

Molecular Recognition Technology:

A GREEN CHEMISTRY PROCESS FOR SEPARATION OF INDIVIDUAL RARE EARTH METALS

Steven R. Izatt

James S. McKenzie

Neil E. Izatt

Ronald L. Bruening

Krzysztof E. Krakowiak

Reed M. Izatt



ucore
RARE METALS



IBC

®

Advanced Technologies

MOLECULAR RECOGNITION TECHNOLOGY: A GREEN CHEMISTRY PROCESS FOR SEPARATION OF INDIVIDUAL RARE EARTH METALS

*Steven R. Izatt¹, James S. McKenzie², Neil E. Izatt¹, Ronald L. Bruening¹, Krzysztof E. Krakowiak¹, and Reed M. Izatt¹

¹*IBC Advanced Technologies, Inc., 856 E Utah Valley Drive, American Fork, UT 84003 USA.*

**(Corresponding author: sizatt@ibcmrt.com)*

²*Ucore Rare Metals, Inc., 210 Waterfront Drive, Suite 106, Bedford, Nova Scotia, Canada B4A 0H3*

ABSTRACT

Separation methods for rare earth elements (REE) are predominantly based on solvent extraction procedures. These methods are low in metal selectivity and generate large amounts of waste resulting in high capex and opex costs. Molecular Recognition Technology (MRT) is a much simpler green chemistry process that uses no organic solvents and carries out separations with highly metal-selective SuperLig[®] products. Minimal waste is generated. The MRT process has been used to successfully separate all sixteen REE (excluding Pm) (1) from a pregnant leach solution derived from the Bokan-Dotson Ridge (Alaska) rare earth metal deposit and (2) individually, from each other. Both separations are made at the >99% level. This paper discusses the MRT-based REE separation results in comparison with traditional separations technology.

KEYWORDS

Rare earth elements, Molecular Recognition Technology, solvent extraction, rare earth metal-selective separations, green chemistry process, capex and opex comparisons

INTRODUCTION

The seventeen rare earth elements (REE, singular or plural) probably have the most confusing and complex history of any group of elements in the periodic table. The search for them and their identification as individual elements constituted an integral part of the development of science and technology during the late 19th century and early to mid-20th century. Several factors made their discovery and identification difficult: the chemical and physical properties of the different elements are quite similar, making their separation from each other challenging; the elements were isolated originally as "earths" or oxides, each of which usually constituted two or more of the individual elements; and the methods of separation and purification depended on laborious fractional precipitation and crystallization techniques, sometimes requiring thousands of separation phases. Difficulties of separation were compounded by a lack of good methods for identification and assessment of purity of the separated elements, and a lack of knowledge through the 19th century and early 20th century of the number of rare earth elements that existed. The first REE to be isolated was yttrium in 1794 from a mineral named ytterbite, found near the village of Ytterby in Sweden. The last REE to be discovered was the unstable element 61, identified in 1947 and named promethium after the Titan who stole fire from the gods in Greek mythology (Scerri, 2013).

During this period, from 1794 to 1947, tremendous scientific progress was made. Moseley (Scerri, 2013) demonstrated in the early 1900, using X-ray spectroscopy, that only one REE remained to be discovered, element 61. The history of the search for element 61, its synthesis in 1947, and the eventual discovery in 1965 that it occurs naturally on Earth in extremely miniscule amounts in the mineral apatite is one of the most fascinating accounts concerning element discovery (Scerri, 2013). The remaining REE had been separated, mostly by laborious fractional crystallization. Charles James was instrumental in separating these metals in the early 1900s. Illustrative of the difficulties involved in working with REE, James used his method to separate large amounts of ytterbium, hitherto considered to be a single element, into two elements now known as ytterbium and lutetium. His methods were used widely by others and remained the best available for separating REE until the successful use of ion exchange (IX) in the 1940s. A National Historic Chemical Landmark was dedicated October 29, 1999 at the University of New Hampshire commemorating the work of James (Separation, 1999).

Ion exchange was the method of choice for REE separations through the 1950s (Gupta & Krishnamurthy, 2005). This method produced small amounts of individual REE of high purity, but there was little demand for these elements until the early 1960s, when color television made its debut and the Eu phosphor was used in large quantities because of its ability to produce the red color needed in this product. The production of REE soared in the next few decades as new uses for these metals in high technology products emerged (Abraham, 2015; Veronese, 2015). Solvent extraction (SX) was used as a method of choice because of its ability to make large scale separations of REE (Gupta & Krishnamurthy, 2005). The U.S. was the predominant producer of REE until the early 1990s, when China overtook it and became dominant in mining REE, processing the ore, and separating the individual metals. China currently dominates the REE industry, supplying nearly 100 % of the pure individual metals (Veronese, 2015) using SX and IX processes.

