

Green Chemistry

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PAPER

Industrial applications of Molecular Recognition Technology to separations of platinum group metals and selective removal of metal impurities from process streams

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Green chemistry procedures using a novel process based on molecular recognition principles are described for the selective separation and recovery of metals in industrial processes. This process, termed Molecular Recognition Technology (MRT), has the capability to make selective separations at various stages in metal life cycles. Results are given for individual platinum group metal separations, recycling of palladium from end-of-life products, copper purification by control of impurity bismuth concentration levels, and purification of H₂SO₄ for use in health-related applications by Hg removal to 0.1 mg/L concentration levels. In each case, the metals are selectively separated in pure form and can be recovered for reuse or environmentally safe disposal. High metal selectivity is obtained using a pre-designed ligand bonded chemically by a tether to a solid support, such as silica gel. Separations are performed in column mode using feed solutions containing the target metal in a matrix of acid and/or other metals. The target metal is selectively separated by the silica gel-bound ligand, leaving other solution components to go to the raffinate, where individual components can be recovered, if desired. Minimal waste is generated. Elution of the washed column with a small volume of eluent produces a concentrated eluate of pure target metal, which is easily separated in pure form. The MRT process uses innocuous wash and elution chemicals and no solvents. Metal recovery rather than dispersal into the commons is essential from a metal sustainability standpoint. A major benefit of metal recycling is reduction in the amount of virgin ore that must be mined to replace discarded metals. As metal use increases, conservation of this valuable metal resource increases in importance. Metal recycling rates are generally low. From end-of-life high-tech electronic products, they are in the 1-5% range. Separation and recovery results presented here show that green chemistry MRT processes have great promise in increasing metal sustainability in industrial processes.

Introduction

Concern over unrecoverable metal loss during metal lifecycles has increased in recent decades as metals have been used in greater numbers and larger quantities, with low recovery and recycling rates.¹⁻⁵ Metals are indestructible, so they remain with us in some form, whether recycled for reuse or discarded into the commons where they are usually unrecoverable with present technologies and, in the case of toxic metals, capable of causing severe environmental and health problems.⁶ Metals are different than other consumer resources such as fossil fuels, agricultural crops, and synthetic products, such as plastics, in being, in principle, recoverable for reuse indefinitely without loss of function. However, in practice few metals are recycled.² Recycling rates range from 80% for Pb to ~50% for platinum group metals (PGM) from autocatalytic converters to <1% for rare earth and other specialty elements, such as In, Te, Re, etc., in

high-tech products. Lack of recovery of metals, especially so-called critical ones, during metal life cycles represents a significant resource loss and has many implications.^{1,3,4} Metals are mined, incorporated into high-tech products, and, usually, discarded with that product into the commons via landfill, incineration, or informal recycling.^{1,3} Reasons for the current metal sustainability situation are complex. However, from a technology standpoint, improvements would be seen if green chemistry principles were more widely applied to metal separations and recovery in various stages of metal life cycles.¹

Green chemistry can be defined⁷ as “the design of chemical products and processes to reduce or eliminate use and generation of hazardous substances.” In their analysis of chemical systems, Anastas and Eghbali⁷ cite work indicating that organic solvents account for most industrial waste in chemical industry and that it is preferable to use systems that minimize use of or do not require such solvents. Principles associated with green chemistry suggest that design of chemical reactions or systems that do not require

intensive energy use is highly desirable and that feed stocks or chemicals used in chemical processes should be conserved rather than discarded into the commons as waste. Introduction of green chemistry practices into chemical industry processes has resulted in important benefits.⁷ Similar benefits are seen where green chemistry principles have been introduced in various steps in metal life cycles.⁸ A major purpose of this paper is to demonstrate that use of clean chemistry principles produces significant benefits to metal separations and recovery in various stages of metal life cycles and to illustrate these benefits by examples taken from commercial operations.

A novel separation process based on molecular recognition principles and incorporating green chemistry principles is described here for the selective separation and recovery of metals in industrial processes with minimal waste generation. This process, termed Molecular Recognition Technology (MRT), is effective at various stages in metal life cycles.^{9,10} The MRT process is based on selective recognition of specific metal ion guests by supported ligand hosts allowing highly selective individual separation and recovery of metals from complex matrices present in industrial feed solutions. Recovery of metals in pure form is desirable, since this avoids their undesirable dispersion into the commons. In this paper, the MRT procedure is described and examples given of its commercial use. Environmental, procedural, economic, metal conservation, and metal resource preservation benefits associated with use of green chemistry principles are discussed and the case made that greater use of these principles in the metals industry can have important effects on improving metal sustainability.¹

Molecular Recognition Technology and its green chemistry approach to metal recovery

Despite wide use in chemical industry processes, green chemistry principles have been applied sparingly in the mining industry and to recovery of metals from end-of-life (EOL) products. Some principles of green chemistry applicable to metal separations and recovery are presented in Table 1.

Green chemistry principles emphasize the importance of preventing waste instead of cleaning it up after it is formed. This statement is at odds with the 'discard into the commons' practice which prevails globally in the mining and recycling industries.¹ Conventional separation processes, such as solvent extraction (SX), ion exchange (IX), and precipitation are, generally, not consistent with the principles outlined in Table 1. Environmental and health impacts from use of these processes can be severe^{1,6} unless care is taken to minimize their environmental effects.

These impacts are usually much larger in non-Organization for Economic Organization and Development (OECD) than in OECD nations where environmental laws are generally enacted and enforced.¹ A primary principle of green chemistry is the use of a safer or no solvent in separation procedures. Solvents and auxiliary substances are used widely in conventional metal processing and recovery procedures. Many added substances become new pollutants or create new pollutants by reactions they undergo. For example, essentially uncontrolled use of Hg in artisanal Au mining,^{1,11} has resulted in extensive Hg pollution worldwide, which is of great concern because of the known negative human health effects of Hg, especially on children.

Emphasis in green chemistry is on renewing materials or feed stocks rather than dispersing them to the environment. Use of conventional methods, generally, results in dissipation, not recovery of metals. Hagelöken³ has emphasized the importance of minimizing losses of metals into residues (commons) during

Table 1 Some principles of green chemistry applied to metals.^a

Prevention	It is better to prevent waste than to treat or clean up waste after it is formed
Safer Solvents and Auxiliaries	Use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary, whenever possible and, when used, innocuous
Design for Energy Efficiency	Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized
Use of Renewable Feed Stocks	A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable

^aAdapted from ref 6

all phases of the life cycle. Residues are defined by him to include "tailings and slags from primary production, production scrap from manufacturing, products discarded during their useful lifetime, non-recycled streams, and slags, effluents, and final waste at end of life."

