

## Economic and Environmental Applications for Recent Innovations of Nonferrous Metallurgy in Some Industrial Nations

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**Abstract**—As ore grades drop at today's large mines, and environmental regulations for waste discharges increase, economics drives new recovery innovations. This paper describes some technological advances in the recovery processes for copper, gold, silver, lead and zinc. It does not discuss pyrometallurgy. Korea, like many nations with industrial economies, consumes large amounts of these metals, and is dependent on overseas suppliers for nearly its entire supply. This paper also discusses how technology for recovery of metal now in Korea, for example from existing wastes, is important. Improved reagents for both leaching and froth flotation of copper minerals, plus bio-oxidation and pressure autoclaving for gold have improved metal recovery. Copper recovery by SX-EW is expanding rapidly, and the method is also commercial for zinc. Biooxidation of encapsulating waste materials and, in some instances, of the desired metal has reached commercial scale. Pressure leaching on a large scale solves specific problems for several metals. Improvements in gold and silver cyanidation include variants of activated carbon adsorption from solution. Zinc and lead still largely depend on flotation for the treatment of ores. However, innovation in hydrometallurgical extraction has been spurred by environmental concerns. Computer modeling and process control worldwide have likely led to the largest improvements in recovery. The limited availability of land, clean water and sites for waste disposal in many countries affects the economics of re-treatment of existing wastes. Some of the new technologies could be combined, for example in modular plants that can be moved between reclamation sites to economic advantage on the Korean Peninsula.

Key words: Nonferrous Metallurgy, Korea, Precious Metals, Waste Dumps, Tailings, Imports, Economics, Grinding, Bio-leaching, Flotation, Solvent Extraction, Pressure Autoclaving, Chloride Leaching, Cyanide, Arsenic, Industrial Nations

### INTRODUCTION

Today nonferrous metals typically are obtained from world-class ore deposits that feed huge processing plants. As feed grades drop, existing mines tend to increase mill throughput. At the same time, environmental concern about "nasty" components of waste streams has increased. Disposal of undesirable components mixed into dilute, large-volume waste discharges has become a significant added cost. While there have been few fundamental changes in nonferrous metallurgy, recent years have seen many innovations and directions based in chemistry. The need for increased recovery of contained metals and more thorough sequestering of deleterious matter, all at lower cost and lower consumption of land and water, will drive commercial-scale innovation.

This paper first reviews some recent developments in the recovery and upgrading of five metals consumed heavily by Korean industry. Table 1 shows examples of the large-scale mill throughput at some large-scale metal mines. Two methodologies characterize the processing: hydrometallurgy (dissolution, concentration and re-

duction to metal), and flotation (physical separation of ore minerals from accompanying waste). This paper does not deal with pyrometallurgy (smelting) and refining processes, which commonly follow flotation and reduce ores to metals. It also does not deal with innovations in ore preparation, which includes fine grinding, sizing, and in some instances roasting of ore.

The consumption of metals in Korea far exceeds the limited, declining domestic mine production (Table 2). The possibility of producing additional metal domestically while carrying out already-mandated environmental remediation and disposal of existing wastes may also be a potential application for new technology. The value (and scarcity) of non-mountainside land, and the need for clean water supplies, is greater in Korea than in many countries. These factors make a difference in the decision whether to merely isolate or move mining waste, or to recover metals from it while removing it.

Per Table 2, Korean industry consumes ever-increasing quantities of copper. Overseas, a variety of partially oxidized copper ores are converted to metal through solvent extraction-electrowinning (SXEW). This method produces 20% of world copper (Acorga Ltd., 2002), and many waste dumps are treated by using conventional sulfuric acid leach treated. However the majority of copper comes from the mineral chalcopyrite,  $\text{CuFeS}_2$ , which is separated from finely ground waste rock by froth flotation. These concentrates are treated by pyrometallurgy at distant smelters. Because of the scale of production, because +99% of the feed is returned to waste streams, and

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<sup>‡</sup>Presented at the Int'l Symp. on Chem. Eng. (Cheju, Feb. 8-10, 2001), dedicated to Prof. H. S. Chun on the occasion of his retirement from Korea University.

