

Journal of Mining and Metallurgy, 41 B (2005) 17 - 32

TEACHING AND LEARNING ADAPTIVE HYDROMETALLURGY- NANOHYDROMETALLURGY

B. Pešić[#]

Department of Materials Science and Engineering,
College of Engineering, University of Idaho,
Mc Clure Hall, Moscow, ID 83844-3024, USA

(Received 29 December 2004; accepted 20 January 2005)

Abstract

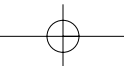
The weakness of the U.S. mining industry has caused a significant decline in academic programs in mining and metallurgical engineering in the U.S. The author's view on the reasons for such weaknesses is presented in a historical prospective covering some key events within the last 30 years. Arguably, the decline of U.S. mining industry is due to many reasons, the most important being the lack of modernization, the difficulty to comply with stringent environmental laws, and global market forces, are the most important. The importance of emerging nanotechnologies is viewed as an opportunity for the evolution of one component of metallurgical engineering— hydrometallurgy—into nanohydrometallurgy, thus extending its viability.

Keywords: Please provide 4-5 keywords

1. Introduction

Extractive metallurgy has three components with overlapping aspects:

[#] **Corresponding author:** pesic@uidaho.edu



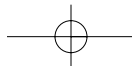
B. Pešić

hydrometallurgy, pyrometallurgy, and electrometallurgy. In combination with pyrometallurgy, hydrometallurgy is an important contributor to the foundation of every extractive metallurgy academic program. As the name suggests, hydrometallurgy as an extractive metallurgy discipline involves the recovery of metals by wet methods, i.e. from aqueous solutions. The third contributor to the extractive metallurgy—electrometallurgy—can also be regarded as a subset of hydrometallurgy, if electrowinning and/or electrorefining of metals is performed from aqueous solutions. If, however, these two electrometallurgical operations are performed from molten salts, requiring much higher processing temperatures, then electrometallurgy may also be classified as pyrometallurgy. (It is not uncommon to hear aluminum electrometallurgical plants referred to as smelters, for example.) Some consider electrometallurgy to be a stand-alone extractive metallurgy discipline.

Hydrometallurgy involves various processing steps, such as dissolution, separation, concentration, purification, and metal winning. Except for separation, which may be physical, each of these steps relies on the chemical principles of oxidation, reduction, solvation, chelation, hydrolysis, etc. Dissolution of metals, ores, and concentrates is usually the first step in a typical hydrometallurgical flowsheet, followed by physical separation of phases, most likely by filtration. Solution purification and concentration steps may involve precipitation, solvent extraction, and ion exchange chemistries. Winning of metals from solutions is most widely achieved by electroreduction in an electrowinning process, or by other reduction methods, e.g. utilization of gaseous reductants, such as hydrogen, sulfur dioxide, etc.

It is important to recognize that each of the above processing steps is also found in traditional analytical chemistry (qualitative and quantitative); thus it is possible to regard hydrometallurgy as applied analytical chemistry, the sole difference being the scale of the involved steps. The identification with analytical chemistry suggests that the solutions to the relevant industrial unit operations may be found in the procedures already developed by analytical chemists.

In the academic world, all hydrometallurgy courses belong to schools with strong mining and extractive metallurgy programs, the strength of which is tied directly to the strength of the mining industry. Due to the ongoing economic globalization the strength of the mining industry has substantially



changed. In some countries, the mining industry has been growing; in others, such as the U.S., the mining industry is struggling for survival. Consequently, many mining schools in this country have been shut down, or barely exist. From the extractive metallurgy (more specifically hydrometallurgy) teaching point of view, it is difficult to maintain the programs in the traditional form unless some programmatic modifications have been implemented. Hydrometallurgy must transform and adapt to the current industrial climate in order to protect its own viability.

