallurgy. Chemical engineering provides useful information on reactor design and process control. There is also appreciable overlap with conventional leaching and much of the expertise of the environmental engineer.

Ion Exchange Processes

The development of processes capable of separating ions in aqueous media was arguably *the* enabling technology responsible for the widespread adoption of hydrometallurgical processes in the second half of the twentieth century (Milbourne and Higgins, 1994). Recognition that the ion exchange and solvent extraction processes developed for processing nuclear materials could be scaled up for base metal processing spurred the development of new reagents. For application in closed loop cycles with relatively concentrated streams, such as found in hydrometallurgical processing of copper, solvent extraction has been more prevalent than ion exchange, because of the more straightforward design of equipment for continuous operation. Furthermore, the finite solubility of solvent extraction reagents in aqueous streams is not generally problematic in closed loops, because losses are limited. However, ion exchange has significant advantages for environmental applications (Jay, 2003). The most obvious technical advantage is the fact that because the functional groups are grafted onto the matrix of a solid substrate, there is a much lower likelihood of them being lost into the solution being treated, and contaminating said solution. A less obvious advantage is the fact that ion exchange is inherently more robust, inasmuch as it presents fewer health and safety concerns when not being overseen by skilled personnel. These and other considerations could be explored as a case study. Table 5a presents other possible case studies. These cover existing or old technologies, such as rare earth separations and the treatment of bleed streams in metallurgical processes (Diniz *et al.,* 2000; 2002), as well as technologies still under development, such as novel ion exchange materials, recovering raw materials from sea water, and using ion exchange to monitor water quality.

Table 5b suggests some of the principles that might be introduced in the context of case studies on ion exchange. Relevant chemistry might include a study of how different functional groups interact with simple cations and anions, along with charged and neutral complexes. Chelation might be considered in the context of the steric constraints imposed by the distribution of reactive functional groups over the resin. Interfacial phenomena such as capillarity and the electrical double layer might usefully be discussed. Thermodynamic principles that might be introduced could include sorption isotherms, calculation of species distributions in solutions to elucidate the influence of solution chemistry on the selectivity of a resin for a given solution component, and a treatment of competitive interactions or undesirable side reactions to understand the effect of solution components in lowering the effective capacity of a resin, or even destroying the reactive functional groups. Ion exchange is governed by rather complex kinetics. While there may be regions where the rate is controlled by the intrinsic kinetics of the ion exchange reaction, such as the outer layers of resin beads near the point where solution is admitted into a column, there are other regions where the rate is controlled by the transport of reacting ions, either by advective transport processes as solution flows through the resin column, or by diffusion as reactive ions move in response to activity gradients between the exterior and interior of resin beads. Thus ion exchange offers an ideal platform for teaching kinetic phenomena. Modeling of these phenomena could then lead directly into chemical engineering principles such as process modeling and reactor and process design, along with study of the manufacture of synthetic ion exchange materials, and the resultant chemical stability of these materials.

Table 5c identifies some fields and industries to which students might look for information relevant to ion exchange. Ion exchange has, of course, long been used for water softening and deionization. Numerous designs exist for commercial units; study of these could be most instructive. Useful information on the chemistry of functional groups and their interaction with ions can be found in the field of solvent extraction, along with expertise on stability and propensity to degradation. A brief introduction to basic principles within polymer science and technology will equip students with information on strategies for controlling the mechanical and transport properties of resin matrices, and the tolerance of different polymers to extremes of pH, ionic strength, and oxidizing agents. Within the earth sciences, much is known about the behavior of zeolites, clay minerals and other naturally occurring ion exchangers (Amphlett, 1964; Bodine and Doyle, 1995), which is particularly relevant to synthetic ion exchangers based on inorganic substrates (Deorkar and Tavlarides, 1998). Geochemical modeling techniques have also developed sophisticated approaches for modeling the ion exchange behavior in soils and sediments.