Mining rare earth metal ores, beneficiation of concentrated leach solutions, and separation of individual REE in China today have many negative externality effects (Abraham, 2015; Veronese, 2015). Solvent extraction methods used have low selectivity for the individual REE resulting in the need for many separation stages and carry-over of impurities downstream with the generation of much waste. Generation of waste during chemical processes is a major target of green chemistry advocates (Anastas & Eghbali, 2010; Izatt, et al., 2015). Solvent use has attracted particular attention due to the flammability and toxicity of most organic solvents, and the need for extensive facilities to remediate them at their end-of-life (EOL) state. In addition, SX separation methods, generally, require use of many corrosive chemicals.

In this paper, Molecular Recognition Technology (MRT) is described. Just as a sequence of separation methods has been used over the past two centuries to meet the changing demand for these metals, both in purity and quantity, MRT has promise to use green chemistry separation techniques to meet the increasing demand from 21st century society for environmentally safe metal separation procedures. MRT is a highly metal-selective green chemistry procedure that has been used to separate individual REE at >99% purity levels from pregnant leach solutions (PLS) derived from the Bokan-Dotson Ridge deposit in Southeastern Alaska (Press Release, 2015, March 2; Press Release, 2015, April 28). Organic solvents are not used in MRT separation processes. An important objective of this paper is to demonstrate that significant savings in capital expenses (capex) and operating expenses (opex) can be achieved by use of MRT, compared to SX, for REE separations. This demonstration is important because global 21st century society is becoming increasingly more environmentally conscious and evidence that separation methods based on green chemistry principles are competitive with more pollutive methods can lead to increased use of green chemistry procedures, increased metal sustainability, and an increased level of conservation of valuable metal resources.

STATUS OF GLOBAL RARE EARTH ELEMENT PRODUCTION

The history of global rare earth production is shown in Figure 1 (Tse, 2011). Prior to about 1960, these elements were, largely, a curiosity. Ion exchange was the method of choice for separation of the REE through the 1950s, when only small quantities were needed (Gupta & Krishnamurthy, 2005). High purities were obtained with IX, but production of large quantities of REE required a different separation procedure. Solvent extraction proved to be a method capable of separating the REE in the quantities needed following about 1960 (Figure 1). In 2015, annual production of REE is more than 120,000 tons annually. Demand for selected members of the REE family is expected to grow in coming decades. This demand will be driven by global population increase, increased affluence of the global population, need to replace end-of-life products containing REE, and production of new products containing REE. Since the recycling rate for products containing REE is < 1% (Reck & Graedel, 2012), increased mining of these metals is assured, with attendant environmental and ecological challenges.

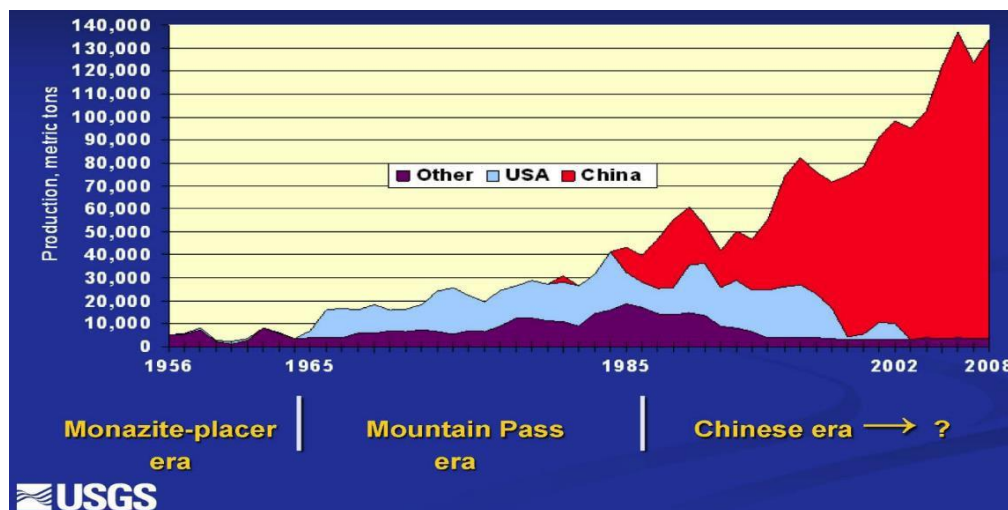


Figure 1 - Global rare-earth-oxide production trends, 1956–2008. The Mountain Pass deposit is in California, U.S.A. Reproduced from Tse, 2011, with permission from the U.S. Geological Survey.