2. Possible Reasons for a Demise of Mining/Extractive Metallurgy in the U.S.A.

Perhaps the turning point for the health of U.S. Mining Industry can be traced back to the 1970s. This decade was politically turbulent (the end of a Vietnam war, the ongoing 'cold war', the Middle East instability), also characterized by severe price instability for raw materials, such as oil, minerals and metals. The high oil prices made many U.S. oil corporations extremely rich. Having achieved control of oil as an important energy resource, the oil corporations boldly moved to control another strategically important resource: minerals. With plenty of cash at hand, major oil corporations went on a shopping spree, buying one mining corporation after another.

For example:

- Anaconda was purchased by Atlantic Richfield Corporation (ARCO) in 1977.
- Standard Oil of Ohio (SOHIO) bought out Kennecott in 1981.
- Gulf Resources controlled the Bunker Hill Mine.
- Duval Corporation, a textbook example for copper production based entirely on hydrometallurgical principles, was controlled by Pennzoil.

The '70s saw exceptional economic volatility, reflected in oil and metal prices [1]. The year of 1973 was the year of greatest economic activity, only to be followed by a severe recession in 1975, with the oil embargo during 1974 being its major culprit. The 1976 and 1977 were years of rapid

B. Pešić

economic recovery. The 1970s have another important event: the birth and growth of the U.S. Environmental Protection Agency (EPA) [2]. The early 1980s were characterized by yet with another severe recession. Flanked by recessionary effects on one side and by the EPA on another, the oil corporations began losing the interest in the metals business. Not keen on investing in the new processing technologies to comply with the tightened EPA standards, the oil corporations shut down many mining operations, or put the mines up for sale. Thus Anaconda, which once was among the companies representing the Dow Jones Index, was shut down in 1983. Gulf Resources shut down the Bunker Hill Mine in 1982, and Duval's plants were fully dismantled in the mid 1980s. Kennecott survived but only after a shut down in 1985, followed by a name-change, and the resumption of operations in 1987 under the new ownership by British Petroleum of America. After spending substantial amounts of money for modernization, BP sold the company to the current owner, Rio Tinto Zinc Corporation.

The period of closures and resale of major U.S. mining corporations resulted in the closures of all mining/extractive metallurgy R&D corporate labs. Kennecott initially reduced the number of labs from two to one located in Salt Lake City, Utah, only to shut it down permanently in the mid 1980s. Anaconda's, Bunker Hill's, Duval's R&D facilities all disappeared with the closure of their respective corporations. Today, with a few symbolic exceptions, the mining corporations in the U.S. are operating without R&D programs of their own. Because the R&D labs were major employers of the university graduates with advanced degrees, it became evident that the market for those with highest education in the profession was quickly disappearing.

The lack of interest for any research related to mining/extractive metallurgy was also growing within the federal and state governments. Thus, the National Science Foundation eliminated a small program for this type of research in the mid 1980s. The U.S. Bureau of Mines, together with the U.S. mining schools, was the only source for the relevant research, but this was soon to change. The prolonged poor health of the U.S. mining industry left an ill effect on the commitment of U.S. government for R&D expenditures related to mineral resources and production. With time, the funding of U.S. Bureau of Mines operations declined. Despite its rich history characterized by significant technological contributions to the mining/extractive metallurgy and the

Teaching and learning adaptive hydromellurgy-nanohydrometallurgy

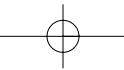
country in general, the 104th Congress in the so-called “Contract with America” decided to close the Bureau; it ceased to exist on March 30, 1996.



Fig. 1 Demolition of Bunker Hill Mine smoke stacks by U.S. Army Corps of Engineers. A symbolic reminder of the decline of U.S. mining industry.

The mining schools affiliated with the U.S. universities were the last place left for any pertinent research. However, faced with industrial clients disinterested in any research, and the loss of federal funding, the U.S. schools with mining/extractive metallurgy programs began experiencing some serious existential problems. Besides the lack of research funding, the loss of a job market compounded the problems with poor student enrollment, which in turn was providing the evidence to the university administrators that the programs are not viable and should be either modified or closed. Consequently, many mining/extractive metallurgy university programs have been shut down in the U.S. in the last 20 years.