Major challenges in the attainment of green chemistry operations in industry lie in the separations area.^{1,7} Separations, as used in industrial chemistry processes, often involve large volumes of organic solvents and hazardous chemicals, which are discarded after use, often with significant environmental consequences. In addition, conventional separation systems such as SX, IX, and precipitation are less effective in recovering metals as their concentration levels decrease.¹ Consequently, metal losses can be significant in separation processes using conventional separation procedures. Metal losses to the commons require that additional ore must be mined and processed to meet increasing demand for metals, especially for their use in high-tech products, which are generally discarded to the environment, often after a single use.^{12,13} Mining ore requires large expenditures of energy and water with resultant environmental concerns.^{1,14,15} Thus, meeting a larger portion of metal demand by recycling and by use of green chemistry processes to conserve metals at the production and recovery stages can result in significant benefits to industry and society.^{1,3}

Highly selective metal separations are achieved in MRT systems by employing pre-designed metal-selective ligands.^{1,9,10} Incorporation of these ligands by chemical binding to solid supports such as silica gel or polymer substrates makes their use in solid phase extraction mode possible. The supported ligand

product is termed SuperLig®. Organic solvents are not used in these MRT systems. MRT has been used in commercial systems for metal separations and recovery for more than two decades. Advantages of MRT systems over conventional separation technologies arise, primarily, from large ligand-target metal binding energies ($\log K$), rapid reaction kinetics, high degrees of selectivity by the bound ligand for target metals even in complex matrices such as highly acidic or basic solution and/or in solutions containing high concentrations of competing ions, use of innocuous solutions throughout, small floor space requirements, marked reduction of metal inventory time, and the ability to carry out selective metal separations and recover pure metals over wide metal concentration ranges from g/L to mg/L.

An early application of molecular recognition to selective host-guest interactions was the pioneering work of Pedersen, for which he shared the Nobel Prize in 1987.¹⁶ Pedersen synthesized a large number of cyclic polyethers¹⁷ and observed that certain of these had remarkable selectivities for specific alkali metal ions. This selective host-guest interaction was quantitated and its range expanded to other macrocycles by us¹⁸ and others.¹⁹ Early work by us with selective transport of metal ions in supported liquid membrane systems²⁰ led to the development of solid supported SuperLig® systems in which the metal-selective ligand was attached by a tether to a solid support, such as silica gel.²¹ This achievement made large scale, selective metal separations possible. A representative example of such a SuperLig® system is shown in Fig. 1. In this case, the SuperLig® System is selective for K^+ , which fits nicely into the 18-crown-6 cavity (good match of cation ionic radius with cavity radius), while Na^+ and Cs^+ do not, their radii being too small and too large, respectively. The fit of the guest metal ions in the host cavity is supported by $\log K$ values valid in methanol at 25 °C for 18-crown-6 interactions with these metal ions,¹⁹ i.e., $Na^+ = 4.36$, $K^+ = 6.10$, and $Cs^+ = 0.99$. Similar principles apply to the selective separations described here.¹⁹ However, ligand, cation, and system parameters which affect the magnitudes of host-guest interactions are numerous and the reader is referred to review articles in which these parameters are discussed.^{22,23}

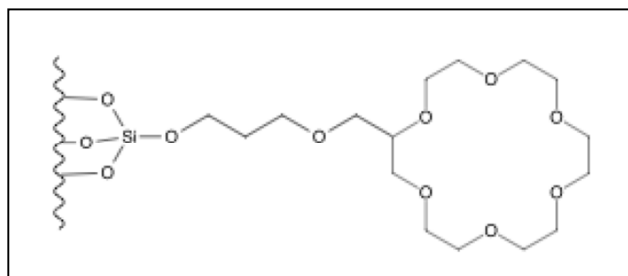


Fig. 1 Representative SuperLig® system consisting of a solid support particle, silica gel, to which a metal-selective ligand, 18-crown-6, is attached by a tether, which is chemically bound to both the ligand and the silica gel.

SuperLig® products consist of small (0.5 mm) particles packed into fixed-bed columns. These columns are present in skid-mounted modular form, and are fully automated for continuous operation. MRT processes operate on a system-cycle basis. A complete system cycle consists of the following sequence: (1)

loading phase—target ion is loaded from feed solution onto an appropriate metal-selective SuperLig® product charged into the column(s); (2) pre-elution wash phase—any remaining feed solution is washed from the column; (3) elution phase—target ion is eluted with a small amount of eluent, forming an eluate solution concentrated in the metal product; and (4) post-elution wash phase—any remaining eluent is washed from the column. The cycle begins again with Step (1).

Pre-determined high selectivity for target metal species is the distinguishing feature of SuperLig® products.^{1,9} High metal selectivity makes possible high loading on the column of only the target metal resulting in direct recovery, upon elution, of that metal in high yield and high purity from matrices containing competing metals that otherwise would contaminate the separated metal leading to additional separation steps downstream. Matrices encountered in metallurgical and metal recovery operations typically include high acid or base concentrations, metals with chemical properties similar to those of the metal to be separated, and high concentrations of common metal salts. Negative effects of these matrices on the ability, using conventional separation methods, to make desired selective separations increase as concentrations of metals to be separated decrease toward mg/L or lower levels. Metal selectivity of conventional methods is generally not high enough under these challenging conditions to effectively remove the target metal from the matrix, resulting in gross inefficiency in the form of poor recovery, low concentration factors, and impure products.¹ Performance can be improved with multiple stages or even use of more than one separation process, but costs mount due to greater needs for space, chemicals, energy, equipment, and labor. Worker safety and health are compromised. The amount of secondary waste production also increases resulting in higher costs for disposal or recycle. Economic consequences of high cost are that industry is unable to recover metal values from challenging matrices, and, in the case of mandated waste treatment of environmental cleanup, devastating economic losses must be borne, often at public expense. Elution of the selectively separated metal from the column in the MRT process provides a pure and concentrated target metal product without need for further purification. The MRT procedure results in minimal waste generation and greater efficiency without use of contaminating or hazardous reagents. The MRT process comes close to zero waste.

Platinum group metals

In 2010, the U.S.A. imported about 94 percent of the Pt and 58 percent of the Pd it consumed.²⁴ South Africa accounted for ~77% of global primary production of Pt and ~41% of global primary production of Pd in 2010. In 2009, Russia accounted for about 42% of global primary production of Pd and 13 % of global primary production of Pt. Wilburn²⁴ has discussed the global distribution and production capacity of PGM. Deposits of PGM are usually mined primarily for their Pt content making future availability of remaining PGM dependent on continued mining of Pt, which, in turn, may be dependent on geopolitical considerations. Recycling PGM can be a valuable secondary source of these metals, which would be independent of

