

**REVIEW OF THE
PHYSICAL AND CHEMICAL ASPECTS OF
LEACHING ASSESSMENT**

Cementitious Barriers Partnership

November 2009

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FOREWORD

The Cementitious Barriers Partnership (CBP) Project is a multi-disciplinary, multi-institutional collaboration supported by the United States Department of Energy (US DOE) Office of Waste Processing. The objective of the CBP project is to develop a set of tools to improve understanding and prediction of the long-term structural, hydraulic, and chemical performance of cementitious barriers used in nuclear applications.

A multi-disciplinary partnership of federal, academic, private sector, and international expertise has been formed to accomplish the project objective. In addition to the US DOE, the CBP partners are the United States Nuclear Regulatory Commission (NRC), the National Institute of Standards and Technology (NIST), the Savannah River National Laboratory (SRNL), Vanderbilt University (VU) / Consortium for Risk Evaluation with Stakeholder Participation (CRESP), Energy Research Center of the Netherlands (ECN), and SIMCO Technologies, Inc.

The periods of cementitious performance being evaluated are >100 years for operating facilities and > 1000 years for waste management. The set of simulation tools and data developed under this project will be used to evaluate and predict the behavior of cementitious barriers used in near-surface engineered waste disposal systems, e.g., waste forms, containment structures, entombments, and environmental remediation, including decontamination and decommissioning (D&D) activities. The simulation tools also will support analysis of structural concrete components

of nuclear facilities (spent-fuel pools, dry spent-fuel storage units, and recycling facilities such as fuel fabrication, separations processes). Simulation parameters will be obtained from prior literature and will be experimentally measured under this project, as necessary, to demonstrate application of the simulation tools for three prototype applications (waste form in concrete vault, high-level waste tank grouting, and spent-fuel pool). Test methods and data needs to support use of the simulation tools for future applications will be defined.

The CBP project is a five-year effort focused on reducing the uncertainties of current methodologies for assessing cementitious barrier performance and increasing the consistency and transparency of the assessment process. The results of this project will enable improved risk-informed, performance-based decision-making and support several of the strategic initiatives in the DOE Office of Environmental Management Engineering & Technology Roadmap. Those strategic initiatives include 1) enhanced tank closure processes; 2) enhanced stabilization technologies; 3) advanced predictive capabilities; 4) enhanced remediation methods; 5) adapted technologies for site-specific and complex-wide D&D applications; 6) improved SNF storage, stabilization and disposal preparation; 7) enhanced storage, monitoring and stabilization systems; and 8) enhanced long-term performance evaluation and monitoring.

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LIST OF ACRONYMS AND ABBREVIATIONS

ACRi	Analytic & Computational Research, Inc.
ANS	American Nuclear Society
ASTM	ASTM International (formerly American Society for Testing and Materials)
BDAT	Best Demonstrated Available Treatment
CEN	European Committee on Standardization
CBP	Cementitious Barriers Partnership
CSF	Chemical Speciation Fingerprint
DOC	Dissolved Organic Carbon
EXAFS	Extended X-ray Absorption Fine Structure
FA	Fulvic Acid
GTLM	Generalized Two Layer Model
HA	Humic Acid
HAO	Hydrous Aluminum Oxides
HFO	Hydrous Ferric Oxides
HMO	Hydrous Manganese Oxides
HY	Hydrophilic content of organic matter
IHSS	International Humic Substances Society
ISO	International Organization for Standardization
LS	Liquid to Solid ratio [L/kg]
NICA	Non-Ideal Competitive Adsorption
ORCHESTRA	Objects Representing CHEmical Speciation and TRANsport model
PA	Performance Assessment
POM	Particulate Organic Matter
PZC	Point of Zero Charge
RCRA	Resource Conservation and Recovery Act
SEM	Scanning Electron Microscopy
SRS	Savannah River Site
TCLP	Toxicity Characteristic Leaching Procedure (EPA Method 1311)
XANES	X-ray Absorption Near-Edge Structure
XRD	X-Ray Diffraction
USDOE	US Department of Energy
USEPA	United States Environmental Protection Agency
USNRC	US Nuclear Regulatory Commission

LIST OF NOMENCLATURE

Roman Variables

a_{aw}	specific surface area of immiscible fluid (air-water) from interface tracer experiments [m^2/cm^3]
$a_{aw,o}$	specific surface area of immiscible fluid (air-water) in an idealized capillary bundle [m^2/cm^3]
C_i	concentration of species i in a material [mg/m^3]
c_i	concentration of species i in the liquid phase [mg/L] or [Bq/L]
D	generalized representation of the diffusion (dispersion) coefficient [m^2/s]
D^{app}	apparent, or observed, diffusion coefficient (diffusivity) [m^2/s]
D^{eff}	effective diffusion coefficient (diffusivity) in a porous media [m^2/s]
D^{mol}	molecular diffusion coefficient (diffusivity) [m^2/s]
D^{int}	intrinsic diffusion coefficient (diffusivity) in a porous media [m^2/s]
D_w	water diffusivity [m^2/s]
F	Faraday constant (96,485 C/mol)
J_i	mass flux of a diffusing species i [$\text{mg}/\text{m}^3 \text{ s}$]
J_i^{diff}	diffusional mass flux of a diffusing species i [$\text{mol}/\text{m}^3 \text{ s}$]
J_i^{elec}	electrical mass flux of a diffusing species i [$\text{mol}/\text{m}^3 \text{ s}$]
\tilde{K}_i	NICA-Donnan median value of the affinity distribution for species i [L/kg]
K_d	linear partition coefficient [L/kg]
\dot{m}_i	source rate term of species i [$\text{mol}/\text{m}^3 \text{ s}$]
N	total number of ionic species [-]
n_i	NICA-Donnan exponent reflecting overall non-ideality of the proton adsorption reaction [-]
n_H	NICC-Donnan parameter of representing the overall non-ideality of the adsorption process [-]
p	NICA-Donnan width of the affinity distribution [-]
R	ideal gas constant (9.841 J/mol K)
$R\langle C_i \rangle$	production rate (sink or source) of species i [$\text{mg}/\text{m}^3 \text{ s}$]
Q_i	NICA-Donnan amount of species i bound to organic matter [mol/kg]

LIST OF NOMENCLATURE (contd)

Roman Variables (contd)

Q_{\max}	NICA-Donnan maximum amount of the species that can be bound to organic matter [mol/kg]
S	specific surface area of the material from gas adsorption experiments [m^2/cm^3]
S_o	calculated surface area of an idealized capillary bundle [m^2/cm^3]
s_i	concentration of species i in the solid phase [mg/kg] or [Bq/kg]
T	temperature [K]
t	time [s]
v	bulk velocity of the liquid or gas phase [m/s]
w	fixed charge density [mol/m^3]
x	1-dimensional spatial variable [m]
z_i	valance state of species i [-]

Greek Variables

γ_i	activity coefficient of species i [-]
δ	constrictivity of the pore network [-]
ε	dielectric constant of the media [C/V m]
θ	water content in the matrix [$\text{m}^3_{\text{water}}/\text{m}^3_{\text{material}}$]
ϕ	total porosity [$\text{m}^3_{\text{pore}}/\text{m}^3$]
ϕ_d	“diffusion through” porosity [$\text{m}^3_{\text{pore}}/\text{m}^3$]
ρ_s	density of the bulk solid phase [$\text{kg}/\text{m}^3_{\text{solid}}$]
τ, τ'	tortuosity based on ratio of diffusional path to straight line path [$\text{m}_{\text{pore}}/\text{m}$]
τ_{sat}^a	tortuosity of a saturated matrix based on ratio of interfacial surface area to idealized capillary bundle [-]
τ_{unsat}^a	tortuosity of an unsaturated matrix based on ratio of interfacial surface area to idealized capillary bundle [-]
ψ	electrodiffusion potential [V]

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ABSTRACT

The objective of this chapter is to provide a summary of the latest developments in leaching from cementitious barrier materials consisting of different concrete formulations and cement stabilized waste forms. The chemical retention of substances in the matrix, which is controlled physically by material hydraulic and diffusion properties and chemically by precipitation/dissolution processes, sorption processes onto iron oxides and organic matter, incorporation in solid solutions and interactions with clay, is addressed. The influence of external factors such as oxidation and carbonation on constituent release can be very important because large pH and redox gradients may exist initially, but the chemistry within and surrounding the matrix will change with time and consequently different release behaviors may occur at over different time intervals. In addition, physical stresses may occur that change the physical and hydraulic properties of the material (this aspect is addressed in other report chapters). From a leaching perspective, the release controlling phases are not necessarily the primary matrix minerals, but also may be phases only present in very minor quantities. An integrated set of tools for testing and evaluation of release is presented, which lend themselves for chemical speciation modeling and subsequent chemical reaction transport modeling. The important role of field verification in lysimeters and test bed studies is stressed and experiences in nuclear waste management are identified.

1.0 INTRODUCTION

One focus of the Cementitious Barriers Partnership (CBP) is to advance the general understanding and prediction of the long-term physical, hydraulic and chemical performance of cementitious materials used for nuclear applications. Since these barriers are designed and implemented to retard the release of

waste materials into the environment, knowledge of the processes and phenomena that control the release of constituents from cementitious barriers and the evolution of the influential properties of cementitious materials and related systems over time and space is central to CBP mission. Thus, this chapter focuses on the mass exchanges that occur across interfaces between the cementitious barrier and surrounding media

and the effect of such exchanges on the ability of the cementitious barrier to retain species of interest.

The Encyclopedia of Science and Technology¹ describes “leaching” as the removal of a soluble fraction, in the form of a solution, from an insoluble permeable solid with which it is associated. In this sense, leaching is a macroscopic process bounding by the mass of a substance passing boundaries of the permeable solid in question. In performance assessments (PAs) developed for the US Department of Energy (USDOE) and US Nuclear Regulatory Commission (USNRC), leaching of radionuclides from a source material through the environment is the primary mechanism that defines doses to a potential receptor. Often descriptions of leaching are based on simple diffusion models with constant diffusivity and source terms. However, within the pore structure of cementitious materials, leaching is a complex coupling of mass transport mechanisms through a tortuous pore system and a wide range of chemical reactions which help to retain constituents within the matrix.