Membrane Processes

One general area that has seen little use in commercial hydrometallurgical processes but is likely to be increasingly important for environmental applications is membrane processes. Here, new materials developments are rapidly overcoming problems that have hitherto restricted widespread adoption. Ideally, a membrane could halt all fluxes besides the one desired, while withstanding operating conditions such as pressure, thermal, osmotic pressure and activity gradients, and abrasion forces, without being susceptible to fouling by fines. In practice, such ideal behavior has not been achieved, and compromises are needed. Some applications that might be considered to study membrane processes are summarized in Table 6a. Fewer of these are commercially relevant that for biohydrometallurgy or ion exchange, reflecting the nascent nature of this technology. Despite having been recognized for over three decades (Li, 1968; 1972), liquid membranes, which represent a potentially elegant configuration of solvent extraction, remain underutilized. Supported liquid membranes, which in principle are more amenable to continuous, commercial use (Sohn and Sohn, 1993; Harrington and Stevens, 2003; Van de Voorde *et al.*, 2003), are relatively rare in practice. Fluidized- and spouted-bed electrowinning, which promise to greatly improve the space-time yields of electrowinning, as well as allowing electrowinning to be done on more dilute streams, such as process effluents, would be most effective if the membranes could be ideally selective, permitting the transport of just one type of ion, while also presenting a low Ohmic resistance (Jiricny *et al.*, 2002a,b). Membrane processes could be invaluable for treating and recycling process water (Ho and Poddar, 2001; Valenzuela *et al.*, 2000: Wang *et al.,* 1998; Wang and Doyle, 1999), or for treating bleed streams in metallurgical processes. Environmental gains could also be reaped from advanced batteries and fuel cells, the ability to detoxify a wide range of process effluents, and biomimetic separations in product manufacture, such as continuously removing fermentation products from a fermentation process producing pharmaceutical products or commodity bioproducts.

Numerous fundamental principles could be addressed in exploring either the successes or the limitations of membrane processes. Osmosis and osmotic pressures may limit the performance of membranes, as may the interaction of colloidal particles with fine pores within membranes. Modern conducting polymers may find application for specific purposes. The thermodynamic concepts of activities, and the difference between concentration gradients and activity gradients might be addressed in this context, as might species distribution calculations. Elementary biology principles could also be introduced; cell walls are some of the most ideal membranes known, and it is instructive to consider the mechanisms whereby desirable species can move across these membranes, while undesirable species are blocked. Organisms capable of withstanding extreme environments, such as *Thiobacillus ferrooxidans* and similar acidophiles, which are proving useful for catalyzing the oxidation of sulfide minerals, are unusually effective in blocking the transport of protons. Membranes might also be used to demonstrate chemical engineering principles such as process modeling, reactor and process design and mass and energy balances.

Despite the limited adoption of membrane processes in hydrometallurgy, considerable success has been achieved in other fields, some knowledge of which should prove useful to students. As shown in Table 6c, these include desalination by reverse osmosis, and water treatment by electrodialysis. Polymer science is pertinent here, because ultimately, the limitations of membranes represent the limitations of the polymers from which the membranes are constructed. Medicine and bioengineering offer success stories. Dialysis of kidney patients, while far from ideal for an affected patient, nonetheless is an outstandingly successful separation process. Significant developments in materials stemming from endeavoring to imitate biological processes provide useful insight. Successful applications of membranes in biotechnology, for example ultrafiltration in the production of biofuels, or the production of protein-based biotherapeutics, are also fields from which useful lessons can be gleaned.

CONCLUSIONS

The field of hydrometallurgy offers many promising approaches for environmental applications, whether the objective is improving the environmental impact of conventional materials production, or replacing processes whose environmental impacts are becoming increasing unacceptable. In order to identify hydrometallurgical strategies that might improve the environment, it is necessary to look at current and future hydrometallurgical approaches critically, to assess their environmental impact along with other possible advantages and disadvantages. Accordingly, teaching and learning environmental hydrometallurgy involves communicating and mastering a way of thinking, as well as teaching tools that can be useful in this endeavor. This presents specific challenges and opportunities. One strategy is to teach principles in the context of judiciously selected case studies. This approach emphasizes the ability to break new ground, and hence is likely to teach students to identify what tools are needed to solve a specific problem, rather than to assume that there is a ready-made solution. In this context, the information and expertise available in related fields should not be overlooked. Students should be encouraged to think creatively, but critically, and to challenge conventional wisdom, provided that they do so rigorously.