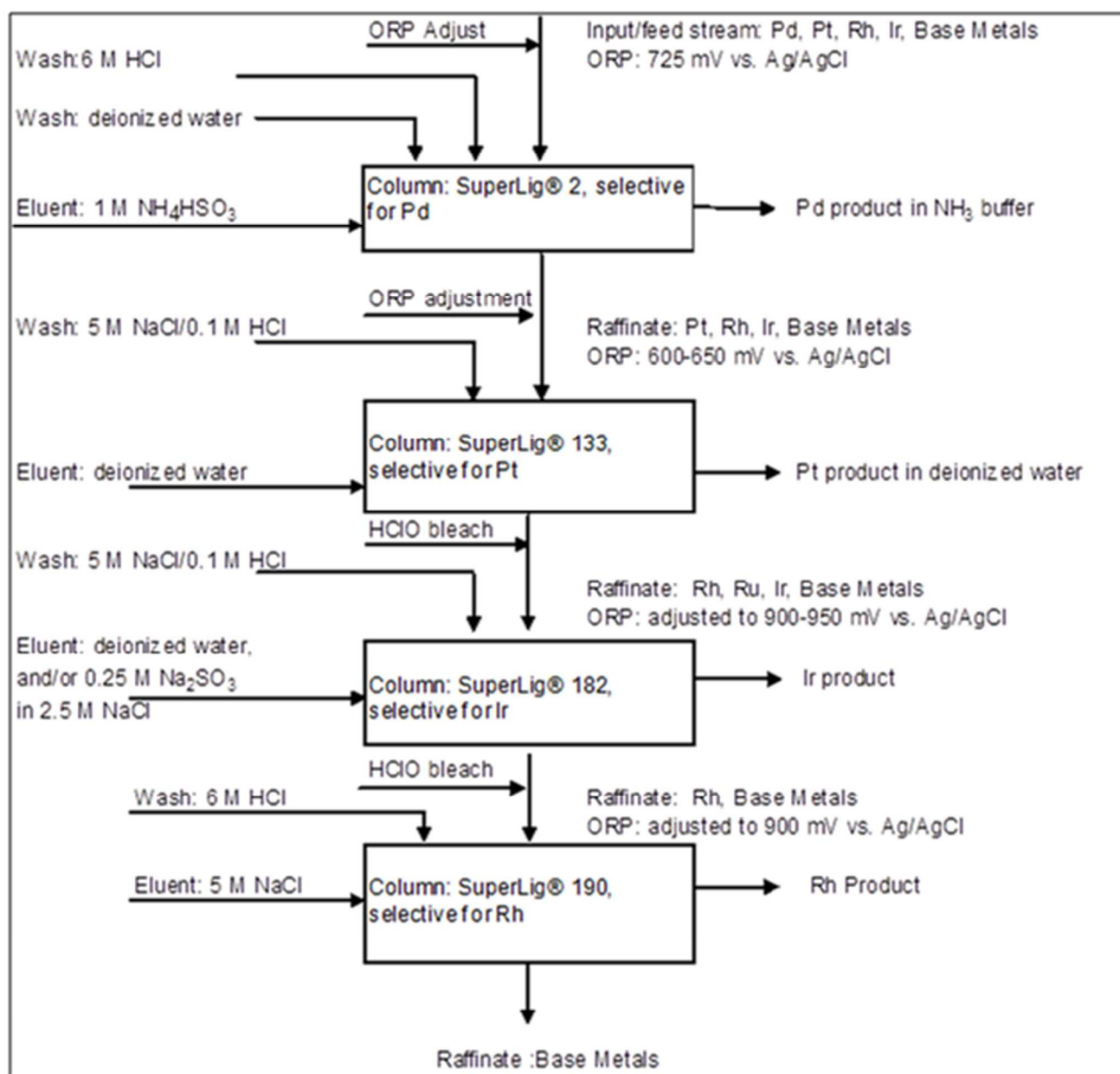


Fig. 2 Sequential separation of Pd, Pt, Ir, and Rh from a base metal matrix.²⁶ ORP = oxidation-reduction potential.

geopolitical concerns, reduce dependence on mined ore, eliminate environmental problems associated with mining and processing virgin PGM ore,¹⁴ and contribute to the supply security of minor and critical platinum metals such as Ru, Ir, Rh, Os and Pd by decoupling their production from that of Pt.³

PGM are required in many commercial, industrial, and military applications for a variety of existing and emerging technologies.^{24,25} Primary uses are in the automobile sector as catalysts for air-pollution abatement in light- and heavy-duty vehicles (Pd, Pt, and Rh), in fuel cells, and in petroleum refining. Other uses are found in the chemical sector as catalysts in nitric acid production; the electronics sector in computer hard discs, sputtering targets, multilayer ceramic capacitors, and integrated

circuits; the glass manufacturing sector in the production of fiberglass, liquid crystal displays, and flat-panel displays; temperature sensing; jewelry; and medical and dental appliances. Palladium, Pt, and Rh have been listed by the National Research Council (U.S.A.) as critical materials because of their limited availability and their potential for supply disruption. The high melting point and corrosion resistance of Ir (highest of all metals) have made it valuable as a component of spark plugs and crucibles. Iridium, Ru, and Os are alloyed with Pt to produce very hard corrosion-resistant alloys. This variety of uses is recent and is expected to expand in the future because of the unique properties of PGM resulting in increased demand for these metals.

Platinum group metal separations

It is desirable to incorporate, wherever possible, green chemistry processes into separations during beneficiation of PGM ores and recycling of PGM from EOL products containing these metals. Impetus is provided by global enactment and enforcement of environmental laws; economic benefits derived from using green chemistry steps in beneficiation processes and for recovery of valuable PGM from all grades of spent products; and conservation of a valuable resource. Sequential separations of Pd, Pt, Rh, and Ir from a typical base metal matrix are presented in Fig 2.²⁶

A key aspect of the separations shown in Fig. 2 is the use of SuperLig® products designed to bind selectively with specific PGM species in the presence of competing metal species. Achievement of individual metal selectivity requires that SuperLig® product design take into account the speciation of the PGM as a function of the anion present and the pH of the solution as well as the relative binding strengths of the several possible host-guest interactions. For example, SuperLig® 2 is selective for the cation, Pd²⁺, allowing selective separation of this cation from remaining PGM, which do not form cations in the solutions involved. Rhodium is separated as an anion, RhCl₅²⁻, using SuperLig® 190, which is designed to selectively separate this particular anion.¹⁰ Selectivity is of critical importance since it eliminates the need for multiple stages downstream and use of hazardous and/or contaminating chemicals. Selective separations in Fig. 2 are single-pass resulting in efficient operations with minimal waste. Time required to make separations is short resulting in reduced inventory time for the PGM over that required in conventional separations. Innocuous reagents are used for wash and elution resulting in clean separations with minimal waste. These PGM separations provide examples of green chemistry processes, which result in economic benefits to the industrial company by eliminating steps, shortening time to make separations, eliminating use of many chemicals, reducing labor costs, reducing environmental impacts, and shortening inventory time for the valuable PGM involved. Target metals are recovered in pure concentrated form from eluate solutions following elution from the column with a small amount of eluent.

Platinum group metal recovery from spent materials^{10,27}

Environmental, economic, and geopolitical reasons for recycling PGM from end of life (EOL) products have been summarized.³ Benefits of recycling include reduction of the environmental burden inherent in mining; mitigation of the environmental impact of mining by decreasing energy demand, CO₂ emissions, land and water use, and impacts on the biosphere; extension of the lifetime and preservation of valuable geological resources; dampening global metal price fluctuations by improvement of demand-supply balance by broadening the supply base; and creation of significant employment potential, including high-tech jobs and infrastructure.

The mining industry is the largest producer of solid wastes globally.¹⁴ It has been estimated that approximately 80 % of

global mine production of PGM since 1900 has occurred since 1980³ and the production rate of PGM is increasing. The relatively low grade of PGM ores, a few grams per ton of ore, means that >99 % of the ore becomes solid waste with potential environmental and health consequences. As available ore grades decline, new sources must be found. These sources often involve extending mining to greater depths with attendant increases in water usage, labor costs, and energy input, largely through increased use of electricity.¹⁴ Electricity is derived, normally, through coal combustion with consequent carbon dioxide generation and emission of dangerous particulates and gases, such as Hg, unless care is taken.

Recycling PGM mitigates the effects of mining virgin ore. However, global recycling rates for PGM are low ranging from 50% (autocatalytic converters) to a few percent (electronic waste such as cell phones and computer motherboards.)^{2,3} Global wastage of PGM from auto catalysts has been estimated to be 900 tonnes annually.³ Low recycling rates are also found with spent petrochemical and other waste, particularly that in which PGM concentration levels are low, i.e., mg/kg levels. Compelling reasons exist for placing added emphasis on PGM recycling in attaining improved metal sustainability.¹⁻³ Application of green chemistry principles⁷ to PGM recycling from low grade resources could significantly increase the effectiveness of PGM recovery.

