J. of Korean Inst. of Resources Recycling
Vol. 17, No. 2, 2008, 3-15
≫總　設≪

生物學的 方法에 의한 廢棄物의 再活用†

Debabrata Pradhan*,** · ✝金東鎭* · 安鍾寬* · 朴庚鎬* · 李承遠**

*韓國地質資源硏究院 資源活用素材硏究部, **忠南大學校 나노工學部 나노素材工學科

Waste Recycling Through Biological Route†

Debabrata Pradhan*,, ✝Dong-Jin Kim*,**
Jong-Gwan Ahn*, Kyung-Ho Park* and Seoung-Won Lee**

**Minerals and Material Processing Division, Korea Institute of Geosciences and Mineral Resources (KIGAM), Daejeon 305-350, Korea.*
***Division of Nano Engineering, School of Engineering, Chungnam National University, Kung-dong, Daejeon 305-764, Korea.*

요　약

다양한 독성 폐기물이 주변 환경에 배출되면 궁극적으로 모든 생명체의 생존에 위협이 된다. 박테리아 및 곰팡이종의 반응을 이용한 미생물침출 및 미생물복원을 포함하는 바이오 습식제련은 환경문제를 극복하는데 적합한 경제성이 있는 잠재기술이다. 미생물 침출은 *Thiobacillus ferrooxidans, Thiobacillus thiooxidans, Laptospirillum ferrooxidans*와 같이 금속과 반응을 일으키는 박테리아를 이용하여 다양한 광물 및 폐기물로부터 금속 성분을 용해하는 것을 말한다. 일반적으로 미생물 침출반응은 직접 및 간접반응으로 나누어진다. 직접반응에서 박테리아는 성장 및 물질대사를 위하여 침출 기질로부터 전자를 받아 황산을 생산하므로써 황화광물을 산화시킨다. 반면 간접반응에서는 철산화 박테리아에 의해 생성된 Fe^{3+}가 황화광물을 산화시킨다. 이러한 침출기구를 통하여 저품위 광물 및 정광, 슬러지, 광미, 플라이 애쉬, 슬래그, 전자 스크랩, 폐밧데리 및 폐촉매 등으로부터 금속을 회수할 수 있다. 생물학적 방법은 폐기물의 매립을 극복할 수 있는 대체기술로서 건강하고 깨끗한 환경 보존에 기여할 수 있다.

주제어 : 미생물 침출, 미생물 균주, 산업폐기물, 황화광물, 폐촉매

Abstract

Different toxic wastes are disposed of in our surroundings and these will ultimately threaten the existence of living organisms. Biohydrometallurgy, which includes the processes of bioleaching and bioremediation through the activities of microorganisms such as bacterial or fungal species, is a technology that has the potential to overcome many environmental problems at a reasonable economic cost. Bioleaching were carried out for dissolution of metals from different materials using most important metal mobilizing bacteria such as *Thiobacillus ferrooxidans, Thiobacillus thiooxidans* and *Laptospirillum ferrooxidans*. According to the reaction, bioleaching is parted as direct and indirect mechanism. In direct mechanism the bacteria oxidize the sulphides minerals by accepting electron and producing sulphuric acid in leaching media for their growth and metabolism. In other hand the indirect bioleaching is demonstrated as the oxidation of sulphides mineral by the oxidant like Fe^{3+} produced by the iron oxidizing bacteria. Through this process, substantial amount of metal can be recovered from low-grade ores, concentrates, industrial wastes like sludge, tailings, fly ash, slag, electronic scrap, spent batteries and spent catalysts. This may be alternative technology to solve the high deposition of waste, which moves toward a healthy environment and green world.

Key words: Bioleaching, microorganisms, industrial waste, sulfide minerals, spent catalysts

† 2007년 7월 30일 접수, 2007년 12월 7일 수리
✝E-mail: djkim@kigam.re.kr

1. Introduction

A feature of the present developed world is that humans purchase an increasing number of new products to maintain a sophisticated life and this causes waste products to be discarded near residential areas. To maintain this demand for new products, industries have accelerated rates of production and this has resulted in huge deposition of industrial wastes that must be disposed of in large waste dumps near the industrial area. The result of this 'consumer culture' and increased waste disposal is pollution of the basic resources that a society requires. Very often this pollution appears first in the fresh water, lakes rivers and ground-water, required by all people in a society. Another feature of increased consumption appears in mine sites where the depletion of concentrated ores has become a challenging issue to supply of the required quantity of the crucial raw material for almost all industries, metals. Wastes, such as house-hold wastes, electronic wastes, secondary minerals, low grade ores, industrial sludge have become the challenging issue for the environment. If the accumulation rate of waste materials continues to increase then within a short time, the environment will not be able to supply the basic necessities for human society.

The accumulation of waste material does however present a challenge and an opportunity to researchers. If these low value wastes can be utilized in an economic way, the environment can be safeguarded and economic opportunities can be realized. Biohydrometallurgical processes will certainly have a role in solving the problem created by wastes. Biohydrometallurgy is a new technology developed in this century. Many researchers have worked in this field which requires a knowledge and understanding of the industrialization through biological and chemical processes. The technique requires harnessing the metabolic activities of suitable strains and optimizing, their growth conditions, such as pH of solution, temperature and material concentration so that the microbes multiply spontaneously and bring the desired changes into effect. In recent years, bioleaching has been shown to be a potential way to remove heavy metals from metal contaminated materials such as anaerobically digested sewage sludge, contaminated river sediment, spent batteries and incinerator fly ash[1-5].

Due to depletion of concentrated ore bodies the present situation demands the development of new technology for mineral processing. Biohydrometallurgical approaches are considered to be a 'green technology' with low-cost and low-energy requirements. Because of these advantages of which also include better efficiency, bioleaching technology has been a notable success for the mining industry[6]. Microbial bioleaching is based on the ability of microorganisms to transform solid compounds to a soluble and extractable form. This may involve enzymatic oxidation or reduction of the solid compound, or an attack on the solid compound by metabolic products[7]. Extraction of metals from low-grade ores, mining wastes, sewage sludge, secondary raw materials and industrial intermediate products using microorganisms have all been reported[8].

Bioleaching is very effective for recovery of gold from refractory gold pyrite and copper from chalcopyrite. Because of the low energy input required in bioleaching processes, they are a feasible and economical technique to recover metals from low-grade ores. Since significant quantities of metals are now found in low-grade ores and mining residues, these are potentially viable sources of metals if low cost extraction techniques can be applied. Biohydrometallurgy can also be applied to other waste materials such as a coal fly ash (CFA), which is produced by coal-operated power plants worldwide. In this application, CFA can be used as a source for metal extraction within appropriate economical constraints[10]. Mine tailings are similar to these materials with respect to the physical and chemical characteristics and biohydrometallurgy is potentially applicable for treatment of these materials. Sediment contaminated by heavy metals is also a growing environmental problem and the need for sediment dredging creates sediment dumps adversely affecting the local environment[11].