**Table 1. Example of major nonferrous metallurgical operations**

Metal	Mine/Mill operation (Name, location, type of deposit, owner or operator)	Type of mill feed and process	Tons/day feed to mill	Quantity of product/yr (in tons, except for gold)	Reported as:
Cu	Morenci, AZ, USA (Open pit "porphyry" Cu, Phelps Dodge )	0.5% Cu, also iron pyrite, Flotation concentration, produce smelter feed	137,300	247,000	Cu Metal
		Cu leaching, SX-EW recovery, electrowinning	-	275,000	Cu Metal
Cu-Au	Grasberg, Indonesia (Open Pit "porphyry" Cu-Au, Freeport McMoran)	0.8-1% Cu sulfide ore with large Au credit. Flotation concentration, feed a smelter	220,700	741,227	Cu Metal
Zn-Pb	Century, Australia (“Sedex” Zn, Pasmaingo, Ltd)	Sulfide ore with 12% Zn, flotation concentration. Also flotation of Pb concentrate	14,000	850,000	Zn Concs.,
				67,000	Pb Concs.
Au (Ag)	Goldstrike, Nevada, USA (Disseminated carbonaceous Au, underground and Open Pit)	Carbonaceous sediments with 4-12 ppm Au. Minor Ag, Hg. Autoclaving or roasting, cyanide leach, pour gold bars	17,000	2,108,000 (also, silver)	Troy Oz. Au

(Data from Company annual reports and websites, late 1990s-2000).

**Table 2. Korean production of nonferrous metals and imports**

		Au (kg)	Ag (kg)	Cu (M/T)	Pb (M/T)	Zn (M/T)
Domestic production	1993	1,438	4,712	0	14,818	27,616
	1994	1,374	8,600	0	4,345	14,243
	1995	1,270	179	123	8,128	15,494
	1996	1,061	0	3	10,262	16,768
	1997	632	42	0	7,264	17,984
	1998	4	957	41	7,117	20,977
	1999	6	1	0	3,644	19,664
Metal imported into Korea	1993	34,435	236,023	571,187	67,338	462,011
	1994	58,336	302,527	426,421	121,078	576,231
	1995	217,102	429,064	468,714	140,653	534,362
	1996	424,381	451,261	347,994	96,026	530,786
	1997	606,152	340,196	518,112	104,524	659,786
	1998	459,244	73,322	973,450	164,829	800,136
	1999	363,757	217,691	1,166,630	178,010	881,885

because byproducts are often important, small innovations have been very significant for both processes.

### COMMUNITION: THE ENERGY INTENSIVE FIRST STEP

Breaking ore into small particles allows physical separation of different minerals, or exposure to chemical or biological reactions. For a typical open pit mining and metal recovery operation, this step consumes 85% of the electrical energy used [de la Vergne, 2001]. Some of the innovations discussed here may allow processing of coarser particles, which reduces power cost substantially. Intrinsic properties of a given ore, such as the hardness or work index with respect to fine grinding, and the size at which the desired metallic minerals are liberated from encapsulation, have great economic sig-

nificance.

The smaller the size of a particle, the greater its proportional surface area. Chemical reactivity, and the tendency of the particle to float on water or form slimes (discussed below) are increased by fine grinding.

### LEACHING AND SOLVENT EXTRACTION-ELECTROWINNING (SX-EW)

Solvent extraction-electrowinning technology for metal extraction has likely seen the greatest degree of technological advance in recent years. SX-EW utilizes the selective transfer and concentration of metal ions from an impure aqueous phase via an organic phase to a second pure aqueous phase from which the desired metal can be recovered.

In the recovery of copper from sulphuric acid leach solutions, for instance, divalent copper ions are selectively captured at the interface of the organic and aqueous phases by a specially designed organic molecule to form a copper/organic complex. This complex is insoluble in the leach solution but soluble in organic solvents. If the organic compound (ligand), has been diluted with, for instance, a hydrometallurgical grade of "kerosene" prior to contact with the leach solution, then the copper complex will transfer into the bulk organic phase. If, in addition, the organic and aqueous are totally immiscible and the ligand is designed to form an organic complex only with the species to be extracted, then a very effective low-energy-consumptive metals separation process results. Proprietary equilibrium modifiers, which improve the efficiency of chelating compounds, are also added at commercial plants [Acorga Technical Library, 2001]. More effective reagents can mean fewer stages of ion exchange.

