THE SEVENTIES—A DECADE OF HYDROMETALLURGICAL ADVANCE

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ABSTRACT

The seventies was a decade of intensive hydrometallurgical activity, firstly for copper recovery, then uranium, and finally gold.

In comminution, semi-autogenous grinding was applied to uranium and gold ores.

In leaching there were extensive investigations into pressure and in-situ systems, and into ammonia and chloride leaching processes.

Solvent extraction became a major unit operation for copper recovery. New reagents and equipment were introduced.

There was a resurgence of ion exchange for uranium as low grade sources were tapped and continuous ion exchange systems developed.

Carbon-in-pulp technology came to the fore for gold recovery with the development of desorption and electrowinning systems.

Electrowinning was widely applied for copper in conjunction with solvent extraction. There was a continued move to greater mechanisation and higher current density.

There were important developments in solid-liquid separation such as high capacity thickeners, belt filters and sand filters.

Many of these trends will continue in the eighties. Interesting new developments can be expected.

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INTRODUCTION

The seventies was a decade of intensive activity in the field of hydrometallurgy. In the early part, the action was centred mainly around copper. The cost of scrap iron for cementing copper from copper oxide leach solutions rose steeply, and the introduction of solvent extraction reagents provided a timely new recovery method. Air pollution became a major concern, leading to a world wide search for hydrometallurgical alternatives to smelting for processing copper sulphide concentrates.

The middle seventies saw a boom in new uranium ore treatment plants and the modernisation and expansion of existing facilities. Flowsheets were developed for low grade ores and for the recovery of uranium as a byproduct from other sources. Environmental considerations were again in the limelight, and the drive to minimise capital costs lead to application of new technology. Surging gold prices towards the end of the decade spawned a new gold rush which is still gathering speed. Carbon adsorption technology developed in the fifties and sixties was embraced for the new generation of plants to reduce costs and to exploit low grade sources.

Hydrometallurgical activity was not only limited to copper, uranium and gold. Developments took place in the processing of a number of other major metals such as nickel, zinc and lead. Environmental constraints, rising energy costs, the trend towards lower grade ores, and spiralling capital and operating

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charges were major forces for change.

Developments took place in every area of the typical hydrometallurgical operation including comminution, leaching, solids-liquid separation and product recovery.

New equipment was applied and new materials of construction were widely used.

COMMINUTION

The major development in comminution was the spread of semi-autogenous grinding to replace conventional crushing and grinding.

The use of autogenous and semi-autogenous grinding mills was already increasing in the sixties for the concentration of iron, copper, lead-zinc and other ores. Australian installations were prominent. Advantages included lower capital investment, reduced labour requirement and decreased steel consumption. Overall operating costs were also generally lower despite the high power consumption.

In the mid seventies, semi-autogenous grinding began to be widely applied to North American uranium ores, for which there were two additional incentives. One was the reduction of the dusting problems associated with a conventional crushing circuit, which constituted a health hazard. The other was the elimination of fine ore bins which were often troublesome when handling moist ores, especially in cold climates. A typical application was described by Lang (1979) for a new mill in Wyoming, USA.

Semi-autogenous mills also appeared in the newer round of gold ore treatment plants in South Africa and the Dominican Republic, and even made their appearance for milling bauxite for the Bayer alumina process in Australia.

The semi-autogenous mills were installed with a variety of classifying devices including cyclones, sieve-bends and high frequency screens.

One of the main disadvantages of semi-autogenous grinding is the need for fairly large scale tests to develop design criteria for scale-up. Sufficiently large samples are frequently unavailable during the early stages of a project.

LEACHING

The early seventies saw a surge of interest in the direct leaching of copper sulphide concentrates due to the growing pressure against smelter emissions, especially in North America. Many research and development programmes were launched involving a variety of leaching approaches, including the use of ammoniacal solutions, chloride solutions, and sulphuric and nitric acids. Some utilized elevated pressures and others attempted to harness bacteria.