Biohydrometallurgy can be applied to all of these environmental problems because they are efficient in their use of energy and cause less environmental problems than chemical methods[12]. The industry sectors are seeking an efficient, economic technique to handle these wastes[13]. Pyrometallurgical and hydrometallurgical techniques are either very expensive, energy intensive or have a negative impact on the environment. For these reasons, interest in biohydrometallurgical techniques is becoming intense.

The bioleaching process may be defined as the solubilization of metals from solid substrates either directly by the metabolism of leaching bacteria or indirectly by the products of metabolism. The interactions between bacteria, metabolic products, CFA particles, and leaching products have been studied[14]. It has been demonstrated that bacterial growth and the amount of metals leached from the CFA residues are coupled through biological and chemical interactions which involve the various components in this system. Oxidation of sulfur in mineral compounds by air naturally results in the formation of sulfuric acid and the subsequent release of toxic metals into the water phase. However, the microbial oxidation of reduced inorganic sulfur compounds, increases the natural spontaneous rate and serves to mobilize metals under controlled conditions, e.g. by bioleaching of low-grade ores, or removal of heavy metals from contaminated soil, sediment, and sewage sludge. Thus, a remediation process for heavy-metal contaminated sediments is being developed and tested on a pilot scale[15]. The effectiveness of bioleaching is highly dependent on the physical, chemical and biological factors in the system. These include (i) carbon source and oxygen supply, (ii) pH, (iii) temperature of leaching environment, (iv) preculture period and inoculum used, (v) resistance of microorganisms to metal ions, (vi) physical and chemical states of the solid residue, (vii) liquid to solid ratio and (viii) bioleaching period [16]. The maximum rate and yield of metal leaching may be achieved when these parameters are considered and optimized collectively.

2. Metal Mobilizing Microorganisms

Wastes utilization and transformation by biohydrometallurgical processes are based on the ability of microorganisms to transform solid compounds and result in the dissolution of extractable elements which can be recovered[17]. Three key groups of microorganisms have been used for bioleaching process; these are autotrophic bacteria (e.g. *Thiobacilli* spp.), heterotrophic bacteria (e.g. *Pseudomonas* spp., *Bacillus* spp.) and heterotrophic fungi (e.g. *Aspergillus* spp., *Penicillium* spp.)[2]. Among the variety of microorganisms those are known to facilitate metal bioleaching reactions, the autotrophic *thiobacilli* species are perhaps the most common[18]. Bioleaching of aluminum and iron from coal fly ash (CFA) by *Acidithiobacillus thiooxidans* bacteria has been considered. The bacterium *Acidithiobacillus thiooxidans* is active at low pH and can endure harsh conditions that exist in concentrated solutions of metals[19]. These particular characteristics make it a suitable microorganism for bioleaching. Specific examples of *Acidithiobacillus thiooxidans* growth in environments containing high concentration of metals are: Zn and Cd up to 600 and 400 mM respectively [20], As^{3+} and As^{5+} 67 and 534 mM, respectively, iron: Fe^{2+} 537 mM and Fe^{3+} 180 mM, and Al^{+3}: 370 mM have been reported[21]. In the case of zinc and cadmium, specific proteins were produced, which were capable of binding these metals[20]. Changes in microbial populations during bioleaching of mineral tailings were determined using terminal restriction fragment length polymorphism (T-RFLP) analysis, and by plating of samples on selective solid media. Both techniques confirmed that *Acidithiobacillus thiooxidans* was present throughout culture incubation but, although the other bacteria identified were iron/sulfur-oxidizing bacteria, the exact identity of these strains varied with the technique used[22]. While the microorganisms associated with mine drainage itself are relatively well documented, those associated with the solid mine wastes are less so. Studies have indicated that *Acidithiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* are the major mineral-oxidizing prokaryotes present in some leached copper ore or spoil heaps, while other reports on commercial bioleaching operations suggest *Sulfobacillus* spp. are important in self-heating heaps where temperatures have been measured at around 50 ^{o}C[23,24]. It is generally considered, however, that the Gram-negative *Leptospirillum /Acidithiobacillus* iron-oxidizers are the principal organisms responsible for mineral leaching in most cases. As environments become more extreme in terms of acidity and/or temperature, the diversity of indigenous acidophilic prokaryotes is reduced, for example thermotolerant *Ferroplasma* spp. (iron-oxidizing Archaea) and *Leptospirillum ferriphilum* become increasingly dominant [25,26]. Metal solubilization from solid wastes or other solids is achieved through a variety of acidophilic and chemoautolithotrophic bacteria

Table 1. Microorganisms used for different types of materials[23-27].

Materials	Major Toxic Metals	Process	Name of Organism
Fly-ash from municipal solid waste	Al, Pb, Zn and Cu	Bioremediation	*A.niger*
Low-grade ore	Cu, Zn and Ni	Bioleaching	*A.niger*
Coal fly-ash	Al	Bioremediation	*T.t.*
Tannery sludge	Cr	Bioremediation	*T.t.*
Industrial waste sludge	Zn and Al	Bioremediation	*T.f.*
Low-grade ZnS concentrate	Zn	Bioleaching	*T.f. and S.t.s.*
Incinerator fly-ash	Al, Zn, Pb and Cu	Bioremediation	*A.niger*
Mineral tailing of copper mines	Cu	Bioleaching	*T.t.*
Sulfidic mine waste	S	Bioleaching	*T.f + SDS*
Mine tailing	Zn, Cu and Pb	Bioleaching	*T.t.*
Contaminant sediments	Cd, Cr, Cu, Ni, Pb and Zn	Bioremediation	*T.t.*
Chalcopyrite	Cu	Bioleaching	*T.f + T.t. + L.f. + Ag*
Low-grade complex sulfidic ore	Zn, Cu and Fe	Bioleaching	*T.f + T.t. + L.f.*
Batteries	Ni, Cd, Li and Co	Bioleaching	*T.f*
Electronic scrap	Cu, Al, Ni, Pb and Zn	Bioleaching	*T.f + T.t. and A.niger + P.simplicissimum*
Metal powder and electronic scrap	Ni, Au and Cu	Bioleaching	*C.v. + P.fluorescens + Bacillus megaterium*
Spent catalyst	Ni, Al, V, Sb and Mo	Bioleaching	*A.niger*

Abbreviation: *Thiobacillus ferrooxidans – T.f., Thiobacillus thiooxidans – T.t., Laptospirillum ferrooxidans – L.f., Aspergillus niger – A.niger, Sulfobacillus thermo sulfidooxidans – S.t.s., Penicillum simplicissimum – P.simplicissimum, Chromobacterium violaceum – C.v., Pseudomonas fluorescens – P. fluorescens*

such as *Acidithiobacillus thiooxidans* and *Acidithiobacillus ferrooxidans*. Other bacteria such as *Leptospirillum ferrooxidans* were reported to bioleach zinc from the marmatite flotation concentrate effectively[27]. The microorganisms utilized in bioleaching for particular metals from different specific materials are reported in Table 1.

