Advances and Perspectives in Electrochemical Metallurgy

by

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Abstract

In time of change, the need to maintain a technically viable foundation is essential to any industrialized economy. A greater degree of flexibility and the ability to respond quickly when business demands such action is also a critical ingredient for survival. A brief review of the state of the art of electrochemical processing is examined in terms of its potential role in providing necessary technology in such a scenario. Factors which may influence the development of scientific advances and future needs are examined. A listing of some of the developments recognized as necessary for the continued growth of metal electrolysis processes is also provided. Examples of specific research and development areas which illustrate some of the unique features of electrochemical reactions in metallurgy and materials science are given.

Introduction

The extensive changes that have occurred in extractive and process metallurgy over the past decade have had a major impact on many aspects of our industry. Any number of factors could probably be cited, but the dramatic shifts in the worldwide political climate and the economic instability it has caused have been primary contributors. As a result, the technical scene has been plagued with a high level of uncertainty as well. In metallurgy, the latter would include the quantity, grade, complexity and availability of ore raw material and their geographical location, stricter requirements on quality, the aging of operating facilities in major industrialized countries and less availability of capital for new, competitive facilities. But in the final analysis, concern with environmental issues and how they affect both current and future prospects may have been one of the most universally omnipresent factors.

The need to eliminate or minimize pollution problems associated with the minerals industry has had multi-faceted ramifications. First there was the need to invest in equipment and processes capable of handling the wide variety of gas, liquid and solid hazardous substances being generated. This meant that less funds were available for the development of new revenue generating products. The magnified focus on the environment also gave impetus to a redirection of research and development efforts. The overtones of the majority of the research, particularly
in universities, became much more environmentally oriented. Emphasis on the treatment of wastes and residues far outdistanced the more classical approaches on the fundamental and applied aspects of primary and secondary metal production. Indirectly this also changed the philosophy of how research was evaluated. The need for a shorter-term and more direct return on research dollars was emphasized. Practicality and specifically quantifiable goals, often best attained by integrating into the direct support of plant operations, became the pattern to follow for many research groups. Simultaneously, there was a downsizing of many technical organizations and an increased interest in cooperative or consortium programs among industries, academia and government.

As pointed out recently, evaluation of research for new processing was no longer based exclusively on a scientific and technical basis. Research was viewed more in terms of a profit center and planning was based more on the possible economic and social impact than on scientific merit. As a result, the goals were oriented to short-term related problems and economics, cost reduction and value added meaning less emphasis was given to fundamental or high-risk projects.

Most assuredly, the changes not necessarily all bad. Improvements in environmental awareness and control have been outstanding and substantial gains continue to be made. Some desirable efficiencies of effort and elimination of less productive segments of the technical community accompanied the reductions in force. But the fact remained that the changes were major and a definite interval of uncertainty was created and is, to varying degrees, continuing to the present time.

But throughout this period, as troubled as it may have seemed, significant progress was made. Gains were not restricted to the area of classical process chemistry but in plant design and environmental control as well. Reviewing some of these advances, in both specific and general terms, and how these changes might influence the processing of metals will be the central focus of this presentation. We are being forced to re-think how the metals industry may best prepare for entry into the next century. One critical feature in this thought process is the judicious selection of possible process alternatives and the determination of importance that technologies such as those based on electrochemical reactions may have in the long term.
Historical Background

The choices available for metal production processes are somewhat limited, being based either on pyro-, hydro- or electrometallurgical principles or their combination. Compared with the other two processes for metal production, electrochemical techniques are relatively new. Both pyro- and hydro- methodologies have long histories and can be traced back thousands of years. Archeological evidence of thermally produced copper dates to about 3000 B.C. and hydrometallurgical heap leaching of copper-containing pyrite with recovery by cementation using iron was reported in the 16th century. The direct recovery of copper from mine water by iron nails is reported to have occurred even earlier, possibly in the 7th century. By contrast, it was not until nearly 1870 that copper was electrolyzed from aqueous solutions. So with a history of some one hundred twenty-five years, metal recovery by electrolysis is a relative newcomer to the process scene.