The College of Mines at the University of Idaho is a specific example of the trend. Regardless of its very rich history, and the fact that the College of Mines was one of the key contributing programs that founded the University of Idaho, the College of Mines ceased to exist on July 1, 2002, after 100 years



B. Pešić

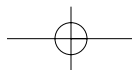
of existence. The mining engineering program was permanently closed, while the metallurgical engineering program, with adequate curriculum modifications, was transformed into a materials science and engineering program.

In contrast to the situation in the U.S., in Canada the major Canadian mining corporations have kept their identities. Moreover, Cominco, Noranda, and INCO, for example, were even able to sustain their own R&D facilities and programs. (Canada is presented here for comparison because of its location; the similar economic forces simultaneously present in both countries can produce comparable results). Despite of definite financial distress throughout the period discussed, the Canadian government never abolished its national laboratory responsible for mining and mineral industries. The mining/extractive metallurgy schools all survived and continue to offer relevant programs. While in the U.S. there was an obvious disconnect between the academia and the mining industry, and between the U.S. Bureau of Mines and the mining industry, the same was not true in Canada. In contrast, the interface between academia, the mining industry, and the government was successfully built and maintained. The mining schools formed Canadian Mining Education Council (CMEC), while the mining industry formed Canadian Mining Industrial Research Organization (CAMIRA), each with the objective to communicate better among themselves, the participating members, and the government, and to deal together on the common issues of funding, research, infrastructure, recruiting, and curriculum.

3. Industrial R&D Investments

If the present trend continues, teaching of hydrometallurgy in the U.S. schools cannot survive unless some modifications are made and hydrometallurgy makes itself more attractive. The hydrometallurgy academics must face the economic reality and the shear strength of market forces. In this regard, it is mandatory to adapt the course curriculum to fit the needs of the stronger industry. For demonstration purpose, let us compare the relatively weak mining industry to the computer industry.

In spite of the fact that mining operations in the U.S. are among the largest



Teaching and learning adaptive hydromellurgy-nanohydrometallurgy

in the world, in reality this industry is small contributor to the overall GDP of the country. Mining is energy intensive, requires the movement of enormous amount of materials, and visually may leave an impression of being of colossal size. Phelps Dodge, the largest copper producer in the U.S., moves close to a million tons of ore a day in their mining operations in order to perform heap leaching, solvent extraction, and electrowinning of copper. If one assumes that the ore contains 0.2% Cu and that all is recovered and sold, that would constitute revenue of about \$1.5B per year, varying somewhat with the price of copper. Although impressive, the revenue number is still small when compared to the revenues by the largest corporations from another industry, the computer industry, such Dell Computer (\$30B/year), Hewlett Packard-Compaq (\$64B/year), and IBM (\$86B/year).

The dramatic difference between these two industries is also reflected in the R&D spending. Mining industry R&D in the U.S. is nonexistent, while the computer industry is driven by innovation, and is thus compelled to invest billions of dollars in research and development (Table 1).

*Table 1. R&D Spending Examples by the Computer Industry in 2002.
In Billions of U.S. dollars [3]*

Motorola	6.00
Intel	5.16
Microsoft	5.26
IBM	4.70
Cisco	5.30
Hewlett-Packard	2.45
Sun	2.32

The computer industry is a genuine leader of innovation. The need for faster computers has forced the industry toward the never-ending miniaturization of electronic components, which can only be achieved by development and implementation of novel technologies. Micron-size components are no longer acceptable, and now the focus is to design the same components on a molecular, or a few atoms scale. This industry has led the U.S. into a completely different world, the world of nanotechnology.