REFERENCES

Amphlett, C.B., 1964, *Inorganic Ion Exchangers*, Elsevier, Amsterdam.

Andreev, P.I., and Pol'kin, S.I., 1981, *Tsvetn. Met.* **5,** p. 14.

Bartlett, R.W., and Malmquist, D.E., 1984, “Changing energy economics in nonferrous hydrometallurgy”, *Journal of Metals*, **36** (8) pp. 45-48.

Bartlett, R.W. 1992, *Solution Mining: Leaching and Fluid Recovery of Materials*, Taylor and Francis.

Bodine, D.L., and Doyle, F.M., 1995, "Removal of Cu^{2+}, Cd^{2+} and Mn(VII) from Dilute, Aqueous Solutions by Oxidized Bituminous Coal", *Treatment and Minimization of Heavy Metal-Containing Wastes,* Ed. J.P. Hagar, B. Mishra, C.F. Davidson and J. L. Litz, TMS, Warrendale, PA, pp. 81-93.

Bosecker, K., (1986) "Leaching of lateritic nickel ores with heterotrophic microorganisms", in *Fundamental and Applied Hydrometallurgy*, eds. R.W. Lawrence, R.M.R. Branion and H.G. Ebner, Elsevier Publishing Co., pp. 367-382.

Braun, E., 1999, "Copper Electroplating Enters Mainstream Processing", Semiconductor International, April, p58

Brierley, J.A. and Brierley, C.L., 1993, "Reflections on and considerations for biotechnology in the metals extraction industry", in *Hydrometallurgy Fundamentals, Technology and Innovation*, eds. J.B. Hiskey and G.W. Warren, SME, Littleton, CO, pp. 647-660.

Brown, M., Barley, B., and Wood, H., (eds), 2003, *Minewater Treatment: Technology, Application and Policy*, IWA Publishing (ISBN 1 84339 004 3)

Crueger, W., and Crueger, A., 1984, *Biotechnology: A textbook of industrial microbiology*, Sinauer Associates, Inc., Sunderland, MA, pp. 112-120.

Dai, X., Chu, C.K., Jeffrey, M., and Brewer, P., 2003, “A comparison of cyanide and thiosulfate leaching for the recovery of gold from a copper containing ore”, C.A. Young, A.M. Alfantazi, C.G. Anderson, A. James, D.B. Dreisinger, and B. Harris (Eds.) *Hydrometallurgy 2003, Proceedings of the 5th International Symposium*, TMS, Warrendale, PA, pp. 123-136.

Deorkar, N.V., and Tavlarides, L.L., 1998, “An adsorption process for metal recovery from acid mine waste: The Berkeley Pit problem, Env. Prog., **17** (2) 120125.

Ding, R., Evans, J. W. and Doyle, F. M., 2003, “An Investigation of the Electrodeposition of Copper Relevant to the Removal of Dissolved Copper from Semiconductor Industry Waste Streams”, in *Electrochemistry in Mineral and Metal Processing VI,* eds. R. Woods, G.

Kelsall and F.M. Doyle, The Electrochemical Society, Pennington N.J., P -2003-18, ISBN: 1-56677-401-2, pp. 326-335.

Diniz, C.V., Martins, A.H., and Doyle, F.M., 2000, "Uptake of Heavy Metals by Chelating Resins from Acidic Manganese Chloride Solution", *Minerals and Metallurgical Processing*, **17** (4), pp. 217-222.

Diniz, C.V., Doyle, F.M., and Ciminelli, V.S.T., 2002, "Effect of pH on the adsorption of selected heavy metal ions from concentrated chloride solutions by the chelating resin Dowex M-4195", *Separation Science and Technology*, **37** (14), 3169-3185.

Dixon, D.G., 2003, "Heap leach modeling – the current state of the art", C.A. Young, A.M. Alfantazi, C.G. Anderson, A. James, D.B. Dreisinger, and B. Harris (Eds.) *Hydrometallurgy 2003, Proceedings of the 5th International Symposium*, TMS, Warrendale, PA, pp. 289-314.