Nearly all REE mining and production was done in the U.S., primarily at the Mt. Pass facility in California, until about 1990 (Figure 1). The rise in REE mining and production in China began in the 1980s

and became dominant by about 2000. The decrease in production at Mt. Pass was due to a number of factors, including the rise of the environmental movement in the U.S., which made the SX procedure used at Mt. Pass uneconomical on the world market. By 2000, the REE market was dominated by China, which had few, if any, environmental restrictions on REE mining or production (Abraham, 2015). REE mining and production in China have created heavily polluted areas, which have attracted international attention (Yang, et al., 2013). China has effective control of global REE mining, beneficiation, and separations. In addition, China has begun to manufacture products using REE, which has put an additional strain on availability of REE for other nations, since Chinese manufacturers have first call on available REE (Abraham, 2015).

Despite the risks of control of the REE market by a single nation, no effective competition exists elsewhere (Veronese, 2015). The Mt. Pass operation ceased in 2002, but was reborn under new ownership in 2008. However, this deposit contained mainly light REE and these were sent to China for separation. In 2015, the Mt. Pass operation filed for bankruptcy, leaving only Lynas as a viable competitor in the global market (Veronese, 2015). Lynas mines REE ore in the Mt. Weld region of Australia and ships this ore to Malaysia for separation of individual members of the REE group. Legal action has been instituted in Malaysia to block the Lynas operation. The fear in Malaysia is that the operation will cause severe environmental damage (Veronese, 2015). IBC Advanced Technologies, Inc. (IBC) has the only other operation that is near production of separated individual REE outside of China. IBC is constructing a pilot plant, commissioned by Ucore (Press Release, 2015, July 8), that is near completion for separation, within U.S. borders, of individual REE (Press Release, 2015, November 11; Press Release 2016, February 17). This operation makes use of a green chemistry MRT approach to the chemical separation of these metals.

GREEN CHEMISTRY MRT APPROACH TO METAL SEPARATIONS

Green chemistry has been defined as the design of chemical products and processes to reduce or eliminate the use and generation of hazardous substances (Anastas & Eghbali, 2010). This definition was formulated in the early 1990s and has since gained acceptance throughout the world, especially in the chemical and pharmaceutical industries (Anastas & Eghbali, 2010). The green chemistry approach is aimed at achieving sustainability at the molecular level. Anastas & Eghbali (2010) consider the most important aspect of green chemistry to be the concept of design. Twelve principles of green chemistry have been set forth as design rules to aid practitioners in achieving the goal of sustainability. These principles apply to a broad range of chemical manufacture and their application has been successful in improving sustainability in the use of chemical substances in a variety of industries.

Principles of green chemistry particularly relevant to achieving metal sustainability in the mining and ore beneficiation industries (Izatt, et al., 2015) are as follows: (1) it is better to prevent waste than to treat or clean up waste after it is formed; (2) use of auxiliary substances, such as organic solvents, separation agents, etc., should be made unnecessary, whenever possible, and, when used, as innocuous as possible; (3) energy requirements of chemical processes should be recognized for their environmental and economic impacts and their use should be minimized; and (4) raw materials or feed stocks used should be renewable rather than depleting, whenever technically and economically practicable.

Despite wide and increasing use in chemical and pharmaceutical industry processes, green chemistry principles have been applied sparingly in the mining and ore beneficiation industries. This is unfortunate, since there is great need for improvement of metal separation and recovery procedures in these industries. Throughout human history, mining has been synonymous with waste generation. Remnants of this legacy are found in every corner of the Earth. In the U.S. alone, it has been estimated that there are as many as 250,000 acid mine drainage sites (Lichti & Mullahey, 1998). In an analysis of the platinum group metal mining industry in South Africa, Mudd (2012) pointed out the large amount of waste generated and

the enormous amounts of energy and water required to mine and process ore to recover desired metals, since ore grade is, usually, 1 % or less. As ore grades decrease and greater depths are required to locate minable deposits, the amount of energy and water required increases dramatically. It would be desirable to reduce the necessity of mining virgin ore by better management of our existing metal supply through reduction of waste generation and achievement of improved recovery rates of metals from waste products. China's rare earth metal mining and processing industries are noted for their widespread pollution of the environment (Yang, et al., 2013).