B. Pešić

4. Nanotechnology- New Technological Horizons

Nanotechnology is regarded as the industrial revolution of the 21st century. It rests on the discovery that *the properties* of materials on the atomic scale are different from those in the bulk. Because all natural systems are governed by the atomic and molecular properties at a nanoscale, the research is now seeking systematic new approaches to develop new products and technologies by controlling matter at the same scale. Due to recognized importance of nanotechnology, many governments are increasing the budgets for the pertinent science and technology development. Thus in 2001, the U.S. administration [4] raised nanoscale science and technology programs to the level of a federal initiative, officially referring to it as the National Nanotechnology Initiative (NNI). The budget for FY 2001 was \$464M, which was increased to \$604M in FY 2002, and projected at \$709.9M for FY 2003.

Among many planned outcomes for the NNI, two are especially important.

1. Establish 10 new centers and networks with a full range of nanoscale measurements and fabrication facilities, and
2. Ensure that 50% of research institutions' faculty and students have access to the full range of nanoscale research facilities by FY 2005.

As a result, the U.S. National Science Foundation (NSF) has made nanotechnology research a top priority in 2002 and 2003, with respective funding levels of \$199 and \$221M [5]. Other countries are in the same race. In Canada, due to collaboration between the government of Canada and the Province of Alberta, about \$120M will be invested to build National Institute for Nanotechnology [6] at the University of Alberta. Overseas, the Taiwanese government has invested \$290M to build a new nanotechnology research center [7].

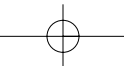
These are only a few examples to demonstrate the major stream for the flow of current and future research dollars. Those involved in research should prepare to adapt themselves adequately.

5. Hydrometallurgy Survival Route-Pathway to Nanohydrometallurgy

There are numerous questions in connection to survival of hydrometallurgy. From the previous discussion, it appears that hydrometallurgy must embrace nanotechnology, but the question then emerges: to what extent? Nanotechnology topics are of little use for typical extractive metallurgy practitioners, and vice versa, nanotechnology is not interested in production of bulk metals and materials. Perhaps the best approach is to have two types of hydrometallurgy. The traditional hydrometallurgy should continue to exist in its original form in the schools that managed to keep the extractive metallurgy programs. This is of little significance for the U.S. schools, but of almost intact importance for the schools abroad. Next, hydrometallurgy has an important opportunity to grow into a new hydrometallurgy, and become an integral component of nanotechnology. The time is right for nanohydrometallurgy.

Would it be difficult for a traditional hydrometallurgist to develop a new nanohydrometallurgy course and research program? The answer is mixed. Regarding the academic teaching, there should be few difficulties because the physical-chemistry principles governing the production of bulk materials are the same as the principles for production of materials on a nanoscale. Actually, a traditional hydrometallurgist may even have some competitive advantage in these efforts, because the fundamental and practical knowledge in many areas is pertinent to nanotechnology. For example, wet etching of silicon wafers in the computer industry is in principle no different than the leaching of ore and minerals in extractive metallurgy. Adsorption processes are very important in many nanotechnologies.

Controlled adsorption of molecules to form uniform assemblies, as a unit step in the overall nanoprocessing, is popularly called the self-assembly of monolayers (SAM). But the chemical principles governing the formation of nanostructures with the SAM approach are no different from the chemical principles of adsorption of collectors and promoters on minerals in a flotation plant. The surface reaction issues with regard to selectivity of bonding, physical or chemical type of bonding, partial or full coverage of a surface, monolayer vs. multilayer stacking of molecules, and hydrophobic vs. hydrophilic surface properties, are identical whether the processing is done on a large or on a nanoscale.



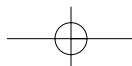
B. Pešić

Colloidal chemistry principles are often used in hydrometallurgy. Understanding colloidal chemistry is also critically important for the development of many nanotechnologies based on sol-gel processing. Sol-gel processing is a wet chemical route to synthesis of a colloidal suspension of solid particles or clusters in a liquid (sol). Subsequently a dual phase material forms, consisting of a solid skeleton filled with a solvent (wet gel) through the sol-gel transition (gelation). Little distinction between traditional and nanohydrometallurgy can be found regarding the application of colloidal chemistry principles.