Good progress in utilizing electrical energy for metal extraction and manufacturing was made through the first two decades of this century. In fact, the basic elements of the processes developed during this period are still being employed. While some substantial improvements and modifications have been made, the basic electrochemistry employed has remained surprisingly similar.

From 1800, when the research of Volta resulted in a power source or "Voltaic Pile," to the turn of the century both basic principles and industrial applications were emerging. The works of Ohm and Faraday were particularly valuable, as were the advancement of other concepts such as ionic theory. Initially, most scientific interest was on the thermodynamics of electrochemical reactions. The Nernst equation and the view that the equilibria involved were not disturbed by electron transfer at the interface were dominant. Transport of species was recognized as a source of irreversibility, but the overall approach was very limited in terms of the possible role of kinetics in the mechanisms.

The important, but extensively empirical, expression of Tafel presented in the 1920's was one of the first correlations presented which related the current flux with the overpotential. Such views deviated substantially from the prevalent school of thought at the time which was dominated by equilibrium considerations. Others, particularly in Russia, followed the kinetic rather than the thermodynamic approach but unfortunately it wasn't until the 1950's that the electrochemical kinetics, as elucidated by charge and mass transfer overpotential, became clearly
entrenched. Electrochemical engineering, emphasizing reactor design and development, then began to emerge in many substantive ways. Theories regarding current distribution and quantitative treatments of fluid flow, mass transport and scale-up of reactors were also presented.

The first formal presentation of electrometallurgy was Addicks treatise in 1921 on copper electrorefining. It wasn't until 1960 that Mantell produced the first textbook on electrochemical engineering and it was another 15 years before texts on electrochemical reactor design were available.

An obvious conclusion is that while the industrial applications for electrolytic metal processes gained early and widespread acceptance, the necessary science to describe the fundamentals advanced much less quickly. So, rather than being a mature technology, electrolysis is in its infancy when judged by the age of the fundamental science governing its use. The critical question then becomes whether or not the growth potential has been fully expended or if significant opportunities exist to elevate electrochemical metallurgy to a new level; one based on an increasing knowledge of the process fundamentals. When attempting to evaluate current advances and place them in proper perspective, it is imperative to determine such basic factors. These decisions will then play a major role in establishing future priorities for research and development directions in metal production. For emerging industrialized nations, evaluating the potential of the various technologies is particularly pertinent and obviously plays a major role in providing perspectives for technical and economic growth.

**Process Categories**

As mentioned, the methods available for extracting and refining metals can be categorized into pyrometallurgy, hydrometallurgy, and electrometallurgy. Whereas the focus of the first two is usually clear, the exact role and place of electrometallurgy is much less obvious. In many instances, electrometallurgy is logically included in hydrometallurgy, particularly when aqueous processing is involved. The boundaries and technical emphasis of thermal pyro-processing and leaching or hydro-processing are clearly delineated by a fundamental scientific base and how it is used to accomplish various steps in a process. Such is not the case for electrometallurgy, and one plausible explanation is that electrolytic processing is never the exclusive or primary means of metal production but follows previous smelting or dissolution processes. In many respects, the inability to identify the precise elements which comprise electrometallurgy is then
understandable. A variety of important industrial processes covering a broad range of applications including electrowinning, electrorefining, plating, leaching, cementation purification, corrosion, high temperature oxidation, flotation and batteries are all electrochemical in nature. But each, more or less occupies its own niche, so including them under one generic heading is not realistic. For that reason, I have chosen to categorize the areas of interest in the context of this presentation as "electrochemical metallurgy." Hopefully, this will be more definitive and consistent with the terminology associated with metallurgical processing, particularly for those involving cathodic deposition.

Processing Advances

Overview

Major technical advances are most often made as a result of the driving force provided by a real or perceived need. As intimated previously, there are currently a number of factors which are causing a realignment and reassessment of metal production. Improved economics and efficiency have always been a goal for industrial processes in the past, but now other political, social and environmental issues compound the complexity of the problem. Although far from complete, the listings in Table 1 contain examples of some of these influencing factors:

<table>
<thead>
<tr>
<th>Factors Which Influence Metal Process Development</th>
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<tbody>
<tr>
<td>Technical Demands</td>
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<tr>
<td>Availability of raw materials</td>
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<tr>
<td>Energy requirements</td>
</tr>
<tr>
<td>Environmental protection</td>
</tr>
<tr>
<td>Final product purity/quality</td>
</tr>
<tr>
<td>Competing materials</td>
</tr>
<tr>
<td>Capital needs</td>
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</tbody>
</table>

It would be impossible to survey all of the recent developments that have evolved to meet the demands of the times. One objective of this paper will be to provide examples of the role and potential of electrochemical alternatives in addressing future processing requirements.

