LEACHING ASSESSMENT OF RED MUD AND PHOSPHOGYPSUM FOR BENEFICIAL USE AS CONSTRUCTION MATERIALS

By

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DEDICATION

To Kenneth B. Kirkland,

for always knowing what needed to be done and doing even more

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ABSTRACT

Beneficial use involves the application of a secondary material from an industrial process, which otherwise may be considered a potentially hazardous waste, as a building block in another process. The application is considered to be beneficial in that the quantity of "waste" material remaining to be managed is minimized by its use. There are significant barriers to beneficial use projects; primarily, the environmental evaluation that determines whether the secondary material will be harmful to human health and the environment. The environmental evaluation is most challenging because there is no universally excepted methodology for evaluating secondary materials. The currently accepted testing methodologies (e.g., single batch tests such as the Toxicity Characteristic Leaching Procedure or TCLP) do not provide the level of mechanistic environmental assessment information required to adequately support the beneficial use determination process.

The intent of this work is to address the issues surrounding beneficial use determinations and to move the field of beneficial use forward through enhanced communication by providing a uniform assessment approach. This thesis presents the use three laboratory leaching tests, under consideration for adoption by the United States Environmental Protection Agency as characterization procedures, as a basis for environmental evaluation of secondary materials for beneficial use. The leaching tests were performed on two mixtures of red mud and phosphogypsum. An initial screening of leaching data is made by comparing test results to documented water quality criteria. Since the leaching test results do not take into account dilution/attenuation factors (DAFs) that are built into water criteria, the screening assessment consisted of calculating the DAF that must be supplied by the release scenario in order to be protective of the environment. Examination of calculated DAFs show that constituent leaching from these two secondary materials would likely not exceed water quality limits under credible environmental scenarios. Although additional work is needed prior to acceptable application of red mud and phosphogypsum as alternative construction materials, the assessment approach of this study provides an indication that advanced leaching tests can facilitate evaluation of potential environmental impacts in a beneficial use scenario.

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CHAPTER I

THESIS OVERVIEW

Introduction

As raw materials continue to be used to grow the global economy, beneficial use of secondary materials will continue to gain interest as viable uses of otherwise wasted materials become available. Beneficial use of secondary materials has yet to gain universal acceptance, mainly due to the public's general aversion to using materials regarded as wastes and because there has not been a universally accepted methodology for determining the human health and environmental risks of using these materials. Once a proven methodology is broadly accepted, the public relations problem may be somewhat easier to manage. This thesis demonstrates the use of a leaching assessment framework as input for beneficial use determinations for use of red mud (waste from aluminum ore processing) and phosphogypsum (waste from phosphate production) as alternative construction materials for levees in Louisiana.

The U.S. Environmental Protection Agency is currently conducting a beneficial use evaluation for red mud and phosphogypsum as alternative construction materials in Louisiana. They have provided an appropriate example BUD framework for this project that could serve as a primer for future BUDs. The framework is presented herein. It overcomes many of the difficulties with beneficial use determinations that are mentioned in this thesis. Most importantly, the framework implements the leaching test protocols proposed by Kosson et al. (2002) to assess the environmental and human health risks for using the secondary materials. This approach addresses many of the concerns expressed by regulators seeking better assessment methodologies for evaluating the beneficial use of secondary materials.

Example Beneficial Use Determination Framework

Red and brown muds are the secondary materials generated from the extraction of alumina from bauxite, an aluminum-containing sedimentary rock. Phosphogypsum is the secondary material generated by the phosphorous fertilizer industry from phosphate-containing sedimentary rock. These materials were directly discharged to water bodies until the mid-1970s. Since then, the materials have been managed in land-based units, either in surface impoundments or as mono-fill landfills. Currently, there are hundreds of millions of cubic yards of these materials located within the state of Louisiana along the Mississippi River, and the individual materials are generated annually at a rate of approximately 3 million cubic yards.

Red and brown mud and phosphogypsum, either as individual materials or as a mixture, are being considered as potential alternate construction materials, possibly in levees and/or levee support systems along the Gulf Coast. The availability of suitable construction material in southern Louisiana is limited, and the United States Army Corps of Engineers (USACE) is currently seeking 100 million cubic yards of clay material to complete construction of hurricane protection levees and floodwalls in southern Louisiana.

Technical Evaluation

In a preliminary geotechnical evaluation funded by EPA Region 6 (MSE, 2008), various mixtures of red mud and phosphogypsum materials do exhibit characteristics of construction materials, as set forth by the USACE. Two additional geotechnical evaluations were performed in this study to determine if these materials (either individually or as mixtures) meet specified physical and engineering requirements, as set forth by the USACE:

- Create several "soils" by mixing red and brown mud with phosphogypsum to create a CH (fat clay) or CL (lean clay) classified material, in accordance with ASTM D2487 and the Unified Soil Classification System, with a Plasticity Index (PI) greater than 10.
- Test the created “soils” (no more than three due to budgetary constraints) that meet the criteria identified under task one for specific physical and engineering parameters to determine if they meet criteria set forth in USACE EM 1110-2-1906 (laboratory soil testing procedures), relevant ASTM standards, and USACE EM 1110-2-1902 (applicability of the various shear strength tests in stability analyses).

Although the specific approaches offered for this evaluation may not be appropriate for every beneficial use project, the basic idea of using relevant methodologies to evaluate secondary materials should be applied to all beneficial use determinations.

Geochemical Evaluation

While the projected cost savings of leveraging secondary materials for beneficial use are considerable, the costs associated with potential damage to sensitive ecosystems or remediation also are very large. Therefore, a level of performance assessment is required that exceeds typical USEPA regulatory evaluation approaches in order to assure that these materials will not adversely affect the environment or human health when placed with the levee system.

Materials characterization was conducted following three proposed draft USEPA leaching assessment protocols developed at Vanderbilt University and in cooperation with the Energy Research Centre of the Netherlands and DHI (Denmark). These leaching protocols are similar in structure and intent to procedures currently in use in several European countries or under development through the European Committee for Standardization, CEN and are based on a published leaching assessment framework (Kosson et al, 2002). The USEPA Office of Solid Waste and Emergency Response is undergoing a review of these methods for publication within their compendium of accepted test methods for solid wastes, SW-846. These tests include equilibrium tests as both a function of pH and liquid-solid ratio as well as a kinetically-controlled tank leaching test. Results from the leaching tests will be used for geochemical speciation modeling and scenario impact assessment using an expert leaching system, LeachXS^{TM}. The LeachXS^{TM} program allows for data management, comparison of material characteristics, geochemical speciation modeling (using the embedded ORCHESTRA model) and scenario-based simulation of environmental impact.

Although some form of material characterization with environmental impact comparison to acceptable criteria is mandatory in support of most beneficial use applications, typical programs either do not specify leaching and assessment approaches or use simplified characterization tests (e.g., TCLP, SPLP) and release assumptions which do not adequately support beneficial use determinations.

Remaining Investigative Procedures

A biological evaluation will be conducted in the near future to determine if red mud and phosphogypsum could potentially be harmful to Louisiana’s delicate aquatic ecosystems. Although it is currently believed that the beneficial use project would be cost beneficial for all stakeholders, an economic analysis will need to be conducted to show how beneficial the project will be. A major potential barrier to the beneficial use of red mud and phosphogypsum relates to which stakeholders will indemnify the materials. As with any beneficial use project, this will have to be resolved by all the stakeholders pursuant to any state and federal regulations. An additional aspect of the beneficial use project will be to discuss the project in an open public forum and disseminate information to the public regarding the benefits and risks associated with the project. It could be a substantial obstacle given the problems with public acceptance that have been discussed in this thesis. It will require input and discussion between all stakeholders to finalize the project.

Thesis Structure

Chapter I introduced the problem with beneficial use projects and an appropriate methodology for beneficial use determinations. Chapter II further explores beneficial use of secondary materials, including the current status of beneficial use programs in the United States on the state and federal level. It also examines significant barriers with beneficial use projects and beneficial use determinations. Chapter III presents a leaching assessment of mixtures of red mud and phosphogypsum. It is a successful example of implementing the beneficial use methodology presented in Chapter I. Chapter III has been written as a separate paper to be published in *Waste* Management. The thesis conclusions may be found in Chapter IV and complete results from the leaching tests are provided in the Appendix.

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CHAPTER II

BENEFICIAL USE OF SECONDARY MATERIALS

Introduction

A serious impact on the U.S. and global economy, garnering more attention each year, is the demand for space – land needed for building, growing, and eventually, storing waste. For generations the United States has been blessed with an abundance of space and, as a result, perhaps, has not been a global leader in waste management practices. However, as raw materials continue to drive the global economy, the desire to utilize waste materials in lieu of raw materials will likely increase in the U.S. Although there are many definitions of beneficial use available (ASTSWMO, 2007), the working definition for this thesis begins with the following from the State of Mississippi:

> *"The legitimate use of a solid waste in the manufacture of a product, or as a product, for construction, soil amendment or other purposes, where the solid waste replaces a natural or other resource material by its utilization"*
> *(Mississippi Department of Environmental Quality)*

In addition, several other criteria are listed below that are considered additions to the Missippi definition to explain the intent of "legitimate use." They are compiled from various sources to provide a complete definition of *beneficial use* for this thesis; their added objective is to serve as a starting criteria for beneficial use determinations.

- The secondary material is nonhazardous as defined by the Resource Conservation and Recovery Act (RCRA) or similar state statute (New York Regulations 360-1.15, Florida Statute 403.7045, Texas Definitions from State Solid Waste Rules, Mississippi Regulations for Beneficial Use of Nonhazardous Solid Wastes);

- The use is merely not a substitute for or escape from disposal, but does, in fact, provide societal and economic benefits (New York Regulations 360-1.15, Texas Definitions from State Solid Waste Rules, Minnesota Administrative Rules 7035.2860, Mississippi Regulations for Beneficial Use of Nonhazardous Solid Wastes);

- The use of the secondary material is technically, chemically and/or physically comparable to the raw material it replaces or is determined to be technically adequate as a virgin raw material for a new process (New York Regulations 360-1.15, Minnesota Administrative Rules 7035.2860, Mississippi Regulations for Beneficial Use of Nonhazardous Solid Wastes);

- The secondary material use is not detrimental to human health and the environment (New York Regulations 360-1.15, Minnesota Administrative Rules 7035.2860, Washington Administrative Code Chapter 173-350-100, Kentucky Regulations 401 KAR 47:150, Mississippi Regulations for Beneficial Use of Nonhazardous Solid Wastes);

- The secondary material must not be stored in anticipation of speculative future markets (Minnesota Administrative Rules 7035.2860, Mississippi Regulations for Beneficial Use of Nonhazardous Solid Wastes); and,

- There is an existing market or reasonable certainty of a market development for the secondary material (New York Regulations 360-1.15, Mississippi Regulations for Beneficial Use of Nonhazardous Solid Wastes).

The purpose of this chapter is two-fold: first to review a selection of beneficial use programs within the United States on the federal and state level, and second, to examine the significant barriers for all beneficial use programs.

Current Status of Beneficial Use Programs in the United States

As presented below, no single major program in the United States serves as the driving force for advancing the application for or assessment of beneficial use. Many of the current programs appear to be loosely connected and unfocused.

U.S. Federal Programs

The United States does not have a universal beneficial use program and BUD criteria have mostly been left to the states to administer (Kosson and van der Sloot, 2000). Two significant exceptions exist on the federal level: The Resource Conservation Challenge (RCC) and the Comprehensive Procurement Guideline (CPG) Program.

Resource Conservation Challenge

In 2002, the U.S. Environmental Protection Agency (EPA) implemented the RCC to provide renewed effort to their commitment to prevent pollution and conserve natural resources and energy by means of managing raw and waste materials more efficiently (EPA, 2009). The RCC is a national program focused on four major areas including municipal solid waste, green initiatives, such as electronics, industrial materials recycling and priority and toxic chemicals. There are several commonalities between the major areas. For example, wastes from each these categories are generated in large quantities in the United States. Additionally, many states already have programs for materials in these categories and there are plenty of stakeholders available to generate funding. A further review of the Industrial Materials Recycling (IMR) Program further illustrates the RCC. The IMR is geared toward three industrial non-hazardous wastes that include Coal Combustion Products (CCPs), Construction and Demolition Materials (C&D) and Foundry Sand. CCPs are being addressed within the IMR Program through a cooperative effort (Coal Combustion Products Partnership - C^2P^2) between the following stakeholders:

- EPA
- American Coal Ash Association (ACAA)
- Utility Solid Waste Activities Group (USWAG)
- Department of Energy (DOE)
- Federal Highway Administration (FHWA)
- Electric Power Research Institute (EPRI)
- United States Department of Agriculture – Agriculture Research Service (USDA-ARS)

In addition, according to the Energy Information Agency (EIA), approximately 50% of the generated electricity in the United States comes from coal (EIA, 2009). In 2007, the United States produced more than 131 million tons of CCPs (ACAA CCP Survey, 2007). Additionally, as of 2007, there were 617 facilities that burned coal to generate electricity in the United States (EIA, 2007). Therefore, it is clear that CCPs are generated in large quantities, sufficient resources and stakeholders are available to investigate potential beneficial uses and finding beneficial uses would certainly lessen the amount of solid waste going to industrial landfills. It also illustrates that the federal government is highly focused on secondary materials generated in large quantities where there are many stakeholders available for funding and liability. This may be a reasonable approach as proper stewardship of these large volume waste streams can go a long way to improving environmental management practices.

Comprehensive Procurement Guideline Program

The CPG Program is part of EPA's continuing effort to promote the use of materials recovered from solid waste (EPA, 2009). Through the CPG Program, EPA is required by RCRA to designate products that are or can be made with recovered materials, and to recommend practices for buying these products. Generally, this means that federal, state and local agencies procuring these products with federal funds are required to buy from the designated list of products made with recoverable materials.

With the recent expansion of the federal government in 2009 through the American Recovery and Reinvestment Act (ARRA), there will be a growing economic marketplace for secondary materials. In 2009, more than $23 billion dollars have been allocated to the Department of Transportation (DOT) as part of a $150 billion dollar infrastructure investment from ARRA (U.S. Government, 2009). DOT and its contractors will be major purchasers under the CPG Program. As the nation rebuilds its infrastructure in future years, federal agencies will likely be under intense public scrutiny to utilize secondary materials as much as possible.

In the CPG program and the RCC program, the focus of each is maintained for materials that are already well researched and evaluated. The programs do little to encourage new innovations and beneficial use of other secondary materials.

U.S. State Programs

According to the Association of State and Territorial Solid Waste Management Officials (ASTSWMO) 2006 Beneficial Use Survey Report (2007), 34 of the 40 reporting states indicated formal or informal decision-making processes or beneficial use programs relating to use of solid wastes. The programs range from statutory or regulatory provisions to agency discretion; however, the report also shows that simply because laws and programs are written does not mean that personnel are available to implement them. According to the report, many states have had programs for more than 10 years, but only 3 states have at least one full-time employee dedicated to beneficial use projects. The majority of states reported less than 10 beneficial use requests annually, yet the time required for the approval process ranged from one quarter of an hour to two years. This implies that sufficient resources are simply not available to review applications in a timely manner, the decision to use a secondary material is excessively complex, potential applicants are not aware of the beneficial use programs or unwilling to participate or some programs are sufficiently inadequate to properly evaluate secondary materials for beneficial use. It is likely a combination of all of these and perhaps others.

Although many states have beneficial use programs, to investigate each would be beyond the scope of this thesis. Four programs have been selected for a deeper review to provide an overview of the general elements included in state beneficial use programs as well as some differences.

Kentucky

Kentucky acquires its statutory authority to regulate beneficial use projects from Kentucky Revised Statutes (KRS) 224.01-010 regarding solid waste and KRS 224.50-760 regarding special waste. Regulations governing beneficial use include 401 KAR 47:150, 401 KAR 45:010, 401 KAR 45:060, and 401 KAR 45:070. These rules permit disposal of certain solid wastes by a practice common to the industry provided the disposal does not violate environmental performance standards and does not present a threat of imminent hazard to human health or substantial environmental impact. A company must submit an application for a registered "permit-by-rule" for beneficial reuse of solid waste or special waste to the Division of Waste Management in the Department for Environmental Protection.

The main components to the application include:

- A description of the waste, its source and quantity generated;
- Toxicity Characteristic Leaching Procedure (TCLP) laboratory analysis;
- A description of how the waste will be managed;
- A description of how the management and reuse of the waste meets the environmental performance standards of 401 KAR 30:031; and,
- Sources and Amounts Log Sheet (provided quarterly).

The rules also specify parameters for operating a beneficial use facility/project and frequently point to the environmental performance standards. The environmental performance standards of 401 KAR 30:031 are used to determine which waste sites pose a reasonable probability of adverse effects on human health or the environment. The regulations include provisions for the following scenarios:

- Floodplains – no allowance for a waste facility located in a floodplain
- Endangered Species – must not be affected by waste facility
- Surface Waters – discharges must not violate surface water standards
- Groundwater – discharges must not contaminate groundwater beyond the point of compliance in excess of the maximum contaminant levels specified in 401 KAR Chapter 8.
- Land Use – restricts waste application within three feet to the surface of land used for food production
- Polychlorinated Biphenyls (PCBs) – restricts PCB concentration to 1 mg/kg with exceptions to residual landfills where the concentration is 49 mg/kg
- Diseases – restricts the land application of sewage sludge and septic tank pumping
- Air – waste facilities must not violate state air pollution requirements
- Safety – restrictions for explosive gases, fire hazards, and facility access
- Public Nuisance – restricts waste facilities from becoming a public nuisance
- Wetlands – prohibits waste facilities from being located in wetlands
- Compliance – prohibits waste facilities from violating any other environmental regulations not specifically mentioned in the environmental performance standards

Kentucky has provided specific regulations to govern all beneficial use activities. There are clear definitions as to what constitutes reasonable probability of adverse effects on human health and the environment.

Mississippi

Mississippi's beneficial use program is relatively new, having been adopted in June 2005. Their regulations allow the Mississippi Department of Environmental Quality (MDEQ) to make beneficial use determinations based on the Mississippi Nonhazardous Solid Waste Management Regulations. These regulations provide exclusions for hazardous wastes as determined by RCRA as well as materials that become hazardous after they are beneficially used. Mississippi provides the following six eligibility criteria:

- The material must be a solid waste from a manufacturing process that would be discarded in a landfill or other waste disposal facility if not beneficially used (i.e. it must be a secondary material);

- The secondary material must be adequately characterized to confirm that the proposed use is adequately protective of the environment and human health and that the secondary material possesses physical and/or chemical properties which make it suitable for the intended use;

- The secondary material must not be a nuisance or have the potential to become a nuisance;

- The secondary material must be used as a suitable replacement for a raw material and provide a benefit comparable to the material it replaces;

- The beneficial use must not solely serve the purpose of disposing of the secondary material; and,

- A proposed beneficial use project must have a demonstrated use and/or market such that speculative accumulation of the secondary material is prohibited.

The regulations define categories for secondary materials considered for beneficial use. Category I uses have a Standing Use Determination that has been preapproved by MDEQ for specific materials and beneficial uses. Category II uses are defined as engineered construction or other civil engineering uses. Category III uses are defined as utilization of secondary material for a soil amendment, soil amendment additive, or direct application to the land. Category IV uses are defined as all other miscellaneous uses that do not fall into any other category. For Categories II, III, and potentially IV, a detailed material characterization is required. At a minimum, the following items which must include the following items:

- Submission of all analytical data identifying the primary chemical constituents and demonstrating the physical characteristics of the material;

- Data showing that the secondary material does not contain constituents that exceed total concentrations in the Beneficial Use Characteristic Standard for eight metals (i.e. As, Ba, Cd, Cr, Pb, Hg, Se, and Ag). If the secondary material exceeds the standard for any constituent, the constituent(s) should be analyzed by TCLP to confirm that the secondary material does not exceed the leachability standards provided in the regulations. An alternate test may be accepted by MDEQ;

- For Category III uses, the pollutant concentrations of a secondary material should not exceed the secondary soil amendment constituent standards provided in the regulations;

- A risk assessment or other constituent standards may be required; and,

- A contaminant risk assessment may be performed for secondary materials that do not meet the above-mentioned criteria.

Additional regulations include that the secondary material must be certified by a professional engineer, licensed in the State of Mississippi, that the material has physical or chemical properties that make it suitable for proposed construction or civil engineering use. The secondary material must also comply with any applicable ASTM or similar standards, and best management practices, if adopted by MDEQ, must be used during the beneficial use project. Upon review of the application, MDEQ will issue or deny a Beneficial Use Determination. In the event the BUD is accepted, the Beneficial Use Regulations also will manage the beneficial use project.

New Jersey

New Jersey Administrative Code (NJAC) 7:26-1.7(g) from the Solid and Hazardous Waste Management Program governs beneficial use projects. The New Jersey Bureau of Landfill and Hazardous Waste Permitting operates the BUD approval process. A Certificate of Authority to Operate (CAO) must be obtained from the Bureau in order to operate a beneficial use project. New Jersey regulations specify that some materials are pre-approved / exempt from the CAO approval process; however, secondary materials not exempt from the process must be determined as non-hazardous according to New Jersey's Solid Waste Regulations (NJAC 7:26(G)) by tests described in the Code of Federal Regulations (CFR) Title 40, Section 261, Subpart C. Other items required in the CAO application include:

- A description of the beneficial use project (i.e. how the material will be used, who will use it, the time frame, etc…)
- For land application, the material must be fully characterized according to the latest Soil Cleanup Criteria (SCC) by a New Jersey certified laboratory or USEPA Contract Laboratory Program. The laboratory must be certified for each parameter tested. Materials must not exceed the most restrictive Direct Contact or Impact to Groundwater (IGW) limits for any contaminant.
- Materials from each area of concern shall be analyzed for contaminants which may be present. The list of required testing parameters includes the USEPA Target Compound List (TCL) / Target Analyte List (TAL) plus 30 scans or the Priority Pollutant (PP) list plus 40 scans, petroleum hydrocarbons and pH.
- Non-aqueous samples must be analyzed according to EPA Publication SW-846, "Test Methods for Evaluating Solid Waste;" however, other analytical methods may be accepted if the organization that developed the method is a recognized expert in developing standardized analytical methods (i.e. EPA, American Society for Testing and Materials (ASTM), etc…).

- The materials may also need to be tested for dioxins/furans in accordance with SW 846, Method 1613B with a 1 ppt detection limit.
- Appropriate documentation from the testing laboratory should be included in the application.
- A proposed sampling plan must also be included in the application. Additional environmental health and risk assessments may be required on a case-by-case basis.
- If radionuclides are suspected, the secondary material must be analyzed by gamma spectroscopy.

Similar regulations are required for out-of-state shipments for beneficial use in New Jersey. New Jersey also requires a CAO if material will be shipped to another state for beneficial use. According to ASTSWMO 2007 Beneficial Use Survey, New Jersey does not allow materials to be stockpiled, requires identification of an end-market, and requires turnover of a certain volume of secondary material.

New York

New York derives its authority to regulate beneficial use determinations through state statutes from sections of its Environmental Conservation Law. The regulations are promulgated through New York's Department of Environmental Conservation (NYDEC). Beneficial Use regulations are found within Title 6: Environmental Conservation, Chapter IV – Quality Services, Subchapter B: Solid Wastes, Part 360: Solid Waste Management Facilities, Subpart 360-1: General Provisions, Section 360-1.15. The regulations specify that secondary materials are considered "solid wastes," and regulated as such, until a beneficial use determination has been granted by NYDEC. New York provides a list of secondary materials that have been pre-approved for specific beneficial uses including: fly ash, compost, wood chips, tire chips, etc.

New York beneficial use determinations are performed on a case-by-case basis. Beneficial use applicants must provide the following items to be considered for a beneficial use determination:

- Description of the solid waste and its proposed use;
- Chemical and physical characteristics of the solid waste and each proposed product. New York regulations do not require specific testing methods; however, the materials shall not exceed state clean-up standards;

- Demonstration of an economic market for the intended use of the solid waste, which includes a demonstration that the product complies with industry standards and specifications for that product; and,
- Demonstration that the management of the solid waste will not adversely affect human health and safety, the environment, and natural resources.

NYDEC uses six criteria to determine if the application will be approved:

- The beneficial use project must constitute reuse not disposal;
- The beneficial use project must be consistent with solid waste management policy;
- The secondary material must function or serve as an effective substitute for a similar raw material or fuel;
- The secondary material must not be required to be decontaminated or processed before being incorporated in the beneficial use;
- The secondary material must have an existing market or reasonable certainty that one will develop; and,
- Other criteria as the department shall determine in its discretion to be appropriate.

Upon approval, New York will no longer consider the secondary material a solid waste.

Summary of Beneficial Use Programs

The United States has two main federal programs focused on beneficial use projects: the Resource Conservation Challenge and Comprehensive Procurement Guidelines. Both concern secondary materials generated in large quantities within multiple states that also have multiple stakeholders. The programs focus on secondary materials that are already well-researched. Despite the two federal programs for secondary materials, comprehensive guidelines for beneficial use determinations do not currently exist. Standardized testing requirements for determining potential human health and environmental effects, based on the specific beneficial use scenario, are particularly needed from the federal level. The goal is not to merely increase the quantity of regulations governing beneficial use, nor to reduce the states' right to make individual beneficial use determinations. Standardized testing ensures that each state has appropriate data to consider the potential human health and environmental effects and provides equal economic opportunities for each state.

The four state programs described above are fairly similar; they have many of the same requirements including: non-disposal mandate, non-hazardous regulation, effective substitute and technically acceptable requirements, existing or developing market, and non-harmful to the environment and human health standard. However, there are considerable differences in the states' determination of those requirements, especially how each determines that a secondary material is not potentially harmful to the environment and human health. Kentucky, Mississippi and New Jersey all specify different testing requirements (TCLP, metals, etc…), while New York does not specify any testing methods. According to the ASTSWMO 2007 Beneficial Use Report, there are many varieties of testing that each state mandates for determining the potential impact to human health and the environment. The states also have different standards for potential impact. Kentucky and New Jersey accept 1 per 1,000,000 excess cancer risk while New York and Mississippi operate on a case-by-case basis. Although states currently have the authority to implement and operate beneficial use programs, there are significant difficulties that plague the states' programs as well as beneficial use in general.

Significant Barriers Regarding Beneficial Use

Several difficulties hinder many beneficial use projects before they even come to a decision-making process. In addition to the programmatic issues with beneficial use projects, merely identifying secondary materials with potential uses is a significant challenge (ASTSWMO, 2007). The following are six limitations in the identification & decision-making processes.

Availability & Economics

The secondary material must be readily available where it can be utilized most beneficially (van der Sloot, 2008); thus, availability favors large volume process wastes as applied within the federal RCC program. Additionally, the materials are likely to be best utilized in the geographic region in which they are generated because of regional resource synergies (Van Beers et al., 2009) which includes transportation costs and costs associated with establishing cooperative relationships. Additional costs may include necessary processing prior to use and transport and landfill costs of associated residual wastes (van der Sloot, 2008). Transportation costs can also be a driver for regional synergy development (Van Beers et al., 2009).

For example, an industry may be inclined to consider a secondary material that is available locally as a substitute for a raw material that is not in order to reduce transportation costs. To the contrary, an industry may be very unlikely to utilize a secondary material if there is an abundance of high quality and relatively low cost natural materials; however, a high quality material is not desirable for a low quality application (Petkovic et al., 2004). A second example is found in Finland where there is an evident need for substitute material because in the most populated areas the depletion of materials, such as natural sand and gravel, has increased transportation costs (Mroueh and Wahlström, 2002).