Perhaps the smallest difference in chemical principles between the hydrometallurgies on a large and a nanoscale is in the area of electrochemistry. Electrons must be delivered to cations on a cathode whether the objective is to produce large tonnage of metal, as in an electrowinning plant, or thin metal films of only a few nanometers thickness, as in a computer hard disk manufacturing plant.

Extractive metallurgy plants are users of large quantities of water in various unit operations (leaching, precipitation, washing, purification, etc.), but the computer industry is an even a bigger user of water. The issue of water quality is essential for this industry, whether water is used for rinsing of wafers or for preparation of ultra pure solutions for electrochemical deposition of thin films. In parallel, the water quality and the solution purification issue is also important in many hydrometallurgical operations for production of large tonnage of metals. Either industry must use identical chemical principles (ion exchange, solvent extraction) for purification purposes. Ion exchange is a key hydrometallurgical unit operation for production of many rare earth metals, but also a key water purification approach by the computer industry.

While the above discussion tries to make a point that there would be little difficulty for a traditional hydrometallurgist to develop a nanohydrometallurgy *course*, the reality is different considering the development of a nanotechnology *research program*. In this regard, there are two major obstacles. One is the requirement for very expensive research equipment infrastructure for analytical and processing purposes. The characterization of nanomaterials requires highly sophisticated (and expensive) equipment, such as transmission electron microscopes, atomic force and scanning tunneling microscopes, scanning electron microscopes



Teaching and learning adaptive hydromellurgy-nanohydrometallurgy

with subnanometer resolution and also electron-beam lithographic capabilities, scanning near field optical microscopes (SNOM), specialized x-ray equipment, film thickness measurement equipment (ellipsometers), magnetometers (equipped for cryogenic measurement conditions), etc. On the processing side, the research lab should have the equipment for patterning by photolithography (mask aligners and steppers) and plasma etching, lasers, and very expensive vacuum pumping systems. Second, the additional expense is that the processing equipment must be placed in laboratories satisfying clean room specifications. The huge expenses involved indicate that individual researchers, and even departments, cannot establish nanotechnology research programs without the commitment by the university administration and the state government to fund the development of needed infrastructure.

If a traditional hydrometallurgist were to develop a nanotechnology research program, some very difficult choices have to be faced, as choosing the area for research is not as trivial, Fig. 2. Nanotechnology research is advancing so rapidly that it is extremely difficult to follow the on going developments. A person must focus on a very narrow research area and be quite self-disciplined to stay on the subject. For example, a computerized literature search will return more than 20,000 research titles with the word “nanotechnology” for the last 5-years alone. A more specific title, research on self-assembled monolayers, will return more than 1,500 titles for research performed just in the last two years. It is not physically possible to read all these papers unless more narrow specialization is used. The often open schedule of scientific symposium sessions, where a researcher is allowed to bring the research title to a session chair within hours of the session beginning, provides further evidence for the rapidly expanding nanotechnology research.

The educational conference [8] “Nanotechnology Business Roadmap for Industry” lists six key nanomaterials technology platforms:

1. Optoelectronics, electronic and nanostructured materials
2. Structural materials and coatings
3. Device fabrication
4. Functional materials
5. Nanobiotechnology
6. Nanoporous materials and energy conversion and capture materials

