

The Application of Molecular Recognition Technology (MRT) in the Nuclear Power Cycle: From Uranium Mining and Refining to Power Plant Waste Separation and Recovery, as well as Element Analysis and Isotope Purification - 9075

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ABSTRACT

This paper reviews the application of Molecular Recognition Technology (MRT) separations technology as an alternative to existing uranium extraction and recovery technologies used in the uranium mining and refining industries. Extraction of deleterious elements from acid mine drainage and aqueous neutral and near neutral mine streams is also discussed as well as applications for MRT in the separation, extraction, recovery and analysis of target elements and ions in power plant and other waste streams and the purification of isotopes such as Pd-103 for brachytherapy.

INTRODUCTION

Molecular Recognition Technology (MRT) separations technology has a wide range of applications throughout the nuclear fuel cycle (Figure 1). This paper provides a summary of various applications for MRT in uranium mining and environmental treatment, conversion, aqueous reactor streams, nuclear waste treatment, analytical applications and purification of isotopes such as Pd-103 for brachytherapy.

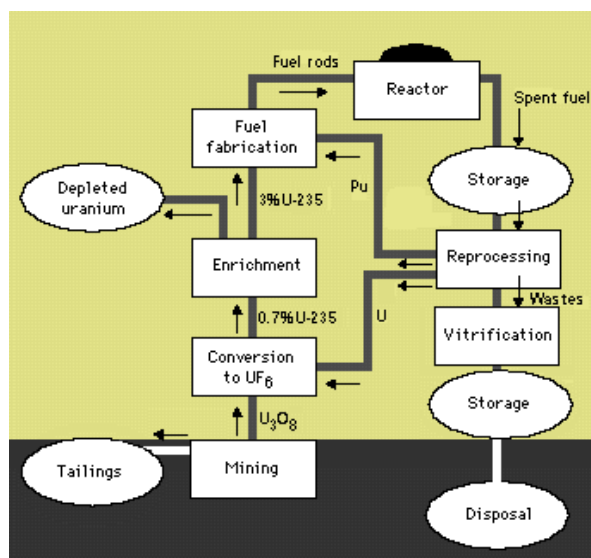


Figure 1: The Nuclear Fuel Cycle (1)

MOLECULAR RECOGNITION TECHNOLOGY (MRT)

The major advantages and benefits offered by MRT over other separation technologies are well documented (2).

MRT uses specially designed molecules, called ligands that are useful for separating, recovering, or purifying ions. The ligands form coordinate chemical bonds with the ion to be separated. MRT utilizes combinations of ion size, chemistry, and geometry to selectively recognize and bind to specific ions in solutions. This is normally accomplished without an exchange of ions. Because of this high selectivity, MRT can bind ions present at very low levels even in solutions of high concentrations of competing ions. This selectivity of ions usually results in very pure products. The ligands can be covalently attached to different substrates including particles such as silica gel, polyacrylate, or polystyrene. The resultant MRT particles are trade named SuperLig[®] when used in industrial applications and AnaLig[®] when used in analytical applications.

SuperLig[®] can be regenerated for a multiple number of cycles, depending on the chemical characteristics of the solution being treated. The ligands can be designed to produce strong interactions or binding constants between the SuperLig[®] and target ion. MRT exhibits very rapid kinetics, high selectivity, efficiency of separation, simple elution chemistry, and the ability to remove ions to extremely low (ppb) levels. These advantages translate to lower capital and operating costs compared to alternative technologies.

EXTRACTION AND PURIFICATION OF URANIUM FROM MINE AQUEOUS PROCESS STREAMS

This section describes the MRT process for the extraction of uranium for value, or for environmental purposes, from uranium solution matrices that may also contain significant amounts of other impurities such as copper and iron. Impurities such as copper may also be recovered for value. Examples of these separations and the primary benefits of the MRT process are given.