Of these only two were applied on a substantial commercial scale. These were Duval's plant near Tucson, Arizona, employing the CLEAR chloride leaching process, and Anaconda's installation at Anaconda, Montana, using the Arbiter ammoniacal leaching process. The decade ended with the CLEAR plant as the sole commercial survivor. As the difficulties with the direct leaching processes became obvious, considerable interest was shown in the more established roast-leach process which gained additional commercial application. Haas (1979) concluded that copper hydrometallurgy had not yet gained the confidence of the industry despite apparently favourable economics.

Heap and dump leaching continued to be popular for low grade copper oxide and sulphide ores in most major copper producing centres and the advent of solvent extraction provided an attractive new way to make a premium product. The intensive uranium activity of the middle seventies stimulated renewed interest into heap leaching of low grade uranium ores. Several plants were built in Spain and North America using either solvent extraction or ion exchange for recovery. When the activity switched to gold, heap leaching was again prominent.

Coupled with carbon adsorption it provided a neat, low cost process for lean ores, which was soon applied in a number of operations.

Widespread interest developed in in-situ leaching, especially for North American uranium deposits, too small for exploitation by conventional mining. A variety of leaching agents were investigated. When commercial operations appeared they generally employed either dilute sulphuric acid or ammonium carbonate solutions. Oxidants included liquid oxygen and hydrogen peroxide. The traditional fixed bed ion exchange technique as well as some of the newer continuous ion exchange processes were employed. Huff et al (1980) reviewed technical and economic aspects of the technology. Deep sea nodules drew world wide attention throughout the decade promising vast new resources of copper, nickel, cobalt and manganese. A number of major research programmes were launched to develop suitable treatment methods. Leaching systems using chloride and ammoniacal solutions were prominent among the touted processes. The decade ended, however, with the unresolved political problems occupying centre stage.

Sulphuric acid leaching under pressure was intensively studied for zinc sulphide concentrates in Canada, while chloride leaching was investigated for lead in the USA. Development work was also carried out on pressure acid leaching for uranium ores in South Africa, resulting in commercial application.

In the field of nickel processing, pressure ammoniacal leaching was commercially applied to nickel sulphide concentrates in Australia, and to laterites in the Phillipines. Roasting followed by ammoniacal leaching was selected for laterites in Australia. Chloride leaching of nickel ores was studied in North America and Europe.

Aluminium is frequently placed in a category of its own, but in fact the Bayer process is one of the historical successes of hydrometallurgy. The seventies saw renewed interest in the exploitation of alternative sources to bauxite, often for political reasons. Processes studied included both alkaline and acidic leaching steps. Nothing emerged, however, to seriously challenge the long established route.

SOLVENT EXTRACTION

Following the successful commercial application of new copper solvent extraction reagents in the USA in the late sixties, the early seventies saw an explosion of worldwide interest.

The first target was the exploitation of copper oxide ores. Traditionally, these were treated by sulphuric acid in heap, vat or agitated leaching circuits, followed by the precipitation of cement copper by precipitation with scrap iron. Solvent extraction coupled with electrowinning provided a direct route to a premium grade product, bypassing the smelter. Although capital costs were higher, the spiralling cost of scrap iron made the solvent extraction approach increasingly attractive. These considerations soon resulted in a number of new plants, some of very large capacity, in North and South America, and Zambia. Hopkins and Lynch (1977) described the Anomax installation in Arizona, USA.

Solvent extraction was a popular unit operation in many of the processes proposed for treating copper sulphide concentrates. It was eventually included in as a key step in the Arbiter process, commercialized by Anaconda.

Designers of copper solvent extraction plants generally drew on experience gained in the fifties and sixties with uranium solvent extraction. This resulted in the well established mixer-settler being chosen as the most suitable contactor. Due to the comparatively high cost of the copper extraction reagents, however, great interest developed in finding a smaller contactor with lower organic inventory. Radically new concepts were investigated at pilot plant scale including the static mixer and electrostatic mixer designs. In addition, further developments of the mixer-settler such as the use of baffles, trays and coalescing media in the settler were investigated. While none of these gained widespread acceptance some offered good prospect for future development. Lewis (1971) described an Australian baffled settler development.

Apart from mixer-settler design, other developments included coalescers for organic clean-up and recovery, and the use of centrifuges for the recovery of organic from so-called crud.