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Once the challenges facing the extraction industry are identified, the methodologies necessary to solve them must be found. Central to this issue is determining the ability of electrochemical processing to meet the needs in the various areas. It is clear from examination of the literature that substantial advances in the development and control of electrochemical processes are being made as the fundamentals become more clearly understood. A better grasp of the basics of oxidation and reduction has resulted in more innovative reaction schemes and advanced plant and reactor design and engineering on an industrial scale. On a small or laboratory scale, the desire to move electrons through a precisely defined conductor to a specific reaction center in a participating chemical species at the reaction surface interface is getting closer to reality.

In reviewing the literature, a variety of both direct and indirect advances in the electrolytic deposition of metals can be identified and a partial listing of some of these are given in Table 2. Areas of both fundamental and applied interest in electrolysis are included.

### Table 2
Areas of Recent Advancements in Metal Electrolysis

1. More sophisticated plant, circuit and reactor designs
2. Innovative insoluble anodes
3. Soluble anode characterization and dissolution mechanisms
4. Less conventional electrolytes
5. Cathode morphology control - nucleation and growth
6. Small scale, integrated production units - waste treatment
7. Organic reagents for selective impurity removal
8. Membrane and diaphragm technology
9. Solution purification
10. Modified wave form processing
11. In-situ characterization of reactions
12. Diagnostic analyses for electrolytes - organic additives
13. Process modelling
14. Instrumentation and process control
15. Environmentally friendly processes
16. High technology coatings
While the items presented in this table refer to the areas of advance, they also serve to provide a perspective of future needs in electrochemical technology as well. Examples of the types of research and development accomplishments that have been reported over the past few years will be given, as well as a few specific examples of research that has been conducted by our group.

**Plant and Process Advances**

The basic design of many electrolytic processes over the years has incorporated sulfate electrolytes with parallel plate electrode geometries and moderate current densities. While highly successful overall, it is considered somewhat primitive by current standards. The production tonnage per unit reactor volume is quite low and rather two-dimensional in nature because of the cell arrangement. The large plant facility areas required have led to metal electrolysis to be termed "metal farming." Whereas pyro-processes employing shaft type furnaces and pneumatic reactor vessels can generate about $3 \times 10^3$ tons/m$^3$/minute, electrolysis of copper and zinc may be nearly an order of magnitude lower. Improving the competitive position of electrometallurgy using more sophisticated and new process approaches is one major current area of technical interest. The use of high current density or enhanced cathode area processes are possible means to attain this end.

Over the past few years there has been renewed interest in the development of less conventional methods for metal electrolysis. In addition a number of plants have undergone extensive remodeling and changes in existing facilities, in more of an evolutionary than revolutionary manner. One notable feature of the new developments is the continuing effort to integrate automated control into the processes. As electronic instrumentation improves, this trend will no doubt become even more extensive.

For example, the improvements reported on operations and control of the BHAS zinc plant are typical of ongoing projects in many non-ferrous electrolytic plants. Their goal was to improve efficiency and maintain production capacity by installing suitable control instrumentation. Key to the new process modifications was the development of on-line analyzers throughout the circuit and improved control of the electrolyte materials balance. Another modernization program was described for the Pasminco Metals zinc plant with similar upgrading facilities. Recently the concept and operation of a new zinc cell house of conventional design
was given. While the process basics remained the same, major improvements in the design and construction of machinery, equipment and process control were reported. Excellent current and energy efficiency averages were obtained. Based on the success of the present operations it was proposed that ultimately the new generation cell house will be fully automated. Inspection, handling, conditioning and control of each electrode is expected to give an optimized electrochemical process. The new, conventional cell house commissioned in 1991 by Asturiana de Zinc, is a good indicator that the basic design and flow sheet used for zinc electrowinning will continue into the near future. However, major technical improvements to upgrade the automation and efficiency of the individual steps will be in evidence.