B. Pešić

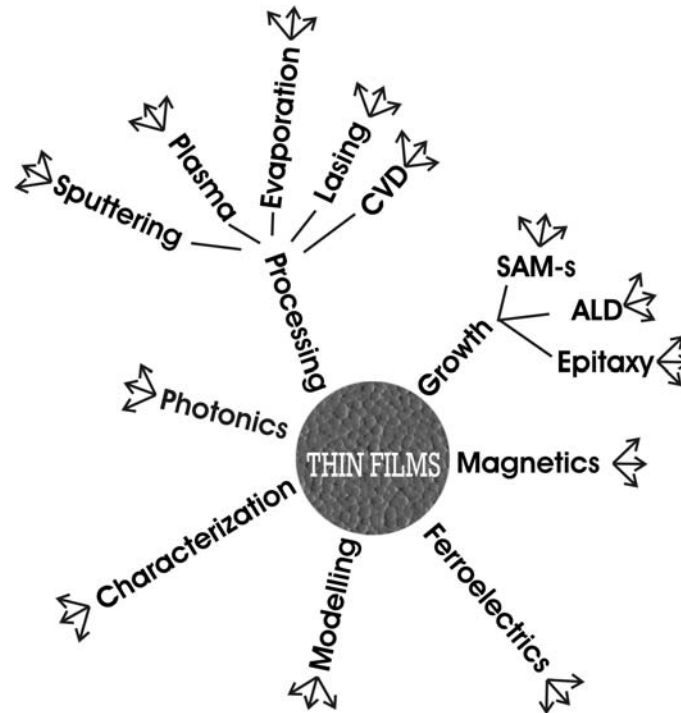


Fig. 2 Depending on the objectives, deposition of thin films can take various research directions. Further activity branching does not stop on the next immediate level. For simplicity, the interconnection between various activities is not shown. Similar directional activity sketch can be made for any other topic in nanotechnology (nanotubes, nanopowders, MEMS, etc.) making the number of subjects in nanotechnology in- exhaustive

Each of these platforms however comprehensive by the research topics and methodologies will require, somewhere in the production steps, the nanohydrometallurgical unit operations. Further, considering synergistic effects among the technological platforms, the business opportunities for nanohydrometallurgy are impressive.

6. *A Personal Approach*

Upon closure of the College of Mines at the University of Idaho, the metallurgical engineering program was moved to college of engineering, where the programmatic emphasis was immediately placed on the materials science and engineering. The commitment of administration to grow materials science program was evidenced by successful funding of several projects via federal appropriation mechanisms. The improvements in equipment infrastructure are significant and the new department is poised to develop and maintain research programs relevant to nanotechnology.

With respect to teaching activities, the author is preparing a new course, Nanohydrometallurgy. Regarding the research activities, the decision was made to select electrochemistry as the focus area. The power of electrochemistry is that it can be well controlled in each direction: electrodeposition and electrodisolution. It can be utilized for production of discrete metallic nanostructures, as well as continuous metallic films. Electrochemical production of desired nanostructures can be achieved either under imposed potentials, or electroless conditions.

Providing that the needed research equipment is already in place, the adaptation to the new teaching and research requirements should not be difficult for a traditional hydrometallurgist. Teaching and research methodologies should be the same, as demonstrated by an example in the current research project on electrodeposition of thin metal films. Figure 3 describes a cyclic voltammetry study of copper on glassy carbon [9]. The scanning range is +500mV to -500mV, and a scan is initiated in a negative direction. The electrodeposition of copper is a typical hydrometallurgical topic for study, and the only difference between the previous studies from this is the additional tool for monitoring the extent of a reaction, the application of atomic force microscopy (AFM).

In Figure 3, the status of the glassy carbon electrode is visualized in various stages or reaction progress. Thus, initially, at +500mV, because there was no reaction occurring, zero current was produced. The surface of the electrode was clean, as shown on the lower right AFM micrograph. When the potential scan passed -200mV, a reduction peak I_c resulted, signifying the electrodeposition of copper. The shape, size and density of produced copper

B. Pešić

can be seen on the lower left AFM micrograph. At -500mV , the scanning direction was reversed, but the reactions were still those of copper reduction, indicating that the copper nuclei growth should continue, which was proven by AFM, as seen in the upper left AFM micrograph. When the oxidation potential for copper was reached, copper dissolved fast resulting in an anodic peak current, I_a . The AFM surface examination of revealed that almost all copper was dissolved, thus justifying the sudden drop of reaction current.