The constituents in cementitious materials, in general, can be categorized by the relative concentration of the element or species present in the bulk solid and the element’s characteristic chemical behavior. For this conceptual model, the constituents of interest are grouped as follows:

- Primary matrix constituents
 - » cations (e.g., calcium, aluminum, silicon, iron)
 - » anions (e.g., sulfate, carbonate, hydroxide)
- Minor constituents at concentrations where mineral precipitation is possible
 - » cations with pH-dependent solution behavior (e.g., manganese, chromium III, barium)
 - » cations with minimal dependence on solution pH (e.g., sodium, potassium),

- » anions with pH-dependent solution behavior (e.g., arsenate, chromate)
- » anions with minimal dependence on solution pH (e.g., chloride)
- Trace constituents at concentrations below the point where mineral precipitation is likely
 - » most radionuclides
 - » trace ionic constituents (e.g., cadmium, mercury)

Leaching from a porous material is an integrated process of mass transport due to gradients in concentration, chemical potential or pressures, combined with all chemical interactions between the solid phase and the pore solution. The release from the solid into the pore water, at every point in time and space, is controlled by a complex set of interactions which include:

- dissolution-precipitation,
- adsorption-desorption,
- cation exchange,
- incorporation into solid solutions, and
- complexation within the aqueous phase.

The mutual interaction between material constituents deposited into precipitates, engaged in competitive sorption to surfaces, or incorporated in solid solutions, implies that individual elements or radionuclides cannot be considered without taking the chemical context dictated by major and minor elements into account. Thus, chemical form of the species (i.e., speciation) determines the ability of the cementitious barrier to retain trace constituents and dictates the compositions of the pore water and gas phases, which are the two phases through which mass transfer results in release.

¹ <http://www.accessscience.com/topic.aspx?searchStr=leaching&term=Leaching>

1.1 Conceptual Model of Cementitious Barrier in the Environment

The following conceptual model of a cementitious barrier material in a generic placement scenario is used for illustrative purposes in subsequent discussions.

1.1.1 Barrier Material – Scenario Description

Fundamentally, cementitious barriers are porous solids consisting of a complex mixture of crystalline and gel-like phases with an interstitial pore solution that is in chemical equilibrium with the solid phase. The relative amounts of the different solid phases that form as a result of hydration reactions are dependent on the components of the “dry blend” or binder, the water/binder ratio, and admixtures included to facilitate placement or handling of the product. If the intent of the cementitious material is to immobilize or retard the release of constituents of concern contained in a waste stream, the composition of the waste also may influence the solid phases of the final wasteform. The physical properties of the matrix (e.g., porosity, permeability, conductivity, etc) will be dependent on both the solid phase composition and on the amount of coarse and/or fine aggregate typically added to the process to increase strength and durability.

Over a given period of performance, a cementitious monolith may be contacted by one or more forms of surrounding media where water, dissolved constituents, and/or gases including water vapor and air (i.e., nitrogen, oxygen, carbon dioxide) are transported between materials. The physical-chemical nature of the materials surrounding the cementitious barrier will depend on the design of the engineered system, but may include an open atmosphere (e.g., air contacting above-ground vaults), soil or granular fill (e.g., unsaturated or water-saturated compacted fill around buried structures), steel (e.g., tank liners), or contained liquids (e.g., for unlined spent fuel pools).

In these scenarios, the cementitious monolith may be structural concrete, grout or a waste form, any of which may have some degree of initial cracking. Figure 1 is a conceptual illustration of release processes, influential physical and chemical factors, and interfacial phenomena that may exist upon placement of a cementitious barrier into the environment.

1.1.2 Water Contact Mode and Moisture Transport

By definition, leaching occurs when the cementitious matrix is in contact with a continuous liquid phase and aqueous constituents are transported across the material interface. Although significant cracking may exist as a result of curing phenomena (e.g., autogenous shrinkage), the initial cementitious barrier is assumed to have lower permeability than the surrounding material, such that the majority of infiltrating or groundwater will flow around the matrix. Over time, physical loads, water-borne chemical reactions (e.g., sulfate ingress and subsequent ettringite precipitation) and thermal gradients imposed on the cementitious monolith may induce physical stresses and the monolith may deteriorate through a series of states from (a) an intact monolith, to (b) a stressed matrix to (c) a spalled matrix (Figure 2). The rate and extent of the physical degradation is material- and scenario-specific, primarily controlled by the stresses induced in the system and the strength of the material. The changes in the physical state of the cementitious monolith will significantly affect the surface area exposed to the environment, mode of water contact (e.g., flow-around or percolation through), and the rate and extent of water and/or gas exchange between the monolith and its surroundings.

The permeability or hydraulic conductivity of the cementitious barrier increases with the degree of degradation, resulting in a larger fraction of water flowing or percolating through the material. If the hydraulic conductivity of the material is low or approximately 1/100 that of the surrounding material,

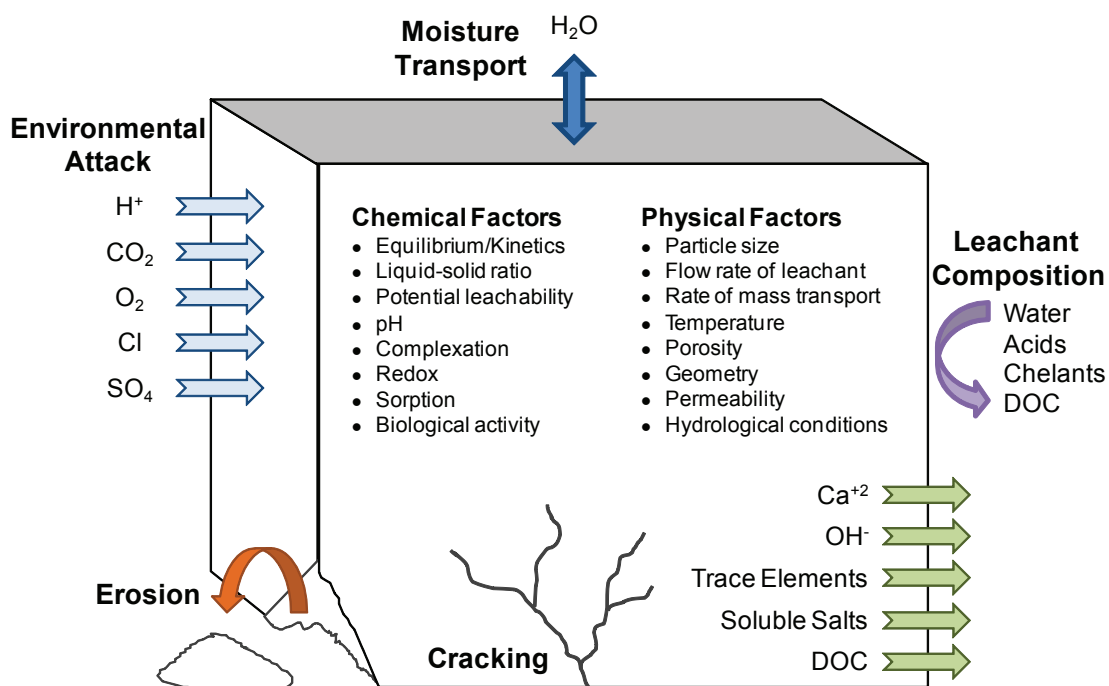


Figure 1. Internal Factors and External Phenomena That Influence the Leaching Process in Cementitious Materials

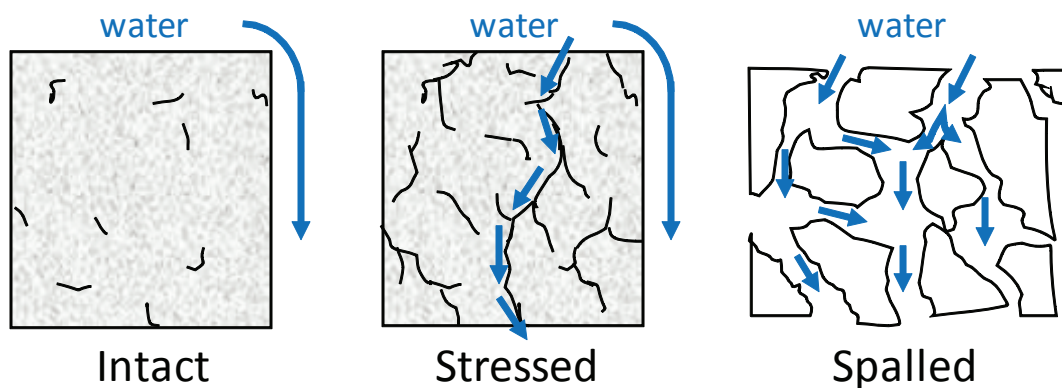


Figure 2. Conceptual Physical Degradation States of Cementitious Material

infiltration due to percolation events or groundwater will preferentially flow around the cementitious mass. However, when the hydraulic conductivity is sufficiently high (e.g., $>10^{-8}$ m/s) and on the same order of

magnitude or greater than that of the adjacent material, water will percolate through the cementitious mass. The same guidelines hold for localized percolation through regions of the cementitious material

(e.g., through continuous cracks or degraded zones). At low permeability, water will be stagnant or move driven by capillary effects in response to gradients in matrix potential (i.e., capillary suction) created by changes in external saturation or evaporation and condensation processes. In low- or no-flow regimes, diffusion will dominate mass transfer and release; while in localized high flow regions around a crack, diffusion may be the release rate limiting step in the diffusion-convection process.

In the absence of large air-voids, the pore of structure cementitious materials may be considered initially saturated if sufficient water is present during curing. Saturation of the cementitious material with water (i.e., extent of pore-filling with water) can vary spatially and temporally. Relative saturation, defined as the fraction of the total pore volume filled with water, is a continuous function taking values between 0 and 1 for completely dry and fully saturated materials, respectively. The following saturation states are important relative to overall diffusive moisture transport through the liquid and vapor phases.

- **Full Saturation** - no gas phase present; evaporation from the surface induces liquid movement within the material
- **Capillary Saturation** - gas phase becomes continuous; diffusion of water vapor starts to influence overall rate of water transport
- **Insular Saturation** - liquid phase becomes discontinuous; vapor phase diffusion dominates transport process
- **Completely Dry** - theoretical construct, typically not obtained in natural systems, where all moisture transport stops.

Drying or moisture transport may occur if:

- the surrounding media is unsaturated with a capillary suction greater than that expressed by the cementitious material,
- the surrounding media is unsaturated and the

adjacent air or pore gas is at less than 100 % relative humidity,

- hydration reactions of the cementitious material and/or phases such as hydrated salts causes self-desiccation.