Therefore, the secondary material must be produced in sufficient quantity in the proper location without incurring substantial costs and/or provide a cost-savings benefit in order to be considered for a beneficial use project. Furthermore, in the event that a secondary material has more than one potential beneficial use, the impact of using raw materials for the uses not chosen should also be considered (Toller et al., 2009). In any case, a comprehensive cost-benefit analysis is necessary to determine the economic, social and ecological benefits of a secondary material (Van Beers et al., 2009).

Technical Evaluation

A technical evaluation for beneficial use of secondary material is dependent on several criteria including, but not limited to, material, proposed use, location, and regulatory requirements. Since different materials have different technical characteristics, one evaluation may not be acceptable for all. Also, the same material used in different applications may need to be tested for different qualities. If the proposed use is located in the State of Mississippi, and, perhaps in many other states, ASTM specifications apply; however, the regulatory framework in Mississippi does not specify which ASTM specifications should be used for which materials and which uses. This is expected because not all beneficial uses require materials with the same physical / chemical characteristics. At a minimum, a technical evaluation may be rather complicated for the proposed beneficial use, and, as done in Mississippi, should be based on a case-by-case basis.

An example methodology used for the mechanical study of secondary materials is presented by Nunes et al. (1996) for crushed limestone aggregate in road foundation construction. The methodology includes two stages associated with technical evaluation:

- General Assessment – conventional characterization and classification tests such as particle size distribution, plasticity of the fraction finer than 425 µm, water absorption, particle density, magnesium sulfate soundness and compactability.
- Testing – Repeated Load Triaxial Tests (RLTT) used to determine both resilient and permanent deformation behavior. Unbound materials failing this test are treated with conventional binders (i.e. cement and lime), or any secondary binder (i.e. pulverized fuel ash, granulated blast furnace slag, gypsum and cement kiln dust). The binder treatment is adjusted to satisfy the repeated load triaxial tests after 28 days of curing and appropriate durability. Durability is investigated by determining the resilient modulus and ultimate strength.

The methodology may be acceptable for the secondary materials and their proposed uses, but it is not universally acceptable for all beneficial use projects requiring technical evaluations. Harmonizing the technical evaluation methodologies between states in the U.S. would be a substantial achievement for the field and remove a significant barrier for future beneficial use projects; however, technical evaluations should still be based on a case-by-case basis.

Environmental Policy

Despite the growing public and political interest in secondary materials, the decision-making process continues to hinder their beneficial use. In the United States, several factors influence the process (ASTSWMO, 2007):

- Lack of information showing that the secondary materials will truly not adversely impact human health and the environment;
- Lack of adequate resources and staff to devote to the BUD process;
- Costs;
- Statutory limitations;
- Public acceptance; and,
- Lack of awareness.

European countries face similar challenges with environmental policy and BUDs. In Finland, an environmental permit is required to utilize secondary materials because the Finnish government only recognizes the materials as waste, and they must be handled according to the Finnish Waste Act. The long and complicated permit process is one of the main barriers impacting the use of secondary materials (Mroueh and Wahlström, 2002; Sorvari, 2008). Environmental policy geared toward beneficial use, and a highly aware public of decreasing natural resources, does not necessarily translate to increased beneficial use projects. For example, Norway has an abundance of natural resources, available space, quality ground water, and small waste volumes. This tends to undermine the discussion of further developing beneficial use programs (Petkovic et al., 2004).

Other European countries have implemented policies to encourage beneficial use and reduce land-filling. The Netherlands adopted the Building Material Decree (BMD, 1995) to provide quality criteria for the application and beneficial use of stony materials and earth used as building materials. Although the legislation does not cover all environmental aspects, it has proved to be an important element in judging the environmental quality of construction materials in a direct or indirect way, and a contribution to the management of secondary materials (Eikelboom et al., 2001). According to Eikelboom et al. (2009), the

BMD is based on the Soil Protection Act and the Surface Water Protection Act. Soil protection policy in The Netherlands uses target values for "clean soil," based on data obtained by analysis of unpolluted soil and data of negligible risk for human exposure and ecological quality, as a reference for describing a clean soil. If the soil is polluted, The Netherlands requires the owner to implement state of the art technology to reduce the pollution to levels "As Low As Reasonably Achievable (ALARA)." The BMD has greatly improved the amount of soil pollution due to leaching of construction materials, from both primary and secondary sources (Eikelboom et al., 2009).

In France, the French Directorate of Roads from the Ministry of Transportation and Equipment set up a working group in 2005 to address the issue of waste and out-of-spec material acceptability as alternative material in road construction (Chateau, 2007). Its purpose was to develop a framework that defines technical and environmental requirements for a proper assessment in beneficial use conditions. It will also provide explanations on the content and the methodological approach in order to enable users to judge the quality of each proposed solution. It is based on EN 12920.

Additional problems are found in testing requirements within environmental regulations. Van der Sloot (2002) explained that tests are often used to satisfy regulations in relevant jurisdictions and limited to the constituents referred to in the regulation. This presents the problem that some constituents of concern may not be tested at all, and others are tested, despite being irrelevant to the material or scenario under consideration, merely to satisfy regulatory requirements.

Public Perception

There is a general public aversion to using, even beneficially, a material called "waste." For example, the biosolids management programs in Oregon and Washington share concerns regarding the perceived health risk associated with land application and contend that negative press from any biosolids program could impact all biosolids programs in the Pacific Northwest (Water Environment & Technology, 2009). Additionally, "Sham Recycling," the practice of using the concept of recycling to convince others that a secondary material has a legitimate application and true value when in fact it does not, by definition, makes the public perception of beneficial use projects much more challenging (ASTSWMO, 2007).

Several materials currently being referred to as secondary materials which were formerly treated as waste has led to much controversy (Kosson and van der Sloot, 2000). Merely changing the name of "waste" to "by-product" or "secondary material" does not improve the market for a secondary material or technical characteristics of that material, but does help decrease negative public perception (Twardowska, 2004). Others believe that, for secondary materials, it is important that they are dealt with in the same way as primary materials, because it is the only way to provide opportunities in marketing them in the construction industry (Eikelboom et al., 2001). As noted on EPA's website, the RCC shifts the view of "waste management" to "materials management" which appears consciously done to help avert negative public perception. To further combat negative public perception of reuse projects, it has been suggested that better opportunities and mechanisms, and a wider scope, are needed (Russell et al., 2006).

Environmental Evaluation

Many secondary materials contain constituents which may be potentially hazardous under certain conditions and, therefore, pose a potential threat to human health and the environment if not managed properly (ASTSWMO, 2007). For example, many industrial processes (i.e. alumina processing, coal combustion, etc.) tend to concentrate constituents in solid residues. Thus, an environmental evaluation is needed to determine if secondary materials pose any threat to human health or the environment. In the case of beneficial use of secondary materials, the environmental evaluation is often not adequately covered by regulatory frameworks or standardized tests (van der Sloot, 2006).

The most often used standardized leaching test is the Toxicity Characteristic Leaching Procedure (TCLP) which was promulgated for use in the RCRA program for classification of wastes as "hazardous" or "non-hazardous." This test has been improperly used to evaluate beneficial uses of secondary materials (Kosson et al, 2002). TCLP may provide general protection from waste materials, but neither TCLP nor any other test performed under a single set of conditions can provide an accurate assessment of waste hazards for all wastes (Kosson et al., 2002). TCLP was not developed to evaluate products with secondary materials and the limit values associated with it are related to land-filling and treatment of waste and therefore unsuitable to judge compliance with environmental quality objectives (van der Sloot, 2008).

Leaching tests are not only the standard for evaluating wastes and secondary materials in the US, but also throughout the world. France, Norway, Belgium and The Netherlands all have evaluation programs based on EN 12920: Characterization of Waste – Methodology for the determination of the leaching behavior of waste under specified conditions (Chateau et al., 2007; Petkovic et al., 2004; Flemish Government Order, 2003; Walloon Government Order, 2001; Building Material Decree, 1995). Leaching tests are used as a tool used to estimate the release potential of constituents from waste materials over a range of possible waste management activities, including during recycling or reuse, for assessing the efficacy of waste treatment processes, and after disposal (Kosson et al., 2002). For a proper understanding of leaching behavior, information on the behavior of major constituents is crucial as they dictate the leaching environment for trace contaminants; however, the emphasis has been too much on heavy metals and too little on oxyanions, which are rather mobile under neutral pH conditions (van der Sloot et al., 2006). They are considered a substantial component to any environmental evaluation for secondary materials. Kosson et al. also proposed a suite of laboratory leaching tests in response to the TCLP criticisms from the EPA's Science Advisory Board (EPA 1991, 1999). The proposed leaching tests are meant to better predict leachability while considering actual waste disposal conditions. Tests that go beyond the single step approach provide insight into mechanistic aspects of leaching, such as solubility control, wash-out phenomena or diffusion controlled release (van der Sloot, 2002).

Testing is often carried out at relatively high liquid to solid ratio (L/S) which does not give insight in behavior under often low L/S conditions encountered in the field (van der Sloot et al., 2006). With the wide variety of leaching tests in use, the fact still remains that there is no way any laboratory test will be able to replicate the various exposure conditions in the field with a reasonable chance of success (van der Sloot et al., 2006). Van der Sloot suggests that geochemical reaction/transport modeling allows better predictions of impact than the usual K_d concept and is potentially very powerful in fostering correct decision making. This approach is consistent with Kosson's suite of laboratory leaching tests and the methodology guideline, EN 12920.

An additional problem with environmental evaluations in beneficial use studies is the inability to communicate test results to others. Different methods applied in various studies from around the world make comparison of test results difficult, even if the same materials have been studied (van der Sloot, 2002). According to van der Sloot (2004), a fair amount of information on a wide range of waste materials was required to satisfy environmental and health related criteria for both disposal and beneficial use. Van der Sloot included material description, composition data, physical properties, leaching data, and biological properties as examples of the information. All countries and industries are faced with similar problems on similar types of wastes, pooling information across boundaries is therefore a sheer necessity (van der Sloot, 2004). As noted in the ASTSWMO 2007 survey, many states rely on data from similar projects to make decisions on beneficial use applications. This necessitates a mechanism to make data from a variety of sources readily available, particularly in the United States where each state has the authority and responsibility to make beneficial use determinations. At the least, horizontal standardization and harmonization of leaching test methods is needed (van der Sloot et al., 1997; van der Sloot and Dijkstra, 2004).

Environmental and Ecological Risk Assessment

Although much attention in literature has focused on the environmental evaluation of the material and to some extent the prediction of its behavior in beneficial use applications or various disposal scenarios, an environmental evaluation, as described above, may be insufficient to determine the environmental impact of using a secondary material (Perrodin et al., 2002; Roth and Eklund, 2003). A supplemental risk assessment (i.e. EcoRA, LCA, ERA, etc…) may also be needed to complete the beneficial use evaluation. For example, the EN 12920 standard does not consider the migration of constituents from the utilization scenario into the surrounding environment and the toxicity to humans or ecological impacts on flora and fauna (Petkovic et al., 2004). Petkovic recommended extending the standard to include a risk assessment step for the material, scenario and land use; however, Petkovic notes that this is only a method for assessing environmental impact of the secondary material in a road structure during the service life of the road.

One method for a broader evaluation of environmental impact of a secondary material is a Life Cycle Assessment (LCA). LCA is a tool for describing environmental aspects and potential impacts throughout a product's life, from raw material acquisition through production, use and disposal (ISO, 1997). An example of the need for local, regional and global environmental impact of beneficial use has been presented by Toller et al. (2009) and previously by Roth and Eklund (2003). Toller used a LCA based approach to assess the environmental impact of ash utilization under different material management/utilization scenarios in which leaching of trace elements as well as other emissions to air and water and the use of resources were regarded as constituting the potential environmental impact from the system studied. Toller found that utilizing the ash in certain scenarios saved more natural resources and energy than when the materials were managed according to the other scenarios investigated, including dumping in a landfill. Similar results (reduced life-cycle environmental impacts when compared to land-filling) were found in a LCA based study on blast-furnace slag and crushed concrete when used for road construction (Mroueh et al., 2000). Although it is not appropriate to apply these results to every beneficial use scenario, it is evident that the LCA method is capable of differentiating between different management scenarios for secondary materials.

It is essential for decision-making that environmental evaluations for beneficial use of secondary materials are further developed to include wider system boundaries, because leaching behavior in a laboratory does not accurately address possible long-term effects on the environment (Roth and Eklund, 2003). Roth and Eklund studied environmental evaluations at different levels of system boundaries. They found that the material level and road environment level would be most appropriate for discussing pollution aspects of a beneficial reuse project, but including life-cycle assessment and industrial system level would include natural resource utilization and be capable of addressing a wider variety of environmental issues.

Ecological evaluations have faced problems similar to environmental evaluations. There is a need for a consistent assessment framework and sharing of information and collaboration in generating information by heath and ecological risk assessors (Suter II et al., 2005). Suter et al. explained that the two main reasons for developing an assessment framework are to improve efficiency and provide better inputs to decision-making. Suter et al. proposed a framework including the following four features:

- Interaction between stakeholders;
- Problem formulation and information sharing;
- Common analysis to reduce waste; and,
- Integrating common results.

Suter acknowledged that more regulations and problems with scale (ecosystem compared to molecular level) will be future problems for ecological risk assessments that will require a collaborative effort to succeed.

Conclusions

Although this is an overview of the general problems facing beneficial use projects, there are probably others, many of which are state-specific or material-specific. However, secondary materials that are successfully matched with a potential beneficial use face even more challenges passing the current criteria for approval. Standardizing the environmental testing would provide comparable results for information sharing between stakeholders and provide more efficient BUDs. Using sophisticated leaching test methodologies such as proposed by Kosson et al. (2002) is also essential to developing more robust beneficial use determination criteria that will provide better estimates of potential environmental and human health impact of secondary materials. This would also provide more assurance to the public that some secondary materials are safe to use beneficially to replace natural resources and lessen the general public aversion to secondary materials regarded as wastes. Although life-cycle assessments and industrial system level environmental impact studies are potential futures of beneficial use criteria, the current methods involving laboratory leaching tests will likely continue to be the standard in the near future and the focus should be to deal with their immediate problems.

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CHAPTER III

LEACHING ASSESSMENT OF RED MUD AND PHOSPHOGYPSUM MIXTURES

Introduction

A significant amount of land and levee loss along the Mississippi River and Gulf Coast of Louisiana has resulted from historical land-use decisions, channeling of the lower Mississippi River, and hurricane and flooding events. Since the 1970s, the rate of land loss in lower Louisiana is estimated to be between 2,000 and 3,000 km^2 per year (Price, 2008). The New Orleans District of the US Army Corps of Engineers (USACE) has initiated a project to rebuild and reinforce the Greater New Orleans Hurricane and Storm Damage Risk Reduction System. In response to a USACE request for 100 million m^3 of fill material, the US Environmental Protection Agency (USEPA) is considering the beneficial use of secondary process materials, e.g., red mud (RM) from bauxite processing and phosphogypsum (PG) from the fertilizer industry, as alternate construction materials. These high volume waste materials are currently managed in surface impoundments or monofills with easy access to transportation along the Mississippi River and the levee construction areas.

The USEPA has recognized that considerable project cost savings could be made by leveraging secondary materials while simultaneously creating an excellent beneficial use for two mostly unused secondary materials. However, the costs associated with potential damage to sensitive ecosystems or remediation are potentially very large due to the magnitude of the project and require a level of performance assessment that exceeds typical USEPA regulatory evaluation. The overall methodology for assessment for beneficial use includes:

- Geotechnical testing;
- Environmental characterization and scenario impact assessment;
- Erodibility testing;
- Toxicological screening;
- Economic evaluation; and,
- Legal assessment.

Red Mud

Red mud (RM) is a byproduct of the Bayer process that is used to extract alumina from bauxite. Bauxite ore is treated with NaOH at elevated temperature and pressure to selectively dissolve Al_2O_3 which is calcined to $Al(OH)_3$. The residue, a highly-caustic ($pH>12$), clay-like slurry (20-40% solids) called "red mud" due to high iron oxide content, is comprised mainly of aluminum minerals with trace constituents based on source materials. Snars and Gilkes (2009, In press) provide a detailed chemical and physical analysis of various red muds and show that all red muds are different and the origin of the bauxite, conditions used in the Bayer process and any further treatment of the residue influence the mineralogy and chemistry of the red muds. Worldwide production of red mud is approximately 70 million tons per year (Aluminum Association, 2000), much of which is managed in large surface impoundments. Red mud has been classified as a hazardous waste by the EPA primarily due to its high pH.

USEPA has been studying potential beneficial uses for red mud since the mid 1970s (Parek and Goldberger, 1976). The Battelle Labs report concluded that there was no cost-effective beneficial use for red mud and that additional investigations should be conducted on the most-likely uses to verify the conclusions or make the potential uses more cost-effective. Additional research has been conducted on red mud since the 1970s, yet no cost-effective bulk application of commercial value has been found (Aluminum Association, 2000). Although beneficial use programs within the United States often cite insufficient data for environmental analysis as the number one concern with beneficial use projects, the Aluminum Association considers negative public perception the top concern for red mud (2000). This shows that although stakeholders may have a common goal, they do not always agree on the main barriers or how to overcome them. According to the Aluminum Association's *Technology Roadmap for Bauxite Residue Treatment and Utilization* (2000), the best option for utilizing red mud is metal recovery – the same as the top priority in the Battelle Labs report 25 years earlier. This suggests that significant progress has neither been made in metal recovery with red mud nor in indentifying improved beneficial use opportunities for red mud.

Recent research suggests that additional opportunities may be viable. For example, red mud has been studied as a coagulant for wastewater treatment (Poulin et al., 2008). Poulin et al. (2008) investigated the potential to transform red mud into a soluble coagulant containing aluminum and iron that would be used for water/wastewater treatment and showed that the solid coagulant produced from red mud has a phosphorus removal capacity similar to commercial coagulants. Red mud has also been evaluated for potential to remediate contaminated mine sites (Bertocchi et al., 2006). Bertocchi et al. (2006) studied the feasibility of immobilizing heavy metals contained in a disused mine tailings dam. The red mud was pretreated (neutralized) with seawater prior to the leaching tests. The test results indicate that the sorption capacity of the two waste materials is strongly influenced by pH. The red mud performed better at low pH values while the fly ash performed better at high pH values. Column tests showed that both waste materials significantly reduce As, Cd, Cu, Pb and Zn release into the eluate. The red mud was found to better remove As, Pb and Zn. Brunori et al. (2005) tested red mud to determine its metal trapping capacity and ability to treat contaminated waters and soils. Red mud was pre-treated with seawater for pH neutralization. The material had a near neutral reaction grade showing the feasibility of using treated red mud in reuse applications without risk to living organisms, from a pH perspective. Based on Italian regulations, the red mud required the additional washing step prior to being used. Experimental results did not show any significant toxic effect. The metal trappings test showed that treated red mud has a high metal trapping capacity. The leaching tests performed on the "trapped" metals showed that once the metals are "trapped" they are not easily removed. Lin et al. (2004) investigated the acid neutralization capacity (ANC) of red mud. The study concluded that red mud could be superior to lime in terms of treatment of unoxidized sulfidic soils and mixing red mud with acidified mine soils could be an effective method for reducing acid mine drainage; however, highly acidic mine soils may require quick lime as well. Altundoğan et al. (2002) used heat and acid treatments of red mud to increase its arsenic adsorption capability. The studies found that red mud can be used as an adsorbent for arsenic in aqueous solutions. The acid treatment improved the adsorptive capacity of red mud compared to untreated red mud. Acid treated red mud may be a cost-effective adsorbent compared to other commercially available adsorbents (i.e. activated carbon and activated alumina).

Although the above mentioned works are a fair sampling of the recent research on red mud, each required a pre-treatment before the red mud was found viable. None of the research provided a beneficial use of red mud that would significantly reduce the amount currently going to impoundments, much less reduce the amounts already impounded. The pre-treatment makes potential beneficial uses much less likely as the regulations within some states do not permit altering the material prior to use. The research may be promising, but it is also evident that there is more work to do.

Phosphogypsum

Phosphogypsum (PG) is a by-product of the chemical reaction called the "wet process," whereby sulfuric acid is reacted with phosphate rock to produce the phosphoric acid needed for fertilizer production. Phosphogypsum is composed primarily of calcium sulfate with trace constituents reflecting the nature of the source rock. Approximately five tons of PG are produced for every ton of phosphoric acid produced (Florida Institute of Phosphate Research, 2009). In 2009, the annual global production of PG was estimated at 280 million tons (Yang et al., 2009).

Tayibi et al. (2009) have provided a synopsis of the environmental impact and management of PG. Phosphogypsum is typically stored in large stacks – approximately 1 billion tons is stored in 25 stacks in the State of Florida (Florida Institute of Phosphate Research, 2009). The EPA banned the use of PG as a raw material in the United States in 1989, citing the level of naturally-occurring radioactivity (amended by EPA final rule June 3, 1992 – www.epa.gov), with the one exception that material with activity levels <10 pCu/g may be used for agriculture soil amendment. However, there has been little to no market for PG in soil applications in the US, due to abundant resources of natural gypsum and strong supply of coal combustion flue gas desulfurization (FGD) gypsum. Although the EPA is currently providing a process for researchers to apply for approval of new uses for PG, and research has shown potential applications for the material, a successful solution to the PG disposal problem has not been found.

As with red mud, PG research suggests that some opportunities to utilize the material may be viable. Due to its similarities to natural gypsum, one of the more likely uses for PG is building materials. For example, PG has recently been studied for its potential use in load-bearing building materials (Yang et al., 2009). Yang et al. (2009) tested autoclaved PG for making load-bearing wall bricks. Both strength and durability of bricks from autoclaved PG (low pressure steam type only) showed that the bricks could be used as load-bearing wall bricks instead of conventional burnt clay bricks. Değirmenci (2008a) studied the utilization potential of PG with fly ash and lime in cementitous binder for the production of interior wall materials. The study determined that calcined phosphogypsum increased the compressive and flexural strength values compared to untreated phosphogypsum and concluded that the cementitous binder can be used for the production of interior wall materials such as bricks and blocks. Değirmenci (2008b) also studied the potential to use phosphogypsum to stabilize adobe. Test results showed that PG can be used as an alternative in adobe stabilization. Calcined PG has been evaluated for potential use to activate fly ash-lime systems (Min et al., 2008). The tests showed that the addition of calcined PG to the fly ash-lime system accelerates the pozzolanic reaction of fly ash and improves the early strength of the binder; however, increases in the ratio of calcined PG to lime caused decreases in the late strength development. The tests also showed that strength development also depends on curing conditions and should be considered for an application. Mun et al. (2007) tested non-sintered cement (NSC) made with PG and waste lime (WL) as the sulfate and alkali activators for granulated blast-furnace slag (GBFS). The tests determined that dehydrate PG was found to be more economical than the use of anhydrite PG to make NSC. Compressive strength of NSC was found to be comparable to ordinary Portland cement at early curing age and higher in later curing age. Singh and Garg (2005) investigated the production of high strength plaster from PG and its use in making flooring tiles. The chemical activators increased the rate of anhydrite dissolution for making high strength gypsum matrix. The MMA improved the density, strength and durability of the anhydrite plaster against water. The study recommended using anhydrite PG for making high strength plaster and flooring tiles. A common theme within these potential uses is that PG is usually pre-treated to make it more usable (Tayibi et al., 2009).

Leaching Assessment Approach

This thesis focuses on environmental characterization and scenario impact assessment of two secondary materials found to meet the geotechnical requirements as levee fill material. The proposed application is that secondary materials will be used as levee “core” material to be covered with clean soil and/or potentially armoring tiles and thus, directly exposed to surface waters. Leaching characterization consisted of three USEPA draft methods designed to provide release controlling parameters under a broad range of conditions. Two equilibrium tests measure constituent release as functions of eluate pH and liquid-solid ratio, while a kinetic-based test determines release rates as a function of leaching time.

Leachate concentrations are compared to water quality criteria benchmarks to determine required dilution and attenuation factors in order to meet the water quality criteria.

Materials

Samples of RM and PG were collected at the production sites along the Mississippi River in Louisiana and delivered to MSE Technology Applications, Inc. (MSE; Butte, MN) for geotechnical analysis and to Vanderbilt University for materials characterization. MSE was responsible for creating mixtures of RM and PG to be tested for geotechnical properties. In all, five mixtures of RM and PG were evaluated for geotechnical properties including plasticity index, unconfined compressive strength, shrinkage drying, standard Proctor compaction, triaxial shear, and permeability.

Of the 32 mixtures evaluated, only two mixtures met USACE specifications as levee fill. Table 1 shows the results of geotechnical characterization of these mixtures (MSE, 2008).

Samples of the two acceptable mixtures were sent to Vanderbilt University for materials leaching characterization. The first mixture, subsequently referred to as material MXA, was simply 100% red mud conditioned to a moisture content of 32.4% (wet basis). The other mixture (MXB) was a 4:1 blend of red mud and phosphogypsum which was then conditioned to a moisture content of 32.4 % (wet basis).

Table 1. Selected Geotechnical Parameters from Mixtures of RM and PG (MSE, 2008).

Parameter	**Test Method**	**MXA**	**MXB**
Compressive Strength	-	510 kPa	100 kPa
Optimal Moisture Content	ASTM 698	32.2 % wet	32.4 % wet
Maximum Dry Density	ASTM 698	1610 kg/m^3	1570 kg/m^3
Hydraulic Conductivity	ASTM D5084	Not tested	3.6x10^{-4} cm/s

Leaching Test Methods

Materials leaching characterization was conducted following three draft USEPA protocols developed at Vanderbilt University in cooperation with the Energy Research Centre of the Netherlands and DHI Water Environment Health (Denmark). These leaching protocols are similar in structure and intent to procedures currently in use in several European countries or under development through CEN. A brief description of each method follows.

Draft Method 1313
Leaching Test (Liquid-Solid Partitioning as a Function of Extract pH) for Constituents in Solid Materials using a Parallel Batch Extraction Test

Draft Method 1313 (USEPA 2009a) is designed to provide aqueous extracts representing the liquid-solid partitioning (LSP) curve of constituents as a function of eluate pH. The protocol consists of nine parallel extractions of particle-size reduced material in dilute acid or base. Particle-size reduction facilitates the approach to solid-liquid equilibrium during the test duration. A mass of solid material equivalent to a specified dry mass (actual value depends on sample heterogeneity and particle size) is placed into nine extraction bottles. Addition of acid or base is based on a pre-test titration procedure to determine the required equivalents/gram yielding a series of eluates in the pH range between 2 and 13. Deionized water is added to supplement the calculated acid or base addition such that the final liquid-solid (LS) ratio is 10 mL/g-dry. The extraction vessels are tumbled in an end-over-end fashion for a specified contact time that depends on the particle size of the sample. Liquid and solid phases are separated via settling or centrifugation and an aliquot is removed for measurement of eluate pH and conductivity. The remainder of the eluate is filtered (0.45 µm filter) by pressure or vacuum filtration and saved for chemical analysis. The eluate concentrations of constituents of interest are reported and plotted as a function of eluate pH. These concentrations may be compared to quality control and assessment limits for interpretation of method results.