SOLVENT EXTRACTION SEPARATION TECHNOLOGY

Use of SX technology has become widespread in mining and ore beneficiation industries during the past half century, notably in the rare earth sector (Gupta & Krishnamurthy, 2005) and across a wide range of industrial metals. Notwithstanding this extensive use, the elimination of solvents is increasingly a focal point for proponents of green chemistry for a variety of reasons, which have been summarized (Anastas & Eghbali, 2010). The elimination of organic solvents represents an important objective for green chemistry because they account for a majority of mass wasted in chemical syntheses and processes. Moreover, many conventional organic solvents are toxic, flammable, and/or corrosive. Their volatility and solubility have contributed to global air, water and land pollution, have increased the risk of worker exposure, and have led to serious accidents including fires that can destroy facilities and shut down production for extended periods of time. Recovery and reuse, when possible, are often associated with energy-intensive distillation and sometimes cross contamination. When environmental regulations are non-existent, ignored, or not enforced, spent organic solvents are often discarded into the commons with serious environmental and health consequences. These negative externalities endanger the wider population as well as the workers associated with the processing of REE. Chinese REE mining and production facilities provide an example of the effects of pollution from use of organic solvents (Yang, et al., 2013). Such problems, and the resulting economic inefficiencies, were, in part, a cause of the closure of the Mt. Pass REE facility in California in 2002 (Abraham, 2015; Veronese, 2015), and, again, in 2015 (Molycorp, 2015).

Solvent extraction is the antithesis of green chemistry. SX utilizes organic solvents that are typically toxic and corrosive, as well as being inherently volatile, flammable, and disposable only as a regulated waste. In addition, SX systems, generally, have low metal recovery rates and low metal selectivity, requiring many stages for effective separations. These inefficiencies require not only more expenditures of reagents, time, space, and labor, but produce large in-process metal inventories, significantly elongating the time required to produce final products. Damage to the environment, resulting from such inefficiencies, are not accounted for in the cost of producing rare earth products (Abraham, 2015; Veronese, 2015). This situation is an example of negative externality, where the cost of producing the rare earth metals is borne, to a large degree, by society at large.

In an effort to address these shortcomings of SX methodologies, chemists have searched for safer solutions for use in the chemical and pharmaceutical industries. Solvent-less systems, water, supercritical fluids, and, more recently, ionic liquids are some examples of these new "green" answers. Where possible, the ideal situation would be to not use any solvent at all, because the decision to include an auxiliary always implies efforts and energy to remove it from a designated system. Efforts have therefore been devoted to developing solvent-less systems. This idea was reinforced by the finding that solvents account for most industrial waste. The observations by Anastas & Eghbali (2010) may be difficult to implement in the mining and ore beneficiation industries where use of SX is deeply embedded. When properly implemented and regulated, SX may have some utility as a separation process; however, its inherent drawbacks severely limit its desirability as a separation technique for the 21st century. It is desirable to use creative thought to

develop alternatives to solvents in the mining and related industries as is being done in the chemical and pharmaceutical industries.

HOW MOLECULAR RECOGNITION TECHNOLOGY WORKS

Early work by us with selective transport of metal ions in supported liquid membrane systems 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. This achievement made large scale, selective metal separations possible, with many commercial applications (Izatt, et al., 2000, Izatt, et al., 2012, Izatt, et al., 2015). A representative example of such a SuperLig[®] system is shown in Fig. 2. 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, *i.e.*, Na⁺ = 4.36, K⁺ = 6.10, and Cs⁺ = 0.99. Similar principles apply to the selective separations described here. However, ligand, cation, and system parameters which affect the magnitudes of host-guest interactions are numerous and the reader is referred to an earlier article for discussion and references (Izatt, et al., 2015).

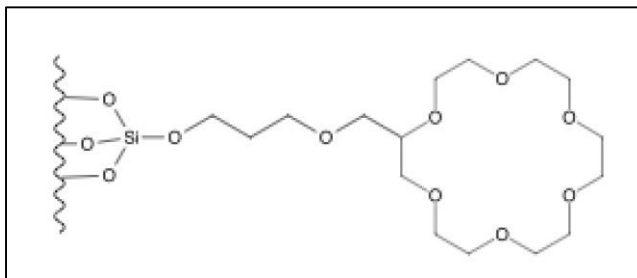


Figure 2 - Representative SuperLig[®] system consisting of a solid support particle, silica gel, to which a metal-selective ligand, 18-crown-6, is attached by a tether, chemically bound to both the ligand and the silica gel

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 (Izatt, et al., 2000; Izatt, et al., 2015). 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).