Ingress of water can occur by:

- capillary suction,
- percolation through interconnected pores and cracks,
- condensation in response to temperature and external relative humidity changes, or
- chemical reactions which generate water.

Although frequently neglected in environmental assessments, significant water exchange by a combination of capillary uptake, vapor migration and condensation has been documented at low-level nuclear waste vaults in Spain (Zuloaga, Andrade & Castellote 2009). As the level and extent of damage to the matrix increases, then water exchange by percolation will increase because of increased hydraulic conductivity if sufficient water is present in the immediate surroundings.

Bulk gas exchange with the monolith will occur in response to:

- changes in barometric pressure (i.e., barometric pumping), or
- displacement during capillary imbibition of water, or
- temperature changes.

1.1.3 Ionic Transport

Leaching, or constituent release as ionic species dissolved in the aqueous phase, occurs in response to gradients in chemical activity between the pore water solution and the external boundary. The release of constituents from a porous matrix results from dissolution of the solid phase into the pore solution,

coupled with mass transport with the pore system (1) by gradients between the interior of the cementitious material and the surroundings (diffusion-controlled release), and/or (2) by convection of the pore water through the solid material by capillary suction or percolation.

In actuality, the impact of leaching on environmental assessment is the net result of a complex combination of water movement within and around a porous solid material and the chemical conditions that occur locally within the material pores and at the external boundary. These chemical conditions are spatially variable and dynamic, changing in response to ingress and release of chemical species and their redistribution between solid and liquid phases in response to precipitation-dissolution, adsorption-desorption, ion-exchange and solution complexation reactions.

1.1.4 Internal Factors

There are several chemical and physical factors that affect the measured rate of leaching from porous materials. Chemical factors primarily influence the concentrations of species in the pore solution, whereas physical factors control the mode of water contact and the rate of mass transport through a pore to the environment.

For inorganic constituents, the master chemical variable is local pH in that many of the solid-liquid partitioning reactions are controlled or influenced by changes in pH. The high pH of cementitious materials is primarily responsible for stabilization of species through formation of solid phases (e.g., precipitates or solid solutions) and for cation binding to negative surface charge on metal oxide surfaces. High pH is indirectly a factor in increasing both inorganic and organic species leaching through mobilization of dissolved organic carbon which may complex with porewater components and increase leachable concentrations.

Permeability of the solid material may be the master physical factor that dictates the mode of water contact and the rate controlling mechanisms of mass transport. Infiltrating water is likely to percolate through highly permeable materials and flow around low permeability fills. In the former case, solid-liquid partitioning will dominate the rate of release while mass transport processes (e.g., diffusion, convection) will control the rate of release in the latter case.

1.1.5 External Stresses

Since the leaching matrix is in direct contact with surrounding materials in the placement scenario, a cementitious material is susceptible to exchange of liquid and gases across the matrix boundary. For example, an initially water saturated material (e.g., as the result of complete hydration during curing) will tend to lose water. If the water loss is significant, gases from subsurface soils or materials can diffuse into the matrix and react with the pore solutions (e.g., carbonation, oxidation). The cementitious material may be contacted with pore solution that is “acidic” or demineralized relative to the pore solution; both of which aggressively influence the durability of the cementitious barrier and the leaching of major and trace constituents. Therefore, examination of interfaces between the environment and the cementitious barrier material and the alteration of leaching mechanisms due to potential boundary reactions become as important as the study of leaching rates from the material under controlled conditions.

1.2 Overview of Leaching Assessment Approaches

A critical aspect of the assessment methodology for environmental performance of cementitious materials is the approach for characterizing leaching rates and interactions at material interfaces. Under current US environmental policy, management and disposal of hazardous and radioactive wastes/waste forms is regulated by local, state and federal agencies.

Assessment methodologies and acceptance criteria for leachability from these materials historically has been based, in part, on screening procedures promulgated by the United States Environmental Protection Agency (USEPA) for hazardous waste classification or stipulated through the USNRC for nuclear waste disposal. Research in Europe and the US provides an integrated leaching assessment framework (Kosson et al. 2002) into the current regulatory context.

This chapter presents conceptual models describing the interdependency between processes, material characteristics and constituent release, constitutive relationships for relevant leaching and chemical retention processes, experimental approaches to determining material-specific leaching characteristics, and integration of experimental data with modeling and simulation. These phenomena will be placed in context of the leaching behavior of typical cementitious matrices as well as identification of knowledge gaps and opportunities for advancement of the current understanding.

2.0 MECHANISMS AND PROPERTIES

Migration of constituents through porous solid media can take place via a combination of several mechanisms; molecular diffusion in the water phase, diffusion in the gas phase, and/or convection of dissolved ions in flowing fluid phases. The generalized mass transport of a species in a porous media can be described using the convection-diffusion-reaction equation:

$$\frac{\partial C_i}{\partial t} = \nabla(D\nabla C_i) - v\nabla C_i + R\langle C_i \rangle \quad (1)$$

where: C_i is the concentration of the species i in a unit volume of liquid [$\text{mg}/\text{m}^3\text{liquid}$], t is time [s], D is the diffusion (dispersion) coefficient [m^2/s], v is the bulk velocity of the liquid or gas phase [m/s], and $R\langle C_i \rangle$ is

the production rate for the species [$\text{mg}/\text{m}^3\text{s}$], typically considered a function of the concentration of the transporting species.

The overall rate of mass transfer and the relative importance of the terms in Eq. (1) are determined by a combination of chemical and physical processes and properties. The following is a brief review of physical properties and processes relevant to leaching from cementitious materials.

2.1 Mass Transport Mechanisms

Leaching from cementitious materials is often considered to be a diffusion-based process where the flux of a species is directly proportional to a gradient in concentration. However, the leaching process in natural systems is influenced not only by concentration gradients but by convection and chemical reaction processes. Chemical processes play an especially important role in the degradation of cement matrices which, in turn, affects the rate of leaching. A well-balanced review of the theoretical and numerical representation of cementitious material based on mass transport and degradation reactions is presented by Glasser, Marchand, & Samson (Glasser, Marchand & Samson 2008).

2.1.1 Convection

When the hydraulic conductivity of the cementitious material is high enough to allow a significant pressure-driven flow of water through the material, dissolved species in the pore solution are carried along with flowing water by a process called convection. Convective transport is not likely to be a significant mechanism for mass transport in intact cementitious material; however, convection will play a role in mass transport when considerable physical damage (e.g., cracking) and disintegration convection are evident. Mechanisms and modeling of convective transport are discussed in the chapter on mass transport processes.

2.1.1.1 Osmotic Pressure

One important issue poorly defined in the literature is the effect of osmotic pressures which may build up in the pore fluid of cement-stabilized matrices with high salt loadings, possibly leading to expansion of the system (Bénard et al. 2008). Osmotic pressure will only be important in systems where there is no free movement of ions possible, as in cases of a semi-permeable membrane with solutions of different salt concentrations on both sides. Rowe et al. (2004) related the movement of water as a result of the osmotic countercurrent due to double layer repulsion in microporous, reactive materials (e.g., clays). To what extent small pores in concrete act as a “membrane” is not clear; however, if osmotic effects are possible, the maximum pressures may be derived from the estimated salt concentrations in the pore solutions.

2.1.2 Diffusion

Molecular diffusion is the autonomous process by which dissolved ions migrate from high to lower concentrations in order to relax existing concentration gradients. Over short distances (e.g., mm to cm scales), the diffusion process dominates mass transport, but becomes increasingly less significant over larger distances. In cracked matrices, liquid phase diffusion can play a role in migration of substances from intact regions towards the crack surface where bulk flow dominates the rate of mass transport. In this way, diffusion can be the rate limiting factor for species that can be transported over longer distances by convection.

Molecular diffusion occurs because of gradients in chemical potential developed within the material relative due to internal heterogeneity or between the material and surrounding media due to external conditions. In turn, chemical potential is related to porewater concentrations through the ionic strength of the pore solution (e.g., through the Debye-Hückel

or Davies equation). Thus, high concentrations within the material relative to those at the boundary or interface cause diffusion out (leaching or release), while higher external concentrations than within the material cause diffusion into the material (ingress).

2.1.2.1 Diffusion Coefficients

In aqueous, non-porous system without bulk phase movement, the one-dimensional (1-D) mass flux of a dissolved species often is described by Fick's first law:

$$J = -D^{mol} \frac{\partial C}{\partial x} \quad (2)$$

where: J is the flux of the diffusing species [$\text{mg}/\text{m}^3 \text{ s}$], $\partial C/\partial x$ is the 1-D gradient of the species [$\text{mg}/\text{m}^3 \text{ m}$], and D^{mol} is the proportionality constant known as the molecular diffusivity or molecular diffusion coefficient [m^2/s].

Molecular diffusivity is a property of the diffusing species and temperature with no consideration for the physical or chemical effects. Values of the molecular diffusion coefficient for a wide variety of species fall typically within a relatively narrow range of $(1-4) \times 10^{-9} \text{ m}^2/\text{s}$ at 25°C (Robinson & Stokes 1959). These diffusion coefficients are determined at infinite dilution and tabulated in the literature (ACG).

Three variants to the molecular diffusion coefficient may be seen in the porous media literature depending on incorporation of various physical and chemical influences. Since the nomenclature associated with diffusion coefficients is widely inconsistent within the literature, the following definitions are used (Walton et al. 1990 and Seitz and Walton, 1993):

The *effective diffusivity* describes the rate of diffusion of a species in a tortuous, porous medium relative to the pore area through which diffusion occurs. Thus, effective diffusivity accounts for tortuosity, but not

for porosity or chemical effects. This form of diffusivity is the diffusion coefficient required in the PORFLOW model (Phifer, Millings and Flach, 2006).

$$D^{eff} = \frac{1}{\tau} D^{mol} \quad (3)$$

where: D^{eff} is the effective diffusion coefficient and τ is the matrix tortuosity [m_{pore}/m]. One variant of the effective diffusivity expression shown in Eq. (3) includes the constrictivity of the pore network (Grathwohl 1998; Saripalli et al. 2002):

$$D^{eff} = \frac{\delta}{\tau'} D^{mol} \quad (4)$$

However, neither tortuosity (τ') nor constrictivity (δ) are measurable parameters and it is likely that these may be lumped into a single tortuosity term (τ) such that the discrepancy between Eq. (3) and Eq. (4) is likely to be minor.