Ewing, W., Evans, J.W., and Doyle, F.M., 2003, "The effect of plating additives on the recovery of copper from dilute aqueous solutions using chelating resins", C.A. Young, A.M. Alfantazi, C.G. Anderson, A. James, D.B. Dreisinger, and B. Harris (Eds.) *Hydrometallurgy 2003, Proceedings of the 5th International Symposium*, TMS, Warrendale, PA, pp. 753-762.

Ferron, C.J., Fleming, C.A., Dreisinger, D., and O'Kane, T., 2003, Chloride as an alternative to cyanide for the extraction of gold", C.A. Young, A.M. Alfantazi, C.G. Anderson, A. James, D.B. Dreisinger, and B. Harris (Eds.) *Hydrometallurgy 2003, Proceedings of the 5th International Symposium*, TMS, Warrendale, PA, pp. 89-104.

Friedrich, S., Platonova, N.P., Karavaiko, G.I., Stichel, E., and Glombitza, F., 1991, "Chemical and microbiological solubilization of silicates", *Acta Biotechnologica*, **11** (3), pp. 187-196.

Gibson, R.W., Fray, D.J., Sunderland, J.G., and Dalrymple, I.M., 2003, "Recovery of Solder and Electronic Components from Printed Circuit Boards", in *Electrochemistry in Mineral and Metal Processing VI,* eds. R. Woods, G. Kelsall and F.M. Doyle, The Electrochemical Society, Pennington N.J., P -2003-18, ISBN: 1-56677-401-2, pp. 346-354.

Grewal H.S., and Kalra, K.L., 1995, "Fungal production of citric acid", *Biotechnology Advances*, **13**, pp. 209-234.

Groudev, S.N., 1987, "Use of heterotrophic microorganisms in mineral biotechnology", *Acta Biotechnol*., **7** (4) pp. 299-306.

Groudeva, V.I., and Groudev, S.N., 1995, "Microorganisms improve kaolin properties", *American Ceramic Society Bulletin*, **74** (6) pp. 85-89.

Harrington, P.J., and Stevens, G.W., 2003, "Recovery of chromium from electroplating rinse water: the development of a hollow fibre solvent extraction process", C.A. Young, A.M.

Alfantazi, C.G. Anderson, A. James, D.B. Dreisinger, and B. Harris (Eds.) *Hydrometallurgy 2003, Proceedings of the 5th International Symposium*, TMS, Warrendale, PA, pp. 1629-1640.

Ho, W.S., and Poddar, K., 2001, "New membrane technology for removal and recovery of chromium from waste waters", *Environ. Prog.,* **20** (1) pp. 44-51.

Huang, J.H., and Alfantazi, A.M., 2003, "Electrowinning of Cobalt from a Sulfate-Chloride Solution as an Option for Treatment of Industrial Effluents", *Electrochemistry in Mineral and Metal Processing VI,* eds. R. Woods, G. Kelsall and F.M. Doyle, The Electrochemical Society, Pennington N.J., P -2003-18, ISBN: 1-56677-401-2, pp. 336-345.

Jay, W.H., 2003, "Application of ion exchange polymers in copper cyanide and acid mine drainage", in C.A. Young, A.M. Alfantazi, C.G. Anderson, A. James, D.B. Dreisinger, and B. Harris (Eds.) *Hydrometallurgy 2003, Proceedings of the 5th International Symposium*, TMS, Warrendale, PA, pp. 717-728.

Jiricny, V., Roy, A., and J.W. Evans, 2002a, "Copper Electrowinning Using Spouted Bed Electrodes. Part I: Experiments with Oxygen Evolution or Matte Oxidation at the Anode" *Metall. & Mater. Trans. B*, **33**, pp.669-676.

Jiricny, V., Roy, A., and J.W. Evans, 2002b, "Copper Electrowinning Using Spouted Bed Electrodes. Part II: Copper Electrowinning with Ferrous Ion Oxidation as the Anodic Reaction", *Metall. & Mater. Trans. B*, **33**, pp.677-683.