An excellent review of tank room data on electrolytic copper refining was given by Schloen. Modernization of existing copper electrorefineries has also been occurring with reports by Southern Copper, Noranda CCR, Phelps Dodge, Falconbridge Kidd Creek Division and others. In most cases, the goals of the development efforts were to increase capacity, efficiency and cost effectiveness or overall product quality. The specific means to attain the various goals varied to some degree but replacement of older equipment, automation of all parts of the operations, improved process control and in-line instrumentation were common to most.

A new copper tankhouse was described by Norddeutsche Affinerie in which the ISA process with permanent stainless steel cathodes was used for the 172,000-ton capacity plant. The trend away from starter sheets also continues in copper operations.

Of course, there is probably no area of greater dynamic activity in copper metallurgy than in solvent extraction-electrowinning. Some factors of importance in the design of copper EW tankhouses were described, listing high quality cathodes, minimal labor and energy requirements, high reliability and attainment of environmental compliance as critical goals. Considerable emphasis continues on obtaining a better understanding of copper cathode growth and the means to control it. Likewise, improved anodes and the quest for lower energy reactions or depolarized oxygen evaluation also continues in conjunction with the need to minimize impurities associated the anode reactions.

There are a number of developments in the design of new processes to replace the conventional sulfate based systems. The use of chloride leaching media has always been an attractive but elusive alternative for treating non-ferrous metal ores, particularly complex sulfides. The CENIM-LNETI proprietary process for the recovery of zinc, copper, lead and
Silver was developed using ammonium chloride to overcome some of the economic and chemical disadvantages encountered with previous processes. The relatively neutral media employed allows good metal separation selectivity using solvent extraction and precipitation techniques. A profitability analysis on the use of the process for various plant capacities was also given.

Técnicaes Reunidas remains active in advancing new hydrometallurgical and electrometallurgical processes for metal recovery, being involved in both individual and cooperative efforts. The emphasis has been on chloric media and current developments include the Cuprex copper and Ledelor lead processes at the demonstration plant scale and the Zinclor zinc process at pilot size. The diaphragm electrowinning cell of the latter has been scaled to industrial size, and electrodes and additives have been optimized.

Solvent extraction is a primary component in the majority of the emerging processes and from all indications this trend will continue in the future. New organic reagents and processes are available for zinc processing in either sulfate and chloride media using DS5846 and Acorga ZNX50 and described recently in the literature. In copper, the Cuprex Metal Extraction Process (CMEP) is another example of the attempt to shift to the combined use of the attractive features offered by solvent extraction and chloride electrowinning. Still another novel scrap electrolytic recovery process, Ecuprex, incorporates a fluoborate solution and an electrochemical dissolution mechanism followed by deposition in a diaphragm cell.

Another flow sheet described to treat zinc bearing materials, particularly waste oxides, is the EZINEX Process. Leaching of the oxide is conducted using ammonium chloride resulting in zinc chloramine complexes which are isolated by the use of a cationic selective membrane. A solution of sulfuric acid circulates as the anolyte but the oxidation reaction is proposed to be chlorine gas evaluation but with immediate reaction with the ammonium ion as shown.

\[ 2 \text{NH}_4^+ + 3 \text{Cl}_2 \rightarrow \text{N}_2 + 6 \text{Cl}^- + 8\text{H}^+ \]

The main advantages of the concept would be for small plants which could be built near the mine site to treat low zinc, high iron sulfides. The ore would initially be smelted in a submerged arc furnace.

Interest remains high in the removal or control of impurities in electrolytes for both quality and environmental reasons. Since the current efficiency and cathode morphology obtained in zinc electrowinning are so directly dependent on solution quality, purification is a
major concern. Likewise, the presence of iron and manganese is detrimental in copper electrowinning and processes to remove them, particularly solvent extraction, continue to be evaluated.