STRENGTHS OF MOLECULAR RECOGNITION TECHNOLOGY IN METAL SEPARATIONS

MRT provides an approach to chemical separations that is consistent with green chemistry principles (Izatt, et al., 2015). Descriptions of the MRT process, including its ability to perform green chemistry separations in an environmentally friendly fashion and several of its commercial applications, are available (Izatt, et al., 2000, Izatt, et al., 2012, Izatt, et al., 2015). The importance of selectivity in making green chemistry separations and the need for improvement in separation technologies to achieve greater global metal sustainability have been presented (Izatt, et al., 2015). The MRT approach forms a basis for improving metal recovery, recycling, and end product fabrication processes during metal life cycles with significant operating advantages and environmental gains over traditional procedures.

Important strengths of MRT processes lead to improved separations behavior. These strengths have been discussed (Izatt, et al., 2012; Izatt, et al., 2015) and are summarized in Table 1.

Table 1 - Strengths of MRT in metal separations

-
1. Pre-determined high selectivity for target metal species makes possible high loading on the column of the target metal from matrices containing competing metals that otherwise would contaminate separated products and require further separations downstream.
 2. Availability of commercially proven SuperLig[®] products for a wide range of metals, non-metals, and anions provides great versatility in the design of selective separations and metal recovery.
 3. Significant operating advantages, since MRT plants are compact, easy to install, and easy to operate.
 4. Rapid metal bind and release mechanisms of the SuperLig[®] products, use of these products over multiple cycles, and avoidance of the introduction of contaminants into the separation process.
 5. Small floor space requirements compared to those used in conventional separation systems. Due to their high selectivity, relatively small quantities of SuperLig[®] products are required resulting in much smaller installations compared with pyrometallurgical and traditional hydrometallurgical operations.
 6. Environmentally and ecologically friendly processes allow SuperLig[®] products to selectively and rapidly separate, concentrate, and recover target and accompanying metals in pure form with minimal carbon footprint. Resulting raffinate streams, with negligible target metal concentration levels, can be efficiently treated within the plant's flow sheet to recover metals of value without need for further processing.
-

APPLICATION OF MOLECULAR RECOGNITION TECHNOLOGY TO SEPARATIONS OF THE RARE EARTH ELEMENTS

(Izatt, et al., 2016)

The entire suite of sixteen REE, Pm excluded, has been separated at the bench level at high purity of >99% using a proprietary MRT procedure (Press Release, 2015, March 2; Press Release, 2015, April 28). A pregnant leach solution (PLS) derived from Bokan-Dotson Ridge, Alaska, feedstock was the feed material for the separations. The PLS was prepared by Hazen Research Inc., of Golden, Colorado from beneficiated ore using a metallurgical process that has been described (Press Release, 2015, March 2). The Bokan deposit has high levels of certain of the 'heavy' REE, such as Dy, Tb, and Y.

The entire set of sixteen REE was initially separated from the non-REE gangue metals present. This initial separation, accomplished at the >99% level, is an important step in the process. Having the entire suite of REE separated from accompanying gangue material simplifies subsequent separation of individual REE since impurity metals are not present downstream. Furthermore, the >99% pure concentrated REE solution contains essentially all of the REE present in the original PLS. This exceptionally high REE recovery rate is a key economic differentiator between MRT and other, less selective, processes and, thus, ensures that minimal amounts of REE are discarded to tailings.

Separation of the set of sixteen REE into individual elements at >99% purities was achieved in a three step process as shown in Figure 3. In Step 1, Sc and Ce are separated from the REE group. In Step 2, light REE (Y, La, Pr, Nd) are separated from heavy REE (Sm through Lu). In Step 3, individual members in the light and heavy groups are separated from each other. Individual REE were collected as carbonates. Elution of the bound REE, as groups or individuals, from the SuperLig[®] columns by small amounts of eluent (acid) produces concentrated solutions of the pure metal(s) for easy and economical salt production.