Koyama, K., Tanaka, M., and Lee, J.-C., 2003, "Copper recovery from waste printed circuit boards", C.A. Young, A.M. Alfantazi, C.G. Anderson, A. James, D.B. Dreisinger, and B. Harris (Eds.) *Hydrometallurgy 2003, Proceedings of the 5th International Symposium*, TMS, Warrendale, PA, pp. 1555-1563.

Li, N.N., 1968, "Separating hydrocarbons with liquid membranes", US Patent 3,410,794.

Li, N.N., 1972, "Liquid membrane separation process", US Patent 3,696,028.

Lingk, C., and Gross, M. E.. 1998, "Recrystallization kinetics of electroplated Cu in damascene trenches at room temperature," *J. of Appl. Physics,* **84**, 5547.

McKenzie, D.I., Denys, L., and Buchanan, A., 1987, "The solubilization of nickel, cobalt and iron from laterites by means of organic chelating acids at low pH", *Int. J. Miner. Process.*, **21**, pp. 275-292.

McNew, E.B., Barnes, J.M., and Torma, A.E., "A biosorption approach to removal of trace concentrations of uranium and heavy metals from aqueous solutions," in S. Chander (Ed.) *Emerging Process Technologies for a Cleaner Environment*, SME, Littleton, CO, pp. 191-196.

Milbourne, J.C., and Higgins, I.R., 1994, “Recovery of uranium using continuous countercurrent ion exchange (CCIX^{TM})”, in *Separation Processes: Heavy Metals, Ions and Minerals*, M. Misra (Ed.), TMS, Warrendale, PA, pp. 3-14.

Natarajan, K.A., Modak, J.M., and Anand, P., 1997, "Some microbiological aspects of bauxite mineralization and beneficiation", *Minerals and Metallurgical Processing*, (May), pp. 47-53.

Nordwick, S., Zaluski, M., Bless, D., and Trudnowski, J., 2003, “Development of SRB treatment systems for acid mine drainage”, C.A. Young, A.M. Alfantazi, C.G. Anderson, A. James, D.B. Dreisinger, and B. Harris (Eds.) *Hydrometallurgy 2003, Proceedings of the 5th International Symposium*, TMS, Warrendale, PA, pp. 1837-1846.

Parkhurst, D.L., and Appelo, C.A.J., 2001, “PHREEQC – a computer program for speciation, batch reduction, one-dimensional transport, and inverse geochemical calculations. Version 2.3.” *U.S. Geol. Survey Water Res. Invest. Report* 99-4259.

Pilone, D., and Kelsall, G.H., 2003, “Metal recovery from electronic scrap by leaching and electrowinning IV”, C.A. Young, A.M. Alfantazi, C.G. Anderson, A. James, D.B. Dreisinger, and B. Harris (Eds.) *Hydrometallurgy 2003, Proceedings of the 5th International Symposium*, TMS, Warrendale, PA, pp. 1565-1575.

Sohn, J.S., and Sohn, H.J., 1993, “Extraction of lithium with a supported liquid membrane”, in J.B. Hisky and G.W. Warren (Eds), *Hydrometallurgy Fundamentals, Technology and Innovation,* SME, Littleton, CO, pp 763-775.

Sukla L.B. and Panchanadikar, V., 1993, "Bioleaching of lateritic nickel ore using a heterotrophic micro-organism", *Hydrometallurgy*, **32,** pp. 373-379.

Thompson, L.C., 1992, “Developments in Mine Waste Biotreatment Processes”, in S. Chander (Ed.) *Emerging Process Technologies for a Cleaner Environment*, SME, Littleton, CO, pp. 197-204.

Turova, E.S., Avakyan, Z.A., and Karavaiko, G.I., 1996, “The role of the bacterial community in transformation of iron minerals in kaolin”, *Microbiology*, **65** (6), pp. 730-735 (pp. 837-843 in original Russian).

Valenzuela, F., Aravena, H., Basualto, C., Sapag, J., Tapia, C., 2000, “Separation of Cu(II) and Mo(IV) from mine waters using two microporous membrane extraction systems”, *Sep. Sci. Technol.*, **35** (9) pp. 1409-1421.

van Aswegen, P.C., 1993, “Commissioning and operation of bio-oxidation plants for the treatment of refractory gold ores”, in J.B. Hisky and G.W. Warren (Eds), *Hydrometallurgy Fundamentals, Technology and Innovation,* SME, Littleton, CO, pp. 709-725.