Intrinsic diffusivity represents the rate of diffusional transport that is hindered by the effective surface area (e.g., porosity) and the tortuous pathway of the fluid phase (e.g., tortuosity). Intrinsic diffusivity does not account for chemical effects on mass transport. The majority of the literature shows the intrinsic diffusion coefficient as (Bear 1979):

$$D^{int} = \frac{\phi_d}{\tau} D^{mol} \quad (5)$$

where: D^{int} is the intrinsic diffusivity [m^2/s], ϕ_d is the “diffusion-through” or connected porosity of the media [m^3_{pore}/m^3] and τ is the geometric tortuosity factor [m/m_{pore}]. The porosity term represents the reduced effective surface area for diffusion while the tortuosity term accounts for the elongated and twisted pathway that a diffusing species must navigate in a porous matrix.

The *apparent diffusivity* describes all physical and chemical effects that hinder the diffusion of constituents in a porous material. Classically, the associated form of the diffusion coefficient is derived from the

closed form solution of the semi-infinite diffusion into to an infinite bath (Crank, 1975) under the assumption that all chemical interactions may be described by a linear partitioning coefficient.

$$D^{app} = \frac{1}{\tau \left[1 + \frac{\rho_s \cdot K_d}{\phi} \right]} D^{mol} \quad (6)$$

where: D^{app} is the apparent diffusion coefficient [m^2/s], ρ_s is the density of the solid phase [kg/m^3_{solid}], ϕ is the total porosity [m^3_{pore}/m^3], and K_d is the linear partitioning coefficient [L/kg_{solid}]. The apparent diffusivity is the rate of diffusion observed from experimental mass transfer tests.

2.1.2.2 Porosity

Since chemical interactions typically are dependent on the solid-liquid surface area, the total porosity is used to describe chemical interactions. However, the porosity used to describe the decrease in cross-sectional area available for diffusion is only a fraction of the total matrix porosity. This “diffusion-through” porosity does not include ink-bottle or dead end pores which do not participate in the mass transport processes. The volume of these non-percolating pores typically is not appreciable in soil systems, but can be as much as significant of the pore structure in cementitious systems. Schaefer et al., suggested a method for determining the fraction of dead end pores in porous media using cyclic mercury intrusion porosimetry (Schaefer, Arands & Kosson 1999).

In cementitious materials, pore size distribution is a continuous spectrum of pore diameters. Gel pores, representing the smallest pore diameters ($5 \times 10^{-4} < d < 0.01 \mu m$), are formed as calcium silica hydrate gels fill in the spaces between crystalline phases. Capillary pores ($0.01 < d < 10 \mu m$) are the void space remaining when the amount of hydration product is insufficient to fill in the original water volume fraction; thus, greater water-binder ratios will result in increased capillary porosity. Gel pores and capillary

pore make up the majority of the pore volume available for mass transport. The combined porosity of gel and capillary pores are considered to represent the “diffusion-through” porosity used to modify the intrinsic diffusion coefficient in mass transport equations.

Larger pore fractions, such as entrained air ($25 < d < 50 \mu\text{m}$) and air voids ($100 < d < 2,000 \mu\text{m}$) occur due to poor consolidation or gaps between course aggregates. In some cases, entrainment of air is purposefully intended to reduce the effects of volume-increase stresses due to precipitation reactions or freezing of water.

2.1.2.3 Tortuosity

In a porous matrix, the actual distance that a species travels through the pore structure is longer than the linear distance in the material, because the travel path through the pores is indirect. In this text, tortuosity is defined as the ratio of the effective travel path to the straight line distance traveled by a diffusing species and, thus, value of tortuosity are always ≥ 1 . When defined as such, the molecular diffusivity is divided by the tortuosity term to yield a reduced effective, intrinsic or apparent diffusivity. Some researchers (Glasser, Marchand & Samson 2008; Marchand & Samson 2009 in press; Truc, Ollivier & Nilsson 2000; Šimunek & Suarez 1994) prefer to define a tortuosity factor in terms of the inverse ratio such that the value is ≤ 1 and the parameter acts as a multiplier of the molecular diffusion. The former definition will be used for all discussions here.

In saturated materials, with high porosity (e.g., $> 20\%$), tortuosity usually is in the range of $1.5 < \tau < 10$ while for materials with low porosity (e.g., $< 10\%$), tortuosity can be significantly higher, $200 < \tau < 500$ in cement mortars (van der Sloot et al. 2001).

The relationship between porosity and tortuosity is material dependent and changes in physical integrity

and pore structure result in changes in tortuosity. Upon aging of mortars, an increase in tortuosity has been observed indicating a continued chemical reaction within the concrete matrix (van der Sloot et al. 2001; van der Sloot 2000). Salt dissolution, precipitation reactions and cracking all affect tortuosity. Partial saturation of the pore space also has a significant effect on the effective tortuosity, with tortuosity increasing in response to decreasing water saturation (Schaefer et al. 1995).

One potential problem with the common definition of matrix tortuosity, is that it is not directly measurable and, therefore, typically estimated empirically by fitting a diffusion equation to observed mass transport measurements of either a nominally inert species (e.g., sodium or potassium) or of chloride under the influence of an applied electrical potential (Samson, Marchand & Snyder 2003).

Saripalli et al. suggested an alternative description of tortuosity in porous media could be directly measured as the ratio between interfacial surface areas (Saripalli et al. 2002). For sample, the tortuosity of a saturated porous matrix would be ratio between solid–liquid surface area (i.e., the “specific surface area”) and the surface area of an idealized capillary bundle:

$$\tau_{sat}^a = \frac{S}{S_o} \quad (7)$$

where: τ_{sat}^a is the area-based tortuosity of a saturated medium [-], S is the specific surface area [m^2/cm^3], and S_o is the surface area of an idealized porous medium (e.g., a capillary bundle) [m^2/cm^3].

In unsaturated media, Saripalli et al. proposed that the

$$\tau_{unsat}^a = \frac{a_{aw}}{a_{aw,o}} \quad (8)$$

where: τ_{unsat}^a is the area-based tortuosity of an unsaturated porous media [-], a_{aw} is the specific immiscible fluid

(air–water) interfacial area determined using interfacial tracers (Saripalli et al. 1997) [m^2/cm^3], and $a_{aw,o}$ is the same quantity for the unsaturated idealized capillary bundle calculated by the geometry of an annulus [m^2/cm^3]. Thus, tortuosity may be determined from measurable or calculable parameters rather than empirical estimation.

2.1.3 Sink/Source Terms

For non-reactive substances that are only present in the dissolved phase, the total concentrations are equal to the dissolved concentrations and the reaction term is zero. For reactive species, however, the concentration in solution of reactive substances is a function of many parallel phenomena, which cannot be readily expressed in a single formula. In many models, the observed diffusivity of all ions is assumed to be constant and independent of the specific ionic species. However, for some problems the difference in diffusivity between ionic species needs to be considered (Li & Gregory 1974). Furthermore, for many species the observed diffusivity is highly dependent on pore water pH and multiple partitioning processes between the pore-water and solid phases.

2.2 Chemical Retention Mechanisms

Although transport can be considered primarily physical in nature, chemical processes are of equal importance in determining migration rates, as chemical processes determine the distribution of reactive substances over different chemical forms (e.g., dissolved, precipitated and gaseous forms). As this distribution can vary considerably in time and space, a good understanding of the chemical retention mechanisms involved in the local distribution of species between solid, liquid and gas phases is necessary to fully describe the leaching process.

In the case of chemical reactions between ions, the driving force for these reactions is not the individual concentrations of ions, but their thermodynamic

activities (i.e., chemical potential). For solutions with a significant amount of dissolved solutes, or with a high ionic strength, which is generally the case for pore solutions in cementitious materials, the ion activity can be quite different from the ion concentration. Ion activity correction models that provide activity coefficients allow calculation of activities from concentrations as necessary to calculate chemical equilibrium conditions. For environmental conditions (surface water, soil solutions) the Davies equation is the most widely used model. The extended Davies equation (Appelo & Postma 2005) also allows a more simple approach to correct for ionic strength. At high salt concentrations ($> 0.5 \text{ M}$), the Davies equation becomes inaccurate. For those conditions, the Pitzer equations (Pitzer 1973) have been developed, which are based on empirical ion–ion interaction terms. However, detailed information on correction parameters is only available for a limited set of substances and elements, and therefore it is in practice not possible to take these corrections into account in most current multi-element speciation models. A simplified Pitzer model for limited species interaction was described by Samson et al. (Samson et al. 1999).

2.2.1 Precipitation

Dissolution of minerals and other precipitated solid phases with fixed stoichiometry occurs in response to under-saturation in the aqueous phase. Precipitation, the reverse reaction, occurs in response to over-saturation in the aqueous phase. In these cases, the maximum dissolved concentration achieved for a dissolved species is controlled by the solubility of the least soluble precipitate or mineral and results in a saturated solution with respect to that species at local equilibrium. As a result, when saturation with respect to a specific species occurs, the total amount of the substance in the solid phase is not proportional to the dissolved concentration. Thus, increasing the amount of the species in the system will not lead to an increase in dissolved concentration, but only to an increase in the amount of the precipitated solid

phase. Conversely, removing some of the species from the system will not result in a lower dissolved concentration until all of the precipitate is completely dissolved. The primary phases of cementitious materials (major matrix constituents, including calcium, silica, alumina, sulfur, iron) will behave according to dissolution-precipitation phenomena. Modeling of dissolution-precipitation processes as linear partitioning processes is not appropriate because of the absence of proportional behavior of the system.

Numerical modeling of dissolution-precipitation reactions is relatively simple in the form of chemical reactions at equilibrium, if thermodynamic data are available. However, for some cases these reactions are kinetically controlled and then reaction rate data is necessary for more accurate modeling.

2.2.1.1 Solid Solutions

Solid solutions are a special form of precipitate in which the composition and element stoichiometry of the precipitate varies with the composition of the solution with which it is in contact. Solid solutions are considered a mixture of different minerals or precipitates. For most radionuclides in cementitious materials, the total mass of the species present is so small that precipitation is unlikely; however, solid solution or inclusion during precipitation of other solid phases may be relevant. The thermodynamic activity of each component in the solid solution is not the same as that for a pure mineral phase, but is a function of the relative fraction of that component in the overall solid solution. For ideal solid solutions, the constituent activity within the solid solution is equal to its mole fraction in the solid solution phase.