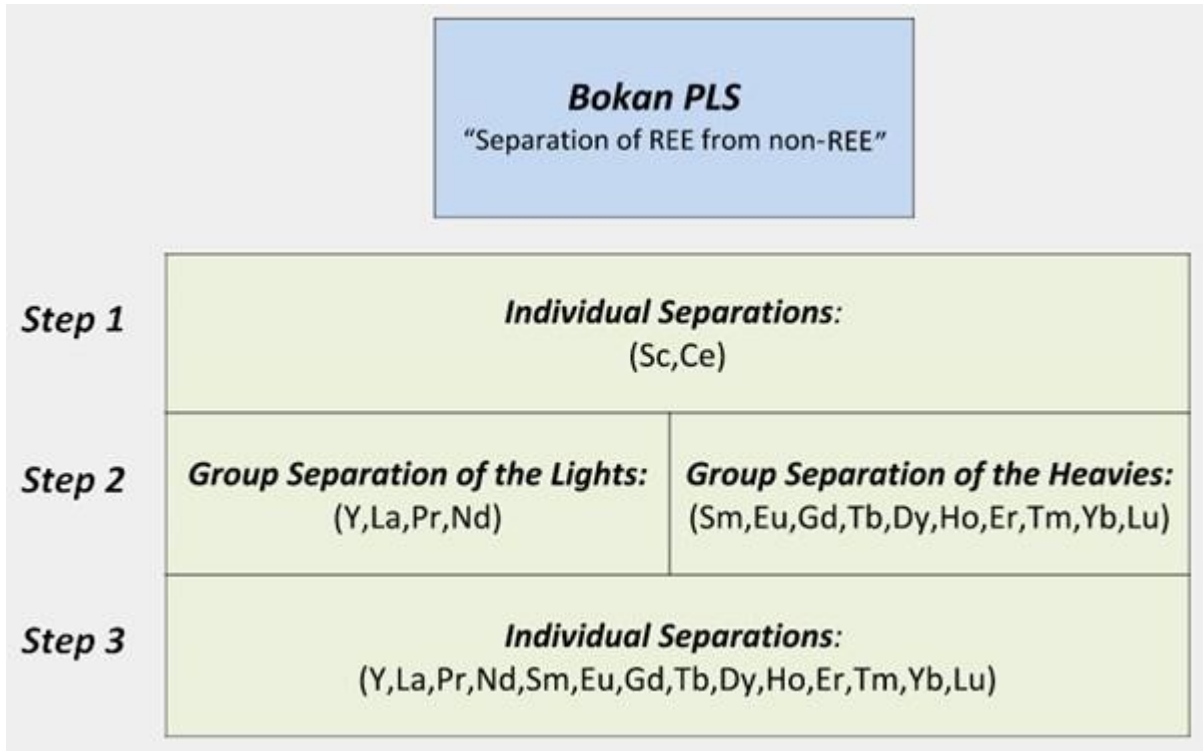


Figure 3 - Scheme for separation of sixteen rare earth elements from Bokan-Dotson Ridge pregnant leach solution and from each other (Press Release, 2015, March 2)

In Table 2, the purity of each individual, separated REE as a carbonate salt, or in solution prior to salt production, is given. The purity of each individual REE in solution was determined at IBC by ICP analysis. Separate analyses of selected carbonate salts were made by an independent analytical laboratory. In all cases, purities exceeding 99% were obtained.

Table 2 - Purity levels of sixteen separated rare earth element salts
(Press Release, 2015, March 2; Press Release, 2015, April 28)

Rare Earth Element	Purity of Carbonate Salt, %	Rare Earth Element	Purity of Carbonate Salt, %
Lanthanum	99.9	Dysprosium	99.9
Cerium	99.5 ¹	Holmium	99.5
Praseodymium	99.9	Erbium	99.9
Neodymium	99.9	Thulium	99.6
Samarium	99.2 ¹	Ytterbium	99.0
Europium	99.9	Lutetium	99.2 ¹
Gadolinium	99.2 ¹	Yttrium	99.4
Terbium	99.1	Scandium	99.1 ¹

¹ Purity reported for solution prior to salt production

A pilot plant is under construction to enable the scaling-up of this separation system to commercial production of individual REE (Press Release, 2015, July 8; Press Release, 2015, November 11; Press Release 2016, February 17). The first phase of the pilot plant has been engineered to accept PLS from

Bokan-Dotson Ridge, with the initial output products being carbonate salts of the critical rare earth elements dysprosium, europium and terbium. The commercial MRT system will have several advantages over conventional processes for REE separations. First, the MRT system is based on green chemistry principles throughout. Minimal waste is generated. No organic solvents are used. Fewer chemicals are used and those used in washing and elution of columns are as benign as possible. Energy requirements are minimal. Second, the high selectivity of the SuperLig® products makes possible separation and recovery of REE from the PLS at >99% purity level, and subsequent separation of individual REE at >99% levels. Results of these high recovery levels are achievement of maximum economic value, minimal loss of REE to the tailings, many fewer stages required to achieve given REE purities, and reduced use of auxiliary substances. Third, the entire MRT operation is physically and operationally simple reducing capital costs. Fourth, the MRT operation requires fewer personnel, equipment, and chemicals thereby reducing operating costs. Fifth, the green chemistry MRT operation should readily meet stringent environmental standards in the U.S. Sixth, Dy can be separated in a targeted manner from the REE without the need to first separate low-value rare earths, such as Ce and La.