3. Mechanism of Bioleaching

Two mechanisms have been proposed, the direct and indirect mechanisms, to explain the process of oxidation of solid metal sulfides by *Acidithiobacilli* species. The direct biooxidation of metal sulfides occurs when microbial cells are attached to the surface of a solid sulfide particle. The name of this mechanism is based on the direct attack on the crystal structure of sulfide by attached microbial cells as part of their metabolism [28]. The attached microbe oxidizes the sulphides at the area of contact between the microbial cell and the sulfide surface. The overall biochemical reaction for direct metal sulfides oxidation can be demonstrated by the following equation (equation 1):

$$MS + 0.5O_2 + 2H^+ \rightarrow M^{2+} + H_2O + S \quad (1)$$

This overall reaction may be separated into two electrochemical half-reactions (equations 2 and 3):

$$MS \rightarrow M^{2+} + S + 2e^- \quad (2)$$

Which are carried out on the surface of the sulfide crystal, and

$$0.5O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad (3)$$

in the cytoplasmic membrane respectively. The electrons are transferred from the surface of the sulfide crystal through the cell wall by means of a chain of several redox proteins such as rusticianin and cytochrome c. In addition to this process, oxidation of sulphides minerals by extracellular metabolism can't be ignored because sulfur oxidizing bacteria excrete organic acids such as those found in the TCA cycle, ethanolamine, amino acid and lipids[29, 30].

The indirect bioleaching mechanism is a two step process based on the chemical oxidation of sulfide minerals by the dissolved ferric ion and itself reduced to ferrous ion during the process (equation 4). The ferrous ions produced by reaction can be reoxidized by microorganisms such as *A. ferrooxidans* according to the biochemical reaction (equation 5). The oxidation of sulphides minerals by ferric iron via this mechanism is regarded as a two step indirect bioleaching process.

$$MS + Fe_2(SO_4)_3 \rightarrow MSO_4 + S + 2FeSO_4 \quad (4)$$
$$2FeSO_4 + H_2SO_4 + 0.5O_2 \rightarrow Fe_2(SO_4)_3 + H_2O. \quad (5)$$

The dissolved iron in solutions cycles between the ferric and ferrous forms according to reactions (equation 4 and 5)[31]. The indirect mechanism is quite complex and reaction is assumed to be the sum of two pathways i.e. thiosulphate pathway and polysulfide pathway. The importance of the two processes depend on the acid solubility the metal sulphides. Thiosulphate mechanism is important during the oxidation of the metal sulfides FeS_2, MoS_2 and WS_2 by ferric iron. The reaction proceeds through the formation of thiosulphate as an intermediate product. The polysulfide mechanism proceeds by an attack of protons on sulphides[32]. The reactions are as following:

Thiosulfate mechanism (FeS_2, MoS_2 and WS_2)

$$FeS_2 + 6Fe^{3+} + 3H_2O \rightarrow S_2O_3^{2-} + 7Fe^{2+} + 6H^+ \quad (6)$$
$$S_2O_3^{2-} + 8Fe^{3+} + 5H_2O \rightarrow 2SO_4^{2-} + 8Fe^{2+} + 10H^+ \quad (7)$$

Polysulfide mechanism (ZnS, $CuFeS_2$ or PbS)

$$MS + Fe^{3+} + H^+ \rightarrow M^{2+} + 0.5\ H_2S_n + Fe^{2+} \quad (n \geq 2) \quad (8)$$
$$0.5\ H_2S_n + Fe^{3+} \rightarrow 0.125S_8 + Fe^{2+} + H^+ \quad (9)$$
$$0.125S_8 + 1.5O_2 + H_2O \rightarrow SO_4^{2-} + 2H^+ \quad (10)$$

From the above equations, it was concluded that the function of bacteria was to produce sulfuric acid and to oxidize minerals by the attack of either ferric iron or by proton. The model of this model is shown in Fig. 1.

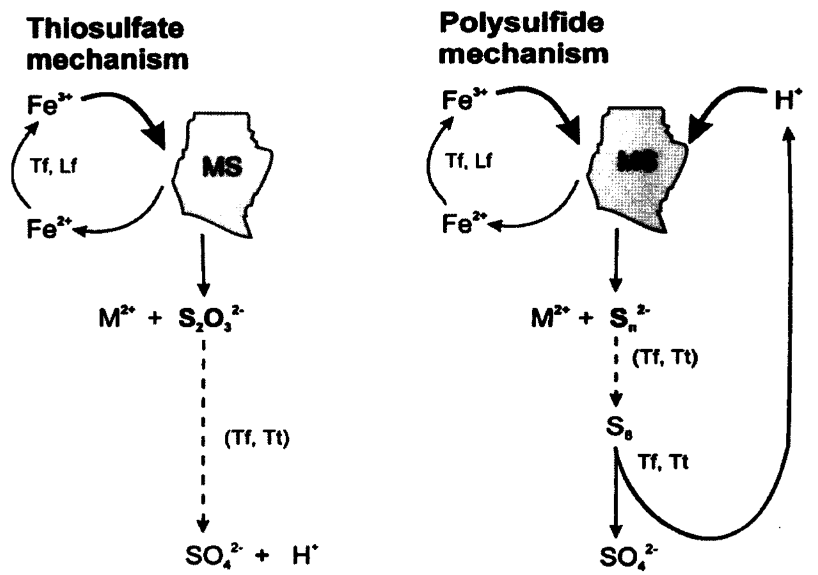

Fig. 1. Two different indirect mechanisms i.e. thiosulfate and polysulfides[32].

4. Bioleaching of Different Wastes

4.1. Low-grade ore

The extraction of metals from low grade ores and refractory gold ores is a multi-billion dollar business worldwide[33] but these refractory, low-grade ores and secondary minerals have problems for mining companies. The use of micro-organisms to recover metals from low-grade ores and mineral concentrates has developed into a successful and expanding area of biotechnology. Bioleaching of base metal sulfides is in use commercially and offers many cost advantages over other techniques such as pressure oxidation. Bioleaching involves the use of iron and sulfur-oxidizing micro-organisms to catalyze the dissolution of the valuable metal species from sulfide ores or concentrates[34-36]. In one study, low-grade sphalerite was treated using native cultures of *Acidithiobacillus ferrooxidans* and *Sulfobacillus thermosulfido-oxidans* in order to determine the ability of these bacteria to the leaching of zinc. The effects of bacterial strain, pH, temperature, pulp density, iron precipitation, and initial concentration of ferric iron on the zinc leaching were evaluated[37]. Bio-oxidation of complex zinc-lead sulfides has been widely investigated using samples of sulfide concentrate, pure galena, or sphalerite minerals[38-40]. Among the bacteria involved in bacterial leaching, *Acidithiobacillus ferrooxidans* has been studied the most intensively and has been the most important in commercial operations treating lead–zinc sulfides.