SepraMet is a metal refinery located in Houston, Texas,¹⁰ which features the use of MRT-hydrometallurgical processes in the selective recovery of PGM from low grade materials using green chemistry principles. These materials, including spent catalyst feeds, are processed in this refinery and accompanying metals recovered using solid phase extraction MRT.^{10,27} Incoming feed may contain unwanted or deleterious elements such as As, Sb, and Fe, which are readily and effectively separated from target species. For example, low-grade spent petroleum/petrochemical catalysts containing Pd can be processed using MRT. Spent catalysts are digested, yielding an acidic solution containing mg/L levels of Pd. This solution is passed directly through the MRT system, without upgrading, and the Pd is selectively bound onto the SuperLig® resin. Following elution from the MRT column, the eluent contains high purity Pd at high concentrations (g/L) that can be sold directly or reduced to Pd metal.

No organic solvents are used in the separation process which is carried out at ambient temperatures with minimal carbon footprint. Low chemical and energy requirements of the MRT system translate into an environmentally friendly process with minimal worker exposure, highly competitive recovery of pure precious metals with low metal inventory time, and low-capital equipment and space requirements. A major environmental benefit is that the metals are recovered rather than being discarded with the catalyst material to a landfill. Effluent from the plant meets all regulatory requirements for discharge.

Bismuth removal from copper electrolyte in production of high purity copper²⁸

A major challenge in the smelting and refining of Cu is the production of high purity product from feed stock containing a diverse range of metal impurities that are deleterious to the final Cu commodity. Pyrometallurgical technologies alone are not sufficient to separate these metal impurities to the extent required. Several hydrometallurgical technologies including bleed streams, crystallization, SX, and IX have been used in copper refineries to meet this challenge with varying degrees of success.^{29,30} Specifications for high purity Cu are increasing as the need for this metal in new high tech devices increases. Failure of the Cu product to meet specifications results in severe economic loss due to the facilities, labor and time required to re-process the Cu while often using the same inadequate impurity metal removal processes. Metal impurities found in Cu ores include Pb, As, Bi, and Sb. During processing, these impurities are found in the electrolyte and their concentrations gradually increase with time necessitating use of some means to maintain their concentrations at acceptable levels. The most critical impurities, which cause grain boundary cracks in wiredrawing are Bi (severe effects), As (deleterious), and Sb (deleterious).³⁰

Environmental and other concerns associated with use of SX, IX, and precipitation for impurity removal are significant.¹ New chemicals are added to the system increasing the number of impurities present. Additional steps and processes are needed to separate the target metal impurity, often with potential health hazards to workers. Following separation, the impurity plus the additional chemicals must be disposed of, usually in landfill or waste receptacles, resulting in potential environmental problems. Altogether, maintenance of acceptable levels of impurity metals in Cu electrolyte presents significant challenges.

The Bi potential is very close to that of Cu, making it possible

to plate Bi on the Cu cathode which adversely affects the quality of the resulting Cu product. Also, as the concentration of Bi in the electrolyte increases, precipitation can result causing quality issues. Therefore, concentrations of Bi and other impurity elements must be controlled inside the tank house. Constant input fluctuations of Bi and other impurities coming from the smelter make control of impurity levels in the electrolyte very difficult but necessary in order to meet ASTM standards or other customer specifications.

Over the period January 2010 through October 2014, the amount of Bi processed in Cu anodes at Asarco's Amarillo, Texas copper refinery (ACR) was appreciable, ranging from ~1600 to ~5500 kg per month with most values being ~3000 to ~3600 kg per month. ACR has studied several methods for electrolyte purification. The method chosen by some other companies in North and South America is to adjust the mole fraction ratio of As/(Sb+Bi) (mol/mol) in order to convert Sb and Bi into the insoluble species, antimony and bismuth arsenate (SbAsO₄ and BiAsO₄).³⁰ These precipitates report at the bottom of the tank house cell mixed with the anodic Cu slimes. This method has the potential to cause environmental issues if not controlled carefully including the use of respirators inside the tank house, a practice that should be avoided due to the extra heat stress this can cause in a hot region like Amarillo, Texas. Disposal or processing/treatment of the residues can attract unwanted attention from environmental agencies and cause public concern since As and many of its compounds are potent poisons.⁶ Other methods for removal of impurities³⁰ are based on adsorption, IX, SX, and MRT. ACR has used MRT successfully for several years to control Bi in tank house electrolyte. The MRT method has the advantage of higher selectivity and

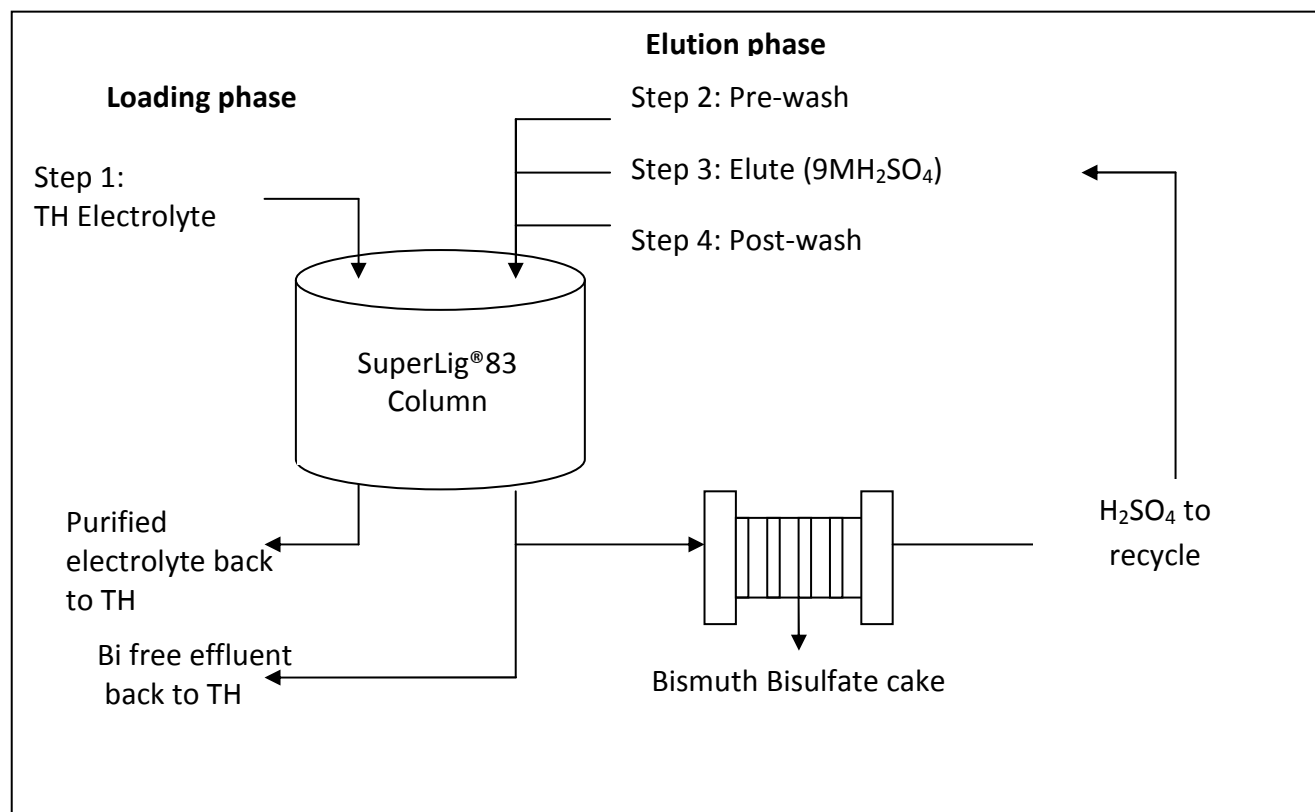


Fig. 3 Schematic flow diagram of the electrolyte purification plant for bismuth removal using Molecular Recognition Technology²⁸
 TH=tank house.

efficiency in comparison with other adsorption methods.