The use of solvent extraction and ion exchange resins is now the technology of choice for extraction of uranium from clarified mine leach solutions, leached pulp and slurries (1, 3). The application of MRT to uranium extraction from these feed streams, as well as to evaporation ponds, waste and environmental streams, offers a viable, highly competitive alternative to solvent extraction and ion exchange resins. Due to the extremely high selectivity of SuperLig[®] materials, MRT offers the potential to dramatically simplify the flowsheet for uranium recovery from these solution matrices. The MRT process can selectively separate the uranium directly from the mine leach solution and produce a concentrated, high purity uranium product.

There are two MRT SuperLig[®] materials available for uranium extraction, SuperLig[®] 171, and SuperLig[®] 191, as described in Table 1 below.

Table 1: SuperLig[®] Materials Available for Uranium Extraction and Purification		
	SuperLig[®] 171	SuperLig[®] 191
Binding Ion	U(VI)	(UO₂)₂
Effective pH Range	Acidic (0 – 1)	Neutral pH (6 – 12)
Elution	8 M H₂SO₄ or similar	Any Strong Acid With Concentration of 0.5 M or Higher

URANIUM SEPARATION FROM A URANIUM SOLUTION CONTAINING SIGNIFICANT IRON AND OTHER BASE METALS

There is a need to extract uranium from feed solutions containing significant amounts of iron, as well as copper, cobalt, and nickel, in a sulfate matrix. These aqueous solutions can be, for example, acid mine drainage solutions in which removal of the uranium is desirable for environmental reasons as well as for recovery for value. Separation of U from Fe in the uranium conversion process is also important. IBC's product, SuperLig[®] 171, is capable of U separation from matrices containing significant iron and other base metals. Reference (4) provides a detailed review of test results demonstrating this capability. In summary, SuperLig[®] 171 removes uranium (as $U(SO_4)_4^{2-}$ anion) to detection levels (5ppm) or lower while rejecting the Fe, Cu, Ni, and Co. Fe, Cu, Ni, and Co levels in the eluent solution were less than 1 mg/L.

The schematic flowsheet for the commercial process is illustrated below in Figure 2. Two SuperLig[®] 171 columns in series are used to extract uranium. Iron and the other base metals present in the feed solution are completely rejected. The large scale system is readily engineered and fully automated.