When the new wave of uranium plants began to be built in the mid-seventies, cross fertilization again took place, and the gains in technology from the copper arena were applied to uranium recovery, including by-produce production from phosphoric acid.

Solvent extraction development was not, however, limited to uranium and copper. Work was also done with other metals such as nickel, cobalt and zinc, resulting in some pilot and commercial installations. Some of these involved the use of alternative contactors such as stirred or pulsed columns.

ION EXCHANGE

Ion exchange was one of the first techniques used for uranium recovery from acid leach solutions in the fifties. Later it was largely replaced by solvent extraction due to the greater selectivity and resistance to poisoning of the tertiary amine extractants.

The seventies, however, saw a resurgence of ion exchange in uranium hydrometallurgy. One major factor was the swing to low grade ores, in-situ leaching, heap leaching and by-produce recovery from copper and leach solutions. All of these involved recovery from low concentraton solutions, the economics of which generally favour ion exchange. Brown and Haydon (1979) found that pregnant solutions containing below 0.35 gpl U_3O_8 are best treated by ion exchange. Another factor was the introduction of new continuous or semi-continuous ion exchange systems, more suitable for large scale plants than the traditional fixed bed columns. A number of these CIX systems reached commercial application, including the Porter system in Namibia and the USA, the Himsley column in South Africa, Canada and the USA, the NIM column in South Africa, the similar USBM column in the USA, and the Higgin's loop in the USA.

Renewed interest was also expressed in resin-in-pulp systems which offered capital cost savings over solvent extraction.

Weak base resins for uranium recovery excited considerable interest for uranium recovery as a replacement for the previously used strong base resins.

The developments in uranium ion exchange spurred interest in its use for other metals. Ion exchange resins for copper and nickel were introduced and tested in the USA, and hold promise for the future.

As stringent anti-pollution regulations came into force, especially in North America, ion exchange was considered for removing residual metallic impurities from aqueous effluents.

CARBON-IN-PULP

Homestake's gold carbon-in-pulp (CIP) plant brought on stream in 1973 in South Dakota, USA was a milestone in the commercialisation of CIP technology. The operation was described by Hall (1974). By the end of the decade plants were underway or planned in all major gold areas including North America, South America, South Africa and Australia. Basic attractions of the technology are reduced capital and operating costs compared with conventional zinc precipitation, especially for low grade ores. Also it is particularly suitable for poor settling ores. An interesting aspect of CIP is the similarity between the design of the adsorption circuit and the resin-in-pulp process used for uranium recovery.

Faced with the prospect of a number of new plants, the South African gold industry together with the National Institute for Metallurgy made a major effort to develop improved technology. This resulted in a number of innovations including a new desorption technique and electrowinning cell. Adsorption technology was also improved by the introduction of integral screens and mechanical agitation systems. Laxen, Becker, and Rubin (1979) reviewed South African developments. In North America, spurred on by work at the USBM, interest turned to faster desorption systems such as the use of pressure and the addition of alcohols, both were adopted for commercial projects.

In parallel with CIP, the carbon adsorption - desorption - electrowinning process was commercialised for heap leaching operations. Following the pattern of uranium ion exchange development, the first adsorption systems were a series of fixed bed type columns. Later, interest in South Africa and North America switched to the application of continuous multi-stage columns.

The oxidation process using chlorine was introduced commercially for processing carbonaceous gold ores, without incurring excessive cyanide consumption. Following this, double oxidation was developed for ores with even higher levels of carbonaceous material. Here, the chlorination step is preceded by agitation with air at high temperature, which serves to avoid excessive chlorine usage.

Research into the CIP process brought greater understanding of the fundamentals, and led to the design of reliable test programmes and scale-up techniques.

Interest began to arise in the use of thiourea as an alternative to cyanide for gold ore leaching. Potential advantages include more selective extraction, faster reaction rate, and operation at low pH levels.

ELECTROWINNING

The success of solvent extraction for copper recovery led to a surge in electrowinning tankhouse construction. Although the solvent extraction - electrowinning combination offered an attractive new route to good quality copper cathode, the early operations were faced with a variety of problems to overcome. Hopkins, Eggett and Scuffham (1973) analysed these and discussed solutions. The major ones to show up quickly were the entrainment of traces of organic into the tank house circuit, the high corrosion rate of the traditional lead-antimony anodes, and the adverse effects of mist suppression foams on solvent extraction.