In cement-based systems, incorporation of elements into ettringite has been shown to have significant influence on pore solution behavior (Klemm 1998; Gougar, Scheetz & Roy 1996). This is particularly relevant for oxyanions such as CrO_4^{2-} , AsO_3^{3-} , MoO_4^{2-} ,

VO_4^{3-} , PO_4^{3-} , SeO_3^{2-} , BO_3^{3-} , IO_3^- , and TcO_4^- , many of which can substitute for sulfate (Klemm 1998; Kumarathansan et al. 1990; Poellmann et al. 1993; Myneni et al. 1997; Perkins & Palmer 2000; Kindness et al. 1994; Zhang & Reardon 2003). Solid solutions are also relevant for Fe, Ba and Sr which can substitute for Al or Ca. In addition, anionic complexes of U are readily incorporated into carbonate solids (Koroleva & Mangini 2005).

Solid solutions can decrease the aqueous solubility of the minor fractions in the solid solution. Although the aqueous solubility of the major constituents in a solid solution will not change significantly, trace elements that form a small fraction of the solid solution may have a much lower solubility than if they precipitated as a separate mineral phase. The extent to which solid solutions reduce the solubility, and therefore the release, of anionic and cationic radionuclides is not clear.

Solid solution modeling parameters for ettringite substitution are provided in another chapter that focuses on thermodynamic databases. These modeling parameters allow description of leaching of these elements and estimation of the order of magnitude of the potential impact of solid solutions on radionuclide leaching. A variety of cement mortars and cement-stabilized wastes with varying concentrations of oxyanions modeled with these parameters have indicated generally good agreement between measurement and predicted concentrations (van der Sloot et al. 2007b). Further experimental investigation of incorporation into and release from solid solutions is warranted to meet CBP objectives.

2.2.2 Adsorption and Surface Precipitation

Adsorption processes are an important form of solid phase association that influence distribution of solutes between dissolved and solid phases, especially for ion concentrations less than the solubility concentration

where precipitation would occur. Adsorption to inorganic surfaces, such as metal (hydr)oxide surfaces, appears to be a multi-component process, with competition for available adsorption sites by ionic species with different charges and chemical binding properties. As a result, adsorption behavior of ions is mutually interdependent with coupled physical and chemical behavior of the system, such that it is difficult to study the transport behavior of trace species without considering the behavior of the major constituents (macro elements) of the system (Goldberg et al. 2007).

2.2.2.1 Adsorption to Metal (Hydr) Oxides

Reactive metal (hydr)oxide minerals exhibit pH-dependent surface charges which result in multi-component adsorption. The surface of reactive oxide minerals is covered with hydroxyl groups that dissociate in water as a function of pH. At higher pH levels, more protons leave the surface, making the surface negatively charged and, thus, more attractive to cations. As pH levels decrease, iron surfaces pass through a point of zero charge (PZC), such that at low pH surfaces become positive, allowing anions to sorb more strongly.

Examples of reactive metal (hydr)oxides relevant to chemical retention and leaching include iron oxides, aluminum oxides, and manganese oxides in both crystalline and amorphous forms. Although these different mineral phases, in many ways, behave similarly, their relative importance in retention of species depends upon matrix properties, the relative solubility of each mineral, and specific sorption reaction constants. For example, Al-oxides are more soluble than iron oxides and dissolve in acidic solutions (i.e., $\text{pH} < 4$). The effect of manganese oxides is generally considered to be less than Fe- and Al-oxides, but is known to be of relevance for some specific systems with elevated Mn levels.

Amorphous forms of ferric, aluminum and manganese oxides are porous, poorly crystalline solids with high specific surface areas. These solid phases have been shown to retain metal species through a combination of surface adsorption and diffusion through microporous particles (Fan et al. 2005). Table 1 presents a comparison of properties of amorphous Fe (HFO), Al (HAO), and Mn (HMO) oxides.

Extensive research in the field of surface chemistry and colloidal interfaces has been completed on characterization and retention mechanisms for metal (hydr)oxides relative to heavy metals and radionuclides (Crawford, Harding & Mainwaring 1996; Charlet & Manceau 1992; Manceau et al. 1992; Axe & Anderson 1995; Axe & Trivedi 2002; Axe et al. 2000; Fan et al. 2005; Thomas et al. 2004; Trivedi & Axe 1999; Trivedi & Axe 2001; Trivedi, Axe & Tyson 2001; Karthikeyan & Elliott 1999; Karthikeyan, Elliott & Chorover 1999; Peak 2006; Tiffreau, Lützenkirchen & Behra 1995).

2.2.2.2 Surface Precipitation

When the sorbate concentration exceeds 1/10 of the solubility concentration and more than half of the total amount of surface sites, accounting for surface precipitation is recommended (Dzombak & Morel 1990). Although the combination of these conditions is not common for in most materials, surface precipitation has been shown to provide an adequate description of local equilibrium and release behavior for specific cases when these conditions are present (Meima & Comans 1998; Dijkstra, van der Sloot & Comans 2002). For most radionuclides, however, it is unlikely that the conditions specified for surface precipitation will be fulfilled as radionuclides concentrations are generally too low. One notable exception is uranium which can be present in high enough concentrations such that it forms discrete surface precipitated phases. Other actinides, having extremely low solubility values, may also form surface precipitates.

Table 1. Selected Characteristics of Amorphous Metal Hydr(oxides) from Fan et al. 2005

	HFO	HAO	HMO
Specific Surface Area [m ² /g]	600 ^a	411 ^b	359 ^a
Porosity [m ³ _{pore} /m ³]	0.5	0.45	0.35
Mode Pore Diameter [nm]	3.8	1.9	2.1, 6.1
Mean Particle Diameter [μm]	13.0	7.5	19.6

^a Dzombak and Morel (1990)

^b Trivedi and Axe (1999)

2.2.2.3 Modeling Oxide Adsorption

In addition to electrostatic interactions, the empty surface “sites” can react chemically with dissolved ions. Therefore, the overall adsorption of ions on oxide surfaces is a combination of chemical and electrostatic interactions. As a result, adsorption of ions on oxide surfaces is not only pH dependent, but also dependent on the presence of competing ions. Describing the adsorption behavior of oxide surfaces requires accounting for these chemical and electrostatic interactions in thermodynamic simulations, referred to as adsorption or surface complexation models.

The Generalized Two-Layer Model (GTLM) presented by Dzombak and Morel (1990) is probably the most widely used multi-component adsorption model for oxide surfaces. The model was initially developed for hydrous ferric oxides (HFO), but is general in nature such that it can be applied to other oxide surfaces. The GTLM, described in detail by Appelo and Postma (Appelo & Postma 2005), is based on the diffuse layer surface complexation model (Stumm & Morgan 1996) with modifications to allow for multiple adsorption site types and surface precipitation. For this model, an extensive set of binding reactions and constants is available for both cation and anion adsorption onto HFO; however, data on specific adsorption parameters for aluminum and manganese oxides are currently lacking. Sorption onto Al-oxide is often modeled with the available sorption reactions

for a HFO surface, using different values for the PZC and site densities (Meima & Comans 1998). A key element in the GTML is the competition for available sorption sites, which is influenced significantly by the concentration the various competing elements. Using the GTLM, adsorption of radionuclides, such as Np(V), U(VI), Se (IV/VI), Co and several others, onto HFO has been shown important (Brendler et al. 2004; Saunders & Toran 1995; Musić & Ristić 1988).

2.2.3 Ion Exchange

Surfaces with constant charges are important in environmental systems and are referred to as ion exchange surfaces (Appelo & Postma 2005). Most important representatives are different forms of clays that have a fixed, negative charge as a result of their chemical structure. In solution, the negative surface charge is compensated for by surrounding aqueous cations forming a diffuse double layer. These counter ions are bound by electrostatic forces and not by specific chemical reactions. Competition between different cations takes place, but is less specific and related to their charge and size. Of all the solid surface interaction processes, ion exchange through the diffuse double layer generally provides the smallest contribution. Due to the non-specific nature of ion exchange, this process is more important for the ions that make up the bulk of the solutes, and is less important for the trace ions. Consequently, it is also of limited

relevance for radionuclides. However, in materials that contain large amounts of clay or zeolites, ion exchange may become a dominant adsorption process when ionic size becomes selective in accessing exchange sites.

2.2.4 Organic Matter Interactions

Another important adsorption surface is formed by organic matter (e.g., solid phase humic and fulvic substances). The surfaces of organic matter also exhibit pH dependent charging behavior but their charge is net negative over the complete pH range. Thus, only cations adsorb significantly to organic particles. Heavy metal cations (e.g., copper) adsorb especially strongly to organic matter, such that solution concentrations of dissolved metals can be decreased by orders of magnitude even at organic matter concentrations as low as 1% by mass (van der Sloot & Dijkstra 2004).

The state-of-the-art model for describing these interactions is the Non-Ideal Competitive Adsorption (NICA)-Donnan model (Kinniburgh et al. 1999) using model parameters described by Milne et al. (Milne, Kinniburgh & Tipping 2001; Milne et al. 2003). The NICA-Donnan model, which describes metal ion binding to natural organic matter, is an example of a relatively simple model that is not straightforward to implement in standard algorithms. The principle equation for the amount of a species bound to organic matter is given by:

$$Q_{i,t} = Q_{\max} \times \left[\frac{n_i}{n_H} \right] \times \left[\frac{(\tilde{K}_i C_i)^{n_i}}{\sum_i (\tilde{K}_i C_i)^{n_i}} \right] \times \left[\frac{\left\{ \sum_i (\tilde{K}_i C_i)^{n_i} \right\}^p}{1 + \left\{ \sum_i (\tilde{K}_i C_i)^{n_i} \right\}^p} \right] \quad (9)$$

where: Q_i is the amount of species i bound [mol/kg], Q_{\max} is the maximum amount of the species that can be bound [mol/kg], C_i is the concentration of species i in solution [mg/L], n_i is an exponent that reflects overall non-ideality of the adsorption reaction, n_H is a parameter representing the non-ideality for the proton adsorption reaction, \tilde{K}_i is the median value of the affinity distribution for species i [L/kg], and ρ is an exponent representing the width of the affinity distribution [-]. As with the Freundlich model of adsorption, the adsorbed concentrations can be calculated, in principle, directly from the aqueous phase ion concentrations.