Draft Method 1314
Leaching Test (Liquid-Solid Partitioning as a Function of Liquid-Solid Ratio) of Constituents in Solid Materials using an Up-Flow Percolation Column

Draft Method 1314 (USEPA 2009b) is designed to provide the LSP of constituents in a granular solid material as a function of LS ratio under percolation conditions. A 5-cm diameter x 30 cm column is moderately packed with solid material. Eluant is introduced to the column in up-flow pumping mode to minimize air entrainment and flow channeling. For most materials, the default eluant is deionized water; however, a solution of 1.0 mM calcium chloride in deionized water is used when testing materials with either high clay content (i.e., to prevent deflocculation of clay layers) or high organic matter (i.e., to minimize mobilization of dissolved organic carbon). The eluant flow rate is be maintained between 0.5-1.0 LS/day to increase the likelihood of local equilibrium within the column. Liquid fractions are collected as a function of the cumulative LS ratio and saved for chemical analysis. The cumulative mass release is plotted as a function of cumulative LS ratio.

Draft Method 1315
Mass Transfer rates of Constituents in Monolithic or Compacted Granular Materials using a Semi-Dynamic Tank Leaching Test

Draft Method 1315 (USEPA 2009c) provides mass transfer rates (release rates) of constituents contained low permeability material under diffusion-controlled release conditions. The procedure consists of leaching continuously water-saturated monolithic or compacted granular material in an eluant-filled tank with periodic renewal of the leaching solution. The vessel and sample dimensions are chosen such that the sample is fully immersed in the leaching solution at a liquid-surface area ratio of 9 mL/cm^2. Monolithic samples may be cylinders or parallelepipeds while granular materials are compacted into cylindrical molds at optimum moisture content using modified Proctor compaction methods. At nine pre-determined intervals, the leaching solution exchanged with fresh reagent water and the previous leachate is collected. For each elaute, the pH and conductivity are measured and analytical samples are saved for chemical analysis. Eluate concentrations are plotted as a function of time, as a mean interval flux and as cumulative release as a function of time. Observed diffusivity and tortuosity may be estimated through analysis of the resulting leaching test data.

Results and Discussion

Materials characterization data for approximately 40 constituents were collected. Integrating this many components into an interpretation of leaching tests is beyond the scope of this thesis; thus, only limited results for seven RCRA metals (i.e., As, Ba, Cd, Cr, Hg, Pb and Se) and five other constituents (i.e. Sb, Be, Ni, Tl, and Zn) will be presented. All leaching tests were conducted on duplicate samples with the exception of mercury, which included duplicate sampling but single rep analysis. Throughout the presented data, each material has a unique symbol shape and color scheme in order to clarify comparisons between materials. First run symbols are shown as follows:

■ RM/PG Mixture A (MXA)
◆ RM/PG Mixture B (MXB)

In general, leaching test concentrations in this report are plotted with method detection limits (MDL) shown as a solid orange line and quantification or method limits (ML) shown as a dashed orange line. Leaching test concentrations found to be below the MDL are plotted at a concentration of ½ the MDL value in order to show that these analytes were indeed measured. For graphs showing cumulative release, which are calculated from leaching test concentrations, the results are plotted in comparison to calculated values assuming all eluate solutions concentrations were ML or MDL values. Release values plotted at or below these lines may not be significant in light of quantificationquantification or detection limits.

Benchmarks

In this thesis, pH and constituent leaching concentrations are compared to Louisiana marine water criteria, LDEQ (State of Louisiana, 2009) for illustrative purposes only. However, direct comparison to published water thresholds is considered conservative since leaching test concentrations do not account for dilution and attenuation that would occur under field conditions. For analytes where no Louisiana criterion was available, benchmarks were set using the National Recommended Water Quality Criteria, NRWQC (USEPA, 2009d) or USEPA Drinking Water Standards and Heath Advisories, DWSHA (USEPA, 2006). While it is unlikely that beneficial use determinations would be based directly on drinking water standards, these values are used as a baseline for comparative purposes only and are provided in Table 2.

Table 2. Benchmarks Used in Comparison to pH-Dependent Leaching Data.

Analyte	**Value** [µg/L]	**Criterion Type**	**Source**
Sb	5.6	HH: H2O+O	EPA NRWQC
As	36	LA MC	LDEQ
Ba	1,000	HH: H2O+O	EPA NRWQC
Be	4	MCL	EPA DWSHA
Cd	10	LA MC	LDEQ
Cr	100	MCL	EPA DWSHA
Pb	8.08	LA MC	LDEQ
Hg	0.025	LA MC	LDEQ
Ni	8.2	LA MC	LDEQ
Se	5	FCCC	EPA NRWQC
Tl	0.24	HH: H2O+O	EPA NRWQC
Zn	81	SCCC	EPA NRWQC

LA MC	Louisiana Marine Chronic concentration
FCCC	Freshwater Criterion Continuous Concentration
SCCC	Saltwater Criterion Continuous Concentration
HH: H2O+O	Human Health for Consumption of Water and Organisms
MCL	Maximum Concentration Level - drinking water criterion

Equilibrium-Based Release as a Function of Eluate pH

The Method 1313 data shows the level of liquid-solid partitioning (LSP) of constituents across a broad pH range. At each pH point, the LSP is driven by the dissolution of mineral phases and changes in chemical reactions (e.g., adsorption or complexation reactions) that increase or decrease the amount of the constituent released into the liquid phase. Where the eluate concentrations are highest can be considered the constituent availability or the maximum constituent release under environmental conditions. The available content (mg/kg) is often orders of magnitude less for many species that are considered environmental risk-drivers. The response at the natural pH point (i.e. the data point where no acid or base is added) indicates constituent concentrations at LS ratio 10 mL/g-dry when the solid material buffering dictates the pH.

Taken as a whole, the Method 1313 results in a continuous LSP curve indicate how constituent concentrations change when pH is controlled by an external source. The shape of the LSP curve (i.e. relative locations of maxima and minima) is representative of the overall speciation of the constituent in the solid phase and has four classical shapes presented schematically in Figure 1 and listed below:

- Cationic Species (e.g., Cd) – LSP curve of cationic species typically has a maximum concentration in the acidic pH range that decreases to lower values at alkaline pH.

- Amphoteric Species (e.g., Pb, Cr(III), Cu.) – LSP curves tend to be similar in shape to cationic LSP curves with greater concentrations in the acidic pH range; however, concentrations pass through a minimum in the near neutral to slightly acid pH range only to increase again for alkaline pH values. Typically, the increase at high pH is due to the solubility of hydroxide complexes (e.g., $Pb(OH_3)^-$).

- Oxyanionic Species (e.g. AsO_4^-, SeO_4^-, MnO_4^-) – LSP curves often show maxima in the neutral to slightly alkaline range.

- Highly Soluble Species (e.g., Na, K, Cl) – LSP curve is only a weak function of pH.

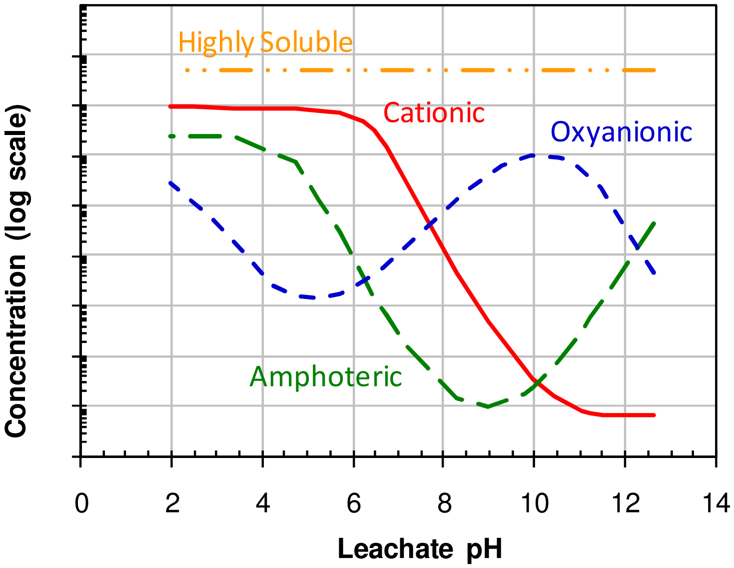

Figure 1. Typical LSP Patterns for Classical pH-dependent Leaching Behaviors (USEPA, 2009d).

The shapes shown in Figure 1 are idealized for simple solid phases and are seldom seen clearly in complex natural systems. However, comparing Method 1313 LSP curves to these idealized shapes is useful for data interpretation by providing a broad-stroke constituent speciation in the solid matrix. A more detailed evaluation of constituent speciation may be made with geochemical speciation models that infer the mineral phases, adsorption reactions, and soluble complexes that control the release of the constituent using Method 1313 data.

Constituent LSP Behavior

A summary of the results of Method 1313 equilibrium-based leaching test as a function of pH are presented in Figure 2 through Figure 4. Eluate pH and conductivity, shown in Figure 2, subplots a) and b), respectively, are used to evaluate how the material responds to acid or alkali intrusion from surrounding materials. In these graphs, base additions are shown as negative acid addition values. The natural pH of MXA (i.e., 100% red mud) is 8.8 close to the upper bound of the Louisiana surface water criteria, but a high pH value is expected in light of the extensive use of NaOH in the Bayer process. Addition of PG lowers the natural pH of the 4:1 red mud/p-gyp mixture (MXB) within water criteria to near neutral.
In the Method 1313 test, eluate conductivity as shown in Figure 2b is reflective of the amount of acid or base added to each extract and, as such, is not particularly useful in environmental assessment. However, the data points at natural pH are useful in that these points indicate the conductivity at the natural release response at an LS ratio of 10 mL/g-dry (i.e., 2.5 mS/cm for PG and 1.5 mS/cm for RM).

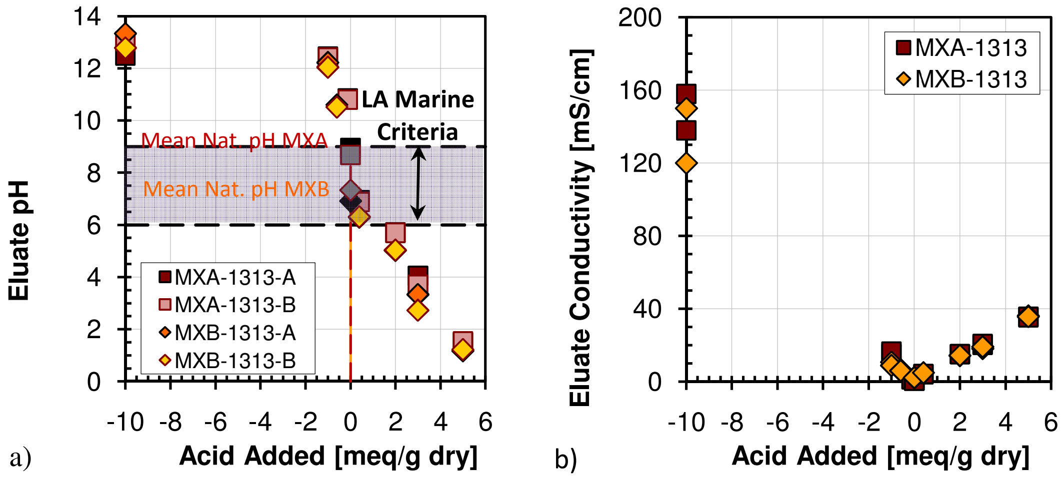

Figure 2. Method 1313 Leaching Data as a Function of pH for MXA and MXB Materials
a) eluate pH (titration curve), b) eluate conductivity.

Method 1313 results for mixtures of red mud and phosphogypsum (MXA and MXB) are shown in Figure 3 and Figure 4. The constituent concentrations at the natural pH are shown as darkened or grayed data points. Comparison of the basic LSP curve shapes in Figure 1 with the Method 1313 leaching test results for MXA and MXB in Figures 3 and 4 shows the following LSP patterns including:

- Cationic – Cd
- Amphoteric – Ba (MXA only), Pb, Ni, Se, Zn
- Oxyanionic – Cr (MXA only)
- High soluble – Hg, Tl (to a lesser degree)
- Mixed – As, Sb, Be

Quality control information, for example, quantification (ML) or detection (MDL) limits, may be plotted to create a “zone of influence” (i.e. upper and lower concentration bounds within a pH range). Data that plots within the zone of influence is not likely to cause an environmental concern in the defined regime once dilution and attenuation factors are applied. In such cases, percolation and mass transport testing may be used to check agreement with the initial screening under specific mechanistic control. Data falling wholly or partly outside of the zone may be of concern and further analysis in the form of percolation and/or mass transport tests is necessary. This approach should be used with caution as the eluate concentrations from the Method 1313 test do not consider dilution and attenuation factors which will result in reduced concentrations in surface waters. Thallium and nickel are the only constituent that fall outside the zone of influence. Generally, the other constituents fall within the zone of influence.

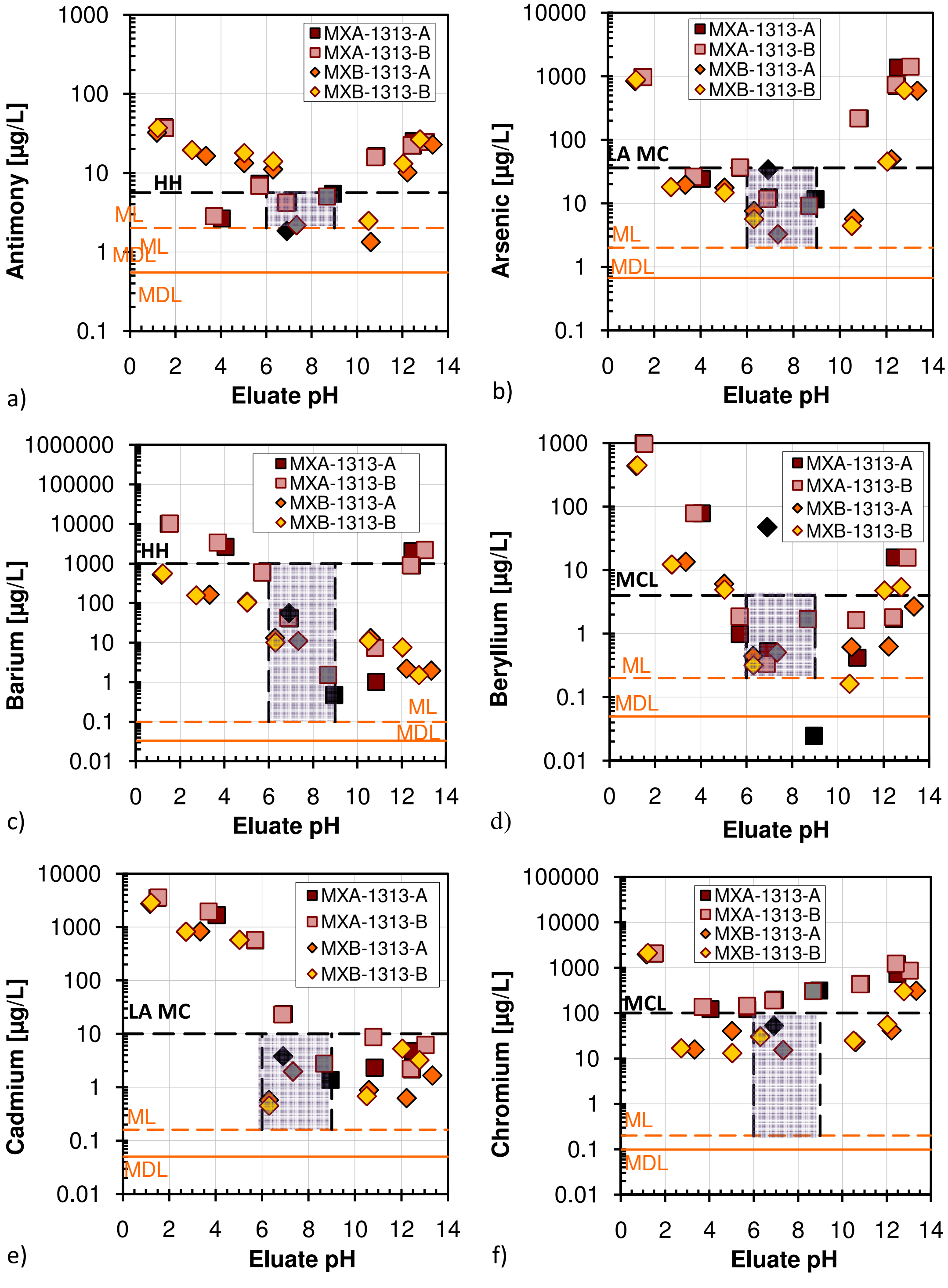

Figure 3. pH-dependent Leaching Data for Selected Constituents in MXA and MXB
a) antimony, b) arsenic, c) barium, d) beryllium, e) cadmium and f) chromium.

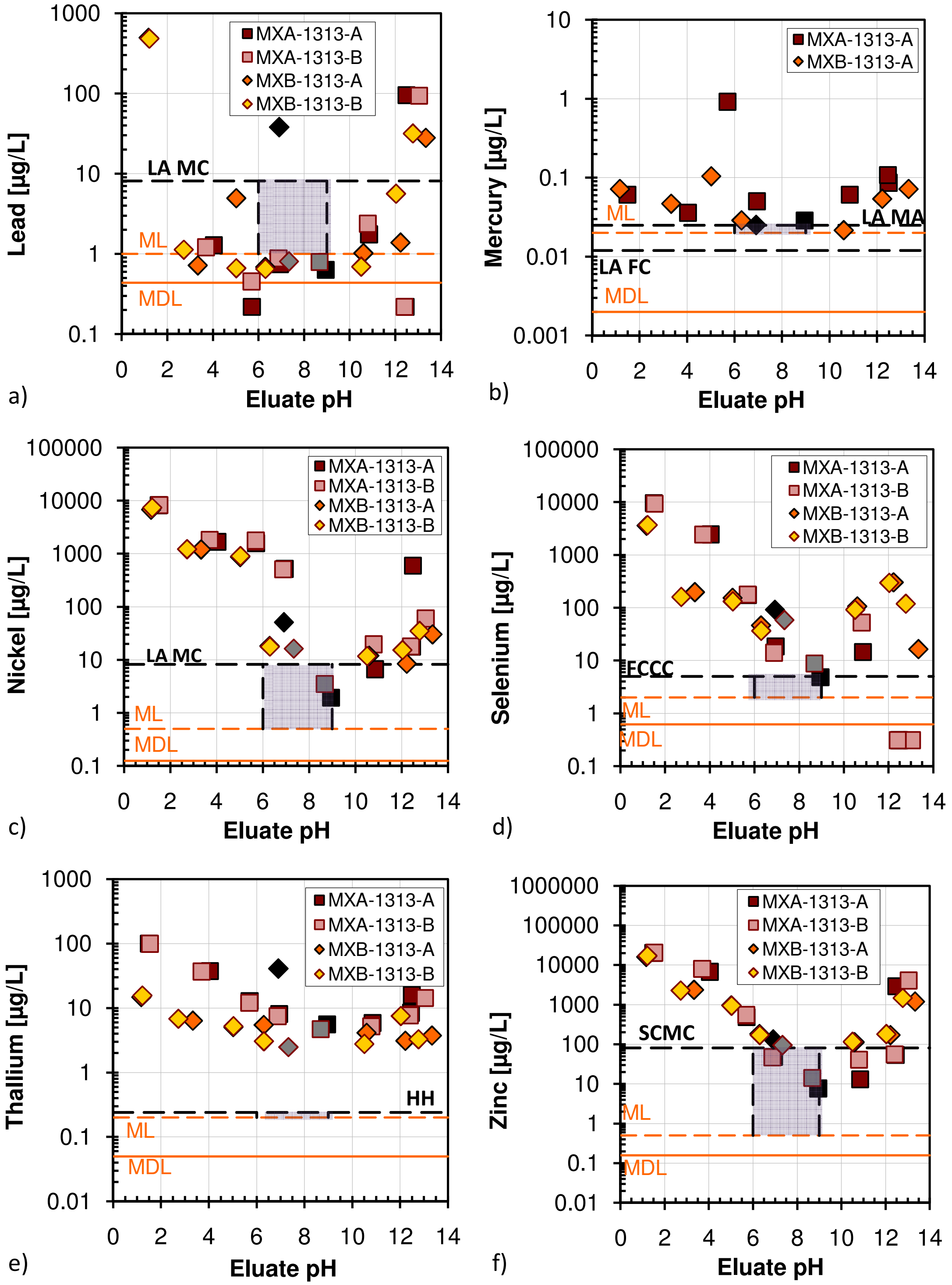

Figure 4. pH-dependent Leaching Data for Selected Constituents in MXA and MXB
a) mercury, b) lead, c) nickel, d) selenium, e) thallium and f) zinc.

Release Estimates at Available Content and Natural pH

The available content of a species in a solid matrix represents that fraction of total content not retained in recalcitrant or geologically stable mineral phases. Thus, the available content of highly soluble species typically is very close to the total content, while often a relatively small fraction of total content for constituents that show LSP curves that are significantly influenced by pH. The Method 1313 data can be used to estimate the available content of a constituent by converting the maximum concentration of the LSP curve to a release basis (mg of constituent / kg-dry material) by multiplying the maximum concentration by the Method 1313 LS ratio (10 mL/g-dry). The same conversion may be applied to the concentration at the natural pH eluate to estimate the release at natural pH. The values for available content and release at natural pH are shown in Table 3. Release of the available content provides a first-order estimate of maximum release under environmental conditions while the natural release provides the potential release if pH conditions do not differ from that of the test.

Table 3. Release at Available Content and Natural pH for Mixtures MXA and MXB.

		MXA		**MXB**	
Analyte	**Symbol**	**Available** [mg/kg]	**Natural** [mg/kg]	**Available** [mg/kg]	**Natural** [mg/kg]
Antimony	Sb	0.37	0.05	0.35	0.02
Arsenic	As	14	0.10	8.6	0.19
Barium	Ba	100	0.01	5.4	0.34
Beryllium	Be	10	0.009	4.4	0.24
Cadmium	Cd	36	0.02	28	0.029
Chromium	Cr	21	3.1	20	0.34
Lead	Pb	11	0.007	4.9	0.19
Mercury	Hg	0.009	0.0003	0.001	0.0002
Nickel	Ni	82	0.027	71	0.34
Selenium	Se	94	0.068	36	0.75
Thallium	Tl	1.0	0.051	0.28	0.22
Zinc	Zn	200	0.11	160	1.1

Equilibrium-Based Release as a Function of L-S Ratio

Selected results of Method 1314 percolation testing are shown in Figure 5 through Figure 9. Complete results are given in the appendix. Eluate parameters (i.e. pH and conductivity) are shown in Figure 5. The pH of eluates from the MXA column increase above Louisiana marine water quality standards at LS less than 5 mL/g-dry, dropping below the upper acceptable limit at high LS (Figure 5a). The pH of eluates for MXB are all well within the pH range of interest. The decrease in eluate conductivity, as shown in Figure 5b, with LS ratio reflects the flushing of soluble salts from the material. Eluate conductivity in MXB is approximately twice that of MXA most likely due to addition of soluble species contained in the PG.

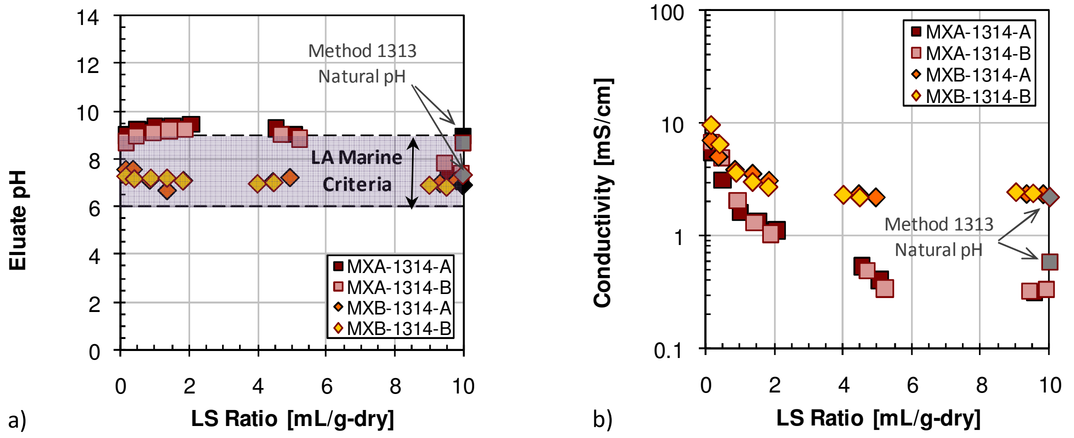

Figure 5. Method 1314 Leaching Data as a Function of LS Ratio for MXA and MXB Materials a) eluate pH (titration curve) and b) eluate conductivity.

Selected data from Method 1314 column tests (Figure 6 through Figure 9) are shown with a line of unit slope which indicates solubility control. All of the constituents presented in this thesis appear to be solubility controlled; however, the cumulative release of many constituents (i.e. As, Ba, Be, Cd, Cr, Pb, Hg, Ni and Zn) flattens as the LS ratio approaches 10 mL/g-dry. The release for those constituents is limited by the equilibrium availability at LS of 10 mL/g-dry, which is expected based on the eluate pH from the column tests corresponding to the natural pH of the materials. Antimony and Thallium are slightly limited by the maximum constituent release under environmental conditions as estimated from Method 1313 tests;

thus, their cumulative release follow the unit slope line and do not flatten until they approach the availability limit.

Comparison of cumulative release in the column test to LSP concentrations can be made if LSP data is represented as a release [mg/kg] by multiplying the LSP concentration [mg/L] by the Method 1313 LS ratio of 10 L/kg-dry. The cumulative release all constituents at LS 10 mL/g-dry, shown in the appendix, are in relatively good agreement with the LSP curves at natural pH.

As with the Method 1313 tests, results from percolation tests can be broadly compared to water quality criteria. Similar to Method 1313, Method 1314 does not account for any dilution or attenuation factors; thus, constituents exceeding the criteria values may not necessarily exceed the criteria in a beneficial use scenario. In general, several constituents were above and below water criteria limits. For example, Sb (MXB only), As (MXB only), Ba, Be, Cd, Pb and Hg (MXB only) were below their respective water quality criteria. Constituents greater than their respective water quality criteria at lower LS ratios included: Sb (MXA only – LS < 6), As (MXA only – LS < 5), Cr (LS < 2), Hg (MXA only – LS < 2), Nickel (MXA only – LS < 2), Se (LS < 5) and Zn (LS < 1). Nickel (MXB only) and Thallium (MXA and MXB) were greater than their respective water criteria limits for all LS ratios. Although mercury for MXA was above the water quality criteria, the eluate concentrations were very near the quantification limit, as is the water quality criteria. It is unlikely that mercury would be above the water quality criteria once a dilution factor is applied to the release concentrations.