In recent years, acid leaching of oxidized (non-sulfide) and chalcocite (Cu<sub>2</sub>S) ores followed by SX-EW has seen the greatest growth and innovation. Ion-specific organic ligands are available at large commercial scale, and continue to improve productivity. Lower costs are often achieved by outdoor heap leaching, rather than leaching

in tanks in a plant. Relatively coarse or agglomerated ore is stacked on a solution-impervious pad and the chosen leach solution is applied. Because the leach solution is more dilute, and does not readily reach every particle of ore on the pad, recovery of the desired metal is often lower by this method.

Metal recovery is typically by electrowinning (EW). Purified copper metal is recovered at the cathode of a series of large cells fed by a solution produced in the second stage of the SX process. This process is known as stripping and is carried out using "spent" or "lean" electrolyte which has been partially depleted of copper in the EW cells. Copper is deposited at the cathode and oxygen is liberated at the anode. This is different from "electrorefining" where the anode reaction is merely the dissolution of a copper electrode, with the electrolyte solution remaining essentially unchanged. Electrowinning uses an insoluble anode so that the deposited copper comes from the solution/electrolyte. In the EW reaction, sulfuric acid is generated which can be recycled back to the leaching process. This is especially important in countries where sulfuric acid must be manufactured from imported raw material.

Until recently, industry has used simple mixer-settler equipment in the SX contacting process. This typically consists of simple mixer boxes, sometimes arranged in series, discharging the organic/aqueous dispersion into a shallow settler typically 1 meter deep. The moving dispersion is allowed to separate by gravity as it passes down the length of the settler. Final phase separation is affected by a simple weir system with the organic phase flowing over the upper weir and into a collection launder and the aqueous phase passing under the upper weir, over a lower weir and into a similar launder. The most recent innovative technology in the copper industry may be the "pulsed column," which replaces the large mixer/settlers in the solvent extraction plant. These cells take up less floor space, less organic is required and the cost is significantly less than the conventional units [Ness, 1999].

Traditionally, oxide and silicate zinc ores have been treated by fuming (pyrometallurgy), sometimes leading to environmental degradation. SX-EW zinc technology recently has become commercial, for example at the new Skorpion Mine (150,000 T/yr of metal) in Namibia [SAEP, 2001]. Here leaching is performed under atmospheric conditions, and the liquors are purified and concentrated by using standard organic compounds prior to electrowinning. Current technology also exists for Pd, Mo, Ge and Ga production, and the removal of As from waste streams.

## BIOLOGICAL PROCESSES IN LEACHING

Optimization of bioleaching, or biodestruction of metallic minerals [e.g. Kawatra and Natarajan, 2001; Free and others, 1991], is now under intense study. Although bacteria have always existed in the copper heap leach process, their importance, especially in iron conversion and copper recovery, is becoming more valued. Different types of bacteria are being gathered from hot springs, ocean floors and naturally occurring acid rock drainage. Some are proving useful additions to leach solutions to achieve optimum oxidation in leach pads under various different temperature and oxygen and sulfide concentrations. Nine copper biooxidation heap leach facilities have been commissioned (all in the Southern Hemisphere) with productions ranging between 1,400 T/d to 20,000 T/d. Commercial appli-

cation to gold processing is discussed below.

## RECOVERY BY FLOTATION: DEVELOPMENTS, AND FUTURE DIRECTIONS

The flotation process utilizes synthetic (typically proprietary) bipolar organic molecules known as promoters and collectors. One end of the molecule has an affinity for specific kinds of mineral grain surface properties. The other attaches readily to a froth or soap bubble, generated by introducing a frothing agent and compressed air. Finely ground ore is agitated and the floated mineral is skimmed continuously from the surface of the flotation cell. This technology, first developed at the turn of the 20<sup>th</sup> century, remains very important, and the copper industry uses it on the largest scale. Chemical engineers continue to test and improve a still-growing variety of mineral-specific flotation collectors. Improvement of these technologies may presently be near a plateau, with research impeded by low metal prices. Copper production costs, most notably in Asia, are also very sensitive to fuel costs. Column cells, which use less energy, are now important. Thus at the scale of a typical large operation (Table 1), every small improvement yields significant rewards. Large amounts of waste, containing significant copper, are stockpiled annually. These also tend to break down in time and can then yield acidic, iron oxide rich drainage [e.g. Alpers and Blowes, 1994; Chon and others, 1990]. Mine and mill wastes are both a liability and a resource for future metal extraction. Chemistry and separation devices to help tame them while the pulverized rock is still in the process stream deserve attention.