Organic matter can be part of the immobile, solid matrix or dispersed as dissolved organic carbon (DOC). Often, the total solid-phase particulate organic matter (POM) is fractionated into a hydrophilic fraction (HY) and more reactive fulvic acid (FA) and humic acid (HA) fractions (van Zomeren & Comans 2007). Each of these functional groups plays some role in the binding process. Ions that are bound by particular organic matter fractions are considered to become immobile and not available for transport by diffusion or convection. Dissolved organic matter is described as small aqueous phase colloidal particles that can significantly bind metal ions. The interaction of soluble cations with DOC increases the concentrations of cations in the aqueous phase and may greatly enhance the transport of cations by convection. However, since these organic matter molecules are much larger than simple ions, diffusion rates of DOC-associated ions are slow relative diffusion rates of free dissolved ions. As with particulate organic matter, fractionation of DOC into HY, FA and HA can be used to describe the mobilization of trace constituents as DOC complexes (van Zomeren & Comans 2007).

In systems considered to be predominantly inorganic, the role of organic matter interaction has been found to be of great importance due to the order of magnitude change in mobility that can occur. In particular,

the fraction of organic matter mobilization as DOC has been shown to play a significant role in relevance to radionuclide mobility and transport (Reiller 2005; Reiller, Evans & Szabó 2008; Reiller et al. 2002; Saunders & Toran 1995).

2.2.5 Inorganic Complexation

Inorganic complexes can be important for the behavior of contaminants. For example, high concentrations of chloride can make cadmium more soluble, and hence mobile, under conditions where it would otherwise be precipitated. Interactions of this type are rather specific and many well known reactions are implemented in thermodynamic databases. When species known to be susceptible to complexation are observed in higher than expected concentrations, mobilization by inorganic complexation is likely to be the cause.

2.2.6 Redox Processes

Reduction oxidation processes are a specific form of chemical reactions in which electron transfer is involved. For many redox processes reaction rates are slow, so reaction kinetics are important. Redox processes are important for reduced materials that are exposed to air, as these will be (slowly) oxidized by oxygen, gradually changing from reduced to oxidized form which may have a large impact on chemical and transport behavior. In thermodynamic databases stability constants for many reduced species are available. The gas-solid interaction (here oxygen-reduced solid) is extremely slow in dry conditions, whereas under moist conditions a much faster oxidation can occur. In modeling such redox changes these aspects should be considered.

2.3 Mass Transport Equations

Within pores, transport can be described as a diffusion process with the flux of species i following Fick's first law of diffusion:

$$J_i = -D_i^{mol} \nabla c_i \quad (10)$$

where: J_i is the flux of species i [mg/m²s], D_i^{mol} is the molecular diffusion coefficient of species i [m²/s] and C_i is the concentration of species i in the liquid phase [mg/L]. This expression is combined with the conservation of mass equation law for species i :

$$\frac{\partial c_i}{\partial t} + \nabla J_i + r_i = 0 \quad (11)$$

where: $\partial C_i / \partial \tau$ is the accumulation rate of species i with time and r_i is the source/sink reaction term. When the reaction term is neglected and the porous material is taken into account, the result is one form of Fick's second law of diffusion describing diffusional transport of a molecular species in the liquid phase:

$$\frac{\partial C_i}{\partial t} = \nabla (D_i^{eff} \nabla C_i) \quad (12)$$

where: C_i is the concentration of the species in the porous material and D_i^{eff} is the effective diffusion coefficient [m²/s]. At the microscale (e.g., within a pore), chemical reactions are expressed as boundary conditions and are not included in the transport equation (Samson & Marchand 1999). Thus, Eq. (12) assumes that only concentration gradients drive the transport of the species.

The microscale transport equation is often extended to the macroscale (e.g., the material scale), by manipulation of the diffusion coefficient term to account for physical and chemical effects of a reactive, porous matrix according the diffusivity definitions described in Section 2.1. In many cases, linear solid-liquid partitioning is assumed and a simplified transport equation is applied to the complex diffusion-reaction process:

$$\frac{\partial C_i}{\partial t} = \nabla (D_i^{app} \nabla C_i) \quad (13)$$

where:

$$D^{app} = \frac{1}{\tau \left[1 + \frac{\rho_s \cdot K_d}{\phi} \right]} D^{mol} \quad (6)$$

The combination of Eq. (13) and Eq. (6) represent a simplified modeling approach for mass transport based on Fick's law. The assumptions of this simplified approach (Marchand & Samson 2009 in press) include:

- Negligible effect of the electrical coupling between the ions
- Minimal influence of chemical activity gradients
- A linear relationship describes all binding interactions
- Insignificant temperature gradients
- Fully saturated porous material without liquid movement

Marchand and Samson (2009 in press) note that these assumptions are rarely valid for mass transport of ionic species through cementitious materials in natural environments, in part, due to the electrical field created by diffusion of ionic species moving at different rates. Several researchers suggest that such effects be taken into account using the Nernst–Planck equation for the flux of ionic species in ideal electrolytic solutions (Marchand & Samson 2009 in press; Samson & Marchand 1999; Samson, Marchand & Beaudoin 1999; Samson, Marchand & Beaudoin 2000; Černý & Rovnaníková 2002).

$$J_i = J_i^{diff} + J_i^{elec} = -D_i^{mol} \nabla c_i - \frac{z_i F}{RT} D_i^{mol} c_i \nabla \psi \quad (14)$$

where: J_i^{diff} is the diffusional flux represented by Fick's first law of diffusion [mol/m² s], J_i^{elec} is the electrical flux resulting from the interaction and relative movement of ionic species in the pore solution [mol/m² s], C_i is the molar concentration of species i in solution [mol/L], Z_i is the valance of species i [-], F is the Faraday constant (96,485 C/mol), R is the ideal gas

constant (9.841 J/mol K), T is the temperature [K], ψ is the electrodiffusion potential [V]. The Nernst–Planck equation holds true for all mobile species in dilute electrolytes (Marchand & Samson 2009 in press).

The electrodiffusion potential can be expressed using the electroneutrality condition (Nguyen et al. 2008), a null current condition, or Poisson's equation (Samson & Marchand 1999):

$$\nabla^2 \psi + \frac{F}{\varepsilon} \left(\sum_{i=1}^N z_i c_i + w \right) = 0 \quad (15)$$

where: ε is the dielectric constant of the media [C/V m], w is a fixed charge density in the domain [mol/m³], and N is the total number of ionic species in solution.

Extension of the Nernst–Planck–Poisson model has been proposed to account for changes in activity coefficients (Samson & Marchand 1999), temperature gradients (Samson & Marchand 2007) and chemical reaction (Černý & Rovnaníková 2002). Marchand and Samson (2009 in press) express a general form of the mass conservation of ionic species in unsaturated porous media as shown in Equation 16 below.

$$\begin{aligned} \frac{\partial(\theta c_i)}{\partial t} = \nabla \left[\theta D_i^{eff} \nabla c_i \right. \\ + \frac{z_i F}{RT} \theta D_i^{eff} c_i \nabla \psi \\ + \theta D_i^{eff} c_i \nabla (\ln \gamma_i) \\ + \frac{\theta D_i^{eff} c_i \ln(\gamma_i c_i)}{T} \nabla T \\ \left. + D_w c_i \nabla \theta \right] + \dot{m}_i \end{aligned} \quad (16)$$

where: θ is the water content in the matrix [m³water/m³material], γ_i is the activity coefficient of species i [-], T is the temperature [K], D_w is the water diffusivity [m²/s], and \dot{m}_i is the source rate term of species i [mol/m³ s].

3.0 LEACHING ASSESSMENT

3.1 Regulatory Approaches

Historically, leaching assessment has been carried out to satisfy the needs of (1) environmental regulatory compliance, for example under the Resource Conservation and Recovery Act (RCRA), and (2) the PA process under the self-regulating authority of USDOE for radionuclides. However, fulfilling each of these assessment needs has required different testing, interpretation, and documentation approaches.

- Under RCRA, wasteforms considered “hazardous” are classified for treatment and disposal following leaching limits established by the USEPA as applicable to a wide range of waste types. Leaching limits pertaining to a select list of 8 metals and some 30 organic species for materials are based on the assumed worst case “plausible mismanagement scenario” of co-disposal with municipal solid waste. The legislation resulted in promulgation of leaching tests, e.g., the Toxicity Characteristic Leaching Procedure (TCLP), and associated pass/fail thresholds based on an assumed dilution/attenuation factor of 100 between the source term and the point of compliance. Initially, leaching tests and release thresholds were intended only as hazardous waste classification approaches. Subsequently, technology-based treatment standards were developed for specific constituents in wastes and waste types based on evaluation of best demonstrated available treatment (BDAT) using TCLP as the reference test. Thus, RCRA compliance has evolved towards technology-based standards in relation to a presumed worst case testing scenario. However, the TCLP approach has been fraught with criticism because of specific test method conditions, inappropriateness of the presumed mismanagement scenario for many waste management decisions, and the inability of TCLP to provide an estimate of leaching under a range of actual waste management scenarios (USEPA 1991; USEPA 1999).

- The release of radionuclides from USDOE wastes is self-regulated through USDOE while the USNRC has the authority for safety regulation of civilian uses of nuclear materials in the United States. Performance assessments document the process of determining release rates and dose to receptors through estimation of anticipated constituent release in relationship to the scenario under which the wasteform or barrier is expected to function. In many cases, performance assessment estimates have taken “conservative” assumptions (i.e., biasing the release estimate towards poorer than expected performance in the absence of more detailed information) to ensure that the design basis of the overall engineered system was protective of human health and the environment. Thus, testing has focused on estimation of release under a range of controlling conditions, with subsequent assessment assumptions to extrapolate results to the anticipated scenario. However, the resulting conservative assumptions also have the potential to be dramatically over-conservative (e.g., overestimating release by orders of magnitude) resulting in overly restrictive treatment requirements and waste acceptance criteria.

3.2 Leaching Tests

Garraabrants and Kosson (Garraabrants & Kosson 2005) discussed different leaching test methodologies and reviewed test methods for leaching assessment of cement-stabilized wastes. In general, leaching test approaches are designed to either simulate release under a specific set of experimental conditions (i.e., attempt to mimic field conditions) or challenge the waste material to a broad range of experimental conditions with the intent to derived characteristic leaching data. Additionally, leaching test methods may be categorized as “equilibrium-based” and “kinetic-based” by whether the intent of the method is to establish equilibrium between a solid and a liquid or measure kinetic parameters such as diffusion coefficients.