The MRT process for Bi removal consists of the following steps as depicted in Fig. 3: (1) electrolyte feed from the tank house is loaded on the columns and Bi is selectively removed by solid phase extraction to the SuperLig® 83 material; (2) the loaded column is washed with hot water to remove residual electrolyte; (3) a small quantity of eluent solution (9 M H₂SO₄) is fed to the column removing Bi as a pure concentrated product, easily recovered as a salt; and (4) the column is washed with hot water to ready it for step (1). In step (2), a hot water wash is used. Hot water does not remove all of the Cu, which may be desired in some Bi-removal operations. If removal of all of the Cu is required, a dilute H₂SO₄ wash may be substituted for the hot water wash in step (2). The 9 M H₂SO₄ is recycled minimizing the amount of waste acid discarded.

In actual operation, electrolyte is drawn from any one of the six commercial modules or from the stripper module and passed to the electrolyte purification plant (EPP) where it enters into a receiving tank. From there the electrolyte is filtered through a 1

20 micron mesh and fed into the columns packed with SuperLig® 83. During this step, Bi is selectively removed from the electrolyte while Bi-free electrolyte is continuously returned to the selected operation module. When loading is complete, the column is washed with two bed volumes (BV) of hot water (4 L water/kg SuperLig® 83), followed by elution with ~3.1 BV of 9 M H₂SO₄. Part of the eluate, ~2.2 BV, is sent to the Bi precipitation tank and the remainder is recycled back into the eluent tank. After precipitation is triggered by dropping the temperature below 42 °C, the product is sent to a filter press to recover bismuth sulfate. On a periodic basis, a 6 M HCl wash is performed to remove Pb and Sb that have built up in the SuperLig® 83 product. Pb and Sb cannot be removed effectively with 9 M H₂SO₄. Other eluent solutions have been studied due to concern about using HCl in the tank house environment, i.e., 9 M H₂SO₄ in combination with thiourea or commercial salt, and have showed some efficiency in improving the removal of these metals, but more study needs to be performed.

The purification plant is not located inside of the tank house,

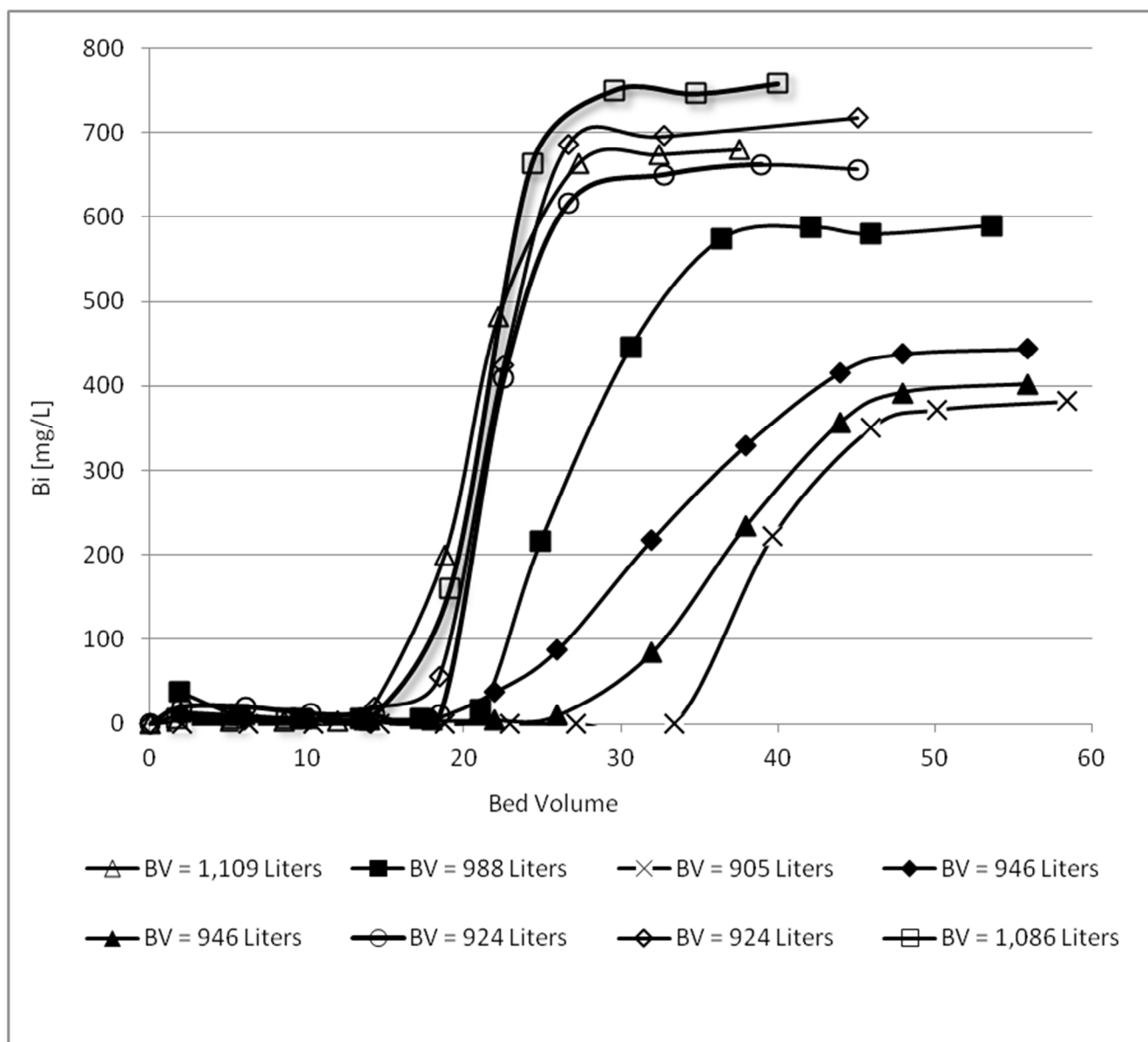


Fig. 4 Bismuth loading profile for different bed volumes and bismuth concentrations using ACR electrolyte.²⁸