Selective flotation refers to floating one mineral while depressing, or leaving behind, others. Addition of a second reagent or changing pH can later float a second mineral. Flotation today also removes and thus neutralizes undesirable components of ores, e.g. carbon, which inhibits leach recovery [de la Vergne, 2001], or other gangue minerals which pollute waste streams or downstream pyrometallurgy. Copper SX-EW plants have recently improved the removal of unwanted organic solution from the copper raffinate and rich electrolyte solution by using flotation cells. This yields significant cost savings in recovered organic.

Given the variety of copper ores and that some of them are not amenable to flotation, extensive research has led to new methods for leaching of ores and waste dumps. The low cost large-scale environment of a dump, like its close relative the gold heap leach, is more difficult to study on a micro-scale than a stream of pulp in a mill. Sulfide-bearing waste and tailings dumps evolve drastically with time [e.g. Garcia et al., 1996; Cathles, 1994; Park and others, 2000; James, 1990]. Their ongoing chemical discharges are now demanding monitoring and remediation. New metallurgical chemistry is being engineered through aqueous solution modeling programs, some of them available over the World Wide Web [e.g. Langmuir, 1997, p. 558-561]. These approaches can identify new paths for chemical reactions. For example, researchers at Montana Tech in the USA have proposed reductive dissolution of copper sulfide minerals by creating cupro-thio complexes under anaerobic conditions. Leaching of common but formerly untouchable minerals such as chalcopyrite is becoming a reality [Prasad and Pandey, 1998]. Applications of better tools to study grain reactions over time, including innovative types of microscopy, help to model complex dis-

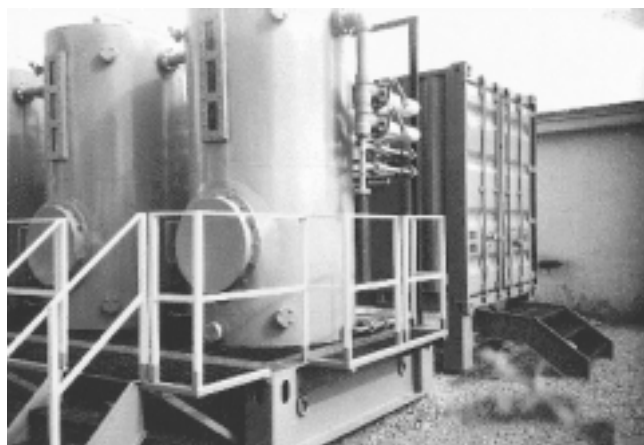
solution.

### PRECIOUS METALS RECOVERY: SIMILAR DIRECTIONS

Many significant gold mines and the few large primary silver mines are nearly similar in scale and raw ore value to copper mines. However, in contrast to base metals, the gold and silver recovered are merely trace elements in the feed. Variants of cyanide leaching are the typical choice for recovery, and the chemistry and environmental safety of the process are well studied [e.g. DeVoto and McNulty, 2000]. A low capital and operating cost is obtained with many low-grade, oxidized ores through heap leaching. Large-scale heap leaching methods have undergone much engineering, and specialized hardware is now available to the metallurgist. There is a trend towards emitters and drip systems instead of the garden sprinklers used in the past. Sprinklers are also now used when there is a need to remove excess solution through evaporation. Innovation has also improved the removal of gold from leach solution by adsorption on activated carbon. Studies of the adsorption mechanism have proved useful. The gold cyanide complex fits cleanly within a plane of graphite atoms [Jones et al., 1989], resulting in efficient adsorption of gold from solution. Refinements have aimed at selectivity, suppression of adsorbent contamination, and optimized granule or fine particle forms of carbon. Today's ores often contain minerals that can also adsorb (rob) gold from pregnant cyanide mill solutions. Synthetic magnetic carbon grains have been proposed by researchers at the University of Utah as a means for quick removal of the activated carbon and its contained gold before in-situ "robbery" of the pregnant solution occurs. Placing the activated carbon, or an adsorbent resin, in the stream of pulped ore is another, now widely utilized innovation for ores that respond poorly to conventional leaching. Carbon-in-leach, or CIL, has allowed much greater and more rapid recovery of gold from some major deposits. A further innovation is the South African carousel unit used for CIL. The activated carbon remains in the stirred tanks as opposed to being counter-currently pumped to progressive tanks. This results in a reduced carbon contact time with pulverized ore, lower carbon, losses, and greater



**Fig. 1. A large gold leaching operation high in the Andes Mountains at Choquelimpie, Chile. The plastic-lined ponds handle pregnant and barren leach solutions (All figures courtesy Kappes-Cassiday Associates, Reno, USA).**



**Fig. 2. A carbon adsorption gold recovery unit, designed for portability, Magistral gold mine, rural Mexico.**



**Fig. 3. The compactness of a small modern plant at an old mine site is illustrated.**

gold recovery.