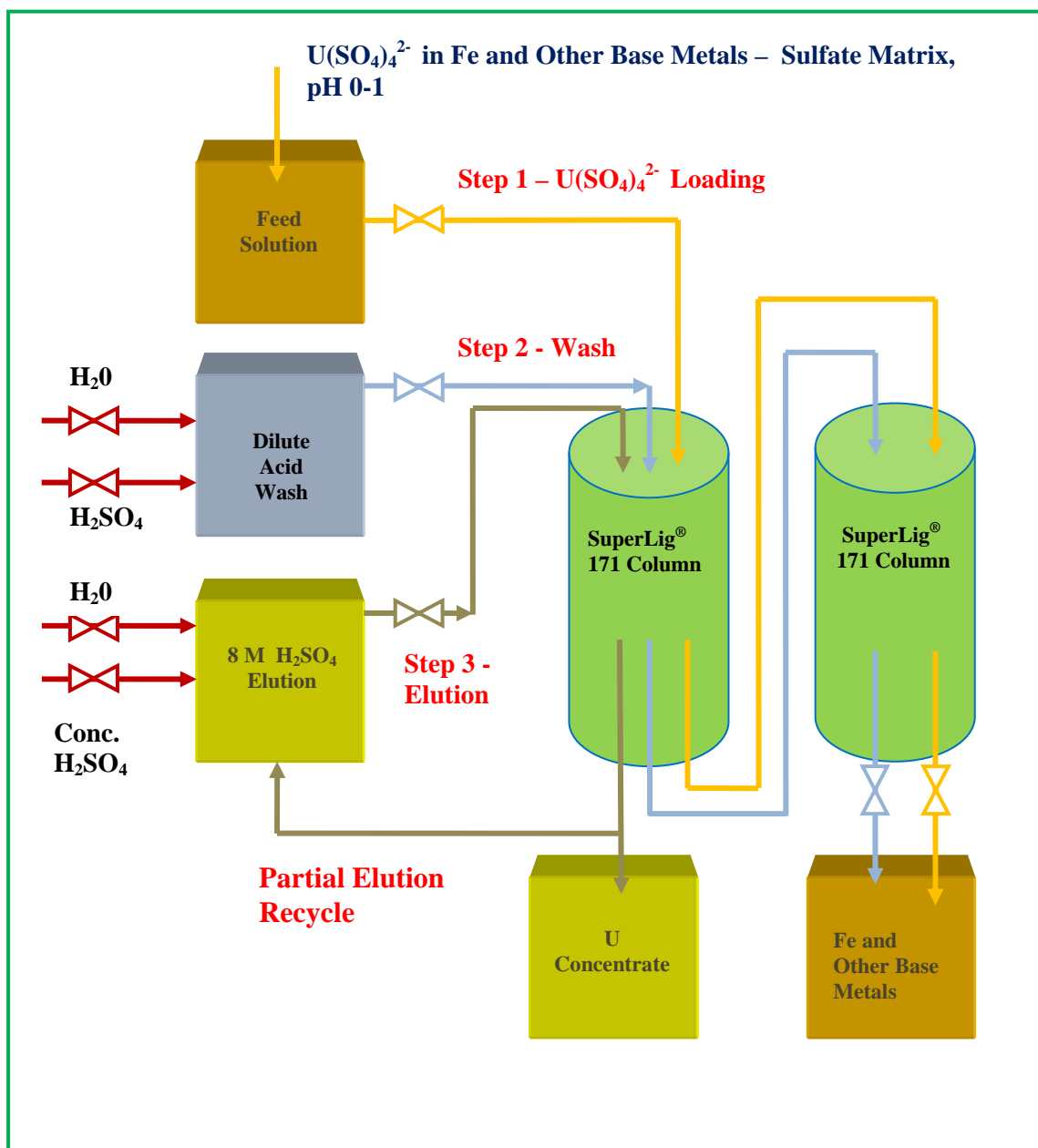


Figure 2: Schematic – Large Scale MRT System for U Extraction (4)

COPPER AND URANIUM SEPARATION FROM URANIUM SOLUTIONS

There is a need to remove copper and uranium from uranium solutions in a sulfate matrix in order to collect the copper and uranium for environmental purposes and for value. These solutions may be, for example, acid mine drainage evaporation pond streams or raffinate streams. IBC has SuperLig[®] products capable of copper and uranium removal from such solutions. Test work was undertaken at IBC to demonstrate this capability for copper and uranium. Two samples consisting of a higher and a lower concentration solution were tested. The results were similar for both. Please see reference (4) for a full review of the test results. A summary is provided below.

The U was removed (as U (SO₄)₄²⁻ anion) using SuperLig[®] 171, while rejecting the Cu, Fe, Co, and Ni. The Cu separation was then performed from the raffinate of the U system. The Cu was readily removed to below detection levels using SuperLig[®] 152. Both the U and Cu are recovered as pure products using sulfuric acid elutions. In a commercial system, the concentrated CuSO₄ product could be sent to electrowinning to produce Cu cathode. The concentrated U product solution in dilute H₂SO₄ would be sent for further treatment to produce a saleable uranium product. As an option, Cu and U can be removed together from the feed stream, utilizing a mixed bed SuperLig[®] system. This would require less system hardware due to the use of fewer SuperLig[®] columns. However, this must be balanced against separate Cu and U recovery, which consumes less acid and produces separate, more highly concentrated and high purity eluant products.