Precipitation and cementation are common techniques used in purification. Reaction kinetics and removal level are of primary concern when cementation is employed and they have been extensively evaluated for many years. Some impurities of interest include Co, Ni, Cu, Cd, Fe, Sb, As, Ge, and Sn with the need to decrease their concentrations to the ppm or even the ppb levels.12,13

The normal kinetic expression for cementation reactions is

\[
\frac{dc}{dt} = k \cdot \frac{A}{V} \cdot C
\]

and it has been found that the area term is the catalytic cathodic surface generated during the reaction and not that of the dissolving metal. Thus, deposit morphology can be a factor in reaction kinetics. Results of recent research showed that temperature, activating agents, pH and solution potential were critical parameters for the industrial operations and the introduction of automation and control into the flow sheet is one priority.

The need to provide more environmentally acceptable means of extracting and recycling lead has caused a significant amount of interest in hydrometallurgical recovery routes. After suitable leaching and purification stages, the lead containing solutions are electrowon. An excellent review14 of some current processes has been given recently in which the problems encountered in electrowinning lead are outlined.

The deposition of PbO₂ at the anode is one of the major undesirable reactions occurring simultaneously with reduction to metallic lead at the cathode. A variety of electrolytes have been proposed with fluoboric and fluosilicic being prominently mentioned, but ammoniacal ammonium sulfate and chloride are also reported. To prevent PbO₂ from crystallizing at the anode various passivating reagents have been used, including arsenic, phosphorous and antimony or oxygen enhancing species such as cobalt. An example of the dramatic influence of P on preventing PbO₂ formations shown in Figure 1. Ion selective membrane cells have also been used with sulfate and EDTA, nitrilotriacetate, oxalic acid or similar complexing agents. Different forms of metallic lead are recovered at the cathode and range from solid, bulk cathode sheets to flakes or powders, depending on the electrolyte used.
While none of the processes described has been commercialized, it is expected that a full-scale operation to electrowin lead will be commissioned during the next decade. Such advances in metal processing are yet another example of the opportunities which exist for the increased use of electrochemical technologies in the future.

Electrocrystallization

One feature common to all electrodeposition processes is the growth of metal at the cathode. However, while the electrocrystallization of metals into large scale bulk deposits is critical to the success of any process, it is probably one of the least understood aspects of electrochemical metallurgy. Unfortunately there is no theory, based on first principles, that adequately explains the process. As a result the majority of the research is very empirical in nature. Most assuredly advances are being made but more emphasis is needed in the area of cathode growth control. Improved in-situ and microscopic characterization techniques show promise for improving our level of understanding of this aspect of electrolysis.

One of the first useful categorizations of metal deposit structure was by Fischer. The concept was expanded into a diagram, shown in Figure 2, by Winand which shows the stability fields of Fischer's deposit types as a function of two parameters. One axis is the ratio of current density to concentration or to limiting current density if the system hydrodynamics are important. Inhibition intensity is the second parameter. The diagram has been effectively utilized for a variety of processes, particularly copper, but attempts have also been made to categorize zinc deposits using this approach. Industrial electrolytic zinc deposits were characterized empirically into four types and compared with previous work. Although the comparisons are somewhat tenuous, there are some correlations to be noted and similar studies can be expected for other deposition systems as well.

A mini-symposium on the use of additives and reagents for the control of copper deposit morphologies was recently held. Most of the interest centered on attempts to gain a better understanding of the role of chloride ions and the organic additives, gelatin and thiourea. Particular attention was given to interactions among these species. In all instances, the need to provide a proper balance among the species present was identified. The conclusions were that various polarization, microscopic and electrochemical sensing devices are available to aid in
characterizing copper electrolytes containing these additives and sensor technology will continue to gain in importance for industrial scale control of copper growth.

Miscellaneous Electrolytic Processes

Whereas most of the previous discussion was centered on new approaches in the more conventional area of electrowinning and electrorefining, other exciting developments have been emerging as well. It would be impossible to adequately describe all of them but some examples will be given to provide insight into the possibilities that exist for unique applications of electrolysis.

A. Electrochemical Synthesis and Surface Modification

The use of electrochemical techniques is becoming more prevalent in synthesis and surface modification applications. In addition to metals and alloys, other high technology materials including semiconductors, superconductors, amorphous films, composites, layered oxides, electropainting, nanostructures, compositionally modulated alloys and conducting polymers are also now becoming prevalent, particularly in the electronics industry. There is little doubt that these deposition processes represent a dynamic addition to the electrochemical family and show tremendous potential for growth. In fact, it would be expected that similar novel processes should continue to evolve as our understanding of electrochemical reactions improve and more sophisticated equipment becomes available to control the desired mechanisms.