Cyanide heap leaching is now a safe, cost-efficient method for production of gold and silver at scales ranging from small to very large, spurred by the rise in precious metals prices in 1980. Figs. 1 to 3 show a large gold heap leach "mill" and small, relatively portable gold and silver recovery units. Similar plants can be applied to removing other substances from crushed waste rock.

Sulfide and sulf-arsenide ores, in which gold and silver may be locked in the structure of metallic waste (gangue) minerals, present other problems. They typically become more abundant as mines are extended further below the earth's surface, and below the water table. In the past, smelting and roasting were used to extract metals from such ores. These produce sulfur- and arsenic-rich high temperature off-gases, which today must of course be treated. Destruction of mineral grains, which encapsulate gold, and sequestering or suppression of deleterious elements (such as arsenic) which also affect gold recovery are now also accomplished by pressure oxidation or autoclaving. This is a popular innovation, though its complexity requires high grade feed and changes in classical grinding technology [Hiskey and Sanchez, 1995]. Huge and increasingly automated autoclaves are now part of high-grade ore reduction plants at large mines, for example in the sediment-hosted gold districts of

northern Nevada, USA. They compete with roasting of refractory ores. The chemistry in a heated, pressured autoclave is complex, varying with pH and minerals present. In an acid medium total oxidation of sulfide sulfur to sulfate, and arsenic to arsenates occurs. An essential feature for many such operations is that arsenic compounds which prevent normal cyanide leaching are not only broken down, but arsenic is sequestered as insoluble compounds while sulfur is discharged at a relatively un-reactive valence state. This technology is now becoming useful with other metals. Canada's Hudson Bay Mining and Smelting now pressure leaches zinc and associated metals, thus eliminating sulfur dioxide off-gases [Wells, 1999].

Bioleaching is another growing technology for destruction of gold-encapsulating minerals [e.g. Brierly, 1999]. With the demand for decreasing discharge of chemicals into the environment, and even



**Fig. 4. Heated agitated leaching tanks for iron chloride leaching of silver and lead, Itos, Bolivia. This facility can process treats 15,000 tons of former waste material per month. Plant was erected to treat 1.8 million tons of tin-tungsten tailings containing approximately 400 tons of silver, and large quantities of recoverable antimony, arsenic, lead and copper.**



**Fig. 5. Interior of Itos plant, Bolivia, showing stainless steel and nonmetallic piping and vessels required to handle hot corrosive leaching solutions. Modern materials make possible handling of fluids that formerly could not be economically contained.**



**Fig. 6. Erection of the Itos plant, using local labor and engineers. International technology transfer and funding are an integral part of metallurgy today.**

the possibility of genetic engineering, this science is rapidly adapting to large-scale metals recovery, especially in gold and copper. Eight biooxidation plants (all in the Southern Hemisphere) have been commissioned to handle gold flotation concentrates. Their capacity ranges between 35 and 1,000 tons per day of concentrate. One gold biooxidation plant has also been commissioned. However, this application is seeing slower growth due to the need to neutralize the acid solution required by the bacteria prior to reaction with alkaline cyanide leach solution.

While silver may also be recovered by using concentrated cyanide, modern materials have allowed recent commercial scale acid-ferric chloride leaching of silver (for example, Cope, 2000). This process dissolves specific minerals refractory to both flotation and cyanide leaching. Figs. 4 to 6 show a plant for the recovery of silver and other metals from old tungsten tailings in Bolivia. Some of these processes do not destroy iron pyrite, and thus help prevent acidic water discharges. Similar leaching technology can also apply to metallurgically difficult lead-bearing ores, but for typical lead sulfide ores conventional flotation followed by pyrometallurgy is presently more cost effective. Much silver is still a byproduct of lead smelting as well as copper precipitation.