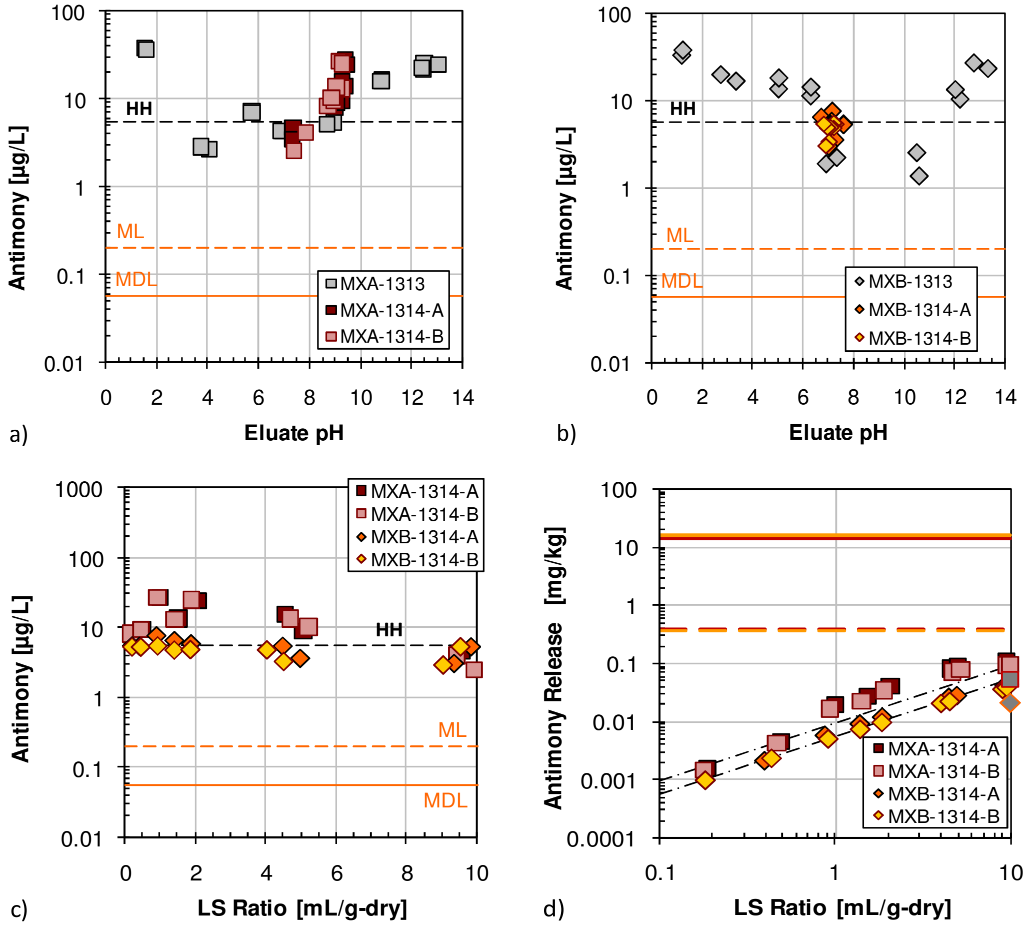

Figure 6. Antimony Results for Method 1314 Percolation Test on MXA and MXB
a) MXA data compared to Method 1314 LSP for MXA, b) MXB data compared to Method 1313 LSP for MXB, c) concentrations as a function of LS ratio, and d) percolation release.

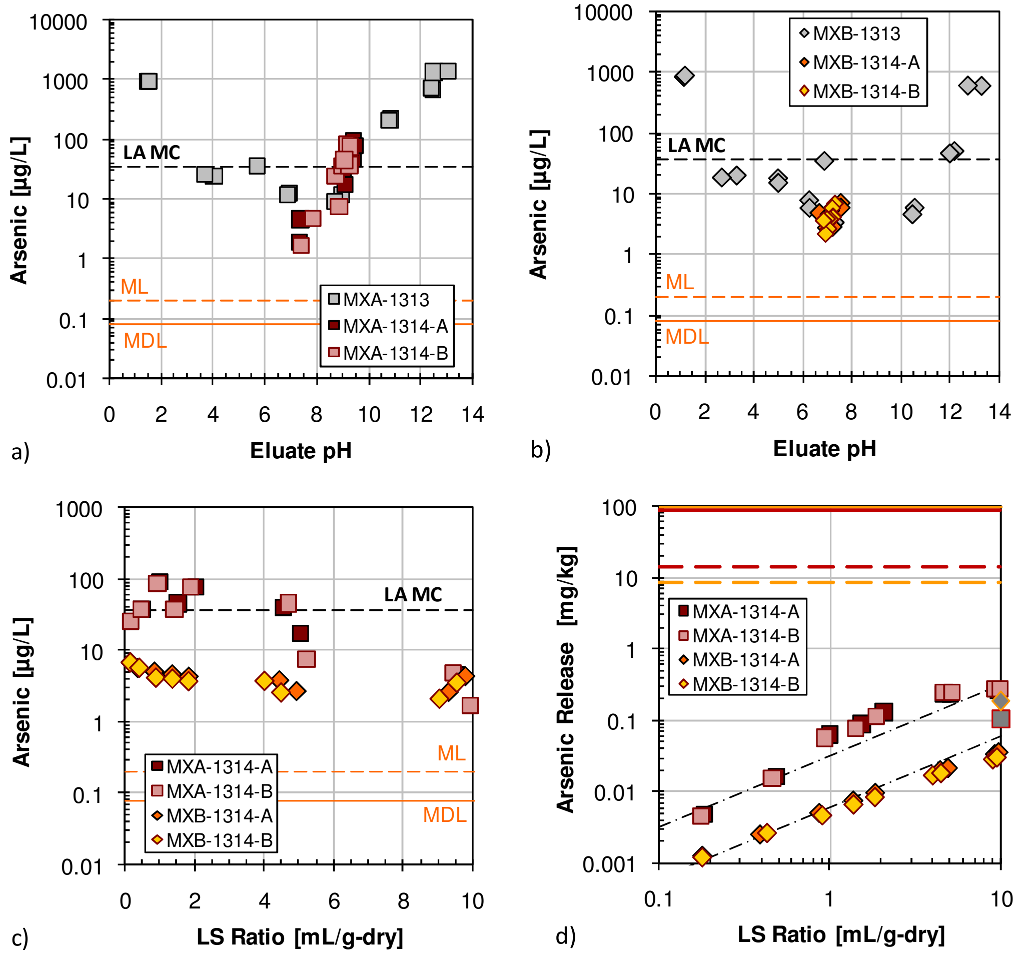

Figure 7. Arsenic Results for Method 1314 Percolation Test on MXA and MXB
a) MXA data compared to Method 1314 LSP for MXA, b) MXB data compared to Method 1313 LSP for MXB, c) concentrations as a function of LS ratio, and d) percolation release.

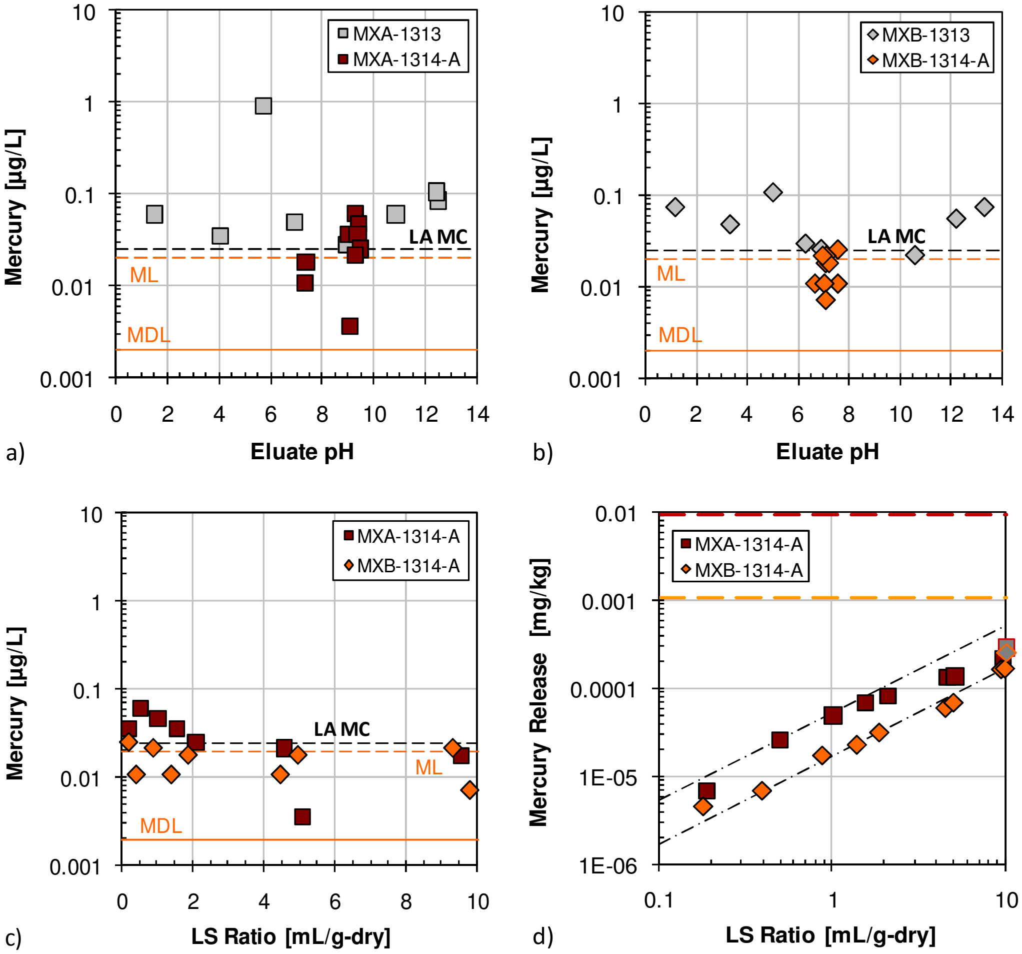

Figure 8. Mercury Results for Method 1314 Percolation Test on MXA and MXB
a) MXA data compared to Method 1314 LSP for MXA, b) MXB data compared to Method 1313 LSP for MXB, c) concentrations as a function of LS ratio, and d) percolation release.

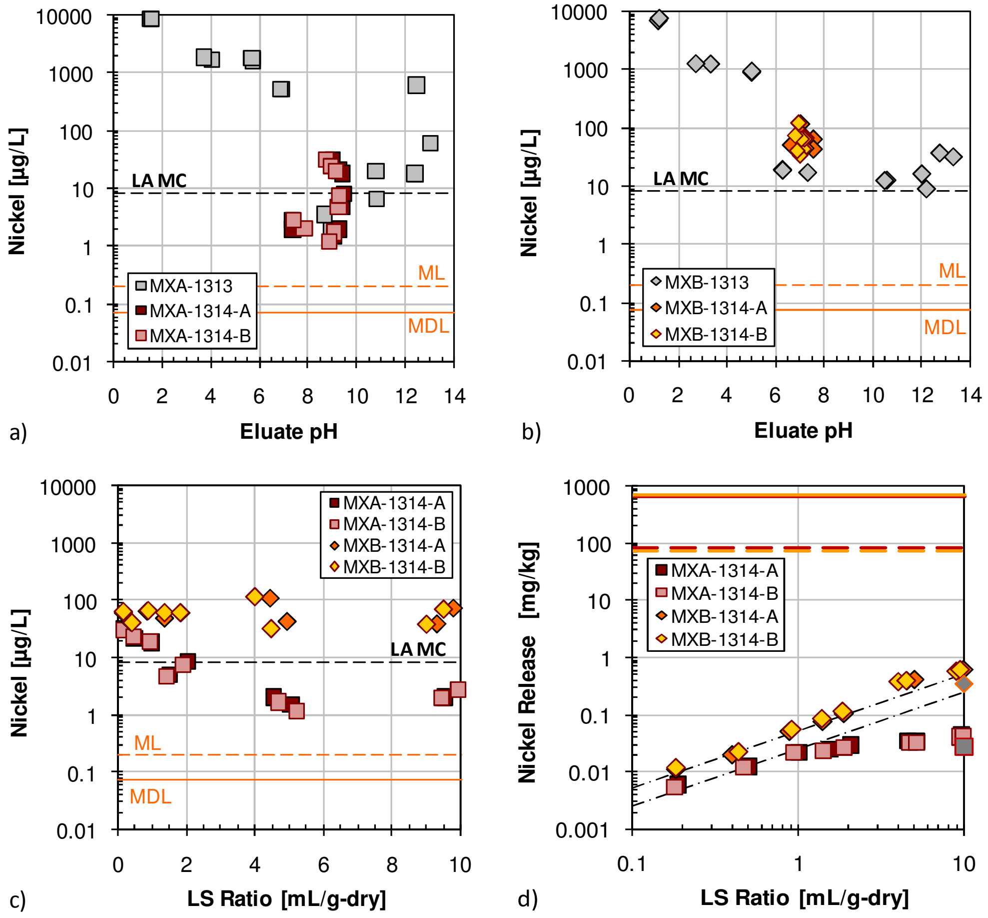

Figure 9. Nickel Results for Method 1314 Percolation Test on MXA and MXB
a) MXA data compared to Method 1314 LSP for MXA, b) MXB data compared to Method 1313 LSP for MXB, c) concentrations as a function of LS ratio, and d) percolation release.

Mass Transport-Based Release from Compacted Granular Material

Figure 10 through Figure 14 show selected results of mass transport testing: complete results are given in the appendix. For this test, granular samples were compacted at optimum moisture content into cylindrical molds. The leaching test followed Method 1315. Through the duration of the tank leach test, eluate pH for both materials, as shown in Figure 10, is within the Louisiana surface water criteria with MXB about one pH unit below MXA. The conductivity of MXB is approximately twice that of MXA due to addition of highly soluble species in the PG.

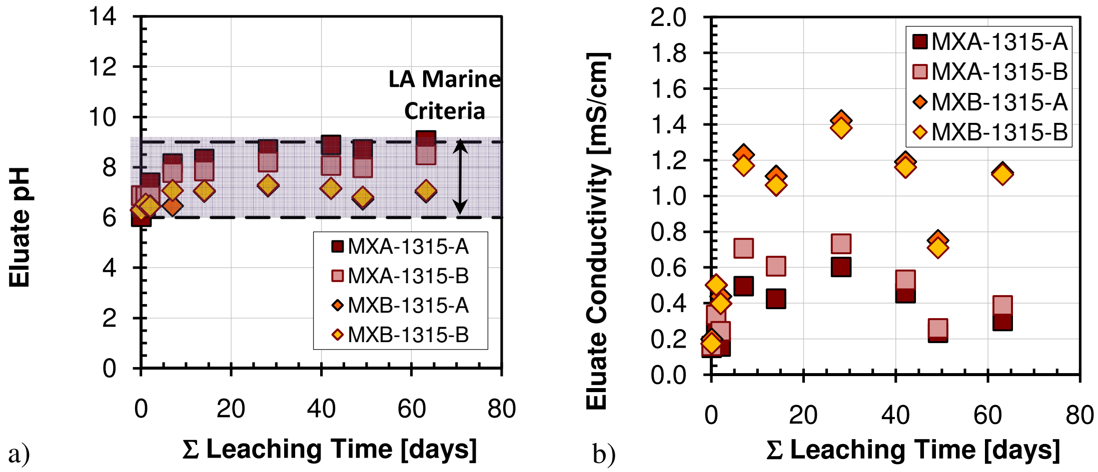

Figure 10. Method 1315 Leaching Data as a Function of LS Ratio for MXA and MXB Materials a) eluate pH (titration curve) and b) eluate conductivity.

Tank leach test results for select constituents (i.e. As, Cd, Cr and Tl) are shown in Figure 11 to Figure 14. The data is presented in four subpanels including a) MXA Method 1315 data compared to Method 1313 LSP for MXA, b) MXB Method 1315 data compared to Method 1313 LSP for MXB, c) Method 1315 concentrations as a function of LS ratio and d) cumulative mass transport release.

As shown in Figure 11d, arsenic follows a diffusion controlled model represented by the dashed line of slope equal to ½. The cumulative release of As in MXB does not follow the diffusion model as closely as MXA due to an initial wash-off as shown in Figure 11c. The higher initial concentration in the tank leachate for MXB causes the cumulative release data to appear flat. Selenium also shows an MXB initial wash-off (Appendix Figure A-14). Cadmium (Figure 12) is diffusion controlled similar to arsenic; however, as shown in Figure 12c, the initial MXA wash-off flattens the MXA cumulative release (Figure

12d). Barium, lead and nickel also exhibit MXA wash-off behavior (Appendix Figure A-7, A-11, A-13, respectively). Chromium exhibits slightly different diffusion controlled behavior than As or Cd. Constituent release of MXA (Figure 13c) is above the water quality criteria while MXB is below the water quality criteria and one order of magnitude less than MXA. Chromium does not show an initial wash-off for MXA or MXB; however, the cumulative release for MXA reaches its availability limit as estimated from Method 1313 tests. The cumulative release would likely flatten if the test were extended. Thallium is somewhat similar to chromium; however, both MXA and MXB are well above the water quality criteria. Additionally, the cumulative release of MXA is nearing availability by the end of the test and the cumulative release of MXB is at its availability. Antimony is the only constituent presented in this thesis that is similar to chromium and thallium. Cumulative release of antimony for MXA and MXB are approaching the availability by the end of the tank leach test. Beryllium and mercury (Appendix Figures A-8 and A-12, respectively) have release rates near or below the quantification limits. Zinc exhibits a distinct behavior (Appendix Figure A-16): the cumulative release is diffusion controlled; however, there is no wash-off for either MXA or MXB and neither MXA nor MXB approach the availability limit.

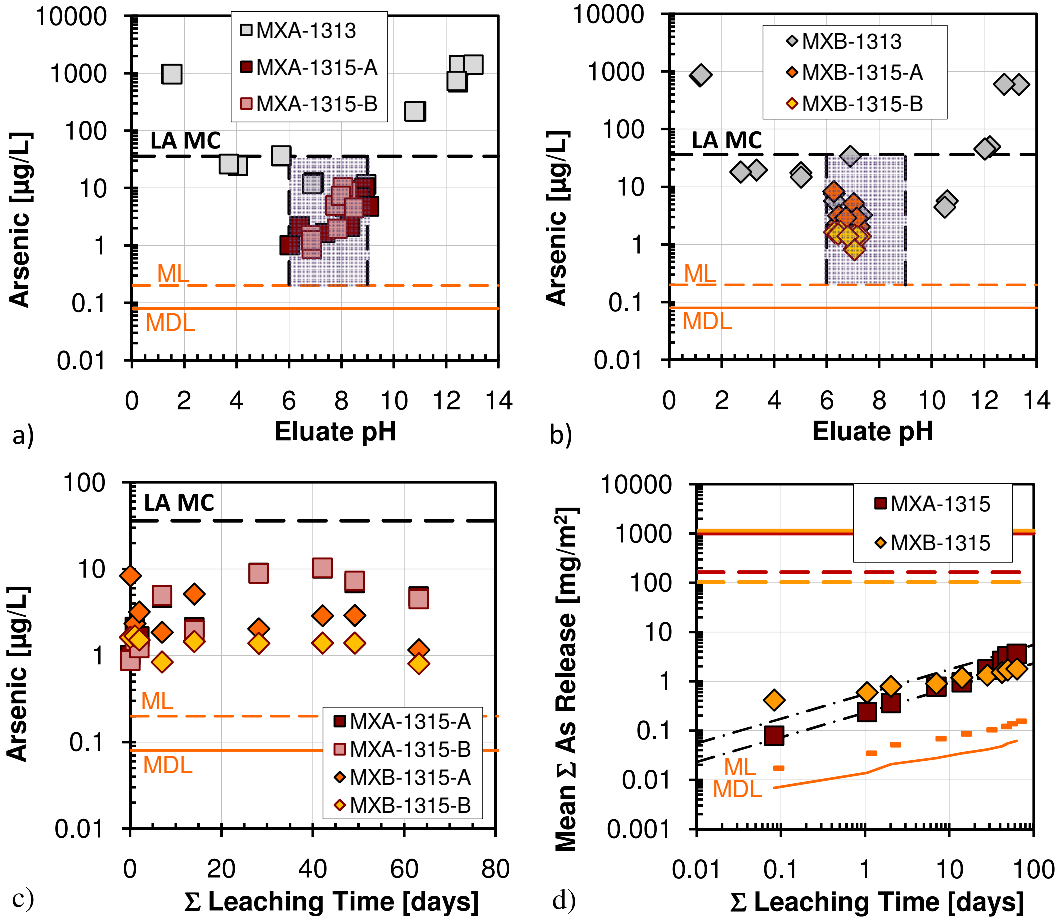

Figure 11. Arsenic Results for Mass Transport Tests on MXA and MXB
a) MXA data compared to Method 1313 LSP for MXA b) MXB data compared to Method 1313 LSP for MXB c) eluate concentrations, d) pH evolution, e) mean interval flux, and d) cumulative release.

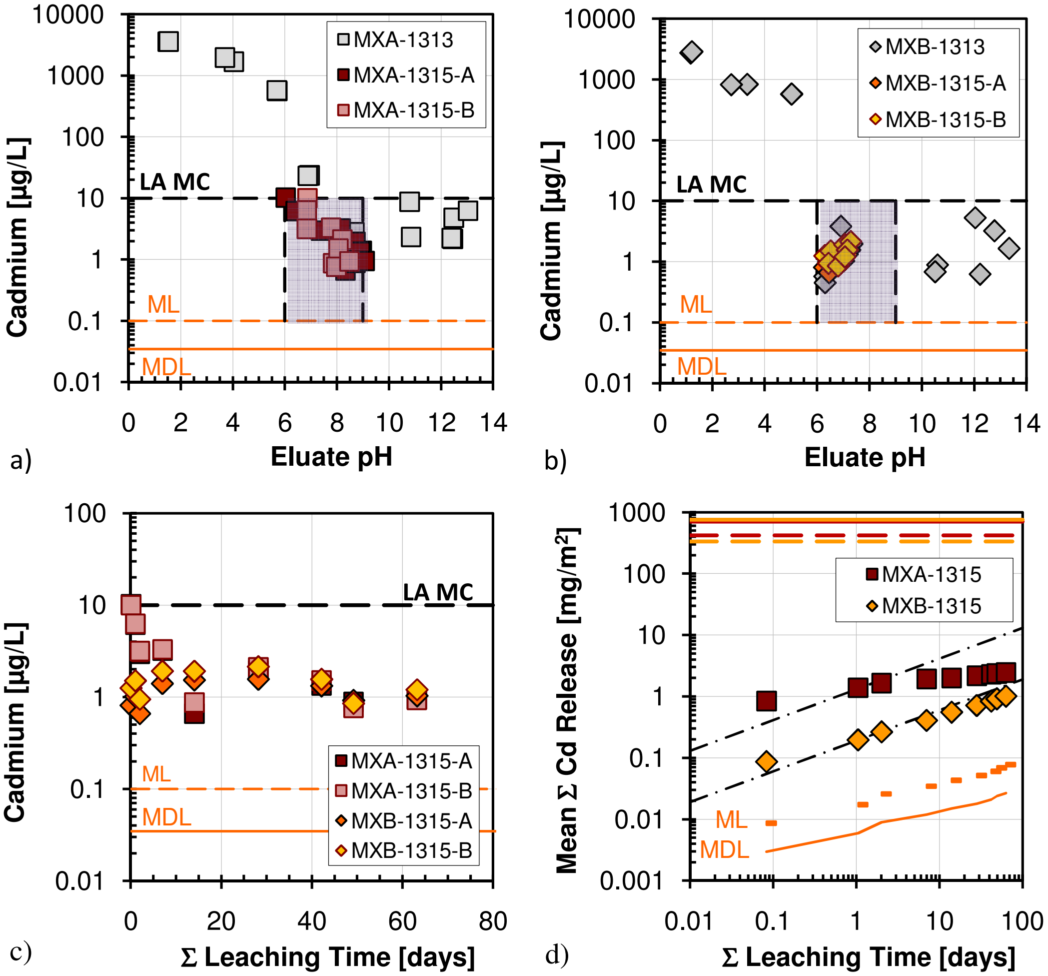

Figure 12. Cadmium Results for Mass Transport Tests on MXA and MXB
a) MXA data compared to Method 1313 LSP for MXA b) MXB data compared to Method 1313 LSP for MXB c) eluate concentrations, d) cumulative release.

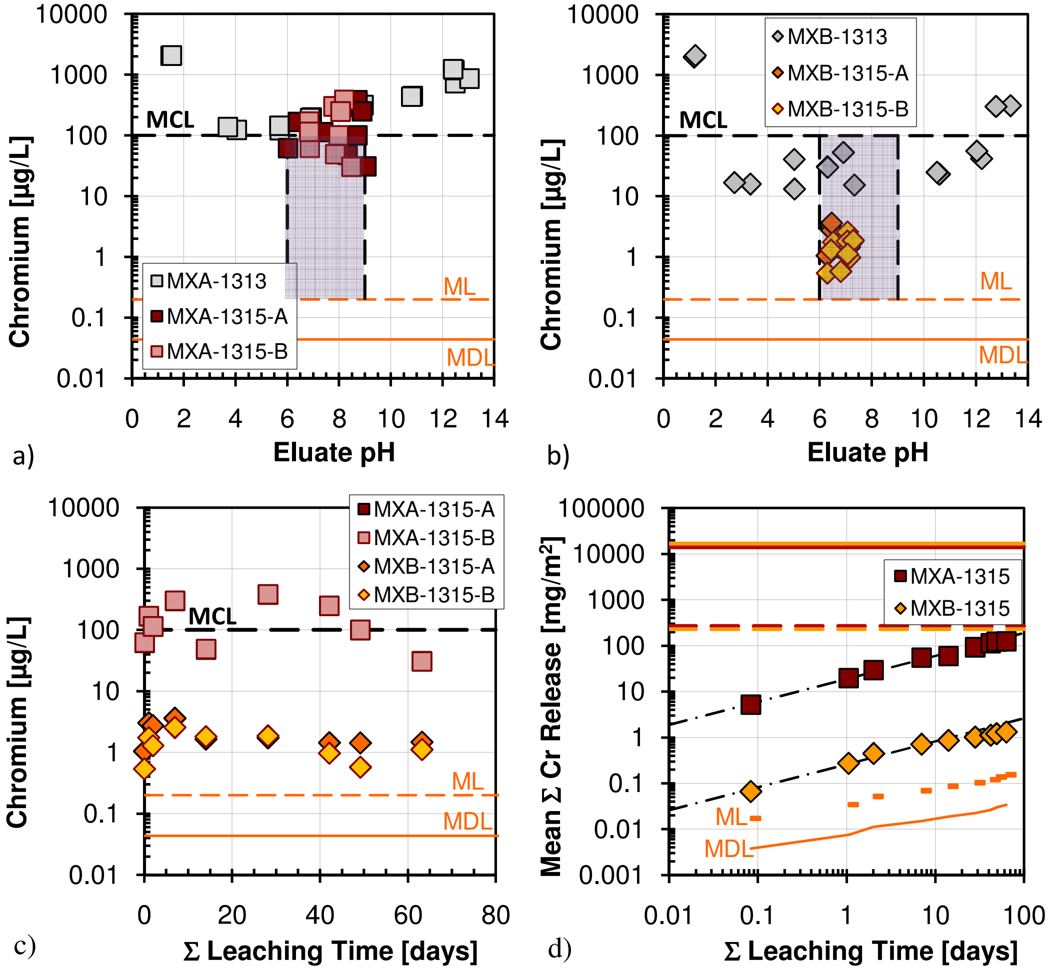

Figure 13. Chromium Results for Mass Transport Tests on MXA and MXB
a) MXA data compared to Method 1313 LSP for MXA b) MXB data compared to Method 1313 LSP for MXB c) eluate concentrations, d) cumulative release.