The increasingly important role of biohydrometallurgy in modern mineral extraction is due to both economic and environmental factors. Bioleaching processes have been investigated as a means of treating copper ores. Chalcopyrite is the most important and abundant copper mineral but it is relatively recalcitrant to chemical and microbiological oxidation due to its special crystal structure and electrochemistry[41-43] It is essential to find some desirable methods to enhance chalcopyrite bioleaching. It has been reported that some as Ag^+, Sn^{+2}, Bi^{+3}, Co^{+2}, Hg^{+2} and Mn^{+2}, exert a catalytic effect and accelerate copper dissolution from chalcopyrite in the presence of *Acidithiobacillus ferrooxidans*. Silver ion appears to have the best effect [44-47]. The positive catalytic effect of silver ions on the bacterial leaching of chalcopyrite containing ores in both shake flasks and column reactors has been studied. The mechanism of silver catalysis [48] indicates that Ag^+ ion rapidly reacts with chalcopyrite as following reaction (equation 11)

$$CuFeS_2 + 4Ag^+ \rightarrow Cu^{2+} + Fe^{2+} + Ag_2S \qquad (11)$$

The Ag^+ ion can be regenerated through the oxidation of Ag_2S by Fe^{3+}

$$Ag_2S + 2Fe^{3+} \rightarrow 2Ag^+ + S + 2Fe^{2+} \qquad (12)$$

4.2. Waste batteries

Microorganisms including the chemoautotrophic, acidophilic, iron and sulphur-oxidizing bacteria *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* use CO_2 as the sole carbon source and ferrous and reduced inorganic sulphur compounds as the energy source[49]. Microorganisms catalyse changes in metal speciation and mobility and are fundamental components of metal biogeochemical cycles, as well as having a role in the cycling of other elements including carbon, nitrogen, sulphur, and phosphorous. Their impact on plant productivity and human health can not be understated. These unique type of life-forms are very important from environmental and economic points of view. It is necessary to find an economic and environmentally friendly process to recycle dry batteries in developing countries. Bioleaching is one of the few techniques applicable to the recovery of the toxic metals from hazardous spent batteries. Its principle is the microbial production of sulphuric acid and simultaneous leaching of metals. A system consisting of a bioreactor, settling tank and leaching reactor was developed to leach metals from nickel-cadmium batteries. Indigenous *Acidithiobacilli*, proliferated by using nutritive elements from sewage sludge and elemental sulphur as substrates, were employed in a bioreactor to produce sulphuric acid. The overflow from the bioreactor was conducted into the settling tank and the supernatant of the settling tank was then conducted into a leaching reactor containing anode and cathodic electrodes from nickel–cadmium batteries[3].

The results showed that this system was able to leach metals from nickel-cadmium batteries while the sludge drained from the bottom of the settling tank could satisfy the requirements of environmental protection agencies regarding agricultural use. Bioleaching of spent lithium ion secondary batteries, containing $LiCoO_2$, was also investigated. The study was carried out using the chemolithotrophic and acidophilic bacteria *Acidithiobacillus ferrooxidans*, which utilized elemental sulfur and ferrous ion as the energy source to produce metabolites like sulfuric acid and ferric ion in the leaching medium. These metabolic products dissolved metals from spent batteries. Based on the EDX and quantitative data bio-dissolution of the cobalt was found to be faster than that of the lithium [50].

4.3. Electronic scrap

The relatively short lifetime of electrical and electronic equipment (EEE) results in the production of significant amounts of waste and discarded materials. In Switzerland, approximately 110,000 tons of electrical appliances are disposed of annually, while in Germany these quantities are 10 times bigger reaching 1.5 million tons [51]. Specialized companies have been formed to be responsible for the recycling and disposal of EEE and the disposal strategy is shown in Fig. 2. The resulting material is subjected to a mechanical separation process after dismantling and manual sorting. Dust-like material is generated during the shredding and separation steps and approximately 4% of the 2400 tons of scrap treated yearly by a specialized company is collected as fine-grained powdered material. Whereas most of the electronic scrap can be recycled e.g. in metal manufacturing industries, the dust residues have to be disposed of in landfill or by incineration. However these dust residues can contain metals in concentrations which might be of economical value and options for reclamation have been investigated. It has been reported that after a prolonged adaptation time, fungi as well as bacteria grew also at concentrations of 100 g L^{-1}. Two fungal strains were able to mobilize 65 % of the Cu and Sn present and more than 95% of the Al, Ni, Pb, and Zn. At scrap concentrations of 5-10 g L^{-1}, *Thiobacilli* were able to leach more than 90% of the available Cu, Zn, Ni, and Al[52]. Pb precipitated as $PbSO_4$ while Sn precipitated probably as SnO. For a more efficient metal mobilization, a two-step leaching process was proposed where biomass growth was separated from metal leaching.

Different cyanogenic bacterial strains (*Chromobacterium violaceum, Pseudomonas fluorescens, and*

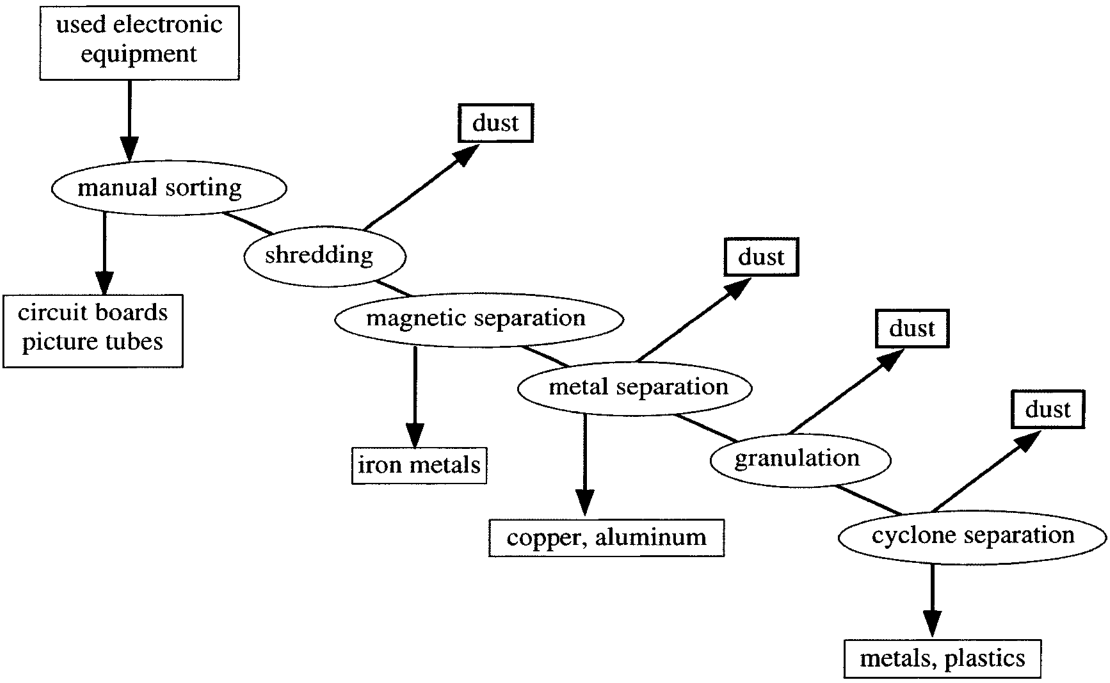

Fig. 2. Schematic treatment process for waste electronic equipment[51].