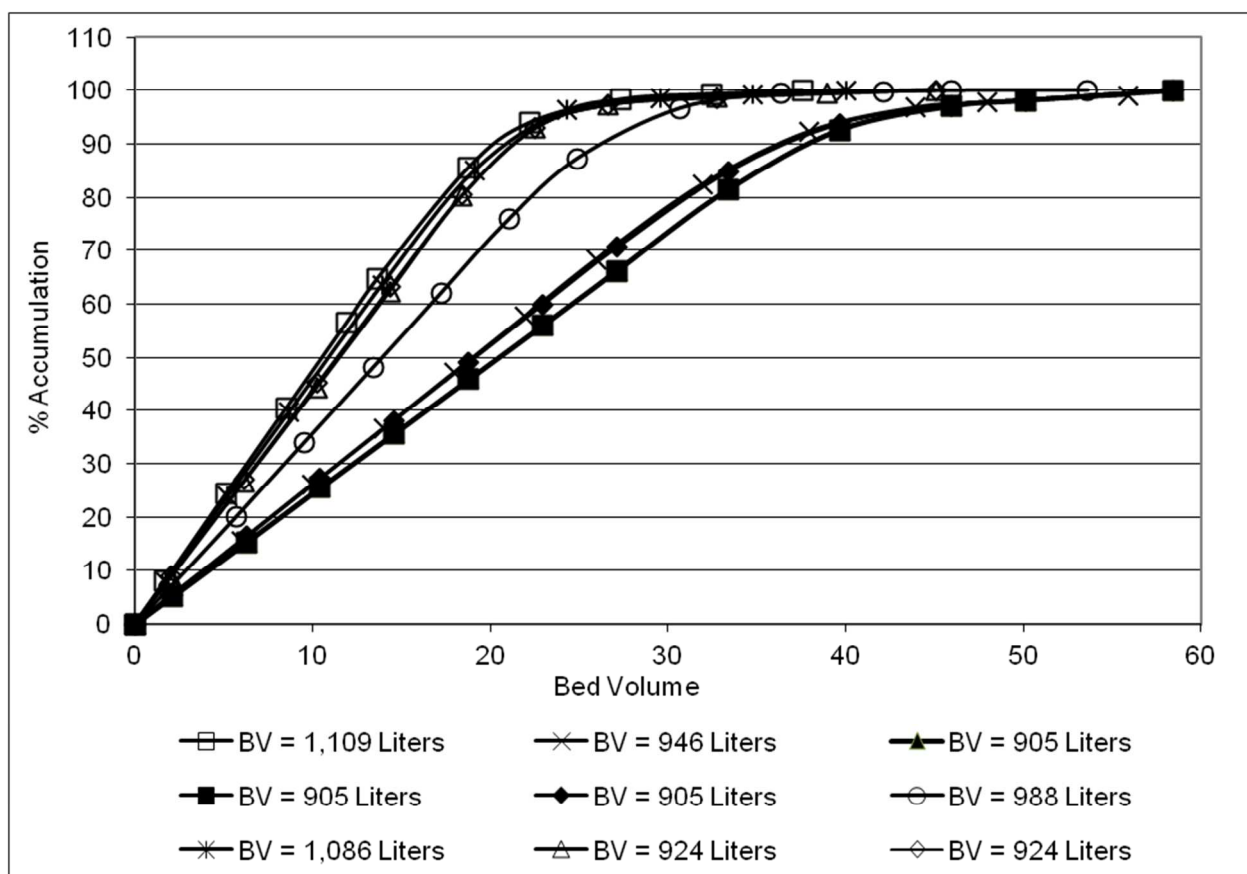


Fig. 5 Bismuth loading capacity (% accumulation) vs bed volume; concentrations of bismuth are < 450 mg/L in lower three curves and > 550 mg/L in remaining curves.²⁸

but adjacent to it, eliminating any potential contamination of the tank house electrolyte. The process is designed to handle 3100 kg Bi per month, running both columns at 100% SuperLig® capacity. Cycle time depends on the Bi feed concentration, flow rate, and column size. In order to increase the Bi removal capacity, it would be necessary to increase the heat transfer capacity or add another heat exchanger to reduce the time for eluent preparation.

The EPP is operated from the control room via control logics from a dual screen monitor. The control room operator is required to visit the purification plant only for routine sampling, cleaning, and emptying of the filter press.

The performance of SuperLig83® was tracked by performing loading and elution profiles through the life of each of the 15 different batches used in either of the 2 columns with a capacity of ~475 kg (± 25 kg), and an average BV of 973 liters. Several loading profiles of a single column are shown in Fig. 4. Each loading profile provides a “snapshot” of how well the SuperLig®83 is removing Bi from the treated electrolyte. This profile is created by taking 50 mL samples from the exiting stream of the column at different times with every sample being evenly spaced throughout the loading cycle. By taking loading profiles, it is possible to monitor both effective capacity of SuperLig 83® and any maintenance issues which impede column performance, such as flow channeling or the need to perform an HCl wash. The maximum loading capacity obtained in the process was 0.18 mmole Bi/kg of SuperLig® 83, with an average loading capacity before 150 cycles of 0.16 mmole Bi/kg of

SuperLig® 83, giving an average uptake capacity of 17.9 kg Bi per cycle at 100% capacity.

The loading capacity of SuperLig® 83 (% accumulation) is independent of BV but dependent on Bi concentration in the electrolyte, as seen in Fig. 5. The loading capacity of SuperLig® 83 is reached after ~30 BV when the Bi concentration is >550 mg/L and ~45 BV when it is <450 mg/L.

The elution profile (example shown in Fig. 6) allows tracking the release of Bi from SuperLig 83® during the numerous stripping cycles. This profile is created by obtaining 50 mL samples drawn 24 times throughout the numerous stages of the 40 stripping cycle. The samples taken at this step are analyzed for Bi and H₂SO₄ concentrations. The Bi elution (Fig. 6) is sharp and rapid, and is accomplished with ~2.2 BV of 9M H₂SO₄ at 63 °C.

Strip 1 refers to the hot wash performed to push the electrolyte out of the column. No acid or Bi is found there. Strips 2-4 are related to the eluant, 9M H₂SO₄, passing through the column. Strips 2 and 3 go to the precipitation tank and strip 4 re-circulates back to the eluent tank to be reused.

Electrolyte purification is a recurrent topic in tank house operations due to the high impact that small concentrations of 50 impurities can have on Cu cathodes. The MRT process has proven to be an important strategic technology for control of Bi impurity. Main benefits to ACR of the process include: (1) The SuperLig® 83 product has high selectivity for Bi and has a high capacity. (2) There is no pick up or loss of Cu during the loading 55 phase. (3) Due to rapid reaction kinetics, very high feed flow rates are possible for Bi loading. (4) The Bi product in the eluant