3.2.1 Common Equilibrium-based Tests

3.2.1.1 EPA Method 1311: The Toxicity Characteristic Leaching Procedure (TCLP)

In context to the above leaching test categories, the current regulatory test for waste classification, the TCLP is an equilibrium-based simulation tests designed to mimic the result of co-disposal of the tested waste with municipal solid waste. The procedure is a single batch extraction of particle-size reduced material (<9.5 mm) with dilute acetic acid in either deionized water or a NaOH buffer depending on the acid neutralization capacity of the material. The liquid-solid (LS) ratio is 20 L/kg of material and the contact time is 18 hours. The extract is considered to be representative of leachate in the simulated release scenario. The USEPA Science Advisory Board (USEPA 1991; USEPA 1999) has recognized several limitations of TCLP including (1) overuse to purposes and materials for which the method was not designed, (2) the fact that end-point pH is not recorded, (3) the method does not account kinetic-effects, and (4) chemical and physical reactions common in many release scenarios are not considered.

3.2.2 Common Kinetic-based Tests

3.2.2.1 ANS 16.1: Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-term Test Procedure

The tank leaching test, ANS 16.1 (ANS 16.1 2003) is the most commonly used US leaching test for solidified low-level (radioactive) waste (LLW) and is one of several tests required by the USNRC to characterize LLW as stipulated in the Waste Form Technical Position. This test method, an adaptation of an earlier test proposed by the International Atomic Energy Agency (Hespe 1971), is a semi-dynamic tank leach test whereby a monolithic material is contacted with

demineralized water with the leachant changed periodically for fresh water following a specified schedule. The test stipulates 7 leaching intervals over a 5 day period but the schedule can be extended to a total of 90 days with intervals at 2, 7, 24, 48, 72, 96, 120, 456, 1,128, and 2,160 hours. Leaching data is interpreted using tables or graphs and effective diffusion coefficient is calculated assuming diffusion-controlled release. However, the experimental parameters of ANS 16.1 have fallen under criticism in that release rates were found to be suppressed, especially during the longer intervals due to elevated concentrations of elements in the leachate (Fuhrmann et al. 1989). Failure to maintain an assumed infinite bath at the monolith boundary may lead to back reactions causing precipitation of secondary products and yield erroneous effective diffusion coefficients. Several variations on this leaching tests address these concerns by adjusting the schedule of exchanges, e.g., USEPA Draft Method 1315, or use of ion-exchange resin to remove ions from solution, e.g., the Simulated Infinite Dilution Leach Test (Schwantes & Batchelor 2006).

3.2.2.2 ASTM C1308: Accelerated Leach Test

ASTM C-1308 (2002) was developed to obtain the net forward rate of release, a material property, as opposed to an environmentally specific release rate. This test is designed to determine if leaching is diffusion-controlled by using a computer code that was developed for the test method (Fuhrmann et al. 1990). It allows computation of a diffusion coefficient from the data and a check of the data against a shrinking core diffusion model. It also can be used to project releases for different size waste forms and for long times based on the observed diffusion coefficient. Elevated temperatures can be used to accelerate leaching, and if modeling shows no alteration in the process relative to room temperature tests, these data can be used to define leaching out to long times. This test is a semi-dynamic procedure that stipulates a cylindrical sample. Large volumes of leachate and frequent leachate changes maintain low concentrations in solution.

Several leaching tests, such as ASTM C1220 (2002), ASTM C1285 (2002), MCC-5s, and MCC-4, were developed for evaluation of radionuclide release from glass or other wasteforms. These leaching tests have limited applicability to cementitious barriers in that glass wasteforms have inherently different leaching mechanisms and characteristics than cementitious materials. Only a few tests have been designed for specifically for wide-based use on cementitious materials.

3.2.3 USEPA Draft Methods

In response to criticisms and misapplication of TCLP for purposes other than hazardous/non-hazardous waste determination, the USEPA recently has been focused on development of alternative test methods to better understand the processes involved in release of contaminants from waste and provide more robust estimates of constituent release under specific disposal and beneficial use scenarios. These methods will not replace TCLP for subtitle D (industrial) versus Subtitle C (hazardous) waste determination under RCRA but rather allow greater flexibility in leaching test applications that do not statutorily specify TCLP (e.g., determinations of equivalent treatment, delisting petitions, treatment effectiveness comparisons, beneficial use determinations). The USEPA draft test methods include:

- equilibrium-based, pH dependence leaching test (Draft Method 1313),
- equilibrium-based, upflow percolation column test (Draft Method 1314), and
- kinetics-based, mass transfer rate test for monolith or compacted granular materials (Draft Method 1315).

Assessment based on test results is scenario-based and follows a leaching assessment framework recommended by Kosson et al. (2002). Some of the methods presented here are similar to methods adopted in Europe under the European Committee on

Standardization (CEN) for waste, mining waste, soil, sludge and construction products (CEN TS14405, 2005; CEN TS 15863, 2009; ISO TS 21268-3, 2007; ISO TS 21268-4, 2008; CEN TC 351 drafts, 2009; see section 3.3.3)

3.2.3.1 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 the liquid-solid partitioning (LSP) curve of constituents as a function of eluate pH and is similar to CEN/TS 14429 (CEN PrEN-14429 2005) used in Europe and ISO/TS 21268-4 (ISO TS 21268-4 2007) developed for soil and soil-like materials. The protocol consists of nine parallel extractions of a particle-size reduced solid 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 (value depends on sample heterogeneity and particle size), is added to nine extraction bottles. 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. 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. The extraction vessels are sealed and 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 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.

3.2.3.2 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 1313 (USEPA 2009b) is designed to provide the LSP of constituents in a granular solid material as a function of LS ratio under percolation conditions and is similar to CEN TS 14405 (CEN PrEN-14405 2005) and ISO 21268-3 (ISO TS 21268-3 2007). A 5-cm diameter x 30 cm column is 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 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.

3.2.3.3 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 in low permeability material under diffusion-controlled release conditions, similar to ANS 16.1 (2003), NEN 7345 (NEN 7345 1995) and PrEN15863 (CEN PrEN-15863 2009). The procedure consists of continuous leaching of a 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/cm². 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 is exchanged with fresh reagent water and the previous leachate is collected. For each eluate, 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.

3.3 Integrated Assessment Approach

Although more than 50 leaching tests have been identified for various purposes and materials, a limited number of carefully selected tests can cover a wide range of possible exposure conditions (van der Sloot, Heasman & Quevauviller 1997). However, test methods alone are not sufficient to evaluate leaching as test results need to be linked to an assessment basis. This linkage requires a conceptual and computational framework to extrapolate laboratory test results to field scenarios.

An integrated assessment approach proposed by Kosson et al. (2002) uses the results obtained from leaching tests, in conjunction with other material and scenario characteristics, to provide the necessary information to describe a source term for assessment modeling. Simplified, semi-empirical and semi-analytical models, which though knowingly over-predict release (i.e., are conservative), can be used for initial screening purposes with the caveat that results be verified against field observations. Coupled chemical reaction-transport modeling is the preferred and most robust option available to provide insight in the long term behavior of materials under changing exposure conditions in the field (Dijkstra et al. 2008; Dijkstra, van der Sloot & Comans 2006; Dijkstra et al. 2005; van der Sloot & Dijkstra 2004; Kosson et al. 2002).

The sequence of steps from problem definition, through test method selection and leaching simulation, to lab-to-field validation (Kosson et al. 2002; CEN EN-12920 2003).

Under the integrated assessment approach, an important distinction is made between the equilibrium-based release mechanisms in the case of granular materials (percolation scenario) versus kinetic-based release mechanisms that dominate release from monolithic materials (flow-around scenario). A generic testing approach has been developed for granular and monolithic materials as shown in the flowchart in Figure 3.

In both cases, constituent analysis in leaching tests should address all major and minor species as well as pH, electrical conductivity, redox potential, and dissolved carbon (organic and inorganic) in order to facilitate speciation modeling. The basis for testing in both percolation and flow-around scenarios is the pH dependence leaching test which provides insight into the chemical speciation of the constituents in the solid phase of the materials by evaluation of constituent release in response to different end-point pH conditions. For granular materials, where the mode of water contact is anticipated to be percolation through the material, release under the natural pH of the material is determined using a percolation test. For low permeability materials (monoliths or compacted granular fills), a tank leach test with leachant renewal is formulated. This testing approach was the underlying methodology behind the development of the USEPA Draft Methods 1313 through 1315 described above; however, analogous leaching tests are available through the CEN and the International Organization for Standardization (ISO).

3.3.1 Defining the Source Term

Environmental model/assessment approaches commonly assume, either explicitly or implicitly, a constant source term² which is not a proper representation of the long-term leaching behavior from cementitious materials in many cases.

3.3.1.1 Constituent Selection

Previous source term descriptions have applied independent release functions to individual constituents. Thus, these models neglect the effect of interactions between elements and changes in mobility due to significant changes in solubility controlling factors. Inclusion of all constituent interactions within the cementitious material, as well as those external stresses that alter the properties of the material or constituent retention, is a daunting challenge. However, accounting for all the additional complexity provides a more realistic and mechanistically-based representation of the source term. Current computational advances, both in hardware and software, are beginning to make this approach practical for many applications.

3.3.2 Material Characterization

In addition to the leaching tests, methods for additional modeling parameters are currently being implemented in standardized protocols (ISO/TC190 Soil, 2008). This effort includes standardization of test methods to quantify reactive surfaces such as hydrated iron oxide surfaces, aluminum oxide surfaces, fractionation of dissolved and particulate organic matter, which are important for speciation modeling and reactive transport.

² In terms of the CBP, “source term” is the representation of the contaminant flux from within the confines of the engineered barrier system to the environment (e.g., vadose zone and groundwater).