The advantages of using electrolytic processing in these applications may vary from almost exclusively technical (e.g., improved or unique properties, controlled dimensions, thermodynamic feasibility, etc) to economic in nature. But whatever the justification, the flexibility provided by such processing techniques certainly merits consideration whenever there is a requirement for deposited films.

One of the other favorable attributes of electrolytic developments is that meaningful evaluations can be conducted on a very small scale using beaker-sized equipment. Since most of the processes are strongly flavored by kinetic control, some very unique research has been initiated with limited physical facilities but quite imaginative ideas.

As mentioned previously, it is beyond the scope of this paper to do adequate justice to the emerging world of electrochemical processing. In the remainder of the presentation a few specific examples from research conducted at UMR will be used for illustration purposes.
Shape Memory Alloys

Recently it was shown that alloys exhibiting the shape memory effect could be electrodeposited. Included were Cu-Zn, Au-Cd, In-Cd and In-TI. Cyanide electrolytes were used for Cu-Zn and Au-Cd and sulfates for the indium alloys. It was determined that pulsed current was helpful in giving denser, more uniform deposits. The phase transformation behavior of the electrodeposited shape memory alloys was, in general, different from that exhibited by equilibrium alloys prepared using conventional thermal/mechanical techniques.

Using In-TI for a comparison, the more non-equilibrium nature of electrodeposited materials can be illustrated. Table 3 shows the structural data and the obvious sluggish thermal transformation of the electrodeposited material from the low temperature martensitic fct to the high temperature austenite. The high temperature X-ray and transformation data in Figures 3 and 4 illustrate the rather remarkable stability of the martensitic phase produced electrolytically since it is partially retained even at 140°C, when the equilibrium material was completely austenitic at 60°C.

APEX Deposition

Addition agents, particularly organics, are effectively employed to control cathode morphology and minimize dendritic growth. One explanation of the role of these reagents is to encourage increased nucleation while limiting crystal growth. Major changes in cathode structure
can be accomplished using addition agents and their use has provided a valuable versatility to plating processes. There are cases however where it would be preferred if the organics could be excluded.

As instrumentation and equipment for electrodeposition processes continues to improve, more subtle polarization schemes can be incorporated into the processes. One application we developed by altering the wave form of the applied current was in the modification of the nucleation mechanism, thereby improving the metal coverage on the substrate without using an organic. In this particular study, the electroplating of tin on a copper substrate for use as an electrical fuse element was evaluated.20

When tin was plated directly on copper the nucleation was progressive and gave a very low density of large crystallites. The addition of a proprietary organic additive gave a good structure but the electrical resistance was not acceptable. During the research it was found that tin plated on a tin substrate gave an excellent morphology, so a substrate crystal mismatch was indicated and improved growth should result if the initial structure was more favorable.

A number of different techniques were used in an attempt to provide a modified surface with more active sites for nucleation for tin on the copper surface. Ultimately, it was found that by using a short pulsed anodic current for 4 seconds to dissolve copper into the diffusion layer prior to pulsing cathodically, as illustrated in Figure 5, the deposit improved dramatically. In fact, when this process (termed APEX for Anodic Pulse Enhanced Crystallization) was used the tin deposit was equivalent to that made using the organic additive, as seen in Figure 6. Many similar opportunities probably exist in related areas where the application of process fundamentals can be used to solve practical problems encountered in a variety of plating situations.

**Galvanic Stripping of Organics**

Another patented process recently developed is concerned with the removal of metal ions from conventional organics used in solvent extraction by spontaneous electrochemical reactions. The technique is called "Galvanic Stripping" and uses solid metals as reducing agents directly in the organic media to strip the cations in a manner similar to cementation.21 The driving force for the reaction is electrochemical which provides an alternative to chemical stripping in selected situations when the latter is difficult or impossible. The surprising feature of the process is that
the short-range electrochemical reactions occur so readily even though the conductivity of the organic solutions is low.