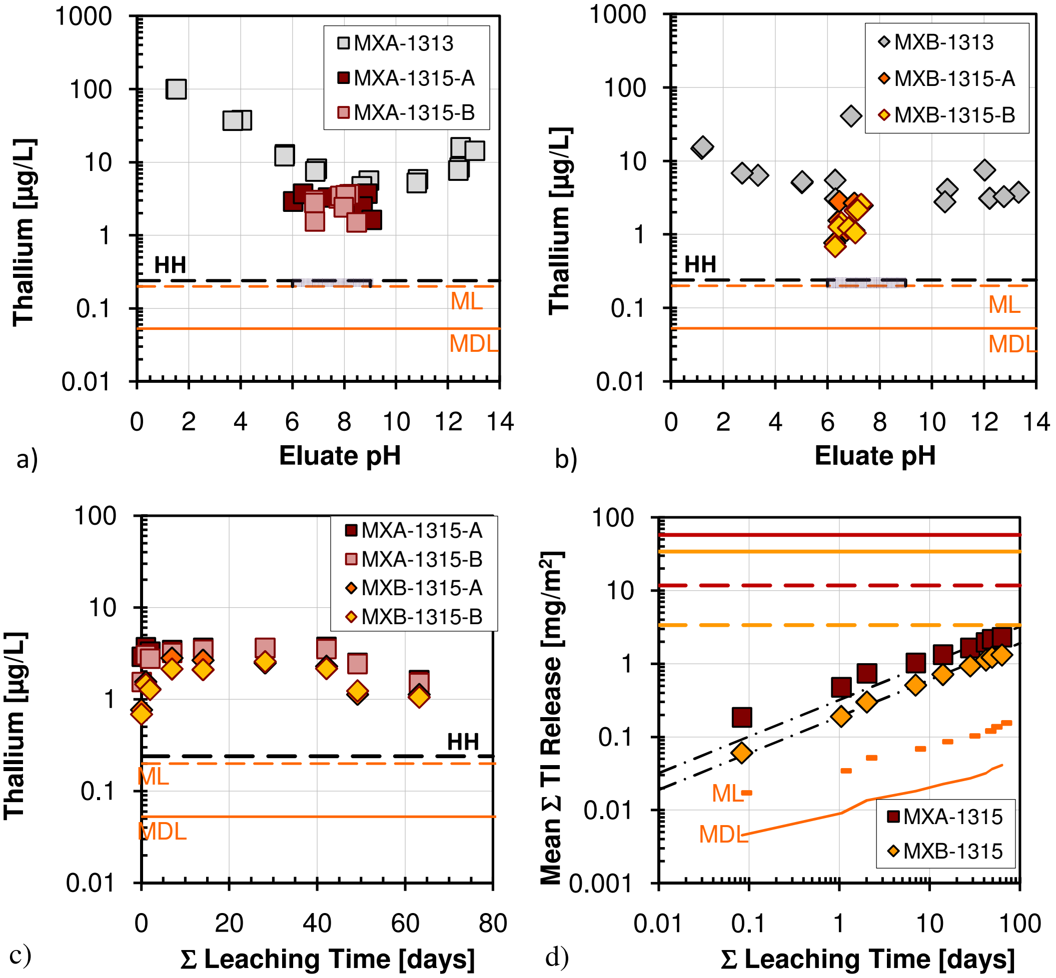

Figure 14. Thallium Results for Mass Transport Tests on MXA and MXB
a) MXA data compared to Method 1313 LSP for MXA b) MXB data compared to Method 1313 LSP for MXB c) eluate concentrations, d) cumulative release.

Effects of Phosphogypsum

For Method 1313 tests, in comparison to 100% red mud (MXA), the addition of phosphogypsum to red mud shown by material MXB appears to decrease the solubility of As, Ba, Cd, Cr, Hg, Ni, and Tl of the pH range between 6 and 9 while increasing the solubility of Sb and Se. The solubility of Be, Pb, and Zn do not seem to be significantly changed by addition of phosphogypsum. For Method 1314 tests, phosphogypsum lowers the release of As, Cr and Hg while increasing the release of Ba, Ni and Zn. The release of Sb, Be, Cd, Pb, Se and Th do not appear to change significantly from the PG addition. Method 1315 tests show that PG lowers the release of Be, Cd and Cr while the release of other constituents does not change significantly from the PG addition. Phosphogypsum also lowers the natural pH of red mud to within water quality criteria, but it raises the eluate conductivity in the percolation and tank leach tests to approximately twice that of MXA most likely due to addition of soluble species contained in the PG.

Screening Evaluation on Water Quality Criteria

A screening evaluation can be conducted based on the percolation and mass transport release data by comparing the maximum constituent leachate concentration to permissible water quality concentrations (i.e. LA marine criteria). The dilution/attenuation factors (DAF) required to meet specifications can be calculated by dividing the maximum Method 1314 / Method 1315 concentration value for each constituent *i*, (C_i^{max}) by the benchmark value (BM):

$$DAF = \frac{C_i^{\max}}{BM} \qquad \text{Equation 1}$$

DAFs less than unity indicate where the maximum concentration value is less than the benchmark value while DAFs over one indicate that the degree of dilution and attenuation required to benchmark values. The DAFs from Method 1314 and Method 1315 concentrations are shown in Table 3 for constituents of MXA and MXB.

Table 4. Dilution and Attenuation Factors Required to Achieve Benchmarks for Method 1314 and Method 1315 Concentrations.

Analyte	**Symbol**	**Percolation**		**Mass Transport**	
		MXA	**MXB**	**MXA**	**MXB**
Antimony	Sb	4.8	1.2	0.88	0.23
Arsenic	As	2.5	0.19	0.28	0.14
Barium	Ba	0.002	0.16	0.002	0.004
Beryllium	Be	0.15	0.16	0.10	0.03
Cadmium	Cd	0.73	0.79	1.0	0.19
Chromium	Cr	25	4.4	3.8	0.03
Lead	Pb	0.89	0.89	0.30	0.16
Mercury	Hg	1.2	0.50	1.1	1.3
Nickel	Ni	3.8	14	0.61	0.78
Selenium	Se	12	6.4	1.0	1.4
Thallium	Tl	41	44	15	11.2
Zinc	Zn	2.4	7.8	0.51	0.82

In general, DAFs for mass transport based tests are relatively lower than DAFs from percolation tests. As shown in Table 3, several of the constituents do not require dilution or attenuation to meet water quality criteria (i.e. As, Ba, Be, Cd, Pb, and Hg – MXB percolation). However, some constituents would require dilution and/or attenuation in order to meet water quality criteria (i.e. Cr, Ni, Th, Se and Zn – MXA percolation). All constituents would comply with a DAF of 50. Although some constituents did not meet water quality criteria during the leaching tests performed for this study, it should be noted that the results from these leaching tests do not account for any potential dilution or attenuation that would be encountered in a beneficial use scenario.

Conclusions

A suite of leaching tests were conducted on two mixtures of red mud and phosphogypsum to provide data to evaluate the potential environmental effects the materials would exhibit when beneficially used as levee fill material. The leaching tests included an equilibrium-based extraction test as a function of pH, a column percolation test as a function of liquid-solid ratio and a mass transport-based tank leach test. Although additional work is needed, preliminary results indicate that red mud and phosphogypsum mixtures may be environmentally acceptable materials to use as levee fill material if the design scenario achieves a reduction in release followed by dilution and attenuation equivalent to a DAF of less than 50. Furthermore, the addition of phosphogypsum appears to reduce the leaching of some constituents, but may also increase the leaching of other constituents. Based on a water quality criteria screening, several constituents will not require a dilution or attenuation factor to meet water quality limits. Other constituents will meet water quality limits with a DAF of 50 or less. This is a preliminary indication that constituents will not exceed water quality criteria if the materials are beneficially used in a levee fill scenario.

Acknowledgements

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CHAPTER IV

THESIS SUMMARY

Major Observations

A universal testing methodology for beneficial use projects is needed in the United States because no federal or state program exists that could function as such. The federal programs that exist are general and not sufficient for beneficial use determinations. The state programs that exist are all different and may not include robust environmental evaluations. A robust environmental evaluation has been identified as the number one obstacle for beneficial use projects; thus, it must be vigorous in order to insure a truly successful beneficial use determination. The EPA has provided an effective testing methodology for beneficial use determinations through their current evaluation of red mud and phosphogypsum. It greatly helps to overcome the barrier associated with the environmental evaluation; thus, it could readily be applied to other beneficial use projects. The leaching assessment framework used in the EPA methodology is an excellent first-step to developing an acceptable environmental evaluation for beneficial use projects.

Future Work

The work presented in this thesis is a good first-step environmental assessment of red mud and phosphogypsum for beneficial use in levee construction. However, additional work needs to be completed to assess fully the potential impact of using the two materials. The results from this thesis are currently being used for geochemical speciation and a scenario specific assessment. Evaluating the materials within their use scenario is essential to overcoming the beneficial use barriers.

Once the environmental assessment is complete, additional work remains before the secondary materials may be beneficially used. A biological / ecological assessment must also be performed, including specie-specific toxicity testing to confirm whether or not the potential leachates may harm marine organisms and other aquatic life. Additionally, a legal assessment must be completed to identify how the materials will legally transfer from the current owners to the end-users. Furthermore, significant effort may be required to convince the public to accept the project. All of the steps should be completed before red mud and phosphogypsum will be beneficially used as levee fill material.

Conclusions

The primary difficulty with beneficial use projects is determining if a secondary material will be potentially harmful to human health and the environment. There are significant other barriers to beneficial use projects, as mentioned in this thesis; however, a solution to the primary issue would ease the other barriers. The environmental evaluation is difficult because there is not a universally excepted methodology for evaluating secondary materials. In addition, the methodologies currently used by states are likely inadequate because they often reduce the evaluation to a single extraction test (i.e. TCLP). Another problem with current methodologies is using an incorrect scenario assessment (i.e. municipal solid waste codisposal for industrial waste in a beneficial use construction application). To address these specific issues with beneficial use projects and move beneficial use determinations toward universally accepted methodologies for environmental evaluations, this thesis is presented as an example of how to use a suite of laboratory leaching tests to perform an environmental evaluation for beneficial use of secondary materials.

The leaching tests were performed on two mixtures of red mud and phosphogypsum. The leaching tests provided key data from equilibrium and mass transport-based perspectives under a range of environmental conditions. From an initial screening based on water quality criteria, constituents leaching from the secondary materials would likely not exceed water quality limits with moderate dilution and attenuation in the beneficial use scenario. Although additional work is needed for this study, it is an indication that advanced leaching tests are needed and can work to better describe the potential environmental effects in a beneficial use scenario.

APPENDIX

Solubility & Release Data

The following pages present the pH-dependent leaching test data for constituents of mixtures of red mud and phosphogypsum alphabetically by analyte. The mixtures consist of 100% red mud (MXA) and 80% red mud/20% phosphogypsum (MXB).

Notes:

- Additions of base are shown in the titration curve as negative acid additions.
- Blackened or grayed points indicate the response at natural pH (no acid or base addition) for replicates A and B, respectively.
- Shaded regions indicate the range of values within the pH criteria for Louisiana surface water (6 ≤ pH ≤ 9) and between the quantifiable limit (ML) and benchmark values when available.
- Benchmark values are shown for comparative purposes only and should not be used as the sole basis for decision-making. Leaching data do not consider dilution/attenuation factors assumed in surface water criteria. The following abbreviations are used:

LA MC	Louisiana Marine Chronic concentration
FCCC	Freshwater Criterion Continuous Concentration
SCCC	Saltwater Criterion Continuous Concentration
HH	Human Health for Consumption of Water and Organisms
MCL	Maximum Concentration Level - drinking water criterion
DWEL	Drinking Water Equivalent Level

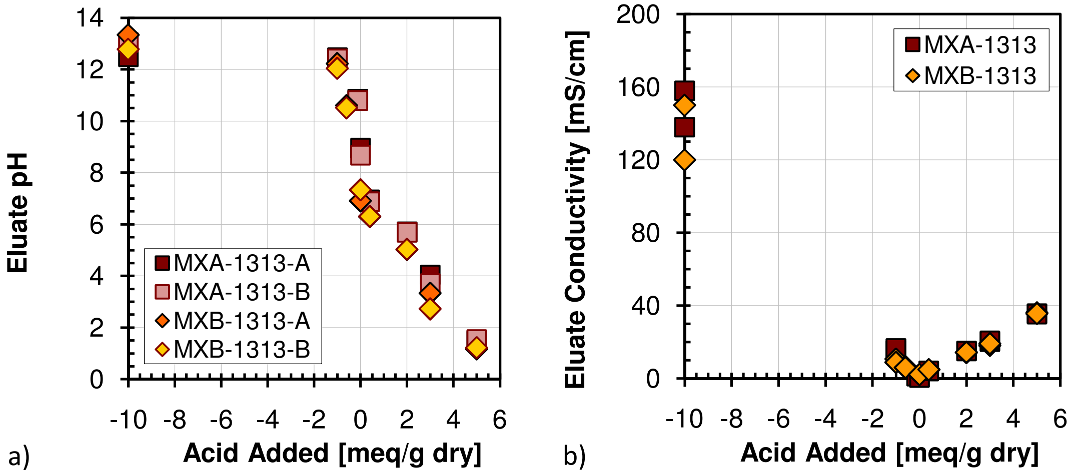

Figure A-1: Method 1313 Leaching Data as a Function of pH for MXA and MXB Materials

a) eluate pH (titration curve), b) eluate conductivity.

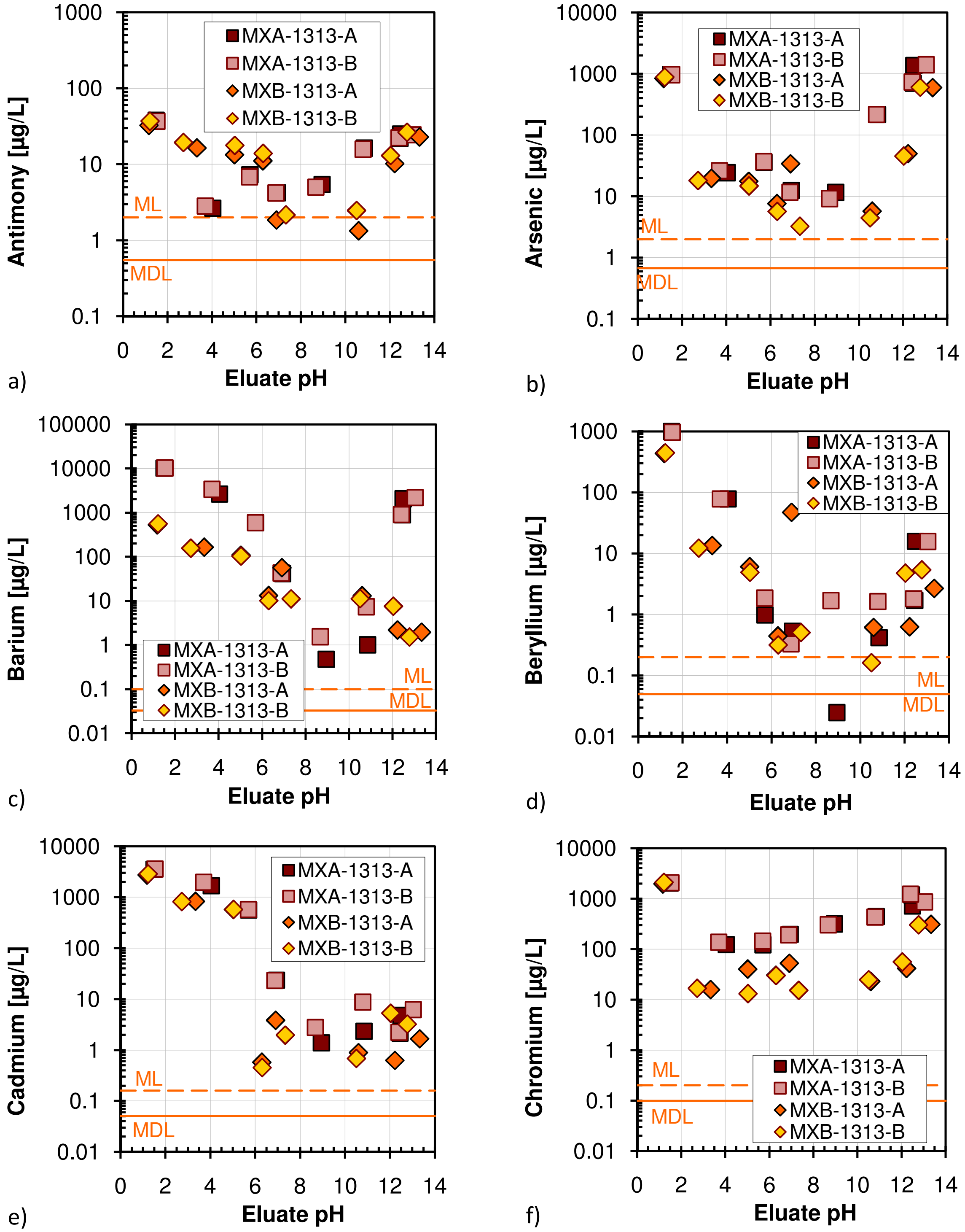

Figure A-2. Method 1313 Leaching Data as a Function of pH for MXA and MXB Materials
a) antimony, b) arsenic, c) barium, d) beryllium, e) cadmium, and f) chromium.

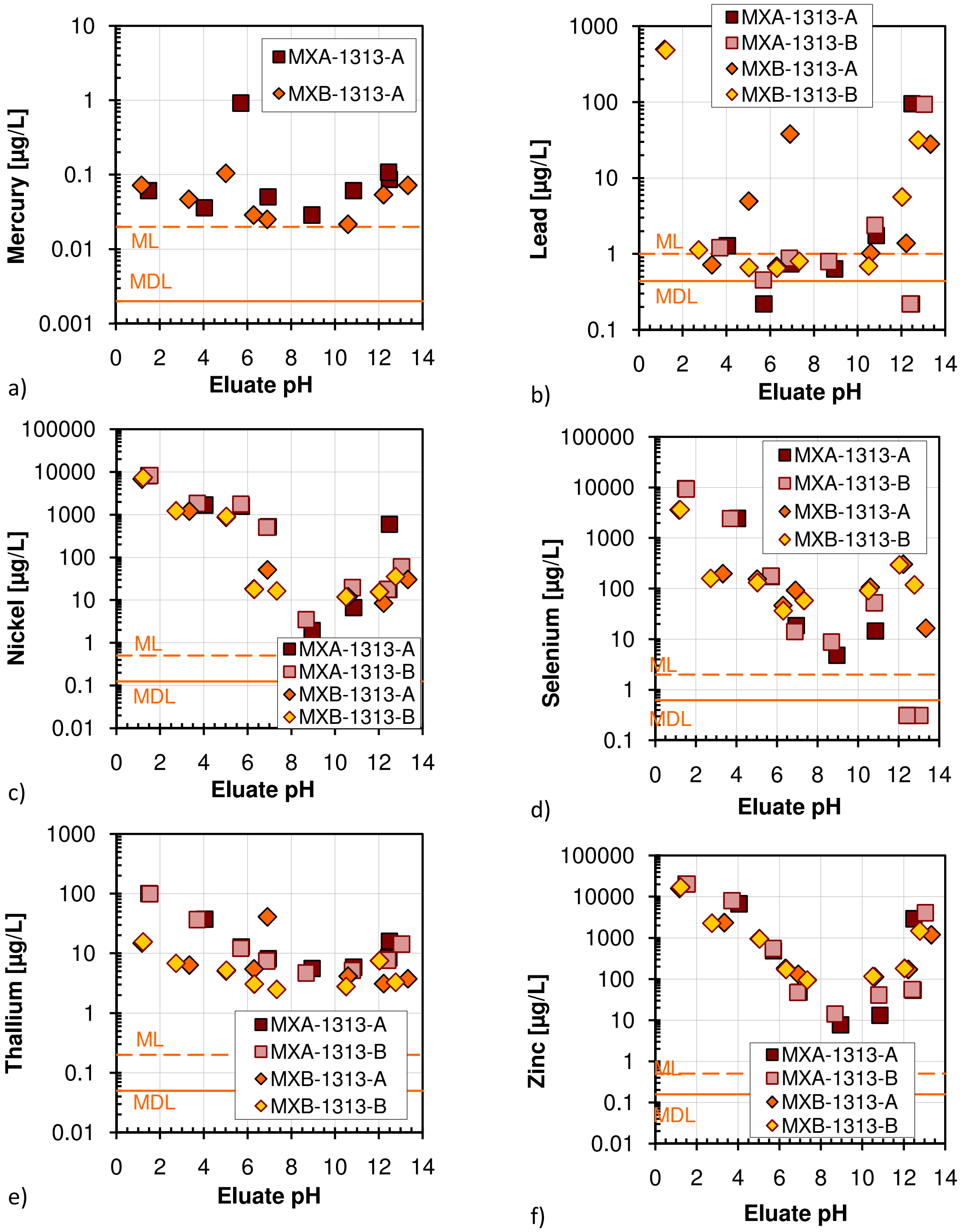

Figure A-3. Method 1313 Leaching Data as a Function of pH for MXA and MXB Materials
a) mercury, b) lead, c) nickel, d) selenium, e) thallium, and f) zinc.

Column Test Data

The following pages present the up-flow column percolation test data for constituents of mixtures of red mud and phosphogypsum alphabetically by analyte. The mixtures are 100% red mud (MXA) and 80% red mud/20% phosphogypsum (MXB). Analyte results are presented in a single figure of four subpanels consisting of a) MXA Method 1314 date compared to Method 1313 LSP for MXA b) MXB Method 1314 data compared to Method 1313 LSP for MXB c) Method 1314 concentrations as a function of LS ratio, and d) percolation release.

<u>Notes:</u>

- Shaded regions (subpanels a and b) indicate the range of values within the pH criteria for Louisiana surface water (6 ≤ pH ≤ 9) and between the quantifiable limit (ML) and benchmark values when available.

- Benchmark values are shown for comparative purposes only and should not be used as the sole basis for decision-making. Leaching data do not consider dilution/attenuation factors assumed in surface water criteria. The following abbreviations are used:

LA MC	Louisiana Marine Chronic concentration
FCCC	Freshwater Criterion Continuous Concentration
SCCC	Saltwater Criterion Continuous Concentration
HH	Human Health for Consumption of Water and Organisms
MCL	Maximum Concentration Level - drinking water criterion
DWEL	Drinking Water Equivalent Level

- The cumulative release (subpanel d) is compared to release at natural pH (grayed points with color-coded edging), available content (dashed, color-coded lines) and total content (solid, color-coded lines).

- Analytical quality control values (subpanels a, b, and c) are provided as quantification limit or ML (dashed orange line) and method detection limit or MDL (solid orange line).

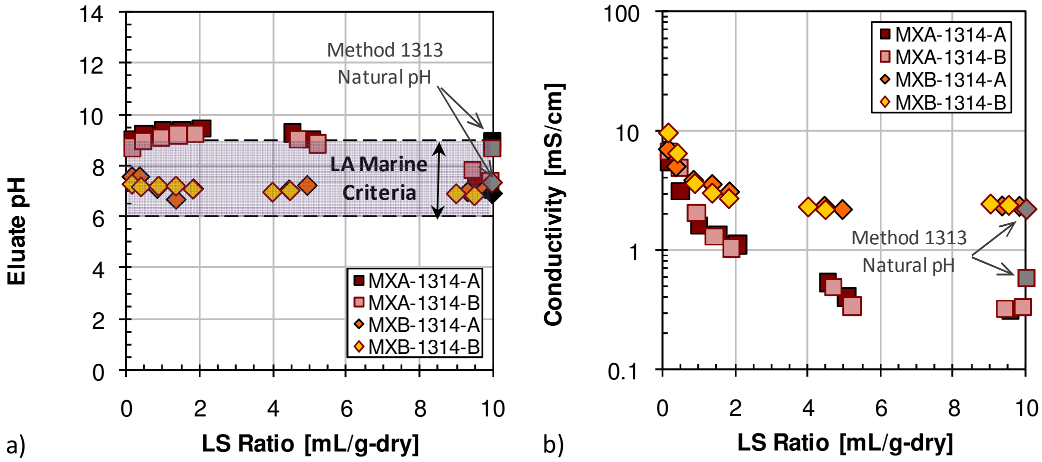

Figure A-4. Eluate pH and Conductivity for Method 1314 Percolation Test of MXA and MXB a) eluate pH as a function of LS ratio, b) eluate electrical conductivity as a function of LS ratio.

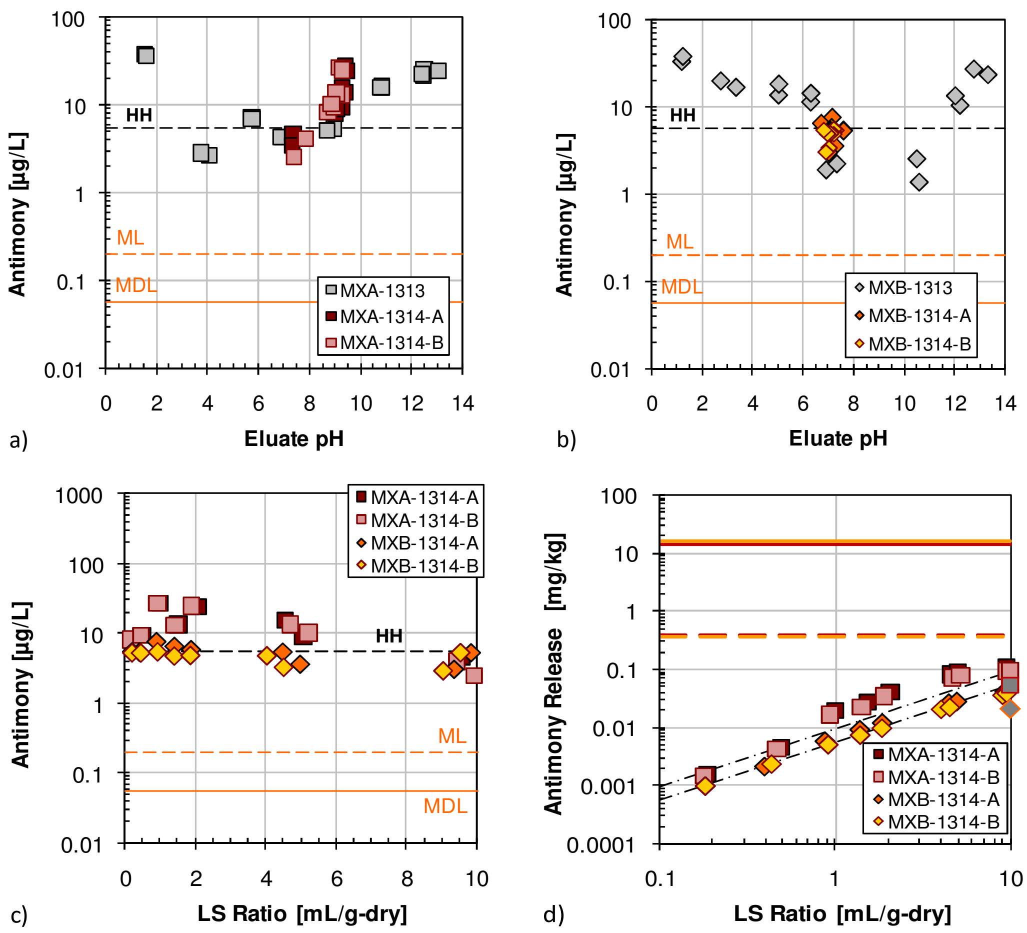

Figure A-5. Antimony Results for Method 1314 Percolation Test on MXA and MXB
a) MXA data compared to Method 1314 LSP for MXA, b) MXB data compared to Method 1313 LSP for MXB, c) concentrations as a function of LS ratio, and d) percolation release.