The accumulation of organic on the solution surface of the cells resulted in undesirable coatings on starting sheets and areas of "burn" on the cathodes. Another problem was the residual odour of kerosene accompanying the final product. Various methods were investigated for keeping organic out of electrowinning including flotation, filtration and coalescence. The most successful proved to be coalescence and sand filtration which were adopted by a growing number of plants.

The relatively high acid level in the electrolyte led to a high corrosion rate of lead-calcium anodes which resulted in high capital replacement cost and unsatisfactory lead levels in the final product. The decade saw intense research into alternative anode materials, especially in North and South America, and Central Africa. These ranged from other lead base alloys to precious metal oxide coated titanium anodes, akin to those used in the caustic-chlorine industry.

Although work was still continuing at the end of the decade, the lead-calcium anode had emerged as the clear leader. The success of a number of plants adopting these anodes served to eradicate the lingering doubt about the ability of the solvent extraction-electrowinning route to produce an acceptably pure product.

Early work revealed that the foams in use in existing electrowinning operations for mist suppression caused problems in the solvent extraction circuit. Because of this, most plants tended to rely on the use of plastic balls to cover the cells. These were reasonably successful for small plants but were not effective enough for large tank houses and for higher current density operations. A practical solution adopted by some was to use a sheet of burlap weave material on top of the balls. Efforts to find a suitable foam remained unrewarded, although some held promise for the future.

The relatively pure solvent extraction electrolytes offered the potential of high current density operation with resulting capital cost savings. This attracted a considerable amount of research, some involving the use of new anode materials. MacKinnon and Lakshmanan (1976) reviewed work on high current density along with other advances in copper electrowinning technology.

The solvent extraction-electrowinning process became of interest for the recovery of nickel and cobalt. A considerable amount of bench and pilot scale work was undertaken, which included research into the processing of sea nodules. One small plant in the USA produced cathode nickel commercially.

The ever increasing cost of labour led to the continuing development of mechanization of electrowinning tank house operations. This was especially in evidence for zinc electrowinning.

LIQUID-SOLID SEPARATION

Solid-liquid separation is an important step in most hydrometallurgical processes. Sometimes it determines the entire success or failure of a new process, and therefore must not be overlooked during the research and development programme.

The seventies saw some interesting new developments in this area of technology, especially in uranium and gold ore processing. Coleman (1980) presented developments in the uranium field.

The first of these was the introduction of high capacity thickeners for commercial uranium plant counter-current decantation (CCD) operations in North America. Developed in the sugar industry, these units were successfully used in coal preparation circuits before adoption for uranium ore processing. Attractions included lower capital cost and the possibility of indoor location in cold climates. In contrast with conventional thickeners they yield a sharp settled bed level. This coupled with short residence time offers the possibility of automatic control and optimization of CCD circuit performance. Lang (1970) described the first uranium mill to use high capacity thickeners for the entire thickening circuit.

In South Africa, where filtration rather than thickening has been the mainstay of the uranium industry, the major development was the appearance of large belt filters. These filters were based on designs proven successful in the phosphoric acid and other fields, but were applied in much larger sizes. Potential advantages included lower capital cost, and smaller buildings and floor areas. The flexibility in being able to incorporate three washing stages on a single machine was another important consideration. A number of large belt filters were installed, in both uranium and gold circuits. The early uranium units experienced a variety of problems resulting in design changes which led to more successful later models.

Belt filtration was also popular with French uranium companies, and considerable interest was shown in North America. In the USA, it became of particular interest for producing "dry" tailings which were strongly favoured by the environmental authorities. Just before the slow down in uranium development the first US company made the decision to proceed with belt filtration.

Another development in filtration was the introduction of high rate sand filters for the final polishing of copper and uranium leach solutions prior to solvent extraction. These units generally require a prior clarification step for satisfactory operation. This led to interest in new clarifiers including high capacity, lamella, and cone clarifyer designs.