COMPARISON OF OPEX AND CAPEX COSTS FOR MOLECULAR RECOGNITION TECHNOLOGY AND SOLVENT EXTRACTION IN SEPARATION AND RECOVERY OF RARE EARTH ELEMENTS (Izatt, et al., 2016)

Items contributing to capex and opex costs associated with use of MRT and SX in separation and recovery of REE are presented in Table 3. Comparison of these items shows that costs are much lower in the case of MRT.

Table 3 - Comparison of MRT and SX capex and opex costs

Item	MRT	SX
	Capex	Capex
Floor space	Small	Large
Equipment cost	Small	Large
	Opex	Opex
Processing costs	Small	Large
Labor	Small	Large
Safety provisions	Small	Large
Spent chemical and waste water discard	Small	Large
REE processing time	Rapid – low metal inventories/working capital	Slow – high metal inventories/working capital
REE recovery rates	High	Low

The lower costs for MRT result from this process being simpler in design, more efficient in operation, more conservative in its use of chemicals, and more environmentally friendly in its use of simple inorganic chemicals, such as dilute acids. No organic solvents are used in the MRT process. High capex and opex costs result when SX processes are used in REE beneficiation and separation processes.

Problems associated with the use of organic solvents in chemical production processes have been discussed above. A major reason for the problems associated with the use of SX in REE processing is the low selectivity and slow reaction kinetics of SX for target REE either in separating these metals from gangue metals or from each other. These deficiencies result in low recovery rates, many separation stages,

extended time periods for effective separations, and the inability to separate individual REE in a targeted manner – resulting in the requirement to first separate low-value rare earths, such as Ce and La. The results are increased capex and opex costs, including low recovery rates and extended processing times that result in high working capital requirements due to ‘in-process’ REE inventories. MRT, on the other hand, has high selectivity, high recovery rates, and rapid processing times for REE separations both from gangue and from each other, as shown in Tables 2 and 3.

The high selectivity of the MRT process and its use of benign chemicals results in markedly lowered capex and opex costs. The number of stages involved in each separation is much lower for MRT than for SX because of MRT’s higher selectivity. The result, as seen in Table 3, is reduced space requirements as well as lower equipment, processing, labor, and waste treatment costs. High REE recovery rates coupled with rapid processing times maximizes the financial rate of return and minimizes working capital needs due to low metal inventories. MRT is a green chemistry process of the type needed in 21st century REE separations where increasingly stringent environmental and health standards must be achieved in concert with intensifying demands for economic efficiency as REE applications continue to expand.

COST EFFECTIVENESS OF MRT COMPARED TO SX AND IX

(Izatt, et al., 2016)

The economy of MRT has been proven in a number of commercial applications involving both base and precious metals (Izatt, et al., 2012). One perceived advantage of less selective technologies, such as IX and SX, over MRT is the low price of the resins or reagents involved in their operation. However, this price is not indicative of the true costs incurred by the use of these technologies. As compared to MRT, the negative externality costs associated with less selective technologies are paid for in more complex capital equipment systems; larger system footprints; limited or no resin re-usability; extensive use of sub-optimal and/or hazardous and flammable chemicals, such as organic solvents, which introduce substantial risk into the process and require complicated operational and environmental protocols; higher energy costs; lack of system flexibility to target specific, commercially important metals early in the flowsheet; higher number of separation stages; increased volumes of eluates, washes, and wastes; larger and more complex waste treatment systems; slower metal binding and release; incomplete and slow extraction and recovery of the target metal; complex pre- and post-treatment regimens; lower metal purities; lower metal recoveries; higher metal losses; and longer retention of valuable metals in the process resulting in high metal inventories and working capital costs. Low selectivity means that traces of impurity metals follow target metals and this translates into the creation of multiple side streams that then need to be processed resulting in higher costs, greater environmental liabilities and increased worker exposure. All of the above factors must be taken into account to determine the true cost effectiveness of a separations technology.

CONCLUSIONS

Greater than 99% of the REE, as a group, were recovered from a PLS derived from the Bokan-Dotson Ridge ore deposit in Southeastern Alaska. This group of REE was further separated into individual REE at the >99% purity level. Separations were achieved using MRT, which is a separation process based on green chemistry principles. No organic solvents are used in the MRT process. MRT has significant process and operational advantages over SX and IX in the separation of REE. These advantages translate into lower capex and opex costs for the MRT process. A pilot plant is under construction for the commercial separation of individual REE from PLS using MRT.

REFERENCES

Abraham, D.S. (2015). *The elements of power: Gadgets, guns, and the struggle for a sustainable future in the rare metal age*. New Haven, CT: Yale University Press.