MRT CAPABILITIES FOR ION REMOVAL FROM ACID MINE DRAINAGE STREAMS

Metals are often present in acid mine drainage streams in levels too low for profitable recovery, or for recovery at all, using conventional processes. The preferred conventional processes have been pH adjustment, coagulation, flocculation, sulfide precipitation, and activated carbon adsorption. These processes all have high capital and operating costs. In the past, the most common procedure has usually been to neutralize the stream with lime and discharge. However, as environmental regulations tighten, this procedure is often not sufficient, as the heavy metal content in the precipitates may well exceed acceptable levels. In addition, the precipitates generated in this process are not stable, and can release the deleterious metals back into the environment. The cost of disposal of these hazardous waste by-products is extremely high. Innovative advanced separation technologies, such as MRT, are now required to meet these standards.

Table 2 below provides a summary of current examples of ions for which MRT has removal capabilities from AMD streams. Please see references (5), (6) and (7) for more details and examples.

Fe ³⁺	Low pH to pH 3
Mn ²⁺	Minimum ~ pH 3.5
Al	Minimum pH 1
Cu	Down to below pH 2
Zn	Minimum ~ pH 2
Ag	Minimum pH 2
Cd	Minimum ~ pH 2
(MoO ₄) ²⁻	pH 0 to pH5
(WO ₄) ²⁻	Minimum pH 2

Ni	Minimum ~ pH 1
Co ²⁺	Minimum ~ pH 1
As ⁵⁺	pH 1 – 7
Pb ²⁺	Low pH and above
Hg ²⁺	Low pH and above
Cl, Br, I	Low pH to pH 5
F	Low pH to pH 6
Sn ⁴⁺	Low pH to pH 2

PURIFICATION OF NEUTRAL AND NEAR NEUTRAL AQUEOUS STREAMS

There is a need in the mining industry, and in numerous industrial applications, for a highly selective, efficient, cost effective separations technology for removal of heavy metal ions as well as other specific target ions such as sulfates, sodium, and sulfide from aqueous, neutral, and near neutral waste streams. It is also very important that this selective separations technology not have any deleterious effects on the downstream raffinate stream. In many cases, the objective is to use the treated water for irrigation purposes, or a similar application. Some ion exchange (IX) resins can offer good binding to heavy metals. However, ion exchange technology is not selective to that class of metals alone. Consequently, other metals may also bind to the IX resin and reduce the efficiency.

In order to avoid generation of a contaminated, often unstable sludge, generated by precipitation techniques, a successful separations technology must be capable of recovering heavy metals and/or other target ions such that they are selectively separated from the waste stream. Also, the technology must allow for the recycle of the recovered product to process, or for sale of the recovered product for value. MRT meets these objectives.

The major advantages offered by MRT for the treatment of aqueous neutral or near neutral streams are given below:

1. Selective removal of ions to extremely low levels, often several orders of magnitude below current discharge limits. These lower limits can usually be obtained without pH adjustment.
2. Selective removal of only the ion of interest in the presence of high concentrations of competing ions.
3. Use of targeted stability constants between the SuperLig[®] and the ion of interest allowing a wide range of elution options for most applications. Eluents can be chosen that are compatible with the plant flow sheet chemistry, and recycle of the elution is usually possible.
4. Use of rapid kinetics, allowing high flow rates.
5. Automation of MRT systems, allowing for continuous operation, and a small system footprint.
6. Use as a polishing system for specific metals and ions that are out of compliance with regard to current and future discharge limits.
7. Minimization of use of process chemicals compared to alternative technologies, due to MRT process simplicity and highly efficient elution curves.

Table 3 below provides a summary of current examples of MRT capabilities for these aqueous neutral and near neutral feed solutions.