Bacillus megaterium) were cultivated under cyanide-forming conditions in the presence of metal-containing solids such as nickel powder or electronic scrap. All microorganisms were able to form water-soluble metal cyanides, however, with different efficiencies. *C. violaceum* was able to mobilize nickel as tetracyano-nickelate $[Ni(CN)_4]^2$ from fine-grained nickel powder. Gold was microbially solubilized as dicyanaoaurate $[Au(CN)_2]$ from electronic waste. Additionally, cyanide-complexed copper was detected during biological treatment of shredded printed circuit board scrap[53]. *C. violaceum* was more effective than *P. fluorescens* or *B. megaterium* at the formation of the tetracyanonickelate complex. Apart from a few previous reports on gold solubilization from gold-containing ores or native gold by *C. violaceum*, these findings demonstrate for the first time the microbial mobilization of metals other than gold from solid materials and represent a novel type of microbial metal mobilization based on the ability of certain microbes to form HCN. Results from the bioleaching of some electronic scrap are given in Table 2 and demonstrate that these types of microorganisms can mobilize metals from different waste electronic scrap. Pulp density was shown to be an important variable in this study[52].

4.4. Spent refinery catalyst

The distillation of crude oil is an essential step in petroleum refining operations. The yield and properties of produced distillates depend on the properties of crude oil, distillation conditions and the type of distillation column. Primary distillates can be subjected to an additional treatment to meet the environmental requirements and the performance specification of fuels produced[54]. The four most important catalytic processes are reforming, hydrocracking, hydrotreating, catalytic cracking and alkylation.

The residue from atmospheric distillation may be subjected to additional distillation under a vacuum to obtain valuable lubricant fractions which also require catalytic hydrotreatment. Non-conventional refineries can process heavy oils and distillation residues. In this case, the catalytic hydrocracking of the heavy feed is usually the first step, followed by hydrotreating of the synthetic distillates. Light hydrocarbon fractions, which are byproducts of several refinery units, can be converted to high octane fractions by catalytic alkylation and polymerization. Thus, several operations employing a catalyst may be part of the one petroleum refinery. The development of refining is closely connected with the growth of the use of catalysts[55]. In the past, refining catalysts accounted for more than half of the total worldwide catalyst consumption. Today, because of the importance of environmental catalysis, refining catalysts account for about one third of the total catalyst consumption.

The Ni-Mo catalyst used in coal liquefaction was also bioleached using *T. ferrooxidans*, denitrifiers, *Sulfolobus* and thermophilic cultures for the recovery of the metal values[56-58]. Vanadium has also been recovered from spent vanadium-phosphorous catalysts using *Acidithiobacillus thiooxidans*[59]. A spent refinery processing catalyst was physically and chemically characterized, and subjected to one-step and two-step

Table 2. Percentage of metal mobilized and metal content of leaching solution (g/L) from different concentrations of electronic scrap[52].

Elements	Scrap concentration, g/L							
	1		10		50		100	
	%	Metal, g/L	%	Metal, g/L	%	Metal, g/L	%	Metal, g/L
Aluminum	62	0.15	57	1.28	42	4.98	43	10.2
Copper	85	0.07	86	0.69	70	2.80	8	0.6
Lead	100	0.02	92	0.18	99	0.99	97	1.9
Nickel	100	0.02	100	0.15	100	0.75	100	1.5
Tin	100	0.02	100	0.23	100	1.15	100	2.3
Zinc	100	0.03	100	0.26	100	1.30	100	2.6

bioleaching processes using *Aspergillus niger*. The leach liquor from this process was analyzed for excreted organic acids along with heavy metal values extracted from the catalyst. Chemical characterization of the spent catalyst confirmed the presence of heavy metal including Al (30-35%), Ni (3-7%), Mo (8-12%) and V (5-10%). In general, the presence of the spent catalyst caused a decrease in the biomass yield and an increase in oxalic acid secretion by *A. niger*. Spent medium of *A. niger* grown in the absence and presence of 2-(N-morpholine)-ethane sulphonic acid (MES), buffer were found to leach almost similar amounts of Al and Ni, while Mo extraction in buffered culture was significantly more effective than the non-buffered culture[60].

In summary, this study showed the potential for use of bioleaching for the extraction of metal resources from spent catalysts. It also demonstrated the advantages of buffer-stimulated excretion of organic acids by *A. niger* in bioleaching of the spent catalyst. Spent refinery processing catalyst is listed as a hazardous waste because the extracts of the catalyst are found to contain heavy metals at concentrations exceeding the regulated levels. One-step bioleaching experiments with 1 wt% spent catalyst (of particle size <37 μm) were carried out using un-adapted and various adapted fungal strains. In contrast to the adapted strains, the un-adapted strain showed no growth in the presence of the catalyst over 30 days of reaction time[61].

5. Bioremediation of Toxic Metals From Industrial Wastes

A consequence of industrial expansion is that large quantities of industrial wastes are accumulating in many countries and cannot be disposed without prior special treatments. In particular, waste products from the mining and metal refining industries, sewage sludges and residues from power station and waste incineration plants can contain heavy metals at high concentrations. For this reason this cannot be disposed into landfill and must be submitted to special treatment in order to reduce metals content. It is now regarded as desirable to consider waste products containing high concentration of metals (copper, zinc, lead, chromium, etc.), as a secondary source of metals. Generally, the metal removal from wastes has been carried out by chemical methods, prevalently acid treatments, at very low pH (1.5-2.0). Recent technologies enabling the removal of heavy metals, namely Pb, Cd, Cr, Ni, contained in dusts coming from electric arc furnaces have been investigated[62]. Such treatments can be favourably employed when the metals are present in significant amounts provided that continuous process control is achieved[63].

Biological solubilization of heavy metals contained in two different kinds of industrial wastes was performed in batches employing a strain of *Acidithiobacillus ferroxidans*. The wastes tested were: a dust coming from the iron-manganese alloy production in an electric furnace (sludge 1) and a sludge coming from a process treatment plant of aluminum anodic oxidation (sludge 2)[64].