Obviously, chemical stripping is preferred but there are instances where certain impurities are difficult to remove or to properly concentrate, resulting in environmental problems. In these instances, the galvanic stripping offers an additional means for separating impurities from the system.

There are two primary embodiments of the process; complete reduction and redox separations which are represented in the following generic chemical equations

\[ R - M_1 \text{(org)} + M_2 \text{(solid)} = R - M_2 \text{(org)} + M_1 \text{(solid)} \]

\[ R - M_1^{+n} \text{(org)} + M_2 \text{(solid)} = R - M_1^{+1} + R - M_2^{+1} \]

The \( M_1 \) represents the metal ion to be removed and \( M_2 \) is the solid metal used as the reductant. The reactions can also be separated into anodic and cathodic half reactions since they are electrochemical in nature. Examples of these types of reactions are:

\[ R - Cu \text{(org)} + Fe \text{(solid)} = R - Fe \text{(org)} + Cu \]

\[ R - Fe^{+3} \text{(org)} + Zn \text{(solid)} = R - Fe^{+2} + R - Zn \]

There are also two flowsheet variations for the process since either separate or simultaneous galvanic stripping can be used. For separate stripping, the solid metal is put into the single-phase organic and is the preferred method when complete reduction is desired. In simultaneous stripping the two liquid phases, organic and aqueous, are mixed with reduction and stripping occurring simultaneously. This method is used more often for redox type reactions. A schematic flowsheet showing these alternatives is given in Figure 7.

A listing of the various Ion/Metal/Organic systems that have been qualitatively evaluated on a lab scale is given in Table 4. Pilot plant scale runs were also made at Cominco on the removal of 0.5 g/l iron from D2EHPA in treating a leach residue to recover valuable by-product metals. Numerous factors such as temperature, metal and surface area, oxygen, etc., have been identified which influence the reaction rate. One which was of particular importance was the notable increase in rate and efficiency provided by a 1.5% Pb-Zn alloy compared to pure Zn as the reductant for iron removal. The results shown in Figure 8 illustrate the strong influence of the alloy, possibly by providing a more favorable second phase site for the cathodic step.
Plans are now being formulated to design and develop a process to use galvanic stripping in the treatment of a zinc leach residue. A conceptual flow sheet utilizing simultaneous galvanic stripping is presented in Figure 9. Preliminary results look promising, further illustrating the novel ways in which electrochemistry might provide solutions to metal recovery problems.

Table 4. Galvanic Stripping of Various Ion/Metal/Organic Systems

<table>
<thead>
<tr>
<th>Extractant</th>
<th>Cation</th>
<th>Loading Anion</th>
<th>Metallic Reductant</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Organic Cementation</td>
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<tr>
<td>D2EHPA</td>
<td>Ag⁺¹</td>
<td>Nitrate</td>
<td>Al, Fe, Zn</td>
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<tr>
<td></td>
<td></td>
<td>Sulfate</td>
<td>Al, Cu, Zn</td>
</tr>
<tr>
<td></td>
<td>Cd⁺²</td>
<td>Sulfate</td>
<td>Zn</td>
</tr>
<tr>
<td></td>
<td>Co⁺²</td>
<td>Sulfate</td>
<td>Mn, Zn</td>
</tr>
<tr>
<td></td>
<td>Cu⁺²</td>
<td>Sulfate</td>
<td>Cd, Fe, Zn</td>
</tr>
<tr>
<td></td>
<td>Pb⁺²</td>
<td>Chloride</td>
<td>Zn</td>
</tr>
<tr>
<td></td>
<td>Sb⁺⁴</td>
<td>Chloride</td>
<td>Zn</td>
</tr>
<tr>
<td>D2EHPA + TBP</td>
<td>Au⁺³</td>
<td>Chloride</td>
<td>Al, Cu, Fe, Zn</td>
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<tr>
<td></td>
<td>Cu⁺²</td>
<td>Fluoride</td>
<td>Al, Zn</td>
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<td></td>
<td></td>
<td>Sulfate</td>
<td>Al, Zn</td>
</tr>
<tr>
<td>Aliquat 336</td>
<td>Au⁺³</td>
<td>Cyanide</td>
<td>Zn</td>
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<tr>
<td></td>
<td>Cu⁺²</td>
<td>Sulfate</td>
<td>Al, Cd, Zn</td>
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<tr>
<td></td>
<td></td>
<td>Fe, Zn</td>
<td>Ni⁺² Sulfate</td>
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<tr>
<td>LIX 854</td>
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<td>Chloride</td>
<td>Zn</td>
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<td>LIX 964</td>
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<td>D2EHPA</td>
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<td>Sulfate</td>
<td>Fe, Zn</td>
</tr>
<tr>
<td>TBP</td>
<td>Ce⁺⁺/Ce⁺²</td>
<td>Nitrate</td>
<td>Cu, Zn</td>
</tr>
</tbody>
</table>