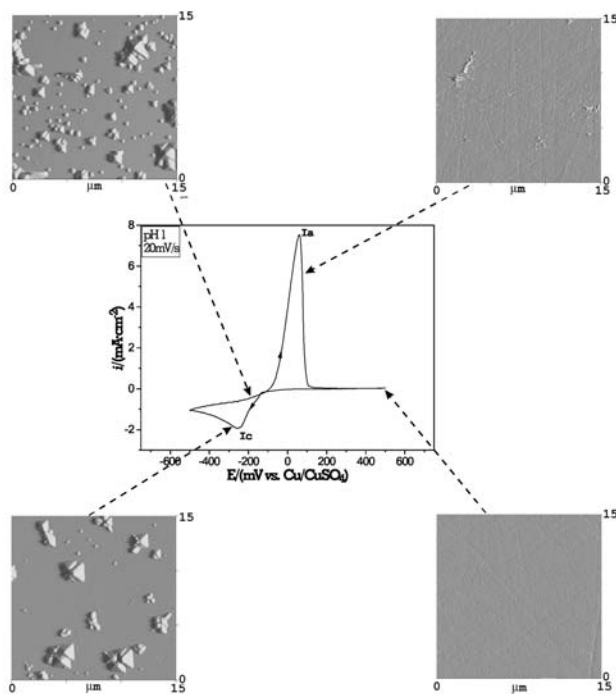


Fig. 3 A novel approach in the studies of electrochemical reactions—Atomic force microscopy was used to monitor copper nucleation, growth and dissolution in various stages of the reaction system. Data from Ref. [9].

The above results, reflecting the mechanisms of copper electrodeposition and electrodisolution, are equally useful to a traditional hydrometallurgist working in a metallurgical plant, as well as to a microprocessor chip manufacturer. *The concluding point is that hydrometallurgy is adaptable and should thrive in both technologies— traditional extractive metallurgy and nanotechnology. Its maturity in each of the technologies is the only distinction.*

7. Conclusions

1. The academic programs covering the subjects of extractive metallurgy are on a relentless trend of being eradicated from the teaching curricula at U.S. universities.

2. The strict federal policies, the economic market forces, poor public perception, the history of treacherous business assimilation of mining corporations by oil conglomerates, and virtually nonexistent collaborative interface between the mining industry, the government, and academia all are the factors that contributed to a precipitous decline of mining industry in the U.S.

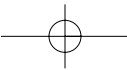
3. In a chain reaction, weakening of the mining industry lead to poor job prospects, which in turn lead to dismal student enrolment in extractive metallurgy and mining schools. To the university administrators, and often the state legislators, enough evidence mounted to start closing these programs.

4. It is not logical to give up on the science of mining/extractive metallurgy in the U.S. It is impossible for a country to be an economic and military super power without having a strong basic industry. History has no evidence of such a precedent. Second, regardless of the promises of nanotechnology, the reality is that the basic industry must always exist to support the new technology.

5. Despite the decline of mining industry in the U.S., hydrometallurgy can evolve into another discipline, nanohydrometallurgy, and thus enhance its viability. The growth of nanotechnology should be viewed as an opportunity for growth of hydrometallurgy.

References

1. U.S. Congress, Office of Technology Assessment, Copper, Technology and Competitiveness, September 1988, NTIS No. PB89-138887.
2. EPA History-The Birth of EPA, <http://www.epa.gov/history>
3. R&D Magazine, January 2002, p. F3.
4. The National Science Foundation. <http://www.nsf.gov>.
5. JOM, June 2002, p. 8.
6. University of Alberta News, NINT Set in Motion as World Class Center



B. Pešić

- for Nanotechnology, (<http://www.engineering.ualberta.ca>).
7. *Materials Today*, November/December 2001, p. 18.
 8. Infocastinc, Nanotechnology Business Road Map for Industry, <http://www.infocastinc.com>
 9. Grujicic, D. and B. Pesic, *Electrochimica Acta*, 47, (2002) 2901-2912.