Zinc is also heavily consumed by Korean heavy industry. The metal is produced domestically, though largely from imported ores. In most mines it occurs with lead, and the different ore minerals must be separated by selective flotation prior to reduction in most smelting processes. Modern zinc plants typically produce metal by electrolytic reduction, often directly from oxidized/roasted feed. For example, the Korea Zinc Co., Ltd. operates large state-of-the-art plants for producing this metal. In the past, relatively high feed grades world wide and low prices for both lead and zinc perhaps limited innovation. But environmental concerns about accompanying trace metals mean some existing technologies, such as the jarosite waste precipitation process, are in need of improvement. Trends in environmental regulations provide added impetus for recovering trace metals accompanying many zinc ores, metals that were formerly disposed of in waste.

All of these processes require water, typically up to 3 tons for each ton of ore processed in a concentration mill [de la Vergne, 2001].

Some of this water is lost at each step, and some is typically locked in "slimes," very fine material with a large surface area, produced by fine grinding, that are discharged as tailings. In countries like Korea, water conservation is becoming a central issue.

### TAILINGS: "NASTY" WASTES OR FUTURE METAL RESOURCES?

The solids in the waste stream from most milling plants typically are impounded, and some ponds have existed for as long as a century. In places these tailings occupy large land areas. Typically finely ground and often reactive when exposed to air or moisture, tailings have traditionally been isolated on unused land or discharged into deep seas. As environmental concerns and the value of flat land increase, the best practices for disposing of tailings are changing. Kral [2001] details a recent large-scale tailings site remediation in a remote area. Over time at many sites, old tailings have also been reprocessed at a profit. The cost of crushing and grinding the material has already been paid. Many of the processes discussed in this article, such as SX-EW, chloride leaching, and flotation, have been applied successfully to metal recovery from old tailings. Modern innovation, perhaps incorporated into modular plants that can be relocated between various small sites, may help in the design of combined recovery and reclamation programs for closed Korean mining sites.

### COMPUTERIZATION AND ECONOMICS

For all of these ore types over the past decade, a large proportion of the improvement in product grade and recovery can be attributed to strong growth in computer technology. Plant control systems, advanced modeling methods, and interfacing with economic analysis [e.g. Brittan and Arthur, 2000] have contributed to improved beneficiation and hydrometallurgy at nearly all nonferrous recovery plants. With development in large-scale fast processing hardware, fuzzy logic, and artificial intelligence software, these improvements will doubtless continue.

For all of these metals, some well-defined deposits are known to have significant resources, but poor extractability. And there are deposits with good ore grades but unusually high or soluble contents of "nasty" undesirable elements. Such ore deposits are a challenge for innovators of technology, at both macro and micro scales. Process mineralogy, or the study of the physical components of ore and waste products, becomes more important. Wherever a metal deposit sits idle, in a nation that must instead import the same metal, foreign exchange is being lost. The totally international pricing of metals thus has important implications for countries where costs, paid in local currency, are low.

For all innovations a critical question is: can laboratory-scale success become economically viable? Pilot plants, small-scale versions of commercial mills, are a necessary testing ground. Korea Institute of Geosciences and Mineral Resources (KIGAM) recently installed a versatile 2 T/hr pilot mill: initially for the study of gold recovery from Korean tailings [Chae, 1999]. Experience and information are also shared worldwide at ever-greater rates.

In the past, nonferrous metallurgists typically were generalists. In the Information Age there is more reliance on chemical engi-

neers. There is new dependence on specialists and new technology from other disciplines, such as bioleaching/microbiology, optical imaging, surface sciences, and every aspect of inorganic chemistry. There is opportunity in Korea to contribute to economic recovery processes for non-ferrous metals worldwide, and to aid in reclaiming land and metals left in unusable condition by past operations. New technology can be applied to "Korea-specific" situations, such as improving the economics of land reclamation.

### ACKNOWLEDGEMENT

The senior author wishes to thank various industry colleagues and members of the metallurgical profession for comments and suggestions. Professors Yong Kang and Jea Keun Lee of the Korean Society of Chemical Engineers urged the preparation of this paper. The Korean Science and Engineering Foundation provided funding and Pukyong National University provided access to superb laboratory equipment in Busan. Dan Kappes of Kappes, Cassiday and Associates, Reno and Joe Stano of Washington Group International, Englewood, Colorado provided helpful comments.

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