Van de Voorde, I., Vander Linden, J., Vanderkerken, S., Dhanens, H., and De Ketelaere, R.F., 2003, "Metal waste prevention by SLM", C.A. Young, A.M. Alfantazi, C.G. Anderson, A. James, D.B. Dreisinger, and B. Harris (Eds.) *Hydrometallurgy 2003, Proceedings of the 5th International Symposium*, TMS, Warrendale, PA, 1971-1981.

Wahlquist, B., Pickett, T., Adams, J., and Maniatis, T., 2003, "Biological water treatment for dissolved metals and other organics", C.A. Young, A.M. Alfantazi, C.G. Anderson, A. James, D.B. Dreisinger, and B. Harris (Eds.) *Hydrometallurgy 2003, Proceedings of the 5th International Symposium*, TMS, Warrendale, PA, pp. 1903-1912.

Wan, R.Y., Brierly, J.A., Acar, S., and LeVier, K.M., 2003, "Using thiocyanate as lixiviant for gold recovery in acidic environment", C.A. Young, A.M. Alfantazi, C.G. Anderson, A. James, D.B. Dreisinger, and B. Harris (Eds.) *Hydrometallurgy 2003, Proceedings of the 5th International Symposium*, TMS, Warrendale, PA, pp. 105-122.

Wang, Y., Thio, Y.S., and Doyle, F.M., 1998, "Formation of semi-permeable polyamide skin layers on the surface of supported liquid membranes", *J. Membrane Sci.* **147,** pp. 109-116.

Wang, Y., and Doyle, F.M., 1999, "Formation of epoxy skin layers on the surface of supported liquid membranes containing polyamines" *J. Membrane Sci*., **159,** pp. 167-175.

Wolery, T.J., 1992, "EQ3/6. A software package for geochemical modeling of aqueous systems: package overview and installation guide (Version 7.0): UCRL-MA-110662-PT-I", Lawrence Livermore National Laboratory, Livermore, California (http://eed.llnl.gov/geosciences/esd/geochem/eq36.html).

York, D.A., and Aamodt, P.L., 1990, "Remediation of contaminated soil using heap leach mining technology", F.M. Doyle (ed.), *Mining and Mineral Processing Wastes*, SME, Littleton, CO, pp. 255-259.

Yoshimura, M, Suchanek, W.L., and Byrappa, K., 2000, "Soft Solution Processing: A Strategy for One-Step Processing of Advanced Inorganic Materials", *MRS Bulletin*, September, pp. 17-27.

Table 1. Comparison of Principles-Oriented and Applications-Oriented Curricula

Orientation of curriculum	**Structure**	**Advantages**	**Disadvantages**
Principles-oriented	▪ Systematic structuring of factual information ▪ Subsequent examination of case studies	▪ Logical, optimal progression of principles ▪ Corresponds to structure of many textbooks	▪ Not always clear how some of the principles apply to a specific case study ▪ Sometimes difficult to see how to approach a new problem
Applications-oriented	▪ Judiciously selected case studies ▪ Thoughtful identification of factual information needed for specific applications	▪ Provides guidance on how one can systematically develop new processes ▪ Easy to update material with cutting-edge examples	▪ Order in which principles are introduced may not be optimal ▪ Any textbook can only be supplemental

Table 2: Comparison of Different Pedagogical Approaches

Pedagogical approach	Advantages	Disadvantages
Straightforward lecturing/examples/ examinations	■ Very effective for accurately conveying factual information	■ Passive for the student ■ Can be boring ■ Colored by experiences and limitations of the instructor
Individual research/ papers/presentations	■ Encourages individual interests and creativity ■ Allows "out of the box" thinking	■ Quality assurance problematic
Team research/papers/ presentations	■ Most representative of real-world problem solving ■ Usually popular with students ■ Inbuilt critiquing encourages critical evaluation of "wild ideas" ■ Enhances likelihood of considering other fields	■ May have uneven distribution of work ■ Difficult to assign individual grades