The incineration process generates bottom-ash and fly-ash as combustion residues. Bottom-ash is the non-combustible material remaining in the bottom of incinerator furnace and constitutes about 10% of the total volume of the waste. Fly ash refers to particles that are retained in the flue gas cleaning system. It is recognized that municipal solid wastes(MSW) incinerator fly ash is more hazardous than bottom ash since it easily becomes airborne and contains high concentration of volatile elements and often includes hazardous heavy metals (e.g. Zn, Cu, Pb, Mn, and Fe)[65]. The high cost and the negative environmental impacts of conventional methods for fly ash treatment have led to the investigation of bioleaching technology as an alternative in the removal of heavy metals from fly ash[66, 67]. Compared with conventional treatment of fly ash, bioleaching confers several advantages such as low capital cost, low energy requirement, reduced landfill space, as well as possible resource recovery.

A mixed culture, obtained from the tailings by enrichment, was shown to leach virtually all the acid-extractable iron from the tailings when augmented with inorganic nutrients. Whereas pure cultures of *At. ferrooxidans* isolated from the tailings was ineffective at enhancing metal mobilization from the mineral waste, in cultures amended with either inorganic or organic (yeast extract) nutrients. Mixed populations of isolates from the Sao Domingos tailings were more effective in leaching the residual sulfide minerals in the tailings, but were again less effective than the mixed enrichment culture. Microbial activity within exposed mine spoil and tailings can result in the mobilization of metals previously bound within the mineral matrix. These solubilized metals can then be washed into local soil and watercourses. Mining of mineral ore and disposal of resulting waste tailings pose a significant risk to the surrounding environment. The objective of this work was to remove heavy metals from mine tailings with the use of bioleaching and meanwhile to investigate the effect of solids concentration on removal of heavy metals from mine tailings by indigenous sulfur-oxidizing bacteria and the transformation of heavy metal forms after the bioleaching process[68].

The multi-stage process based on the bioleaching of heavy metals using microbially produced sulfuric acid. In the core stage, solid-bed leaching of sediments supplemented with elemental sulfur (S^0) was performed. The acidophilic bacteria oxidize the S^0 to sulfuric acid, which intern dissolves the heavy metals. The final pH resulting from the addition of 2% S^0 was found to ensure sufficient removal of the target heavy metals from the sediment but to suppress the mobilization of mineral components[69]. The application of microbially produced sulfur (biological sulfur) may offer advantages. The sulphides material appears as a waste product during the microbial treatment of sulfide-containing waste waters, e.g. from metal refineries, and the biotechnological desulphurization of flue-gases from coal-fired power plants or of H_2S-rich digestion gases from sewage sludge treatment. Its price is marginal compared to the costs of elemental sulfur and other substrates often used in bioleaching[70]. If this waste product can be used as a substrate for the sulfur-oxidizing bacteria, the costs for bioleaching treatments could be considerably reduced and the deposition as a chemical waste will be avoided.

6. Conclusions

From the article it can be demonstrated that bioleaching is an advanced technology to extract valuable metals from wastes. There are different types microorganisms that can be used for different waste sources. Use of the chemoautotrophic bacteria *Acidithiobacillus ferrooxidans, Thiobacillus thiooxidans* and *Leptospirillum ferrooxidans* is more common that the use of heterotrophic bacteria such as *Sulfobacillus* and *Pseudomonas* species. Use of heterotrophic fungal strains such as *Aspergillus* and *Penicillum* species have an important role for treatment of fly ash, electronic scrap and spent catalyst.

Two types of mechanisms are proposed for bioleaching. The direct mechanism deals with acceptance of electrons directly from reduced minerals by l attachment of bacterial cells to the mineral surface; hence electron can easily transfer from metal surface to different proteins and enzymes of the living organism for the growth and metabolism ultimately oxidized metal transfer to leaching medium. The indirect mechanism is the reaction between ferric iron and/or proton produced by the microorganism with the target minerals. There are two pathways proposed to define indirect leaching and their relative importance varies with the solubility of the raw material. The bacterial strains are mostly iron and sulfur oxidizing bacteria, which produce sulphuric acid and ferric iron in leaching medium. However the bioleaching action depends on various parameters such as pulp density, pH, inoculums volume, particle size, and percolation of leach liquor. As the process catalysts, the microbes, reproduce naturally often using the waste as a substrate, the operating cost can be reduced dramatically when compared to the conventional process. Biological processes can be economically feasible even when applied to low-grade ores of metal content less than 1%. Not only this is valuable for application to low-grade ore but also to wastes such as electronic scrap, spent batteries, spent catalyst, industrial tailing, river sediments and fly ash. By-products from biological processes are usually much less than those produced by alternate processes and adverse environmental effects are minimized.

The quantity of waste is increasing day by day in the modern societies. Bioscientists need to exercise more regarding the sustainability of zero waste in the environment. In 21st century pollution is already proving to be the major drawback for industrial development. Governments of developed countries are encouraging an integrated approach for ideas to treat the waste materials for betterment of the society. Industries in the developed societies will come under increasing pressure to be more adventurous and willing to consider alternative technologies for waste control. We can confidently say that the application of biotechnology to degrade wastes will help in environmental protection in various ways.

Acknowledgement

This work was supported by the Korea Foundation for International Cooperation of Science & Technology (KICOS) through a grant provided by the Korean Ministry of Science & Technology (MOST) in 2007 (No. K20602000004-07E0200-00410).