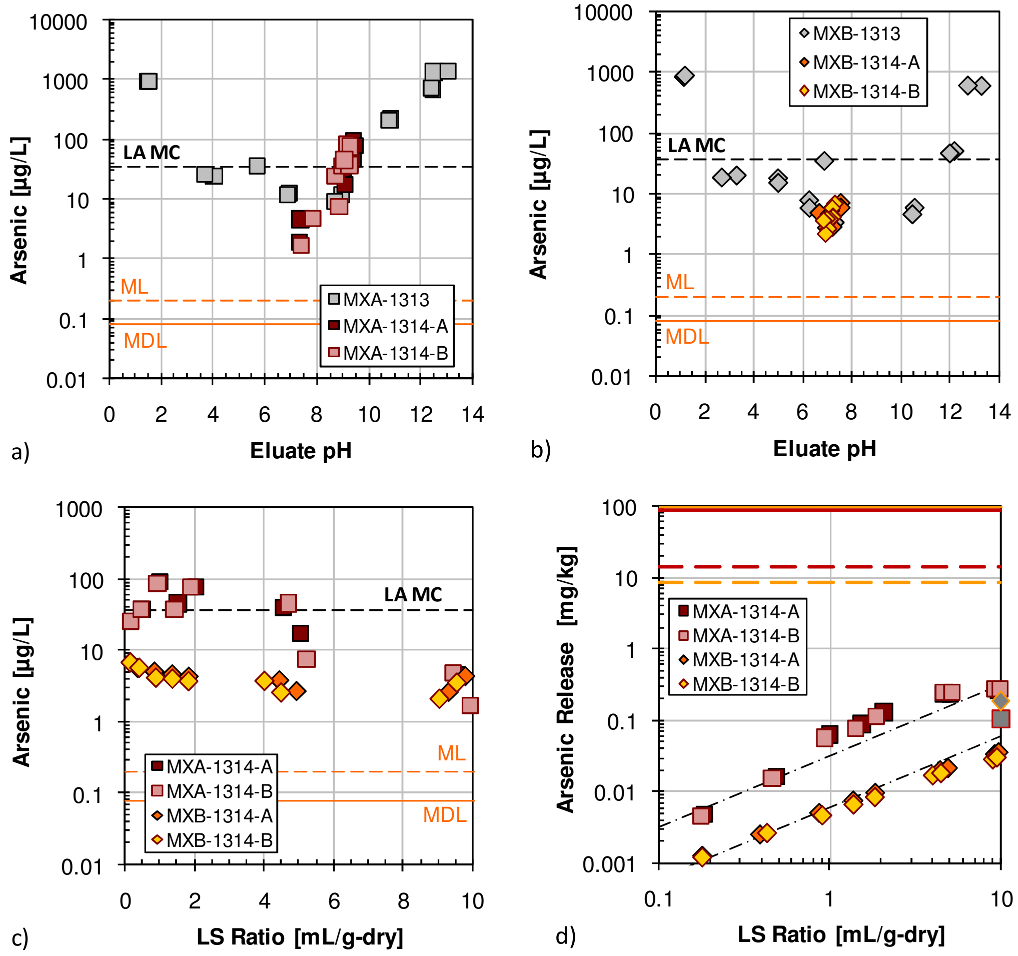

Figure A-6. Arsenic Results for Method 1314 Percolation Test on MXA and MXB
a) MXA data compared to Method 1314 LSP for MXA, b) MXB data compared to Method 1313 LSP for MXB, c) concentrations as a function of LS ratio, and d) percolation release.

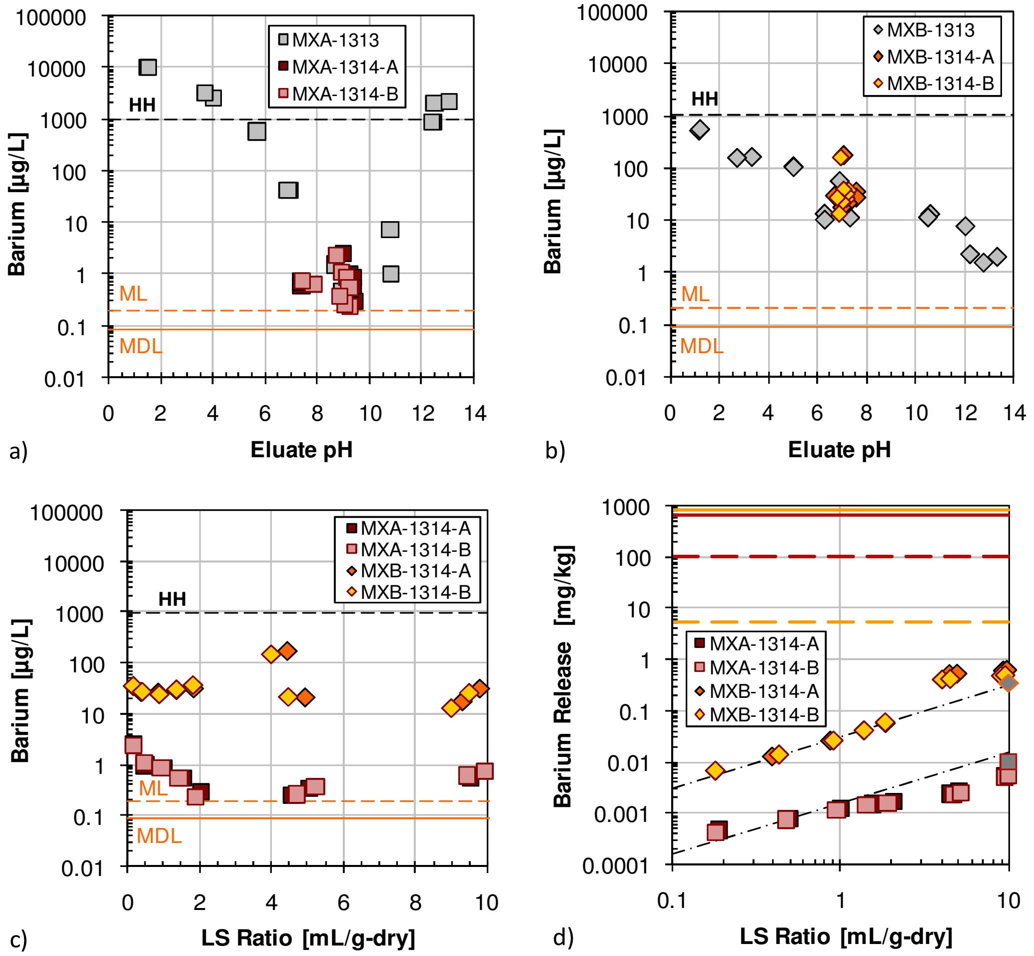

Figure A-7. Barium Results for Method 1314 Percolation Test on MXA and MXB
a) MXA data compared to Method 1314 LSP for MXA, b) MXB data compared to Method 1313 LSP for MXB, c) concentrations as a function of LS ratio, and d) percolation release.

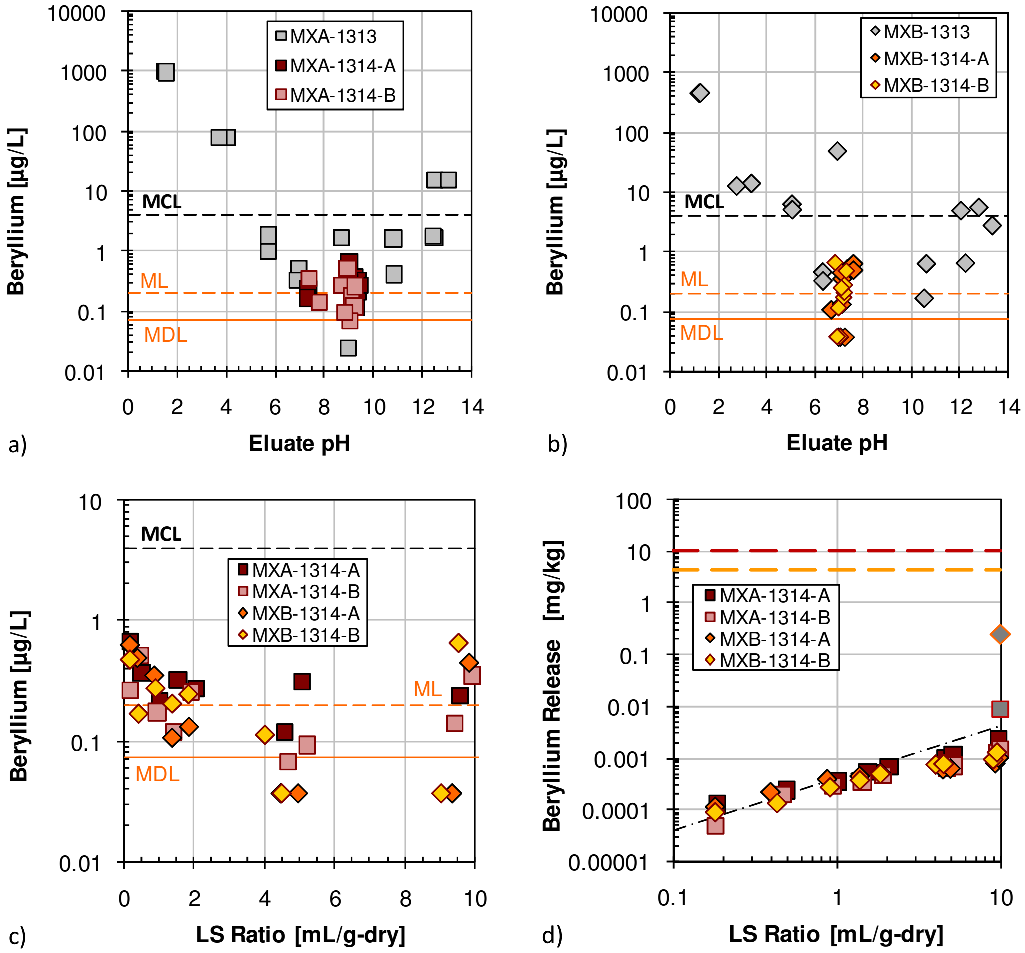

Figure A-8. Beryllium Results for Method 1314 Percolation Test on MXA and MXB
a) MXA data compared to Method 1314 LSP for MXA, b) MXB data compared to Method 1313 LSP for MXB, c) concentrations as a function of LS ratio, and d) percolation release.

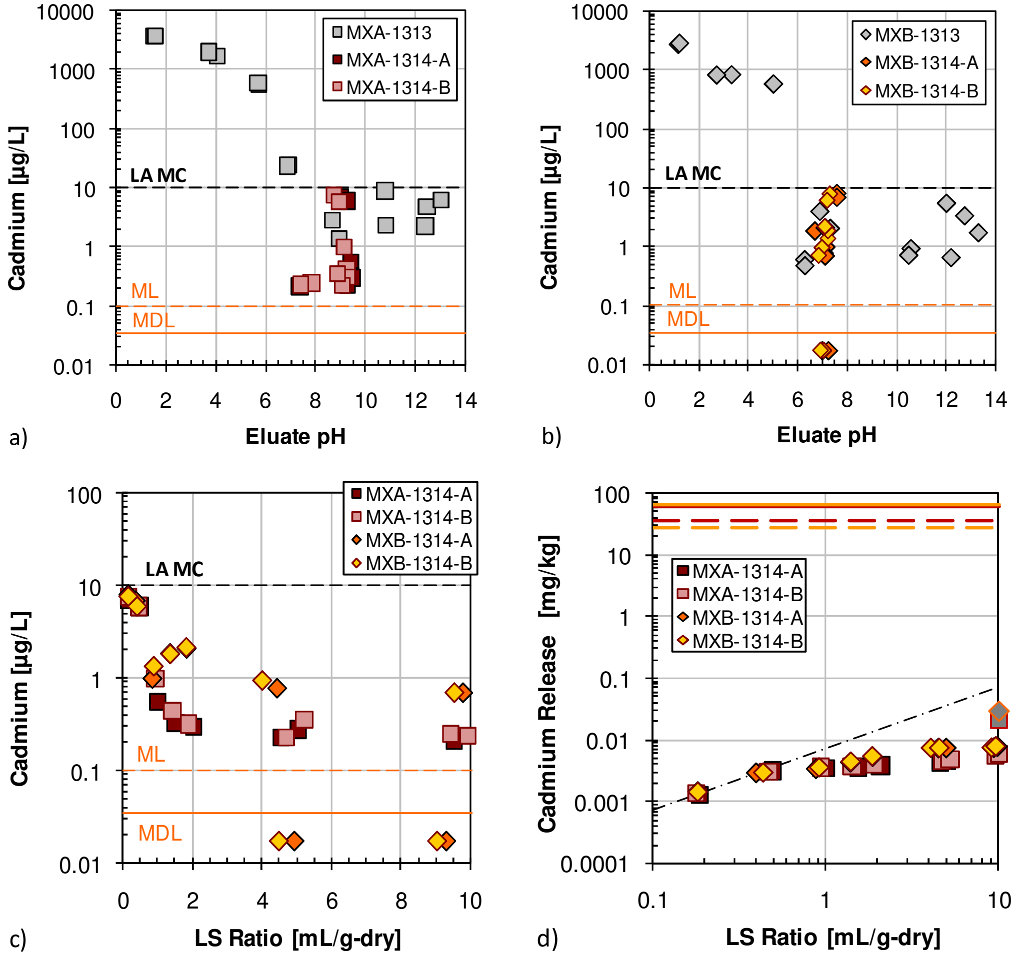

Figure A-9. Cadmium Results for Method 1314 Percolation Test on MXA and MXB
a) MXA data compared to Method 1314 LSP for MXA, b) MXB data compared to Method 1313 LSP for MXB, c) concentrations as a function of LS ratio, and d) percolation release.

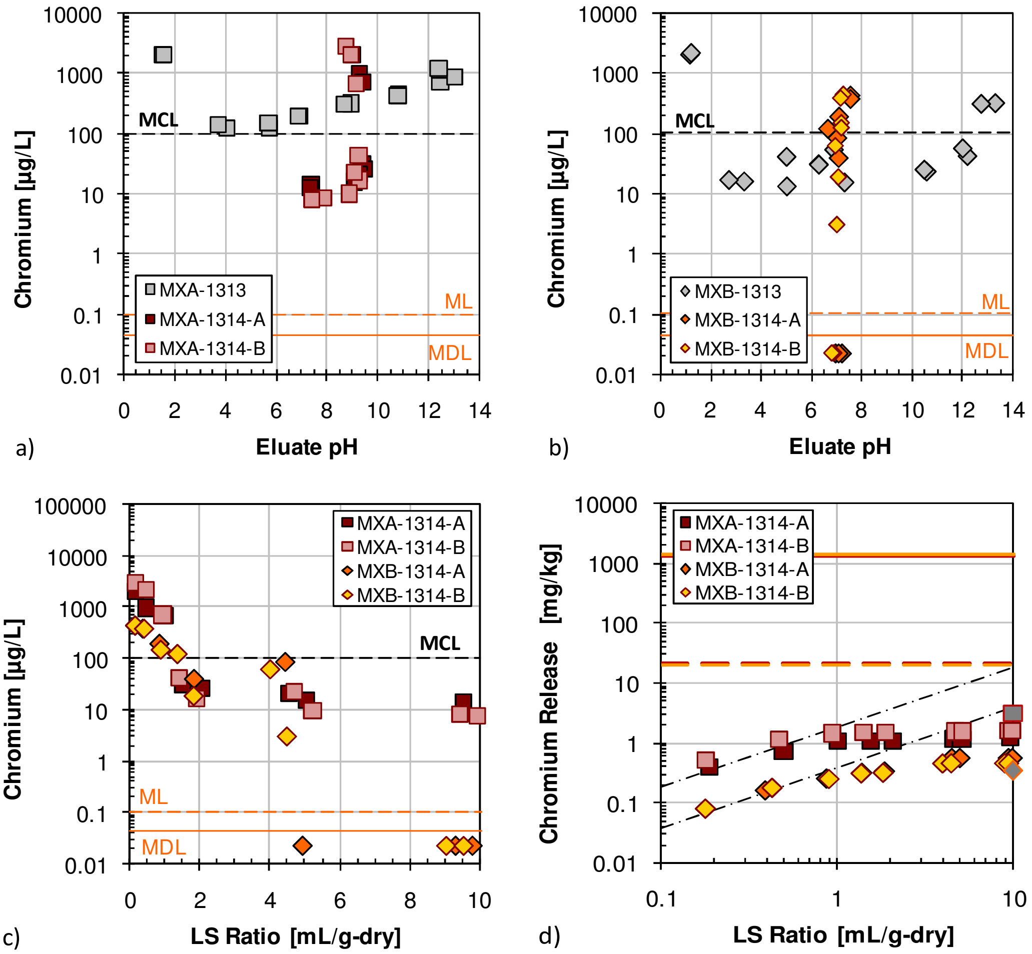

Figure A-10. Chromium Results for Method 1314 Percolation Test on MXA and MXB
a) MXA data compared to Method 1314 LSP for MXA, b) MXB data compared to Method 1313 LSP for MXB, c) concentrations as a function of LS ratio, and d) percolation release.

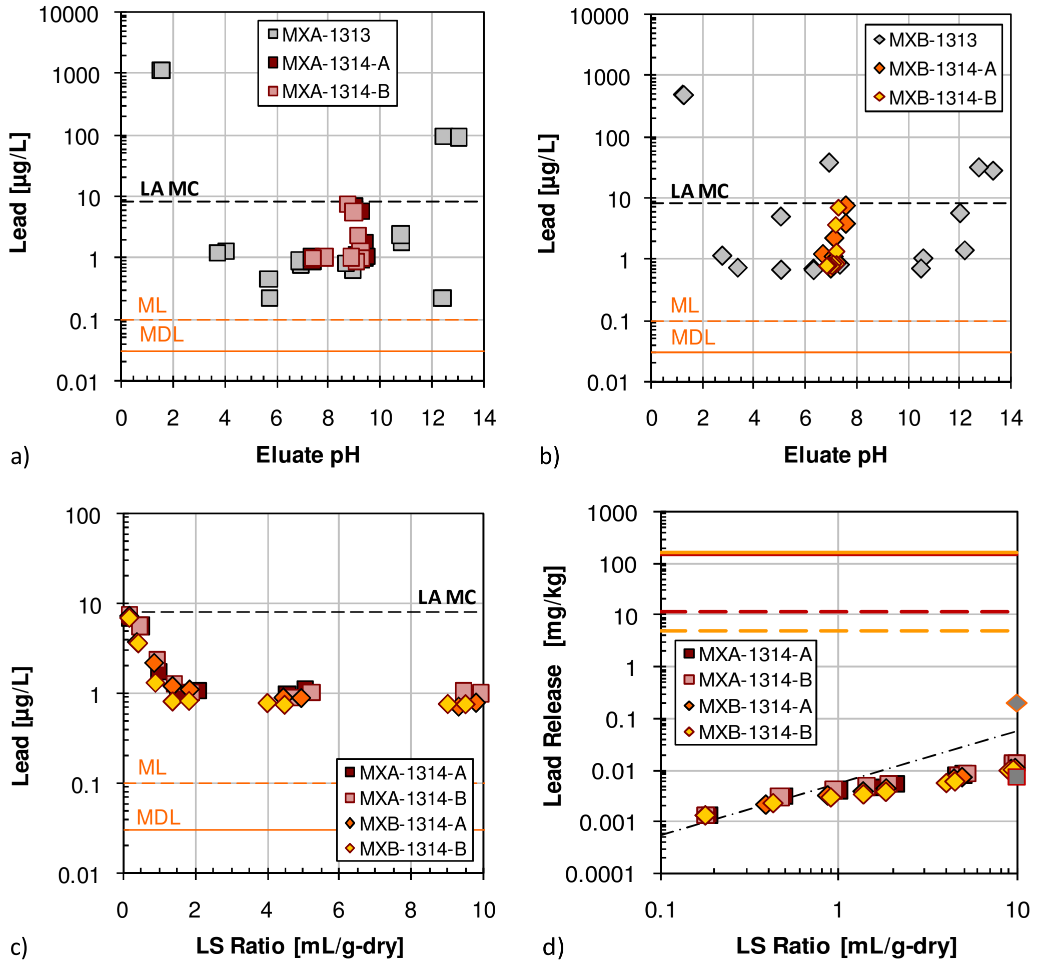

Figure A-11. Lead Results for Method 1314 Percolation Test on MXA and MXB
a) MXA data compared to Method 1314 LSP for MXA, b) MXB data compared to Method 1313 LSP for MXB, c) concentrations as a function of LS ratio, and d) percolation release.

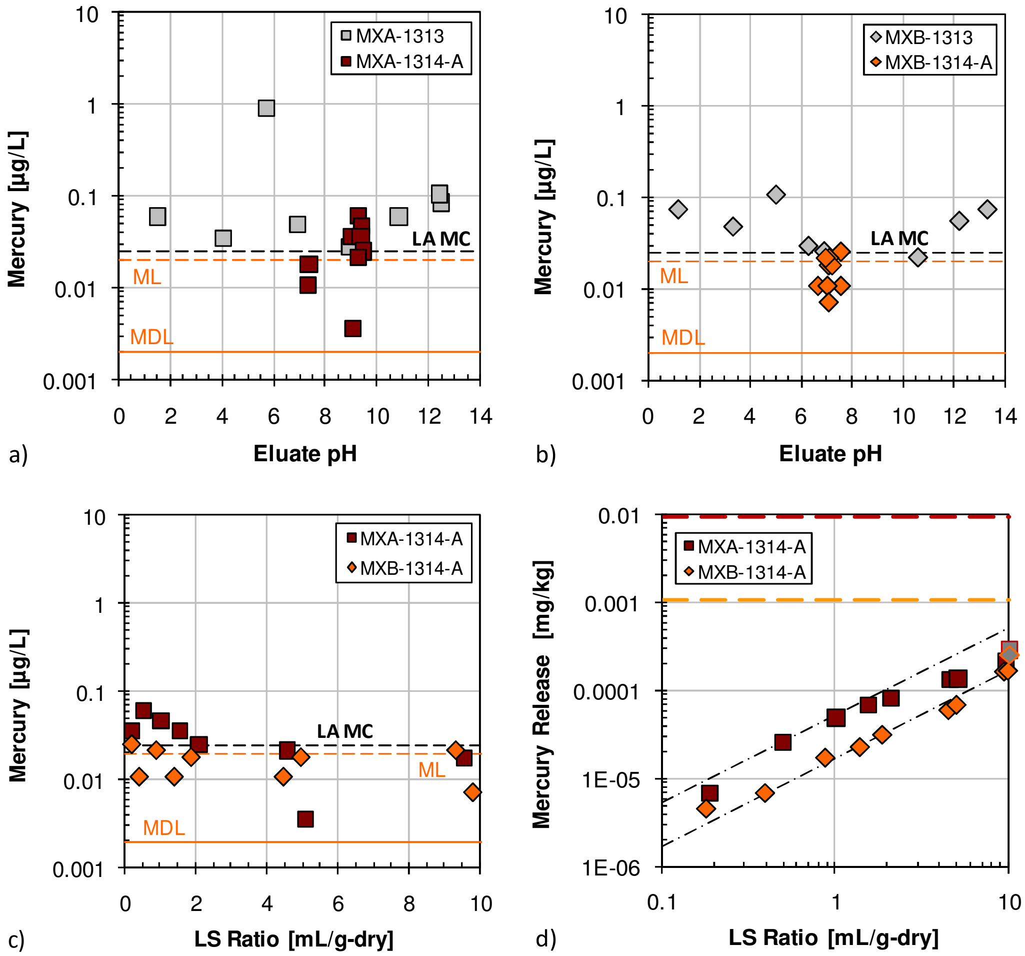

Figure A-12. Mercury Results for Method 1314 Percolation Test on MXA and MXB
a) MXA data compared to Method 1314 LSP for MXA, b) MXB data compared to Method 1313 LSP for MXB, c) concentrations as a function of LS ratio, and d) percolation release.

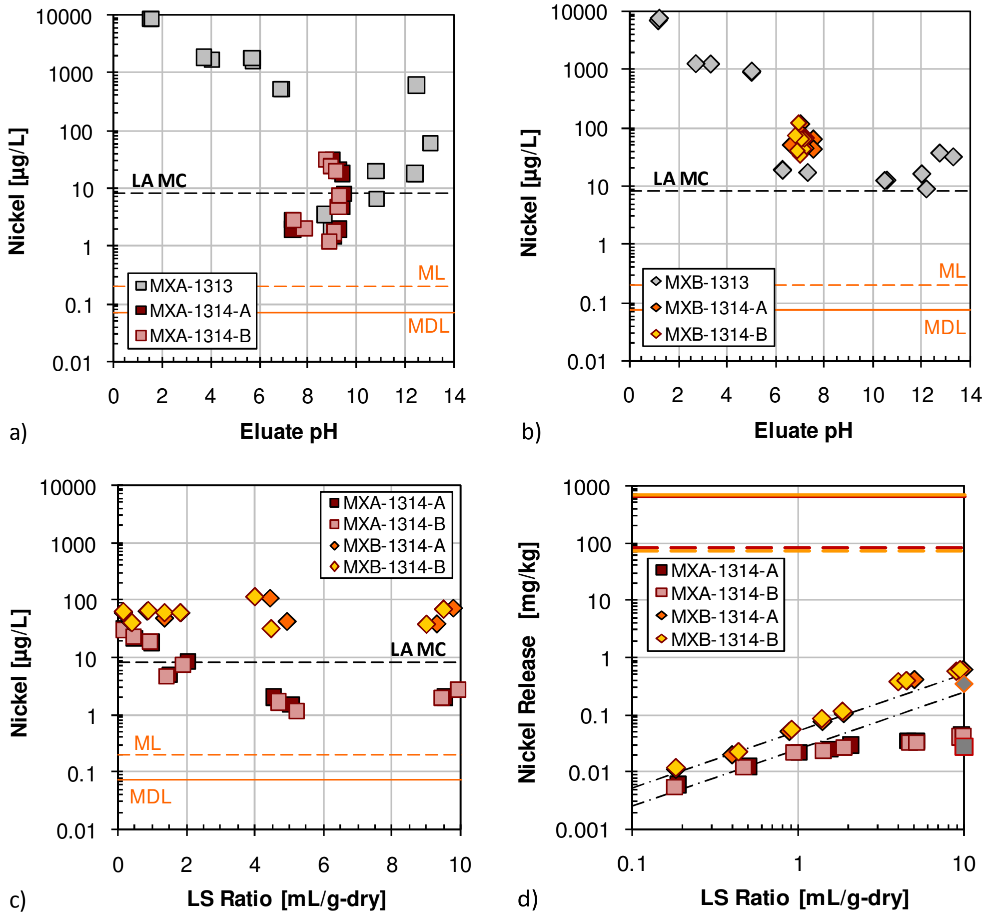

Figure A-13. Nickel Results for Method 1314 Percolation Test on MXA and MXB.
a) MXA data compared to Method 1314 LSP for MXA, b) MXB data compared to Method 1313 LSP for MXB, c) concentrations as a function of LS ratio, and d) percolation release.