Table 3a: Possible projects in biohydrometallurgy

Environmentally Compliant Hydrometallurgy	Hydrometallurgy for Environmental Compliance
Oxidation of refractory gold ores	Biodegradation of toxins such as cyanide
Treatment of laterites and bauxites with heterotrophs	Direct and indirect removal of metals from effluents by bacteria, organisms and biological materials
Upgrading of industrial minerals	Biological alternatives to solvents and etchants

Table 3b: Principles that might be tackled in the context of biohydrometallurgy

Microbiology	Chemical Thermodynamics	Kinetics	Systems Analysis
Classification of microorganisms	Quantitative description of different environments	Rate models	Economic analysis
Substrates, nutrient and environmental requirements	Favorable and unfavorable processes	Identification and manipulation of rate-controlling step	Current and future regulatory issues
Adaptability of microorganisms and colonies	Energy balances	Catalysis	Assessment of environmental impact

Table 3c: Fields and industries related to biohydrometallurgy of which students should be cognizant.

Environmental Engineering	Chemical Engineering/Pharmaceuticals	Fermentation technology
Sanitary engineering	Reactor design	Bulk commodities – citric acid, etc.
Bioremediation of toxic spills	Process control	Winemaking and brewing
	Raw material selection/costing/acquisition	

Table 4a: Possible projects in conventional leaching

Environmentally Compliant Hydrometallurgy	**Hydrometallurgy for Environmental Compliance**
Cyanide leaching of gold ores and non-cyanide lixiviants	Washing of soils contaminated by radionuclides
Heap and *in situ* leaching of oxidized copper ores	Steam injection for removal of non-aqueous phase liquid (NAPL) contaminants
Leaching of non-bauxitic aluminum ores	Use of “lixiviants” to replace organic solvents for cleaning

Table 4b: Principles that might be tackled in the context of conventional leaching

Geological engineering	**Chemistry**	**Kinetics**	**Systems Analysis**
Fluid flow in geological media	Electrochemical mechanisms and driving forces	Electrochemical kinetics	Economic analysis
Design, construction and maintenance of engineered barriers to flow	Stoichiometry, mass balances and side reactions	Analysis of rate models	Current and future regulatory issues
Sampling of groundwater and soils	Comparison of lixiviants	Longevity of different species in the environment	Assessment of environmental impact

Table 4c: Fields and industries related to conventional leaching of which students should be cognizant.

Geology	**Chemical Engineering**	**Environmental Engineering**
Geochemical modeling	Reactor selection, design and modification	Remediation of contaminated sites
Ore-body formation and weathering processes	Process monitoring and control	Landfill construction

Table 5a: Possible projects related to ion exchange

Environmentally Compliant Hydrometallurgy	Hydrometallurgy for Environmental Compliance
Treatment of bleed streams in metallurgical processes	Selective removal of metals from effluents
Rare earth separations	By-product recovery
Recovery of raw materials from sea water	Processing of nuclear fuels
Comparison of overall environmental impact of ion exchange and solvent extraction routes	Monitoring of water quality

Table 5b: Principles that might be tackled related to ion exchange

Chemistry	Thermodynamics	Kinetics	Chemical engineering
Interaction of different species with functional groups	Sorption isotherms	Reaction kinetics	Manufacture of synthetic ion exchange materials
Chelation and steric limitations	Influence of solution chemistry on selectivity	Transport kinetics	Process modeling
Interfacial phenomena	Adverse effects of solution components		Reactor and process design

Table 5c: Fields and industries related to ion exchange of which students should be cognizant.