References

1. J.W.C. Wong, L. Xiang, X.Y. Gu, and L.X. Zhou, 2004: Bioleaching of heavy metals from anaerobically digested sewage sludge using FeS_2 as an energy source. Chemosphere, **55**, 101-107.
2. S.Y. Chen, and J.G. Lin, 2004: Bioleaching of heavy metals from contaminated sediment by indigenous sulfur-oxidizing bacteria in an air-lift bioreactor: effects of sulfur concentration. Water Res. **38**, 3205-3214.
3. N.W. Zhu, L.H. Zhang, C.J. Li, and C.G. Cai, 2003: Recycling of spent nickel-cadmium batteries based on bioleaching process. Waste Management, **23**, 703-708.
4. T.J. Xu, and Y.P. Ting, 2004: Optimization on bioleaching of incinerator fly ash by *Aspergillus niger* - use of central composite design. Enzyme Microb. Technol. **35**, 444-454.
5. M. Paul, A. Sandstrom, and J. Paul, 2004: Prospects for cleaning ash in the acidic effluent from bioleaching of sulfidic concentrates. J. Hazard. Mater. **106B**, 39-54.
6. S.Y. Shi, Z.H. Fang, J.R. Ni, 2006: Comparative study on the bioleaching of zinc sulphides. Process Biochemistry, **41**, 438-446.
7. H.L. Ehrlich, 1992: Metal extraction and ore discovery. In: Lederberg J, editor. Encyclopedia of microbiology, San Diego: Academic Press. **3**, 75-80.
8. F. Schinner, and W. Burgstaller, 1989: Extraction of zinc from industrial waste by *Penicillium* sp. Appl. Environ. Microbiol. **55**, 1153-1156.
9. M.R. Hoffmann, R.G. Arnold, and G. Stephanopoulos, 1989: US Patent 4880740.
10. R.F. Wilder, P.J. Barrett, L.W. Henslee, and D. Arpi, 1986: Recovery of metal Oxides from Fly Ash, EPRI CS-3544, Palo Alto, CA, USA, Vols. 1-3.
11. A. Seidel, 1997: Mechanism of metals bioleaching from coal fly ash inconcentrated suspension by *Thiobacillus thiooxidans* bacteria. D.Sc.Thesis, The Technion, Haifa, Israel.
12. A.E. Torma, and K. Bosecker, 1982: Prog. Ind. Microbiol. 16, 77.
13. N.M. Catherine, K. Mahtab, F.G. Bernard, 2004: Bioleaching of heavy metals from a low-grade mining ore using *Aspergillus niger.* J. Hazard. Mater. **110**, 77-84.
14. A. Seidel, Y. Zimmels, and R. Armon, 2001: Mechanism of bioleaching of coal fly ash by *Thiobacillus thiooxidans.* Chem. Eng. J. **83**, 123-130.
15. H. Seidel, C. Loser, A. Zehnsdorf, P. Hoffmann, and R. Schmerold, 2004: Bioremediation process for sediments contaminated by heavy metals: feasibility study on a pilot scale. Environ. Sci. Technol. **8**, 1582-1588.
16. K. Bosecker, 1997: Bioleaching: metal solubilization by microorganisms. FEMS Microbiol Rev. **20**, 591-604.
17. W. Krebs, C. Brombacher, P.P. Bosshard, R. Bachofen, and H. Brandl, 1997: Microbial recovery of metals from solids. FEMS Microbiol Rev. **20**, 605-617.
18. T. Gehrke, J. Telegdi, D. Thierry, and W. Sand, 1998: Importance of extracellular polymeric substances from *Thiobacillus thiooxidans* for bioleaching. Appl. Environ. Microbiol. **64**, 2743-2747.
19. J.T. Staley, M.P. Bryant, N. Pfenning, and J.G. Holt (Eds.), 1989: Bergey's Manual of Systematic Bacteriology. Williams and Wilkins, USA. 3, 1857.
20. K. Sakamoto, M. Yagasaki, K. Kirimura, and S. Usami, 1989: Resistance acquisition of *Thiobacillus thiooxidans* upon cadmium and zinc ion addition and formation of cadmium ion-binding and zinc ion-binding proteins exhibiting metallothionein-like properties. J. Ferment. Bioeng. **67**, 266–273.
21. M.N. Collinet, and D. Morin, 1990: Characterization of arsenopyrite oxidizing *Thiobacillus*. Tolerance to arsenite arsenate ferrous and ferric iron. Antonie van Leeuwenhook. **57**, 237-244.
22. G. Bryan, B. Christopher, K. Hallberg, and B. Johnson, 2006: Mobilization of metals in mineral tailings at the abandoned São Domingos copper mine (Portugal) by indigenous acidophilic bacteria. Hydrometallurgy. **83**, 184-194.
23. P.R. Norris, N.P. Burton, and N.A.M. Foulis, 2000: Acidophiles in bioreactor mineral processing, Extremophiles. **4**, 71-76.
24. J.A. Brierley, and C.L. Brierley, 2001: Present and future commercial applications of biohydrometallurgy, Hydrometallurgy. **59**, 233-239.
25. B.M. Goebel, E. Stackebrandt, F.G. Priest, A. Ramos-Cormenzana, B.J. Tindall, 1994: Bacterial Diversity and Systematics. FEMS Symposium, Plenum Press, New York. 131-273.
26. C. Demargasso, P. Galleguillos, L. Escudero, V. Zepeda, D. Castillo, E.O. Casamayor, 2003: Proceedings of the Copper 2003, 5th International Conference, Santiago, Chile. 6 (book 1), 131-140.
27. S.Y. Shi, and Z.H. Fang, 2005: Bioleaching of marmatite flotation concentrate by adapted mixed mesoacidophilic cultures in an air-lift reactor. Int. J. Miner. Process. **76**, 3-12.
28. M.P. Silverman, H.L. Ehrlich, 1964: Microbial formation