Table 3: Current Examples - Ions for Which MRT has Removal Capabilities from Aqueous Neutral and Near Neutral Streams	
Fe ³⁺	Neutral to basic
Fe ²⁺	Neutral to Basic

Mn ²⁺	Neutral to Basic
Al	Neutral to Basic
Cu	Neutral to Basic
Zn	Neutral to Basic
Ag	Neutral to Basic
Cd	Neutral and Basic
B	Neutral and Basic
Ni	Neutral to Basic
Co ²⁺	Neutral to Basic
As ³⁺ , As ⁵⁺	~ pH 7
Pb ²⁺	Neutral to Basic
Hg ²⁺	Neutral to Basic
Cl, Br, I	Effective under certain conditions
Sn ⁴⁺	Neutral to Basic
Na	Neutral to Basic
SO ₄ ⁻	Neutral to Basic

PURIFICATION OF NEUTRAL AND NEAR NEUTRAL AQUEOUS STREAMS AT POWER PLANTS

Erosion, corrosion and stress corrosion are major problems in nuclear power plants. The corrosion products can include copper alloys, zirconium, iron, cobalt, zinc, chromium, and nickel. IBC has developed a wide range of SuperLig[®] products that are effective for recovery of various ions from neutral and near-neutral aqueous solutions. Examples of current MRT capabilities are provided in Table 3 above.

NUCLEAR WASTE TREATMENT

A comprehensive review of the application of MRT to selective separation of anions and cations from nuclear waste is provided in references (8) and (9), which describe the use of IBC's SuperLig[®], MacroLig[®], and AnaLig[®] MRT products to efficiently and selectively separate and recover cesium, technetium, strontium, and radium from radioactive waste solutions. Distinct advantages, including high selectivity, rapid kinetics and system compatible elution chemistries, of these MRT products are provided over conventional separation techniques. Highly selective separations are described and results given for the target ions over chemically similar ions often present at much higher concentrations. The separations are performed in solutions of high or low pH that usually contain high concentrations of salts. Other separations involving components (Hg²⁺, Pb²⁺, (UO₂)²⁺, Pu (IV), I⁻, and Bi (III)) of radioactive and mixed waste are noted.

Representative data for the selective separation of cesium and technetium from actual Hanford tank waste using SuperLig[®] materials are also discussed in references (8) and (9). IBC has developed individual SuperLig[®] materials with high selectivity for a number of radioactive ions including Cs⁺, Ra²⁺, Sr²⁺, TcO₄⁻, Pu(IV), Am³⁺, and Cm³⁺.

The following characteristics of MRT provide compelling reasons for using SuperLig[®] versus other solid phase materials, or other techniques such as precipitation (9):

- High selectivity and strong binding strength allow for efficient separations and recoveries under difficult and varying conditions.
- The SuperLig[®] materials exhibit reasonable radiolytic stability.

- Once absorbed on SuperLig[®], the target radionuclide is elutable at high efficiencies with very small volumes of eluent.
- Elution chemicals are simple and can be used at dilute concentrations – for example, dilute nitric acid for cesium, and ordinary water for technetium.
- Elution chemicals are system-compatible with the remaining processing steps.

THE USE OF MRT ANALIG[®] MATERIALS FOR ANALYTICAL APPLICATIONS

Laboratories today use methods such as sedimentation, liquid-liquid extraction, or ion-exchange extraction to accomplish separation of the metals prior to ICP analysis. However, these techniques require many extraction steps and can be labor- intensive, driving up laboratory costs.

Analytical solid phase extraction (SPE) using AnaLig[®] addresses these issues by providing highly selective and quantitative separation of target ions, after which they can be readily detected by ICP-OES. Additionally, this sample preparation method can be automated, further simplifying the sample preparation procedure.

AnaLig[®] products rely on utilizing MRT, a highly selective chemistry. The selectivity of MRT is very useful for analytical separations and pre-concentration in the laboratory. Various AnaLig[®] product formats are shown in Figure 3 below.