Copper Nucleation and Surface Modification

The combination of surface modification and metal deposition is another area of interest, with numerous potential applications in improving morphology and thin film properties. A study of the influence of plasma and thermally oxidized titanium surfaces on copper nucleation was conducted. It had been previously demonstrated that anodized titanium, with various surface oxide phases, had a substantial effect on copper deposition overpotential, crystal growth and surface coverage.
Plasma and thermally treated surfaces had similar effects, with differences of 100 mV or more in nucleation overpotential being observed. A series of tests was performed using a single cathodic pulse for various times. The copper deposits made on untreated, 100°C and 400°C oxygen plasma treated and 400°C low pressure thermal oxidation titanium surfaces are shown in Figure 10. The nucleation mechanism was shown to shift from diffusion controlled, progression nucleation to instantaneous nucleation. The improvement in grain size and surface coverage is obvious and the role of surface modification clearly identified.

Another approach that offers promise in metal deposition developments is the scanning tunneling and atomic force microscopes. In addition to providing atomic resolution in selected cases, it is also capable of doing in-situ studies, directly in the aqueous or organic electrolytes. Examples of the microscopy showing atomic resolution of a HOPG graphite surface is shown in Figure 11. The image in Figure 12 is of a copper nucleus deposited on the graphite. The results are promising and work is continuing on similar projects.

Conclusions

In summary, there is strong evidence of a considerable degree of technical activity in a wide variety of electrochemically related processes. Most of the developments involve metals in some way, either as the film being deposited or the substrate used.

Of particular importance is the apparent new and unique applications of electrolytic processes in both materials science and advanced technologies as well as in the more conventional metal extraction industry. As our understanding of the fundamental science of the interphase reactions occurring at electrode surfaces increases, advances can be expected to follow.

Far from being a mature technology, relegated to marginal improvements in existing processes, electrochemical metallurgy shows every sign of being a vibrant and exciting force in the technology of the future. It is now necessary to provide the level of research and development effort required to insure attainment of these goals.

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References

6. B. J. Lederboer, ibid, 563-574.
8. R.F. Dalton and P.M. Quan, ibid, 347-355.

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Figures

Figure 1. Effect of P on preventing PbO₂ formation.

Figure 2. Simplified diagram showing different possible types of polycrystalline electrodeposits as a function of J/C₆⁺ and inhibition intensity.

Figure 3. Intensity profiles of electrodeposited In-24 at.% Tl alloy on heating.

Figure 4. Relationship between thallium content and phase transformation temperature.

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Figure 5. Schematic diagram of square-wave pulsed-current schedule: (a) cathodic pulse, (b) APEX.

Figure 6. Tin deposited on a copper substrate using (A) DC, (B) DC plus organic additive, (C) APEX process.
Figure 7. Galvanic stripping flowsheet showing the simultaneous and separate stripping alternatives.

Figure 8. The effect of pure and leaded zinc dusts on iron stripping from D2EHPA.

Figure 9. A conceptual flowsheet utilizing simultaneous galvanic stripping to treat an oxidized iron-zinc residue.
Figure 10. Copper deposited at -600 mV (vs. Hg/Hg$_2$SO$_4$ ref.) on pretreated as-received titanium substrates, (a) as received for 5 s, (b) 100°C O$_2$ plasma (P) for 180 s, (c) 400°C O$_2$ (P) for 5 s, (d) 400°C low O$_2$ pressure for 5 s. Magnification = 1000X.
Figure 11. Micrograph of HOPG surface.

Figure 12. Copper deposited from sulfate electrolyte onto HOPG surface.