Anastas, P., & Eghbali, N. (2010). Green chemistry: Principles and practice. *Chemical Society Reviews*, 39, 301-312.

Gupta, C.K., & Krishnamurthy, N. (2005). *Extractive metallurgy of rare earths*. New York, NY: CRC Press.

Izatt, N.E., Bruening, R.L., Krakowiak, K.E., & Izatt, S.R. (2000). Contributions of Professor Reed M. Izatt to Molecular Recognition Technology: From laboratory to commercial application. *Industrial & Engineering Chemistry Research*, 39, 3405-3411.

Izatt, R.M., Izatt, S.R., Bruening, R.L., Izatt, N.E., & Moyer, B.A. (2014). Challenges to achievement of metal sustainability in our high-tech society. *Chemical Society Reviews*, 43, 2451-2475.

Izatt, R.M., Izatt, S.R., Izatt, N.E., Krakowiak, K.E., Bruening, R L., & Navarro, L. (2015). Industrial applications of Molecular Recognition Technology to green chemistry separations of platinum group metals and selective removal of metal impurities from process streams. *Green Chemistry*, 17, 2236-2245.

Izatt, S.R., Bruening, R.L., & Izatt, N.E. (2012). Status of metal separation and recovery in the mining industry. *Journal of Metals*, 64, 1279-1284.

Izatt, S.R., McKenzie, J.S., Bruening, R.L., Izatt, R.M., Izatt, N.E., & Krakowiak, K.E. (2016). Selective recovery of platinum group metals and rare earth metals from complex matrices using a green chemistry-Molecular Recognition Technology approach. In R.M. Izatt (Ed.), *Metal sustainability: Global challenges, consequences, and prospects*. Oxford, U.K.: Wiley. In production.

Lichti, G., & Mulcahy, J. (1998). Acid mine drainage—environmental nightmare or asset? *Chemistry in Australia*, January/February, 10-13.

Molycorp (2015). Molycorp shuts down Mountain Pass rare earth plant, August 26. Retrieved on January 10, 2016, from <http://www.mining.com/molycorp-shuts-down-mountain-pass-rare-earth-plant/>

Mudd, G.M. (2012). Sustainability reporting and the platinum group metals: A global mining industry leader. *Platinum Metals Reviews*, 56, 2-19.

Press Release (2015, March 2). Molecular Recognition Technology: Environmentally friendly, cost efficient separation of each individual rare earth element. Retrieved on November 16, 2015, from <http://ucore.com/ucore-successfully-separates-entire-suite-of-individual-rare-earth-elements-at-high-purity>

Press Release (2015, April 28). Ucore updates on the separation of individual rare earth elements. Retrieved on September 22, 2015 from <https://ucore.com/ucore-updates-on-the-separation-of-individual-rare-earth-elements>

Press Release (2015, July 8). Ucore commissions design and construction of SuperLig[®]-One pilot plant. Retrieved on November 25, 2015, from <http://ucore.com/ucore-commissions-design-and-construction-of-superlig-one-pilot-plant>

Press Release (2015, November 16). Ucore updates on SuperLig®1 pilot plant construction. Retrieved on February 20, 2016, from <http://ucore.com/ucore-updates-on-superlig1-pilot-plant-construction>

Press Release (2016, February 17). Ucore updates on preparations for SuperLig®-One pilot plant. Retrieved February 20, 2016, from <http://ucore.com/ucore-updates-on-preparations-for-superlig-one-pilot-plant>

Reck, B.K., & Graedel, T.E. (2012). Challenges in metal recycling. *Science*, 337, 690-695.

Scerri, E. (2013). *A tale of seven elements*. New York, NY: Oxford University Press.

Separation of Rare Earth Elements by Charles James (1999). National Historic Chemical Landmark, Dedicated October 29. University of New Hampshire, Durham, NH. Retrieved on December 2, 2015, from <http://www.acs.org/content/acs/en/education/whatischemistry/landmarks/earthelements.html>

Tse, P-K. (2011). China's rare-earth industry: U.S. Geological Survey Open-File Report 2011-1042, 11 p., available only online. Retrieved on January 13, 2016, from <http://pubs.usgs.gov/of/2011/1042/of2011-1042.pdf>

Veronese, K. (2015). *Rare: The high stakes race to satisfy our need for the scarcest metals on earth*, Amherst, NY: Prometheus Books.

Yang, X. J., Lin, A., Li, X.-L., Wu, Y., Zhou, W., & Chen, C. Q. (2013). China's ion-adsorption rare earth resources, mining consequences and preservation. *Environmental Development*, 8, 131-136.