Figure 3: AnaLig[®] Product Formats

AnaLig[®] products have been used in a number of applications including for the detection and analysis of radioactive elements (plutonium, strontium, cesium, technetium, radium and uranium) (8,10) as well as for a wide range of base and precious metals sample preparation applications (12, 13). Examples of these applications include the following:

- Alkali elements and alkaline earth elements
- Halides
- Heavy metals (e.g., mercury, cadmium, chromium, arsenic and lead)
- Transition metals (e.g., iron, zinc, nickel, cobalt, gallium, indium, bismuth, aluminum, and molybdenum)

AnaLig[®] materials for these applications are highly selective and can be used to eliminate matrix interferences or to pre-concentrate analytes for laboratory applications. Examples of the use of AnaLig[®] materials are given in references (8), (10), and (13). Reference (8) describes the use of Rad Disks[™] using AnaLig[®] for the separation and detection of Sr and Ra. Reference (10) describes the use of IBC's AnaLig[®] Sr-01 and AnaLig[®] Tc-02 molecular recognition technology products to more effectively and selectively separate and recover strontium and technetium from radioactive waste solutions as compared to traditional commonly applied methods using Eichrom's Sr Resin and TEVA Resin. Different concentrations of Ca²⁺, Ba²⁺, Pb²⁺, and K⁺ interfering ions on Sr²⁺ sorption were tested. Reference (13) describes an automated online preconcentration system for the determination of trace amounts of lead using a Pb selective AnaLig[®] Pb-01 resin minicolumn and ICP - Atomic Emission Spectrometry (ICP-AES). The lead, after being concentrated on the column, is eluted with 0.06 M nitrilotriacetic acid (NTA) solution (pH 9) and injected into the nebulizer of ICP-AES for quantification. The accuracy of this method was validated by determining lead in the standard reference material of river water (SLRS-4), and the applicability of this method to the determination of lead in environmental river water samples was demonstrated. The determination of Pb from other high background matrix samples, such as seawater, can also be accomplished using this method.

PURIFICATION OF Pd-103 FOR BRACHYTHERAPY

Purification of isotopes for medical and other uses can be readily accomplished using MRT. For example, an IBC product, AnaLig[®] Pd-03, is used by manufacturers of brachytherapy seeds in both the United States and Europe for purification of the Pd-103 isotope (14). Pd-103 brachytherapy is used to treat prostate cancer. This is an important and widely used therapy involving the insertion of radioactive Pd-103 directly into the prostate gland. The therapy is especially useful for patients with aggressive prostate cancer. The MRT product is used to separate and purify the palladium prior to preparing the pellets involved in the treatment. Metal purity at a high level is essential in this case. The palladium composition offers distinct advantages over iodine-based seeds. In addition to brachytherapy, Pd-103 is used for treatment of vascular disease, macular degeneration, and other diseases.

KEY ECONOMIC ADVANTAGES OFFERED BY MRT SEPARATION PLANTS

There are many problems associated with conventional separations approaches such as ion exchange, solvent extraction, evaporation, and precipitation, to element recovery and concentration. These problems include slow kinetics, lack of selectivity, interference by matrix ion concentrations, loss of solvent to the environment, high energy input, and difficulty of engineering design.

The ideal separations method for metals has the following features:

- Does not introduce or produce new pollutants
- Does not exchange one pollutant for another
- Is efficient for any solution concentration even at ion concentrations in the ppb/ppt range in high concentrations of matrix ions.
- Is highly selective for the target ion in various solution matrices
- Is highly selective for the target ion even when other similar ions are present at greater concentrations
- Can be used to concentrate a separated ion
- Can be automated and placed in a real time process flow sheet

MRT offers all of the above features. In each MRT application, one must determine the overall economic benefit that is contributed to the process by the MRT system. MRT is currently used in numerous commercial applications worldwide in precious and base metals processing and refining applications. All of these commercial systems underwent an extremely rigorous evaluation procedure to prove them to be economic before project implementation.