Centrifuges gained widespread popularity for dewatering of yellow cake pulp prior to drying. These were generally the horizontal solid bowl type.

MATERIALS OF CONSTRUCTION

The seventies was a decade when plastics and other synthetic materials came of age in the mining industry in general, and in hydrometallurgy in particular. For high temperature and pressure applications, however, special alloy steel and more exotic metals such as titanium held sway.

For non acid abrasive applications around the comminution area, perhaps the major development was the introduction of urethanes. They also found application for lining copper oxide ore leaching vats where corrosion protection was provided by an inner resin layer.

Soft rubber lining, along with wood, continued to be popular for agitated leaching tanks operating in acidic environments at low temperatures and atmospheric pressure. For higher temperatures, various synthetic rubber linings were applied. They are excellent corrosion barriers but are difficult to bond to the tank wall. High pressure leaching was the domain of special alloys and titanium.

Fibreglass reinforced plastic (FRP) was found to be an ideal low cost material for many corrosive solution applications. It found a particular niche for solvent extraction mixer-settlers and associated tankage because of its ability to cope with the combination of acid and organic. For very large mixer-settlers containing sulphuric acid solutions, stainless steel was generally found to be more economic. Polypropylene was found to be another useful material for solvent extraction circuits.

High density polyethylene became increasingly used for tailings lines. Their impressive list of plusses include resistance to abrasion, corrosion and organic attack, low friction coefficient, low cost and ease of field installation. On the negative side it is limited to relatively low temperatures and pressures.

FRP and polyvinyl chloride (PVC) were extremely popular for acidic solutions at modest temperatures. More expensive plastic lined steel pipe was used at higher temperatures and pressures, especially when stainless steel was unsuitable, such as for chloride solutions.

Plastics also began to find their way into pump manufacture for corrosive applications. Commercially applied materials included FRP, PVC, Teflon and others.

WHAT ABOUT THE EIGHTIES?

Developments in hydrometallurgy will of course be largely dependent on market trends; but other factors such as environmental constraints and the rising cost of energy will continue to be major motivating forces.

In leaching, there will likely be renewed interest in hydrometallurgical alternatives to the copper smelter. The incentive will be greatest for the smaller, more remote deposits. Pressure leaching may be given serious consideration as experience is gained in commercial plants for zinc and uranium ores.

Chloride systems will also be of major interest. The exploitation of deep sea nodules should move closer to commercial reality.

New and improved copper solvent extraction reagents are already in competition for future projects. Their increased range of properties will give more flexibility to developers of hydrometallurgical processes. Solvent extraction could also feature in lateritic nickel projects. On the equipment field new solvent extraction contactors are likely to reach commercial application. The new combined mixer-settler (CMS) is already in operation for uranium recovery in South Africa.

In ion exchange, further refinements of continuous systems are likely. There is likely to be increased interest in the development of resins for the recovery of base metals such as copper and nickel from low grade sources, and for effluent clean up. Magnetic resins, under development in Australia, may offer interesting new possibilities. Further development in resin-in-pulp for uranium recovery are also likely.

Carbon-in-pulp is rapidly becoming a standard process for gold and silver recovery. Further process developments will almost certainly occur, such as new desorption and electrowinning systems. Chemical reactivation of carbon could also be an area of interest. There is likely to be an increased research effort into the use of thiourea for gold extraction, possibly coupled with CIP.

High capacity thickeners will continue to make inroads, and the trend will continue towards fully automatic CCD circuits. As the uranium industry revives, renewed interest is likely in belt filters, especially where there is environmental pressure to produce "dry tailings for burial. Cone type clarifyers should gain widespread acceptance.

The interest in electrowinning of copper from solvent extraction electrolytes can be expected to continue, together with the trend towards greater mechanization. Following Copper Refineries' success at their Townsville operation, there is likely to be world wide interest in the elimination of starting sheets. There is also likely to be continued interest in novel electrowinning processes such as the fluid bed cathodes.

The swing to plastics and other synthetic materials of construction will probably continue, and new materials are likely to be introduced.

Finally, the industry will hopefully be stirred by new and unexpected developments which are always a necessary ingredient for real progress.

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