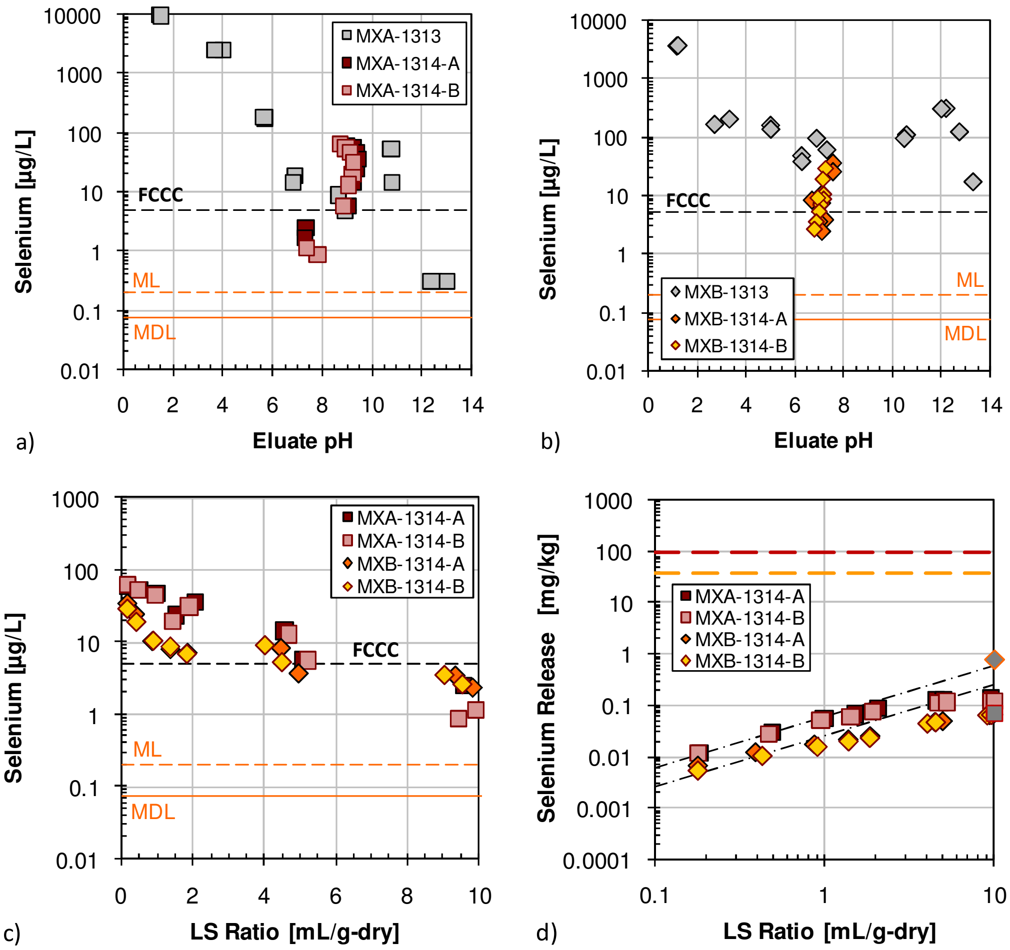

Figure A-14. Selenium Results for Method 1314 Percolation Test on MXA and MXB.
a) MXA data compared to Method 1314 LSP for MXA, b) MXB data compared to Method 1313 LSP for MXB, c) concentrations as a function of LS ratio, and d) percolation release.

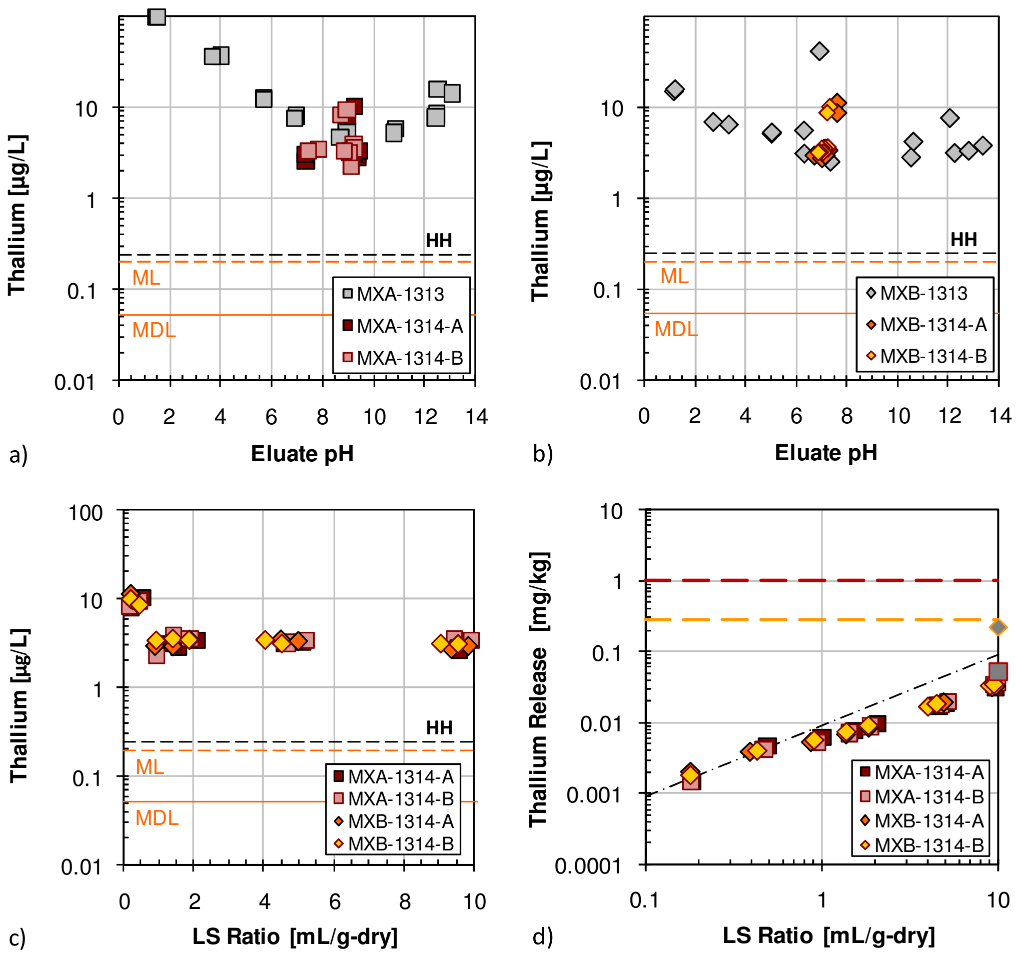

Figure A-15. Thallium Results for Method 1314 Percolation Test on MXA and MXB
a) MXA data compared to Method 1314 LSP for MXA, b) MXB data compared to Method 1313 LSP for MXB, c) concentrations as a function of LS ratio, and d) percolation release.

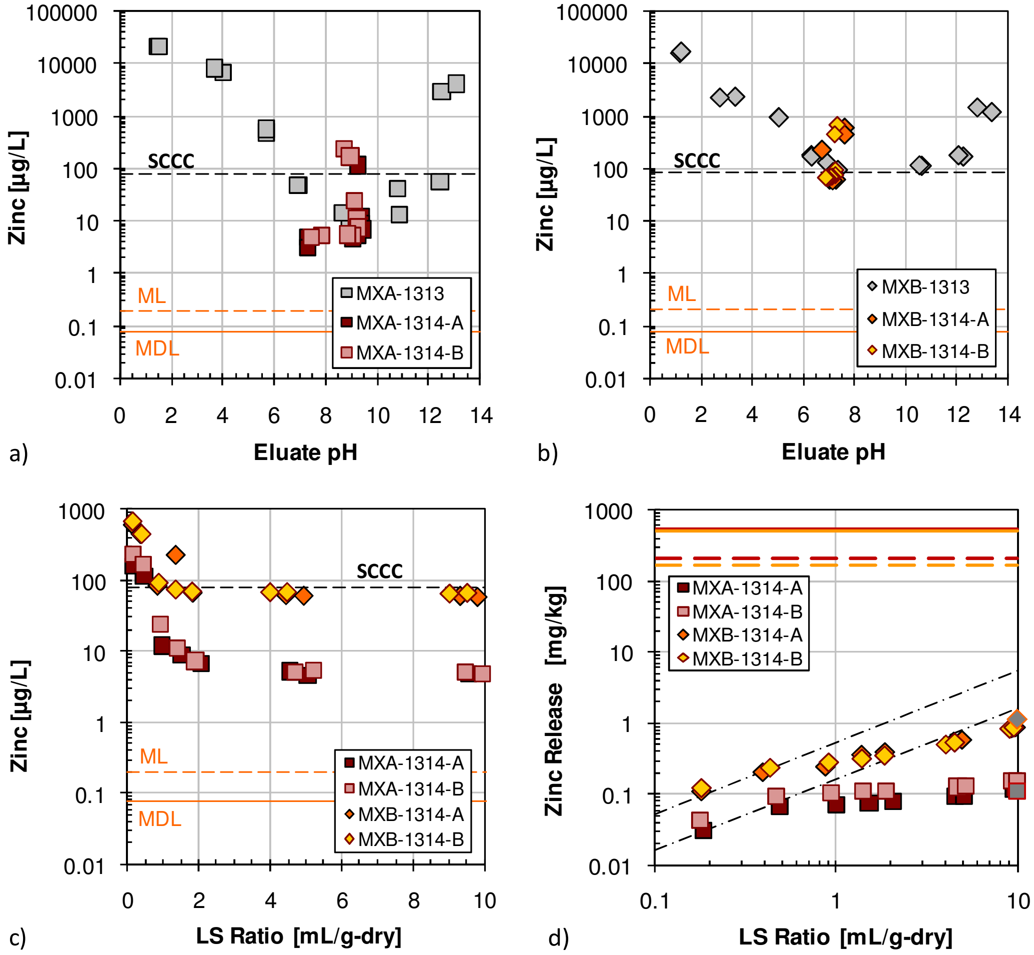

Figure A-16. Zinc Results for Method 1314 Percolation Test on MXA and MXB
a) MXA data compared to Method 1314 LSP for MXA, b) MXB data compared to Method 1313 LSP for MXB, c) concentrations as a function of LS ratio, and d) percolation release.

Mass Transport Data

The following pages present the Method 1315 mass transport test data for two mixtures of red mud and phosphogypsum alphabetically by analyte. The mixtures are 100% red mud (MXA) and 80% red mud/20% phosphogypsum (MXB). Analyte results are presented in a single figure of four subpanels consisting of a) MXA Method 1315 date compared to Method 1313 LSP for MXA b) MXB Method 1315 data compared to Method 1313 LSP for MXB c) Method 1315 concentrations as a function of LS ratio, d) cumulative mass transport release.

Notes:

- Shaded regions (subpanels a, b, and d) indicate the range of values within the pH criteria for Louisiana surface water (6 ≤ pH ≤ 9) and between the quantifiable limit (ML) and benchmark values when available.

- Benchmark values (subpanels a, b, and c) are shown for comparative purposes only and should not be used as the sole basis for decision-making. Leaching data do not consider dilution/attenuation factors assumed in surface water criteria. The following abbreviations are used:

LA MC	Louisiana Marine Chronic concentration
FCCC	Freshwater Criterion Continuous Concentration
SCCC	Saltwater Criterion Continuous Concentration
HH	Human Health for Consumption of Water and Organisms
MCL	Maximum Concentration Level - drinking water criterion
DWEL	Drinking Water Equivalent Level

- The cumulative release (subpanel d) is compared to available content (dashed, color-coded lines) and total content (solid, color-coded lines).

- Analytical quality control values (subpanels a, b, and c) are provided as quantification limit or ML (dashed orange line) and method detection limit or MDL (solid orange line). In figures for cumulative release (subpanel d), quality control lines are used to show calculated response if the concentration in all eluate fractions were limited at ML (dashed) or MDL (solid) values.

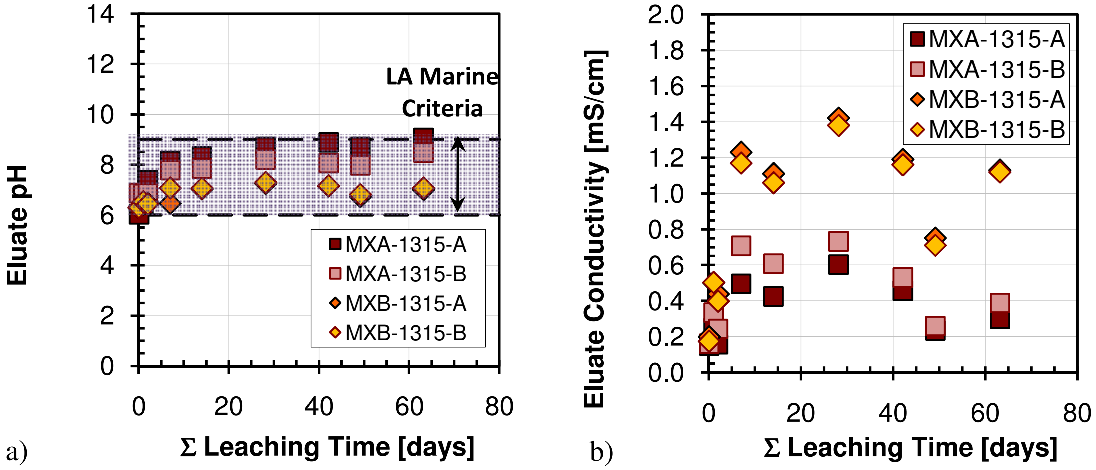

Figure A-17. Method 1315 Leaching Data as a Function of LS Ratio for MXA and MXB Materials a) eluate pH (titration curve) and b) eluate conductivity.

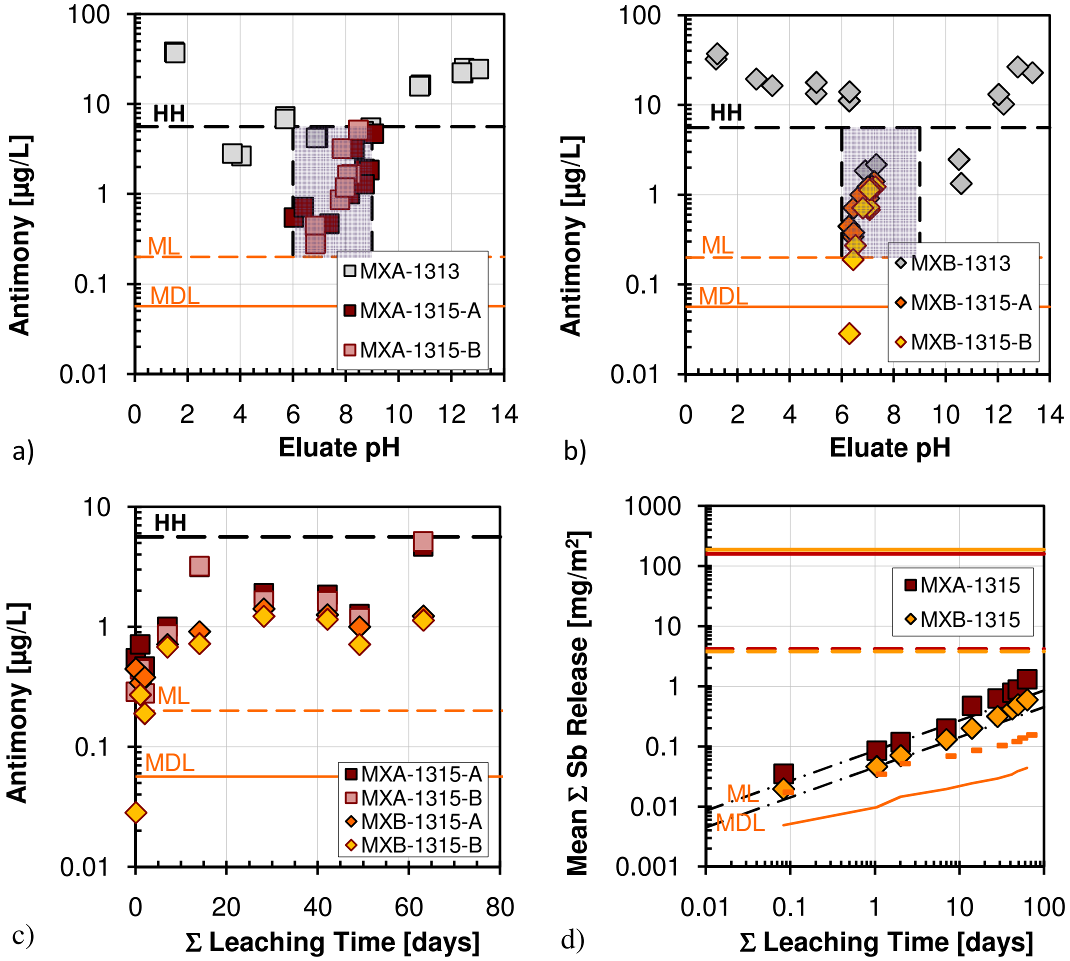

Figure A-18. Antimony Results for Mass Transport Tests on MXA and MXB
a) MXA data compared to Method 1313 LSP for MXA b) MXB data compared to Method 1313 LSP for MXB c) eluate concentrations, d) cumulative release.

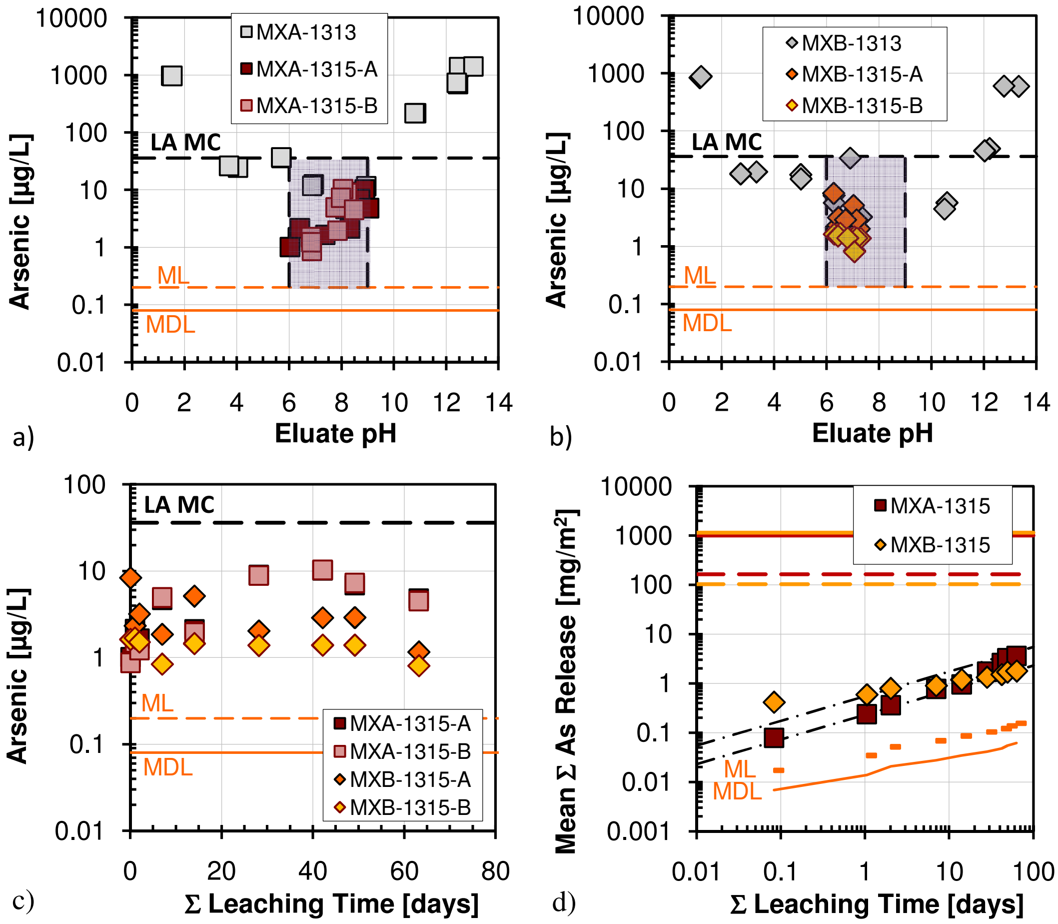

Figure A-19. Arsenic Results for Mass Transport Tests on MXA and MXB
a) MXA data compared to Method 1313 LSP for MXA b) MXB data compared to Method 1313 LSP for MXB c) eluate concentrations, d) cumulative release.

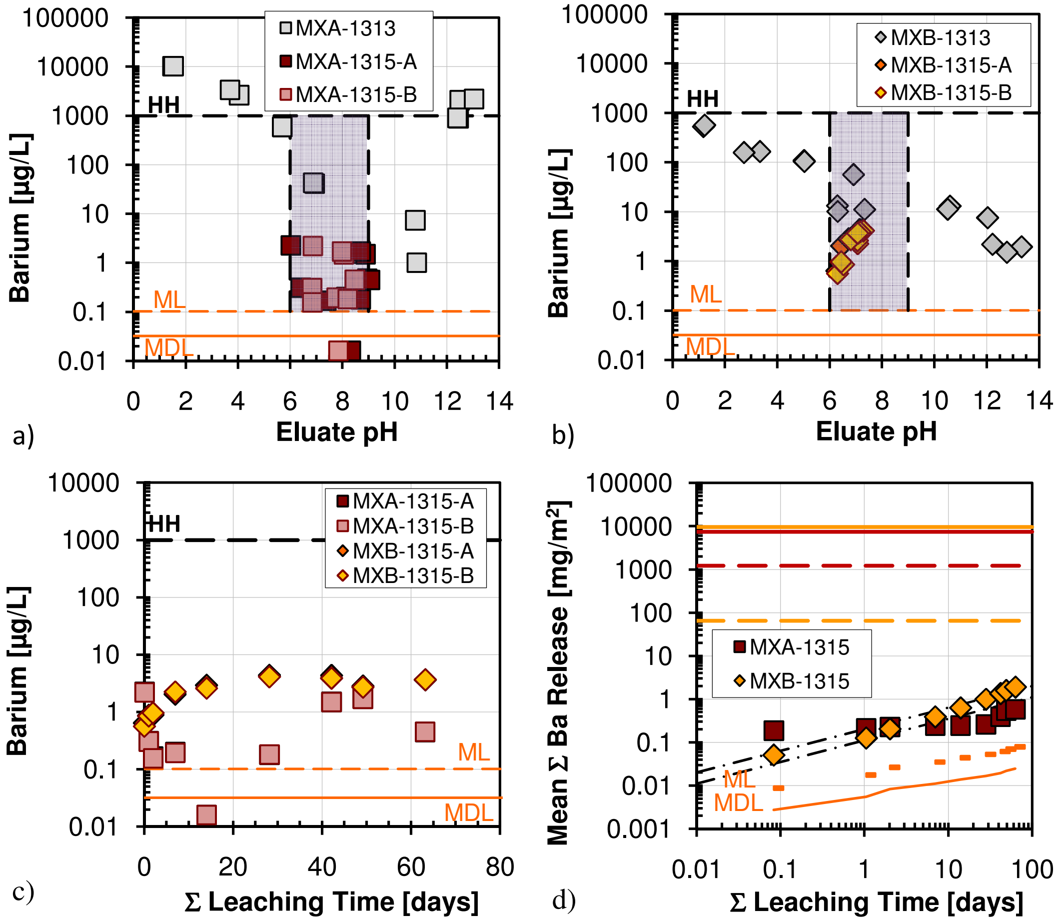

Figure A-20. Barium Results for Mass Transport Tests on MXA and MXB
a) MXA data compared to Method 1313 LSP for MXA b) MXB data compared to Method 1313 LSP for MXB c) eluate concentrations, d) cumulative release.

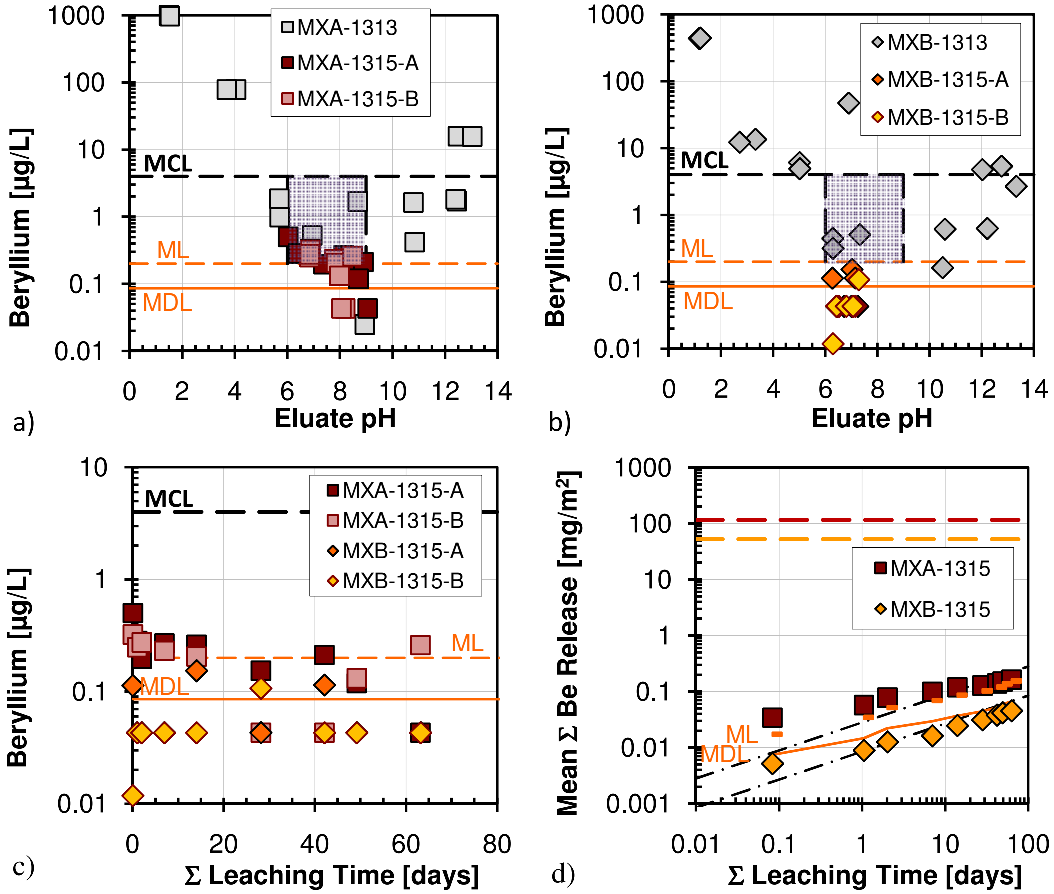

Figure A-21. Beryllium Results for Mass Transport Tests on MXA and MXB
a) MXA data compared to Method 1313 LSP for MXA b) MXB data compared to Method 1313 LSP for MXB c) eluate concentrations, d) cumulative release.