Water Treatment	Solvent Extraction	Polymer Science and Technology	Earth Sciences
Deionization	Chemistry of functional groups	Control of mechanical properties of matrix	Clay minerals and zeolites
Water softening	Expertise on stability and degradation	Control of transport properties of matrix	Ion exchange behavior in soils and sediments
Design of commercial units		Tolerance of different polymers to extreme chemical conditions	

Table 6a: Possible projects related to membrane processes

Environmentally Compliant Hydrometallurgy	Hydrometallurgy for Environmental Compliance
Emulsion and supported liquid membranes	Advanced batteries and fuel cells
Fluidized- and spouted-bed electrowinning	Detoxification of effluents
Treatment and recycling of process water	Biomimetic separations in product manufacture and synthesis
Treatment of bleed streams in metallurgical processing	

Table 6b: Principles that might be tackled related to membrane processes

Chemistry and Physics	Thermodynamics	Biology	Chemical engineering
Osmosis and osmotic pressure	Activity coefficients; concentration and activity gradients	Transport processes in cells	Process modeling
Colloid chemistry and interfacial phenomena	Species distribution calculations	Mechanisms whereby organisms withstand extreme environments	Reactor and process design
Electronic conductivity in polymers	Barriers to spontaneous processes		Mass and energy balances

Table 6c: Fields and industries related to membrane processes of which students should be cognizant.

Water Treatment	Polymer Science and Technology	Medicine and bioengineering	Biotechnology
Desalination by reverse osmosis	Control of transport properties for different species	Dialysis for kidney patients	Ultrafiltration separations in biofuel production
Reduction of BOD in wastewaters	Control of mechanical properties	Biomimetic materials	Production of protein-based biotherapeutics
Electrodialysis processes			

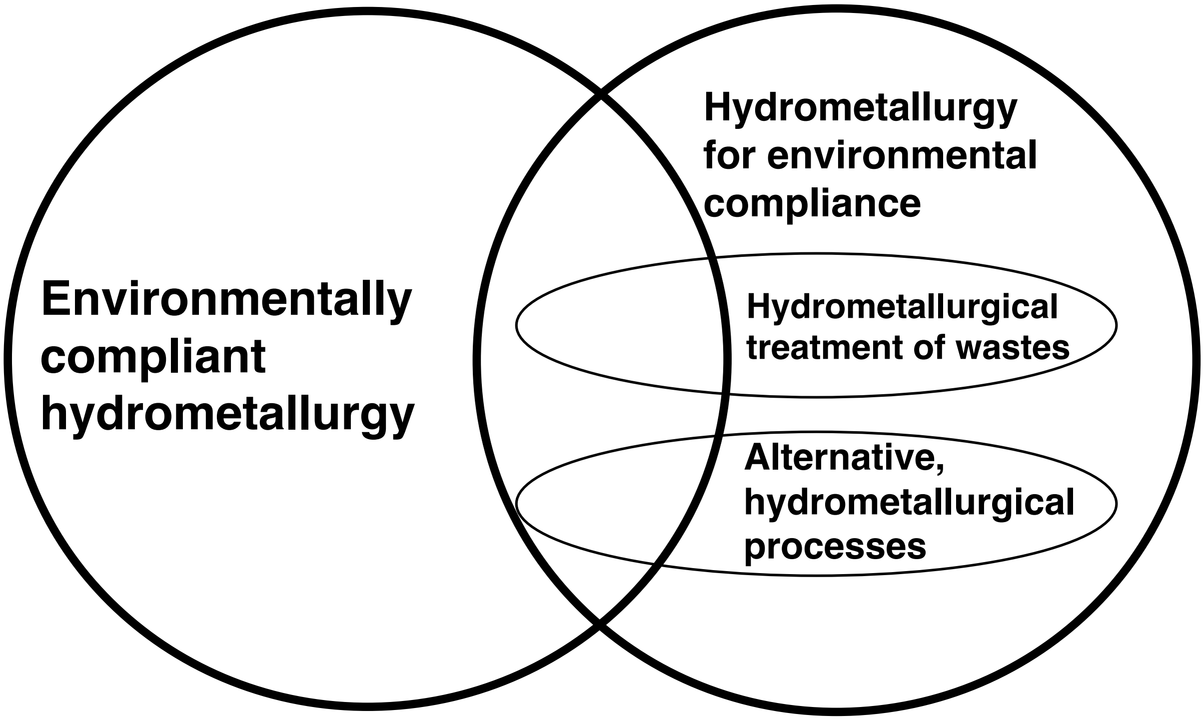

Figure 1: Conceptual view of the field of environmental hydrometallurgy