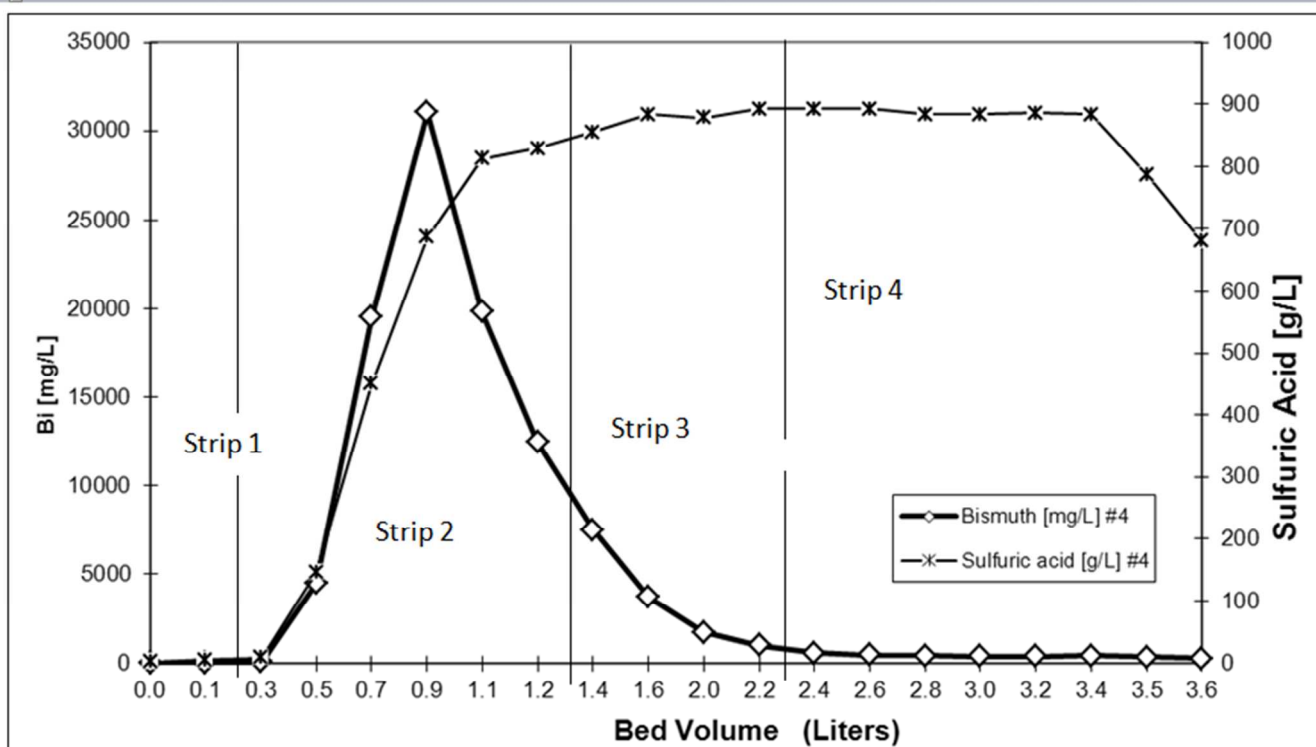


Fig. 6 Typical bismuth elution profile using 9M H₂SO₄.²⁸

solution is very concentrated and readily precipitates to form a high purity bismuth bisulfate precipitate that can be collected by filtration. (5) The bismuth bisulfate has a significant market value that makes a sizeable contribution to reduction of operating costs. (6) Recovery of Bi for reuse avoids its wasteful discharge into the environment. (7) The number of BV used to remove Bi from SuperLig® 83 is low making it possible to have a smaller purification plant than would be the case when other methods for Bi removal are used.

10 Mercury separation and recovery from commercial sulfuric acid.³¹

Due to its affinity for sulfur, Hg is found enriched over its crustal abundance in sulfide ores of Zn, Pb, Cu, Au, and Mn.³² When these ores are treated in thermal processes, such as smelting and roasting, the Hg present volatilizes and will appear in downstream products such as H₂SO₄, which is generated at most of these operations from by-product SO₂.³³ Consequently, Hg eventually finds its way into commercial products such as fertilizer, where the potential damage to the environment, farm animals, and humans, especially children, is severe.⁶ Large increases in mining activity during the past century have resulted in a corresponding increase in (often) unregulated Hg dispersal into the environment with consequent environmental and health challenges.^{11,34} It is important to eliminate or minimize Hg dispersal into the commons from these massive worldwide metallurgical operations.

Without any treatment for Hg removal, approximately half of the Hg originally present in the ore will be found in the product acid.³³ Partial removal of Hg upstream in the process is desirable

and normally achieved, but significant amounts, especially in non-OECD nations, report to the product acid. The present standard for commercial H₂SO₄ is <1 mg Hg/L while a content of <0.5 mg L⁻¹ is required if the H₂SO₄ is used in products such as fertilizer that may be linked to the food chain.³³ Removal of Hg to these levels is challenging to current commercial separation methods. Conventional processes for Hg removal involve gas adsorption.³³ Gas adsorption processes require very high capital investment costs, and are not flexible enough to deal with changes in Hg input levels. Also Hg levels present in the gas must be related to predicted Hg levels in the H₂SO₄. Possible hydrometallurgical processes that may be used for Hg removal, such as precipitation, SX, and IX become less effective as the concentration of Hg in the H₂SO₄ decreases.¹

An MRT green chemistry process is effective in Hg separation and recovery from H₂SO₄ solutions. The MRT process is used for bulk Hg removal and as a 'polisher' for Hg in these solutions. A lead-trail column MRT pilot test program was conducted at a base metal smelting location³⁵ to remove Hg from a plant H₂SO₄ stream of general composition 93% H₂SO₄. Mercury concentrations in the feed were in the range of 100 to 200 mg/L. Used in bulk removal mode, the MRT system maximizes removal of Hg from the feed stream, reducing the Hg concentration to the mg/L concentration level, and, in some cases, to concentrations as low as 1.0 mg/L. Use of the MRT system in polishing mode, with up to five MRT columns in series, allowed the Hg concentration to be further reduced to <0.1 mg/L.

Results for bulk removal of Hg (present at 140 mg/L) from peroxidized H₂SO₄ for a three columns-in-series system are given in Fig. 7. The early part of the loading curve (column 1) for a pilot plant (0.5 kg SuperLig® 88 per column) system is shown. In column 1, the early part of the breakthrough curve is

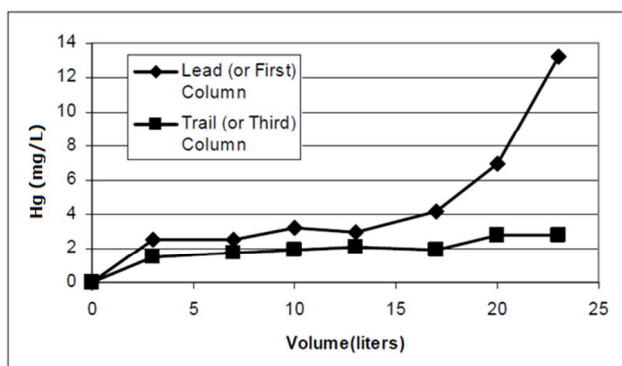


Fig. 7 Pilot plant loading curve results for bulk removal of Hg, initially present at 140 mg/L, from peroxidized H_2SO_4 for a three columns-in-series system.³⁵

presented. The Hg present in the output from the third column-in-series is reduced to a few mg/L. Pilot plant results are given in Fig. 8 for polishing of Hg in a five column-in-series system.

Mercury content in the feed ranges up to 1.0 mg/L, and the system operates through 1144 bed volumes. Mercury content in the exiting column 5 is < 0.1 mg/L.