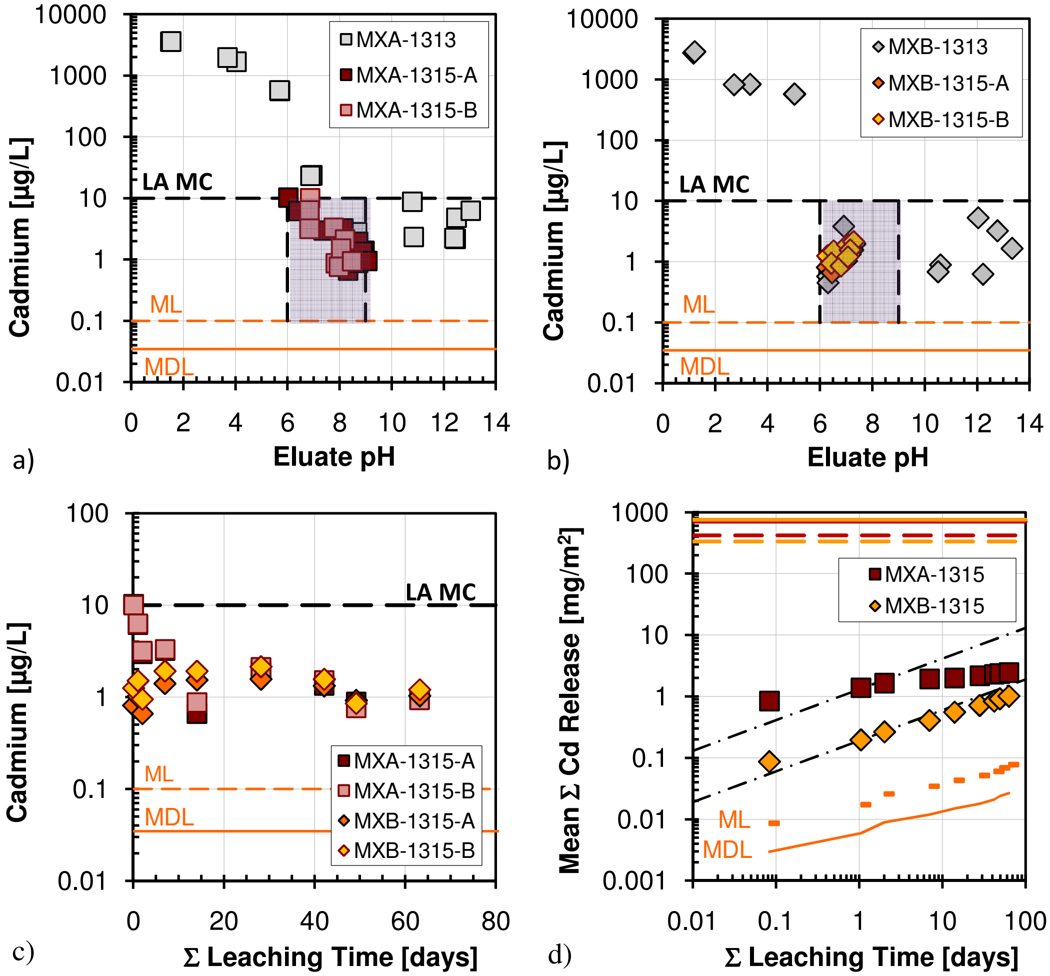

Figure A-22. Cadmium Results for Mass Transport Tests on MXA and MXB
a) MXA data compared to Method 1313 LSP for MXA b) MXB data compared to Method 1313 LSP for MXB c) eluate concentrations, d) cumulative release.

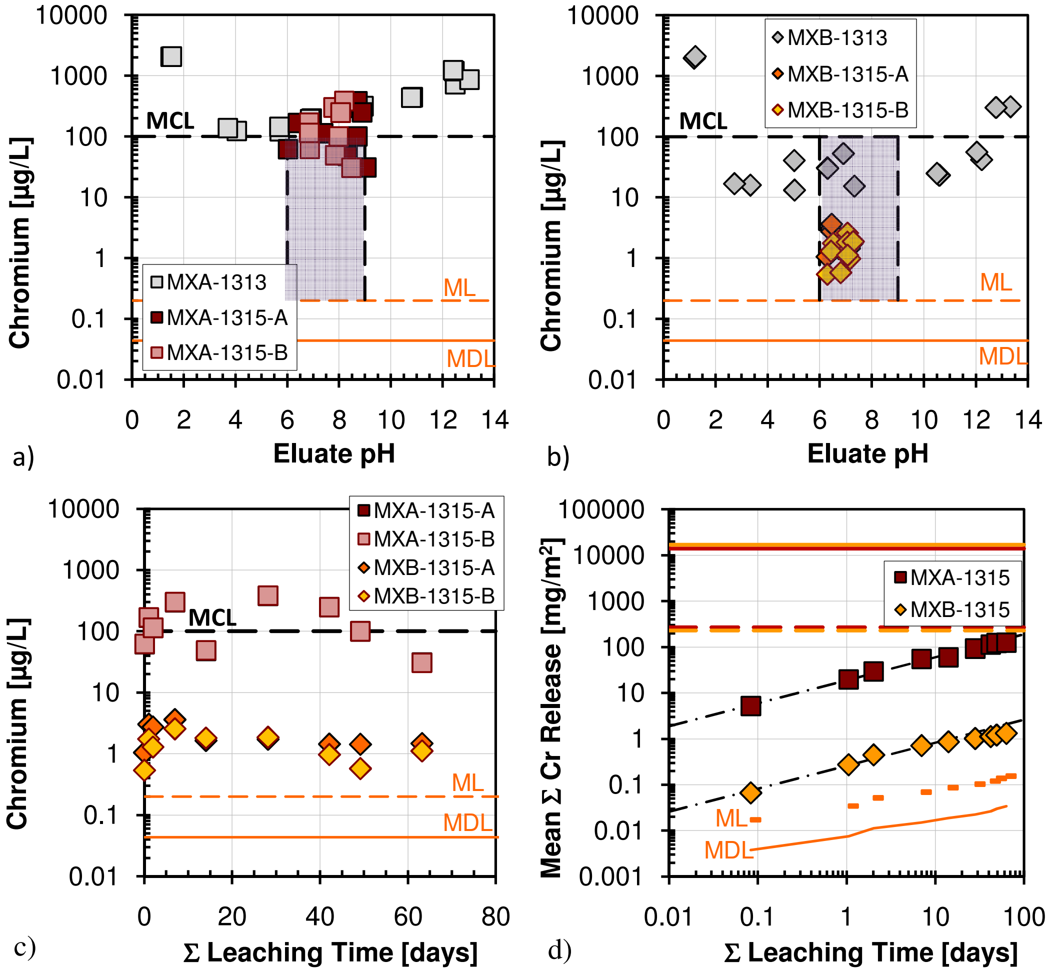

Figure A-23. Chromium Results for Mass Transport Tests on MXA and MXB
a) MXA data compared to Method 1313 LSP for MXA b) MXB data compared to Method 1313 LSP for MXB c) eluate concentrations, d) cumulative release.

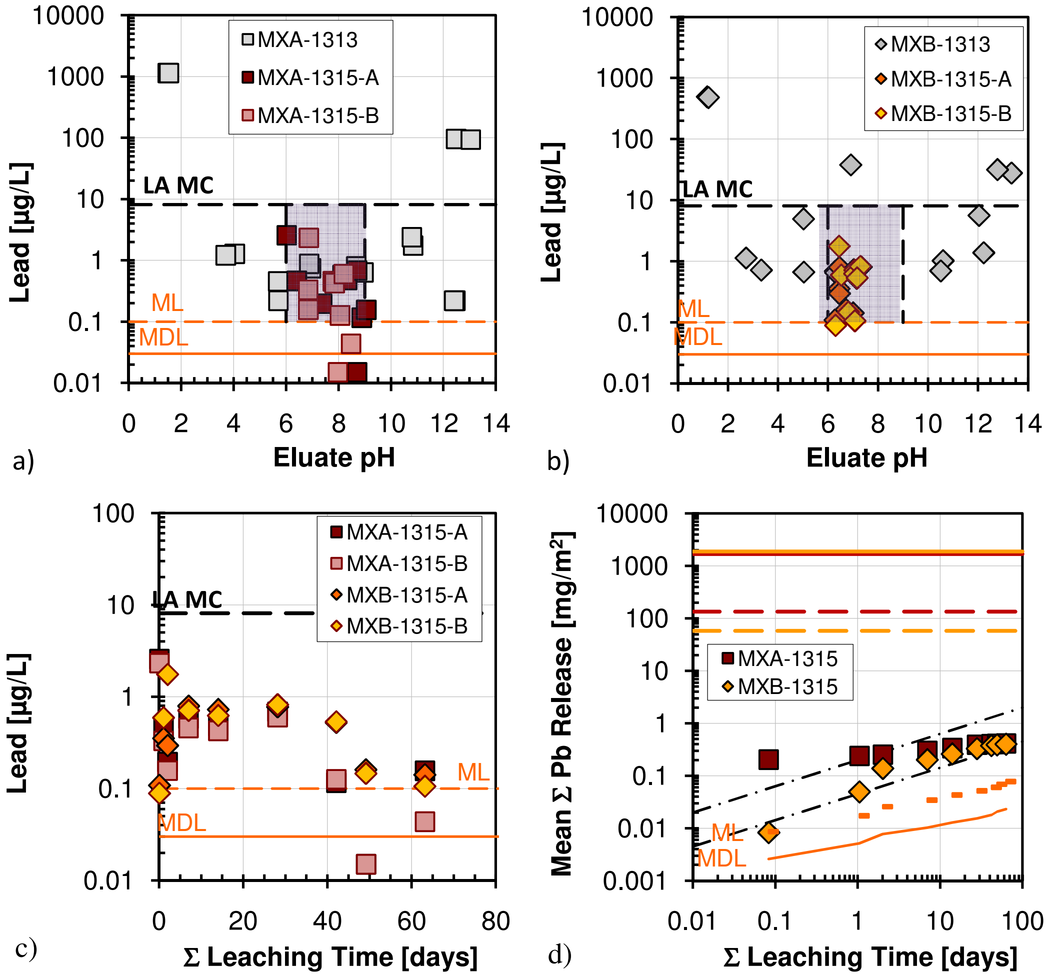

Figure A-24. Lead Results for Mass Transport Tests on MXA and MXB
a) MXA data compared to Method 1313 LSP for MXA b) MXB data compared to Method 1313 LSP for MXB c) eluate concentrations, d) cumulative release.

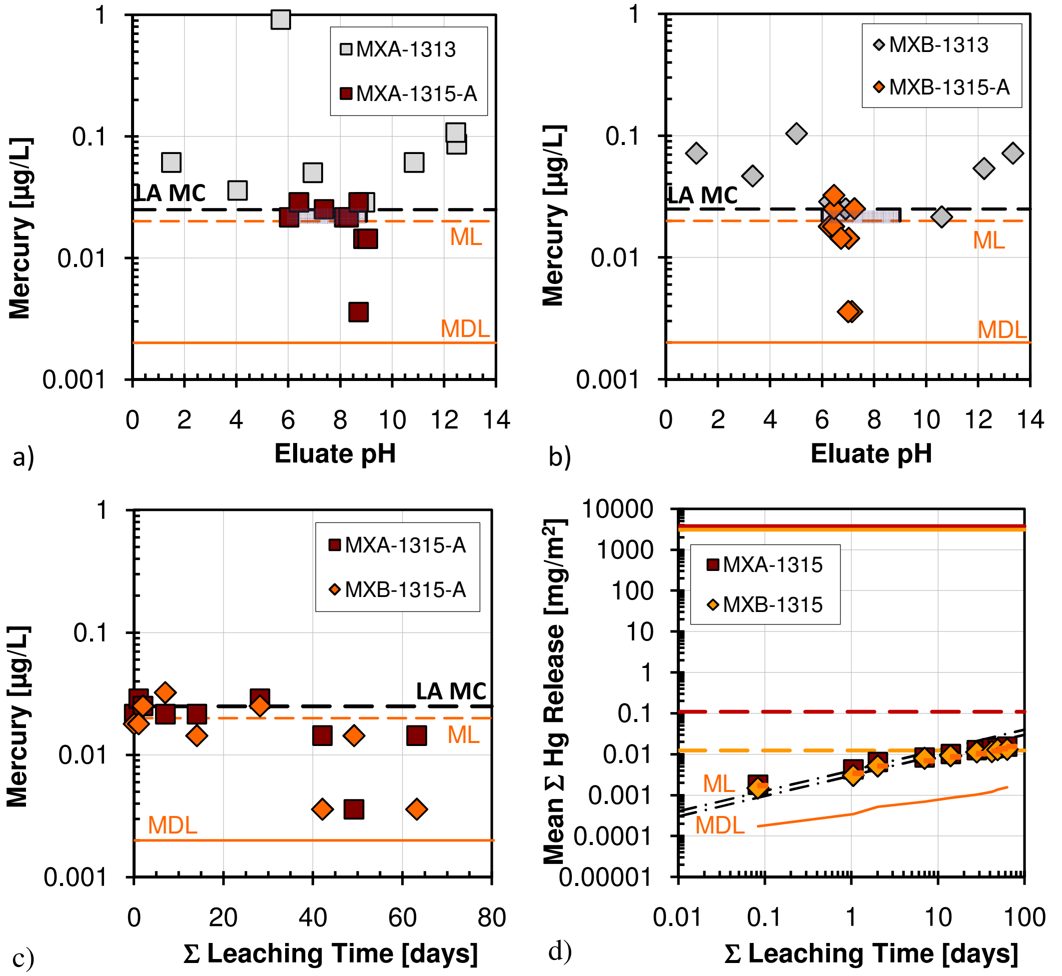

Figure A-25. Mercury Results for Mass Transport Tests on MXA and MXB
a) MXA data compared to Method 1313 LSP for MXA b) MXB data compared to Method 1313 LSP for MXB c) eluate concentrations, d) cumulative release.

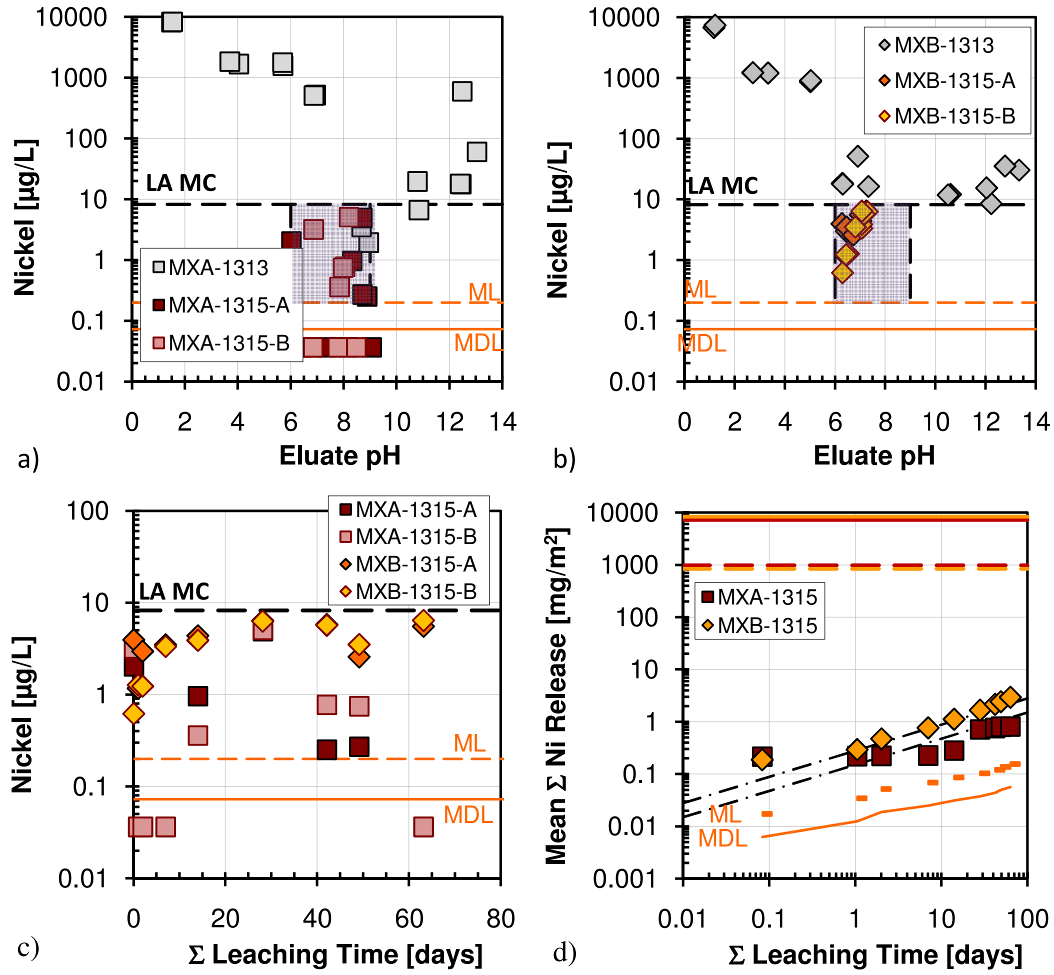

Figure A-26. Nickel Results for Mass Transport Tests on MXA and MXB
a) MXA data compared to Method 1313 LSP for MXA b) MXB data compared to Method 1313 LSP for MXB c) eluate concentrations, d) cumulative release.

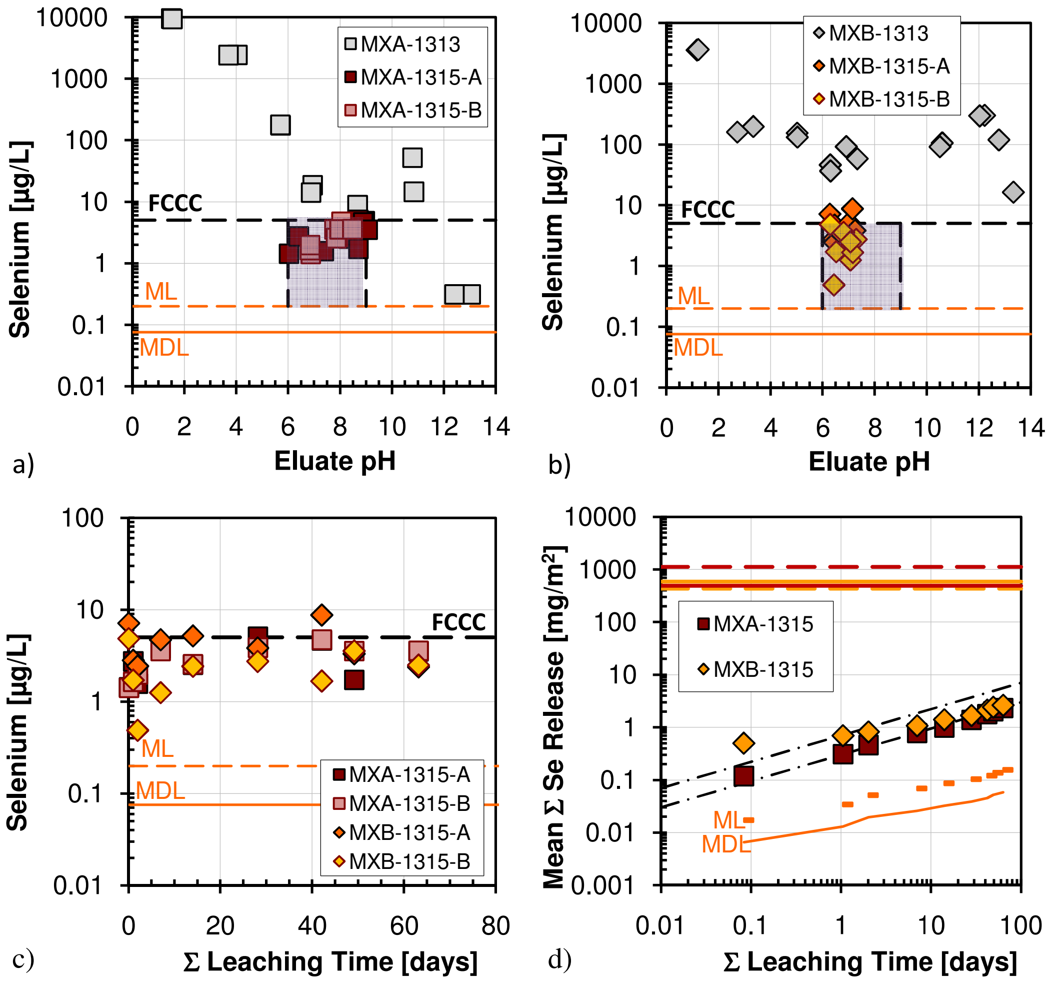

Figure A-27. Selenium Results for Mass Transport Tests on MXA and MXB
a) MXA data compared to Method 1313 LSP for MXA b) MXB data compared to Method 1313 LSP for MXB c) eluate concentrations, d) cumulative release.

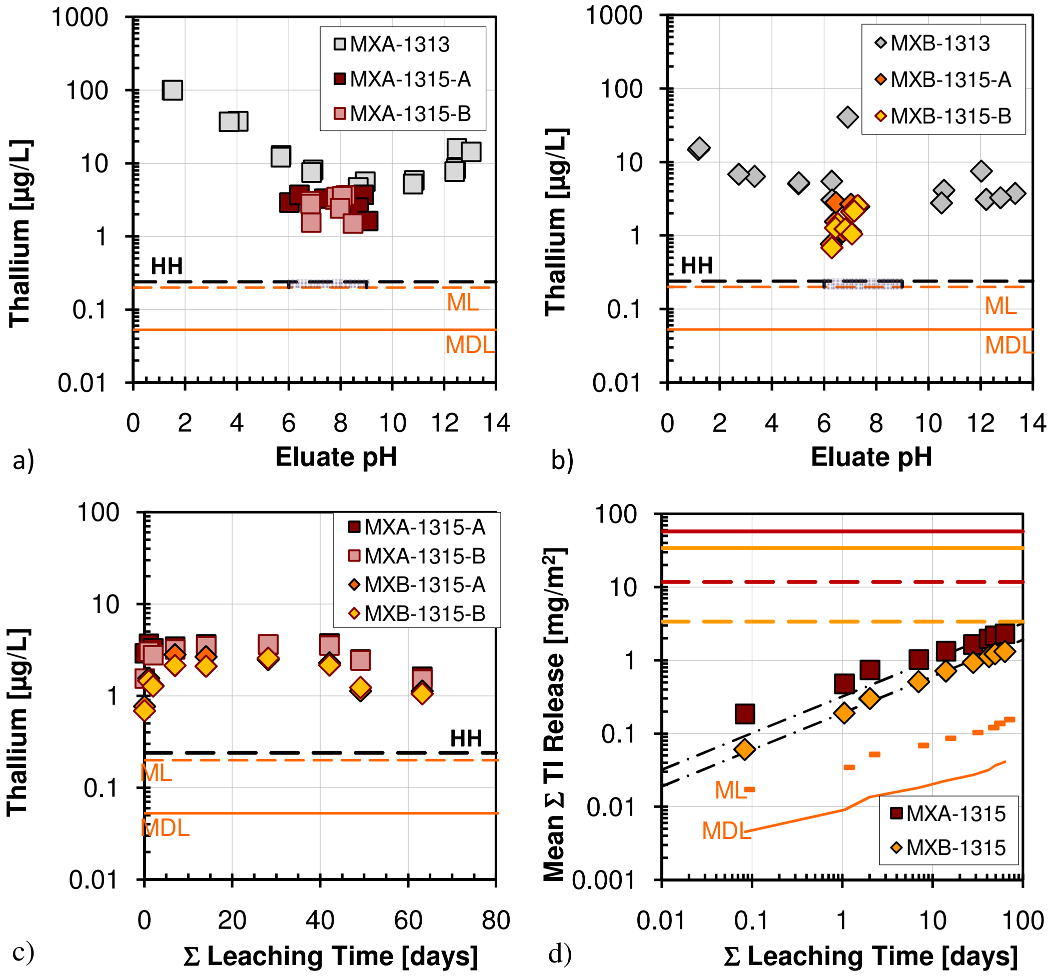

Figure A-28. Thallium Results for Mass Transport Tests on MXA and MXB
a) MXA data compared to Method 1313 LSP for MXA b) MXB data compared to Method 1313 LSP for MXB c) eluate concentrations, d) cumulative release.

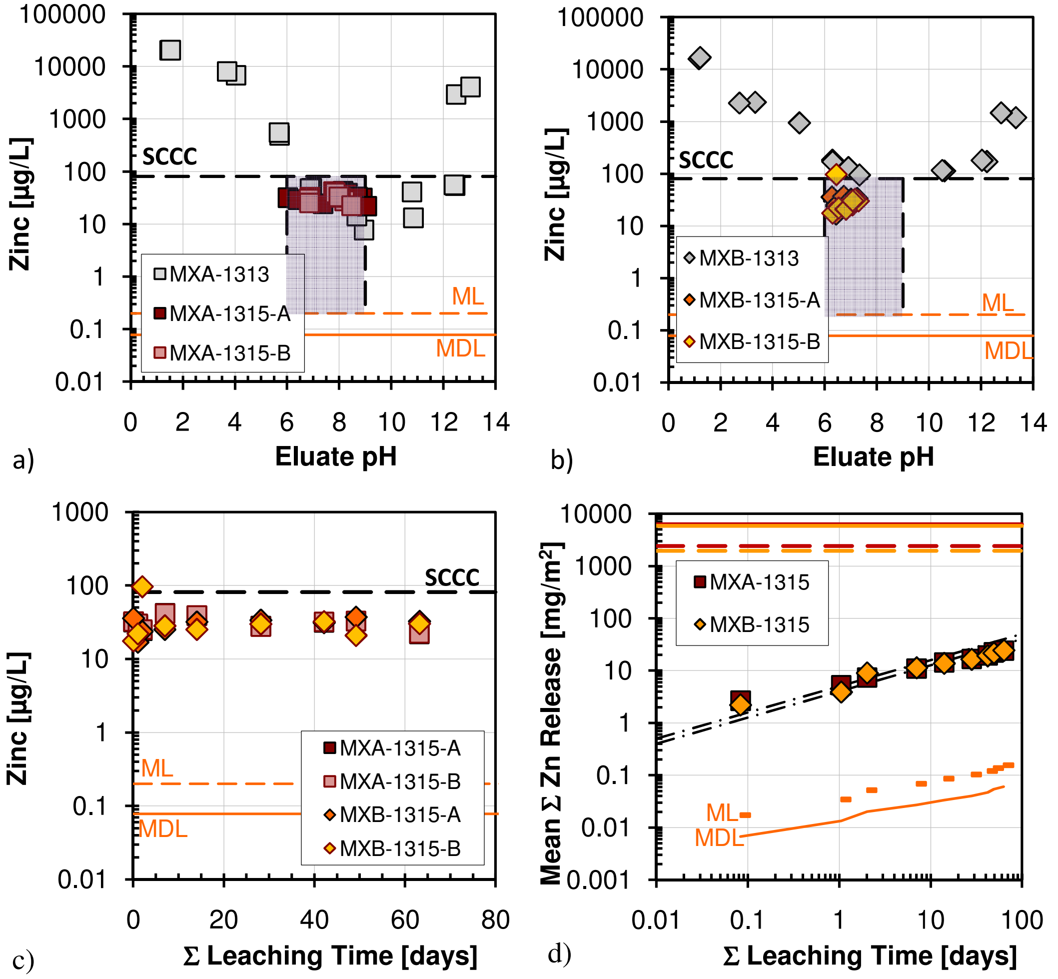

Figure A-29. Zinc Results for Mass Transport Tests on MXA and MXB
a) MXA data compared to Method 1313 LSP for MXA b) MXB data compared to Method 1313 LSP for MXB c) eluate concentrations, d) cumulative release.