REFERENCES

1. World Nuclear Association, "The Nuclear Fuel Cycle," www.world-nuclear.org/info/info3.html, 2008.
2. N.E. Izatt, R.L. Bruening, K.E. Krakowiak, and S.R. Izatt, "Contributions of Professor Reed M. Izatt to Molecular Recognition Technology: From Laboratory to Commercial Application," *Ind. Eng. Chem. Res.*, 39, 3405-3411, 2000.
3. Areva, "Nuclear Fuel Cycle – Uranium Extraction and Conversion," www.cri.ca/nuclear_energy/datagh/cycle/extraction.htm, 2008.
4. S.R. Izatt, R.L. Bruening, N.E. Izatt, J.B. Dale, "The Application of Molecular Recognition Technology (MRT) for Removal of Uranium and Other Significant Impurities Such as Iron and Copper from Uranium Solution Matrices," ALTA 2008 Uranium/Copper Conference, Perth, Australia, June 16 – 21, 2008.
5. R.L. Bruening, N.E. Izatt, W. Young, P. Soto, "Environmentally Clean Separations Technology for the Mining Industry", III International Conference on Clean Technology for the Mining Industry, University of Concepcion, Santiago, Chile, May 15 – 17, 1996
6. J.B. Dale and N.E. Izatt, "The Use of Molecular Recognition Technology (MRT) For Treatment of Mining and Metallurgical Effluent Solutions," *Effluent Treatment in the Mining Industry*, Department of Metallurgical Engineering, University of Concepcion, Chile, pp. 257- 298, 1998.
7. S.R. Izatt, J.B. Dale, N.E. Izatt, R. L. Bruening, "An Update on the Application of Environmentally Friendly Molecular Recognition Technology (MRT) for Separations in the Mining Industry," Clean Technologies for the World Mining Industry, 8th International Conference, Santiago, Chile, April 13 – 16, 2008.
8. S.R. Izatt, R.L. Bruening, K.E. Krakowiak, and R.M. Izatt, "The Selective Separations of Anions and Cations in Nuclear Waste Using Commercially Available Molecular Recognition Technology (MRT) Products," WM'03 Conference, Tucson, Arizona, February 23 – 27, 2003.
9. M. Johnson, S.R. Izatt, R.L. Bruening, D.J. McCabe, N.M. Hassen, and G.L. Goken, "Selective Separation of Cesium and Technetium from Hanford Tank Waste Using SuperLig® Particles," Exchange '97 Conference, Miami, FL, December 1-5, 1997.
10. B. Remenc, "The Selective Separation of ⁹⁰Sr and ⁹⁹Tc in Nuclear Waste Using Molecular Recognition Technology Products," *Czechoslovak Journal of Physics*, Vol. 56 (2006), Suppl. D, pp. D645-651, 2006.
11. Y. Furusho, K. Namiki, M. Yamada, T. Kitade, N.E. Izatt, A. Sabarudin, and S. Motomizu, "Solid Phase Extraction and ICP-AES Determination of Trace Level Pb in High Matrix Plating Solution," Japan Society of Analytical Chemistry Conference, Poster Session P1097, Utsunomiya University, Utsunomiya, Japan, May 19 – 20, 2007.
12. Y. Furusho, S.R. Izatt, R.L. Bruening, N.E. Izatt, and S. Motomizu, "Use of Molecular Recognition Technology (MRT) Products for Analysis of Gold and Platinum Group Metals," International Precious Metals Institute, 32nd Annual Meeting, Phoenix, Arizona, U.S.A., 7 – 10th June, 2008.

13. A. Sabarudin, N. Lenghor, Y. Liping, JiangXi Y. Furusho, and S. Motomizu, “Automated Online Preconcentration System for the Determination of Trace Amounts of Lead Using Pb-Selective Resin and Inductively Coupled Plasma – Atomic Emission Spectrometry,” *Spectroscopy Letters*, 39: 669 – 682, 2006.
14. Theragenics Corporation, “Therased® Treatment All Seeds Not Equal,” www.theragenics.com, 2008.