A representative curve for elution of bound Hg from a

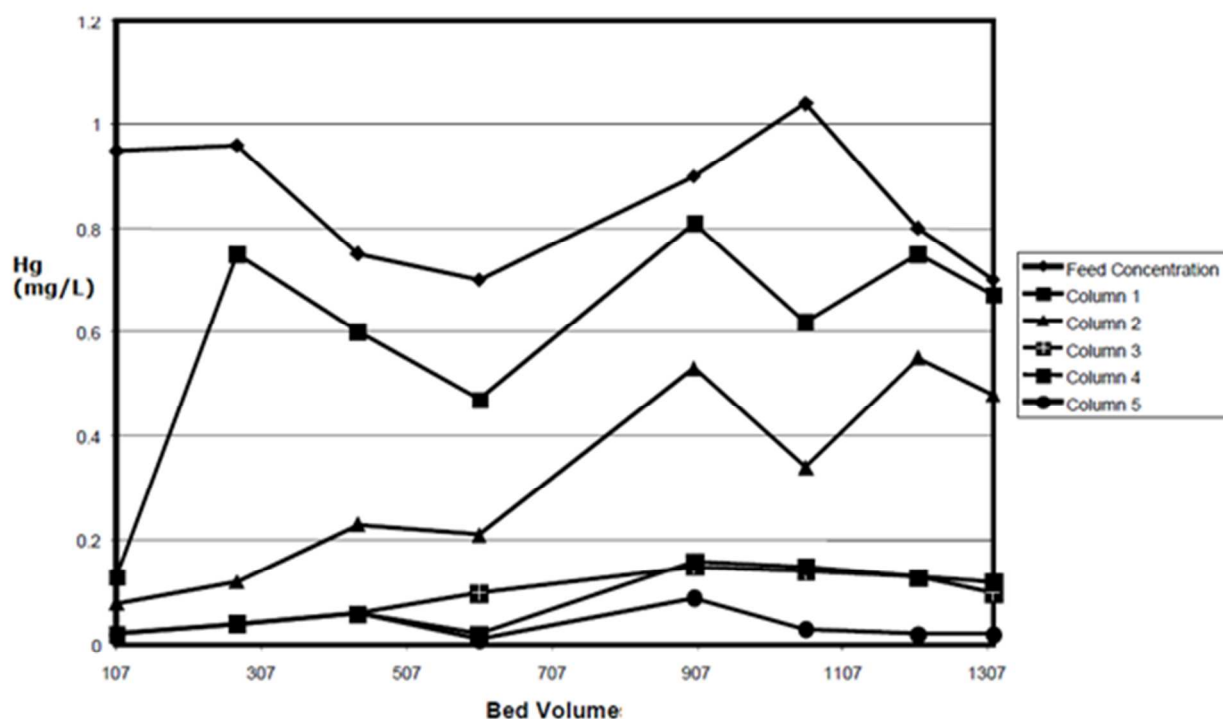


Fig. 8 Pilot plant results for a five column-in-series Hg polishing system.³⁵

SuperLig® 88 column is presented in Fig. 9. The eluent is 0.5 M thiourea, 0.1 M H_2SO_4 . The elution curve is extremely sharp with essentially complete elution of Hg being achieved in less than six bed volumes. The Hg concentration peaks above 250 mg/L. In normal operation, the first third of the eluate is sent to Hg recovery. The remaining two-thirds of the eluate is sent to recycle, to be used as the first and second parts (thirds) of the next elution. The eluate is neutralized with NaOH to produce sulfide ion and urea. The sulfide precipitates Hg as HgS , which

is readily collected as a solid and either marketed or disposed of in an environmentally safe manner. A number of compounds can be used as eluents, including (a) 6 M HCl and (b) 5 M NaCl plus 0.1 M HCl. However, thiourea is usually the preferred eluent, since its use results in a significant reduction in wash and elution volumes. The MRT process uses innocuous wash and eluent solutions throughout the operation.

The MRT green chemistry procedure is effective for Hg removal and recovery from H_2SO_4 solutions. Main benefits to the industrial company of the process include: (1) liquid phase acid product is treated, eliminating need for large, high capital cost gas handling equipment; (2) sustainable levels of Hg are achieved at the < 0.1 mg/L concentration level in H_2SO_4 solutions, a level which cannot be assured by other processes; and (3) a pure Hg product is recovered, which can be marketed or disposed of in an environmentally safe manner avoiding unsafe discharge of Hg to the commons.

Conclusions

Clean chemistry MRT processes make possible selective separation and recovery of metals at various stages in metal life cycles. Examples are given for selective individual separations of

metals from industrial feed solutions. PGM were separated from each other and individually recovered in the pure state. Palladium was separated and recovered in pure form from spent petrochemical catalysts. Bismuth was selectively removed from Cu electrolyte and recovered in pure form as a bismuth salt. Mercury was removed from a concentrated H_2SO_4 solution and recovered in pure form. The Hg concentration level in the H_2SO_4 solution was reduced to 0.01 mg/L. These examples illustrate important green chemistry features of the MRT system as used in

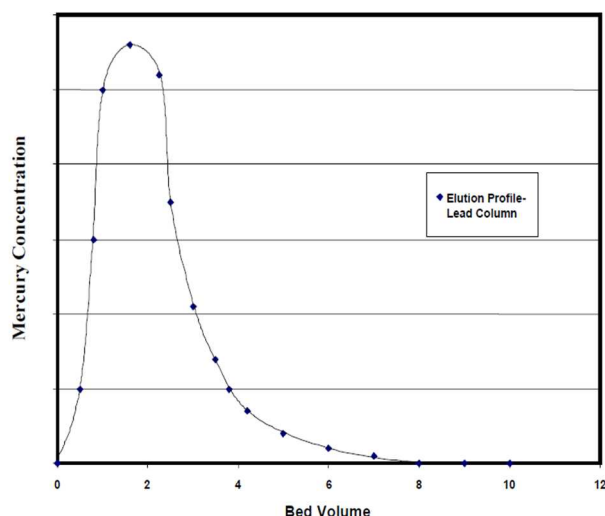


Fig. 9 Representative curve for elution of bound Hg from a SuperLig® 88 column.³⁵

commercial separations (refer to Table 1). First, separation and recovery processes were accomplished with generation of minimal waste. Second, no organic solvents were used in the operations. Third, innocuous reagents were used in all wash and elution steps. Reagents used are compatible with industry requirements. Fourth, MRT processes require minimal energy input since columns and gravity are used. Fifth, elimination of process steps and auxiliary substances used in conventional separation procedures result in cost savings in labor, chemicals and equipment that otherwise would be required. Sixth, pure, recoverable metal products result from MRT operations. Recovery of these products reduces the need to mine virgin ore to replace the metals, thus conserving valuable resources and eliminating additional environmental impacts of mining. Benefits of recycling metals as opposed to dissipation of them to the commons have been discussed.^{1,3} Finally, removal of Hg to the 0.1 mg/L concentration level is significant. The ability of MRT processes to achieve this separation at this low concentration level on an industrial scale suggests that means could be devised to separate and recover Hg and other toxic metals such as Cd and Pb from environmental and industrial streams, where they are now being discarded. Recovery of these toxic metals at these concentration levels has great potential value to human health and to environmental welfare. The conclusion is reached that expanded use of green chemistry principles in recovering metals from all stages of metal life cycles can have important effects on global metal sustainability.

Experimental

Compositions of feed streams are indicated in the figures. All chemicals used were reagent grade. Metal concentrations were determined using ICP and/or atomic absorption spectrophotometry. All determinations were made at or near ambient temperature.

An Agilent 4200 Microwave Plasma Atomic Emission System was used to analyze for most of the metal impurities in the ACR

electrolyte. Copper, H₂SO₄ and HCl concentrations were determined via titration. Typical analyses for ACR electrolyte solutions are (g/L): Cu (50), H₂SO₄ (175), As (3.5), Sb (0.3), Bi (0.6), Cl (0.045).

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Notes

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Selective precious and specialty metal separations and recovery using molecular recognition processes are described for commercial mining and recycling operations.