and degradation of minerals.. In: Umbreit, Wayne W. (Ed.), Adv. Appl. Microbiol. **6**, 153-206.
29. D.K. Ewart and M.N. Hughes, 1991: The extraction of metals from ores using bacteria, Adv. Inorg. Chem. **36**, 103.
30. J. Barrett, M.N. Hughes, G.I. Karavaiko and P.A. Spencer, 1993: Metal extraction by Bacterial Oxidation of Minerals, Ellis Horwood, Chichester.
31. A.W. Breed, G.S. Hansford, 1999: Studies on the mechanism and kinetics of bioleaching, Minerals Engineering, **12** **(4)**, 383-392.
32. A. Schippers, W. Sand, 1999: Bacterial leaching of metal sulfides proceeds by two indirect mechanisms via thiosulfate or via polysulfides and Sulfur, Appl. And Environ. Micribiol., **65(1)**, 319-321.
33. E. Rawlings (Ed.), 1997: Biomining: Theory, Microbes and Industrial Processes,Heidelberg, R.G., Landes and Springer-Verlag, Austin.
34. H. Deveci, A. Akcil, and I. Alp, 2004: Bioleaching of complex zinc sulphides using mesophilic and thermophilic bacteria: comparative importance of pH and iron. Hydrometallurgy. **73**, 293-303.
35. M.X. Liao, and T.L. Deng, 2004: Zinc and lead extraction from complex raw sulfides by sequential bioleaching and acidic brine leach. Miner. Eng. **17**, 17-22.
36. M.Q. Qiu, S.Y. Xiong, W.M. Zhang, and G.X. Wang, 2005: A comparison of bioleaching of chalcopyrite using pure culture or a mixed culture. Miner. Eng. **18**, 987-990.
37. S.M. Mousavi, S. Yaghmaei, M. Vossoughi, A. Jafari, R. Roostaazad, and I. Turunen, 2007: Bacterial leaching of low-grade ZnS concentrate using indigenous mesophilic and thermophilic strains. Hydrometallurgy. **85**, 59-65.
38. O. Garcia Jr., J.M. Bigham, and O.H. Tuovinen, 1995: Sphalerite oxidation by Thiobacillus ferrooxidans and *Thiobacillus thiooxidans*. Canadian Journal of Microbiology. **41**, 578-584.
39. G.R. Chaudhury, and R.P. Das, 1987: Bacterial leaching complex sulfides of copper, lead and zinc. Int. J. Miner.Proces. **21**, 57-64.
40. S.S. Bang, S.S. Deshpande, and K.N. Han, 1995: The oxidation of galena using *Thiobacillus ferrooxidans*. Hydrometallurgy. **37**, 181-192.
41. F.K. Crundwell, 1988: The influence of the electronic structure of solid on the anodic dissolution and leaching of semiconductor sulphide minerals. Hydrometallurgy. **21**, 155-190.
42. F. Habashi, 1978: Chalcopyrite: Its Chemistry and Metallurgy. McGraw-Hill, New York.
43. A.J. Parker, R.L. Paul, and G.P. Power, 1981: Electrochemistry of the oxidative leaching of copper from chalcopyrite. J. Electroanal. Chem. **118**, 305-316.
44. A. Ballester, F. Gonza'lez, M.L. Bla'zquez, and J.L. Mier, 1990: The influence of various ions in the bioleaching of metal sulfides. Hydrometallurgy. **23**, 221-235.
45. A. Ballester, F. Gonza'lez, M.L. Bla'zquez, C. Go'mez, and J.L. Mier, 1992: The use of catalytic ions in bioleaching. Hydrometallurgy. **29**, 145-160.
46. P.C. Banerjee, B.K. Chakrabarti, S. Bhattaacharyya, and A. Das, 1990: Silver-catalyzed hydro-metallurgical extraction of copper from sulfide ores from India mines. Hydrometallurgy. **25**, 349-355.
47. M.E. Escudero, F. Gonza'lez, M.L. Bla'zquez, A. Ballester, and C. Go'mez, 1993: The catalytic effect of some cations on the biological leaching of a Spanish complex sulphide. Hydrometallurgy. **34**, 151-169.
48. J.D. Miller, P.J. McDonough, and H.Q. Portillo, 1981: Electrochemistry in silver-catalyzed ferric sulfate leaching of chalcopyrite. In: Keaton, M.C. (Ed.), Process and Fundamental Consideration of Selected Hydrometallurgical Systems. SME-AIME, New York. 327-338.
49. P.R. Norris, 1990: Acidophilic bacteria and their activity in mineral sulfide oxidation. In: Ehrlich, H.L., Brierley, C.L. (Eds.), Microbial Mineral Recovery. McGraw-Hill, New York.
50. D. Mishra, D.J. Kim, D.E. Ralph, J.G. Ahn, and Y.H. Rhee, 2007: Bioleaching of metals from spent lithium ion secondary batteries using Acidithiobacillus ferrooxidans, Waste Management (Article in Press).
51. R. Bosshard, 1998: Metallru¨ckgewinnung aus Elektronikschrott mit Hilfe von Bakterien. Diploma thesis, ETH Zurich, Switzerland.
52. H. Brandl, R. Bosshard, and M. Wegmann, 2001: Computer-munching microbes: metal leaching from electronic scrap by bacteria and fungi. Hydrometallurgy. **59**, 319-326.
53. M.A. Faramarzi, M. Stagars, E. Pensini, W. Krebs, and H. Brandl, 2004: Metal solubilization from metal-containing solid materials by cyanogenic *Chromobacterium violaceum*. Journal of Biotechnology. **113**, 321-326.
54. K. Inai, 1994: Rev. Inst. France Petrol. 49(5), 521.
55. G. Martino, 1994: Bull. Sot. Chim. Fr. 131, 444.
56. P. Joffe, G.T. Sperl, 1993: DOE rep., PC-92119-T4.
57. K.A. Sanback, 1995: DOE Rep., PC/92119-T6.
58. K.A. Sanback, P.M. Joffe, 1993: DOE Rep., PC-92119-T2 and T3.
59. L. Briand, H. Thomas, A. de la Vega Alonso, E. Donati, 1999: Vanadium recovery from solid catalysts by means of Thiobacilli action. In: Amils, R., Ballester, A. (Eds.), Proceedings of the International Biohydrometallurgy Symposium (IBS), Part A. Elsevier, Amsterdam. 263-271.
60. D. Santhiya, and Y.P. Ting, 2005: Bioleaching of spent refinery processing catalyst using *Aspergillus niger* with high-yield oxalic acid. Journal of Biotechnology. **116**, 171-184.
61. D. Santhiya, and Y.P. Ting, 2006: Use of adapted *Aspergillus niger* in the bioleaching of spent refinery processing catalyst. Journal of Biotechnology. **121**, 62-74.
62. A.D. Zunkel, 1997: Electric arc furnace dust management: a review of technologies. Iron and Steel Engineer. March, 33-38.
63. M. Nemati, STL. Harrison, GS. Hansford, and C. Wess, 1988: Biological oxidation of ferrous sulphate by

Thiobacillus ferrooxidans: a review on the kinetic aspects. Biochem. Eng. J. 171-190.

64. C. Solisio, A. Lodi, and F. Veglio, 2002: Bioleaching of zinc and aluminium from industrial waste sludges by means of *Thiobacillus ferrooxidans*. Waste Management. **22**, 667-675.
65. TT. Eighmy, Jr J.D. Eusden, JE. Krzanowski, DS. Domingo, D. Stampfli, and JR. Martin, 1995: Comprehensive approach toward understanding element speciation and leaching behavior in municipal solid waste incineration electrostatic precipitator ash. Environ. Sci. Technol. **29**, 629-646.
66. PP. Bosshard, R. Bachofen, and H. Brandl, 1996: Metal leaching of fly ash from municipal waste incineration by *Aspergillus niger*. Environ. Sci Technol. **30**, 3066-3070.
67. H.Y. Wu, 2002: Bioleaching of heavy metals from MSW incineration fly ash by *Aspergillus niger*. Master Thesis. National University of Singapore (NUS).
68. Y.G. Liu, M. Zhou, G.M. Zeng, X. Li, W.H. Xu, and T. Fan, 2007: Effect of solids concentration on removal of heavy metals from mine tailings via bioleaching. J. of Hazard. Mat. **141**, 202-208.
69. C. Loser, H. Seidel, P. Hoffmann, and A. Zehnsdorf, 2001: Remediation of heavy metal-contaminated sediments by solid-bed bioleaching. Environ. Geol. **40**, 643-650.
70. J.F. Blais, R.D. Tyagi, and J.C. Auclair, 1992: Bioleaching of metals from sewage sludge by sulfur-oxidizing bacteria. J. Environ. Eng. **118**, 690-707.

Debabrata Pradhan

- 현재 충남대학교 나노소재공학과

安 鍾 寬

- 현재 한국지질자원연구원 자원활용소재연구부 선임연구원

李 承 遠

- 현재 충남대학교 금속공학과 교수
- 당 학회지 제13권 6호 참조

金 東 鎭

- 현재 한국지질자원연구원 자원활용소재연구부 책임연구원

朴 庚 鎬

- 현재 한국지질자원연구원 자원활용소재연구부 책임연구원
- 당 학회지 제10권 3호 참조