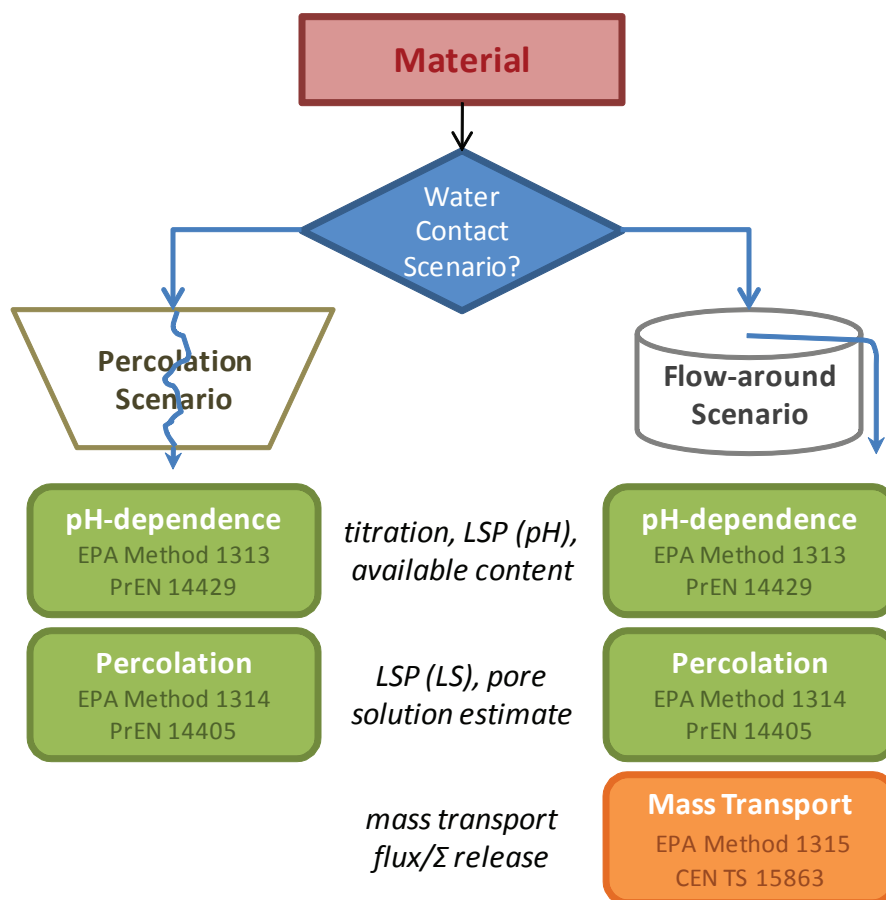


Figure 3. Flowchart Indicating Test Method Selection Based on Material Type Used in Integrated Assessment Approach

3.3.2.1 Redox Titration

The redox capacity of a material is an important property of the material that allows the quantification of the overall rate at which oxidation may occur when balanced against the rate of oxygen ingress for a given scenario. For reducing materials like reducing grouts it is important to be able to assess the reducing capacity of the material (expressed in mol/kg) as it determines the resistance of the matrix to oxidation. In the Netherlands, a procedure (NEN 7348 2006) is described based on exposing a material to an excess of Ce (IV) in 2M sulfuric acid and back titration with Fe(II) as originally proposed by Angus and Glasser (Angus & Glasser 1985).

A similar procedure for measuring reductive capacity for cementitious materials using Cr(VI) in NaHCO_3 followed by slurring with NaSO_4 to desorb chromate (Lee & Batchelor 2003) showed a 20× decrease in reductive capacity on blast furnace slag compared to the Angus and Glasser procedure (Serne 2006). However, the values determined according to the Angus and Glasser method match better with the reducing capacity independently calculated from the sulphide content, which is the main contributor to the reducing capacity relevant for impact on the environment. In blast furnace slag reducing capacity values in the order of 300–400 mmol O_2/kg have been measured (van der Sloot et al. 2007a).

3.3.2.2 Reactive Oxide Phases

The quantification of reactive sorptive surfaces proceeds by selective extractions. The amount of amorphous and crystalline iron (hydr)oxides in the materials to be studied can be estimated by a dithionite extraction (Kostka & Luther 1994). The amount of amorphous aluminum (hydr)oxides can be estimated by an oxalate extraction (Blakemore, Searle & Daly 1987). The extracted amounts of Fe and Al can then be summed and used as a surrogate for hydrous ferric oxides (HFO) in the geochemical speciation modeling (Meima & Comans 1998).

3.3.2.3 Organic Matter Characterization

The quantities of “reactive” organic carbon in the solid phase (i.e., HA and FA) can be estimated by a batch procedure (van Zomeren & Comans 2007), which is derived from the procedure currently recommended by the International Humic Substances Society (IHSS) for solid samples (Swift 1996). In brief, the procedure is based on the solubility behavior of HA (flocculation at pH <1) and the adsorption of FA to a polymer resin. This fractionation allows identification of the most relevant sub-fraction of DOC, because not all parts constituting DOC are equally reactive towards the substances of interest.

3.3.2.4 Solid Analysis

Discerning the structure and chemistry of the solid phases of cementitious materials (including containment structures and waste forms) and how those materials change with time is important to understanding their long-term behavior. Many of the techniques to study solids are x-ray methods and their sensitivity is limited by the intensity of the source of x-rays. Synchrotron based methods take advantage of very high fluxes of x-rays and the ability to supply x-rays of specific energies to provide techniques that have revolutionized the analysis of the solid phase. Detailed descriptions of these techniques can be

found in several reviews (Sparks 2004; Fenter et al. 2002; Brown & Sturchio 2002). A few applications relevant to study of cementitious waste forms are briefly given below.

Elemental analysis of materials on the microscopic scale is an important tool in assessing behavior of cementitious materials. Scanning Electron Microscopes (SEM) and microprobes provide excellent images but detection limits for elemental concentrations are typically 1,000 mg/kg or greater. Synchrotron microprobes can provide elemental analyses with spot sizes as small as about a micrometer and detection limits of less than 1 mg/kg. With this sensitivity, geochemical processes can be explored. Locations and associations of elements in a complex system can be resolved. For example, adsorption of contaminants on individual minerals in a soil can be determined as can their incorporation into new phases such as secondary weathering products. An example is shown in Figure 4 which illustrates the incorporation of U and As into calcite during column leaching experiments with a tank backfill grout (Fuhrmann & Gillow 2009). Arsenic was readily incorporated into the calcite as was U. Apparently U was available for incorporation earlier in the experiment but not later. Calcite continued to grow around older calcite containing U.

Determining the oxidation state of elements, e.g., U, Tc and I, whose redox sensitive behavior controls their mobility, is an important tool in designing materials and systems for waste disposal. X-ray absorption near-edge structure (XANES) spectroscopy allows determination of oxidation states and co-ordination chemistry of individual elements in complex solid and liquid samples. For example, XANES can determine the speciation of contaminants under different conditions or over time as a reagent is added to a system. XANES analysis can be coupled with elemental mapping on microprobe systems so that images can be produced showing the distribution of elements in different oxidation states or in association with different ligands (see examples in Sparks, 2004).

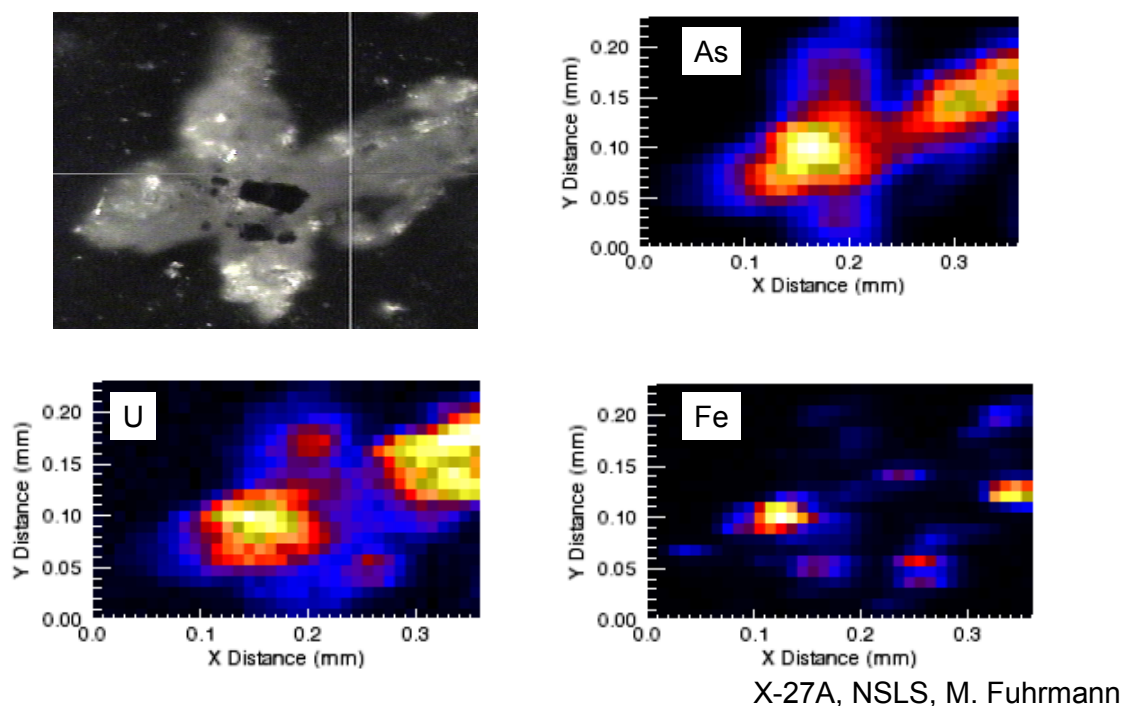


Figure 4. Distribution of Trace Species in Secondary Calcite Growth Found in Column Leaching Experiments of Tank Backfill Grouts. (1000 pore volumes of leachate through grout G-21 designed for filling high-level waste tanks at West Valley, New York)

These techniques can be used to determine distribution of waste species in grouts and other cementitious materials. For example, the distribution and elemental associations of reduced forms of Tc and I can be determined in newly produced reducing grouts. As these materials are exposed to accelerated aging conditions, the oxidation state and possibly the speciation of Tc and I can be determined as oxygen and carbon dioxide enter the system, secondary weathering products form and reducing species (e.g., Fe (II)) are depleted. For example, Luckens (Lukens et al. 2005), used extended X-ray absorption fine structure (EXAFS) to show that Tc(IV) in the form of Tc_3S_{10} in reducing grouts will slowly oxidize to the readily mobile TcO_4^- when oxygen can diffuse through the container. Oxidation does not take place when oxygen is not available, demonstrating that the high nitrate content of the waste does not oxidize Tc (Lukens et al. 2005; Allen et al. 1997).

3.3.3 Interpretation of Leaching Data

Following the testing approach shown in Figure 3, characterization of the leaching behavior of monolithic materials like cement-stabilized waste is carried out by a combination of two equilibrium-based leaching tests (i.e., a pH dependence leaching test and a percolation test) and kinetics-based monolithic leach test. This combination of leaching tests allows for many conclusions to be drawn about leaching behavior, including long-term leaching of a monolith and after full disintegration of the monolith to granular rubble. The approach to interpretation and integration of leaching tests is described in reference to the leaching test data for lead leaching in a cementitious material, presented in Figure 5 and in Figure 6.

The first two graphs in Figure 5 show the relationship between pH-dependent leaching and release from

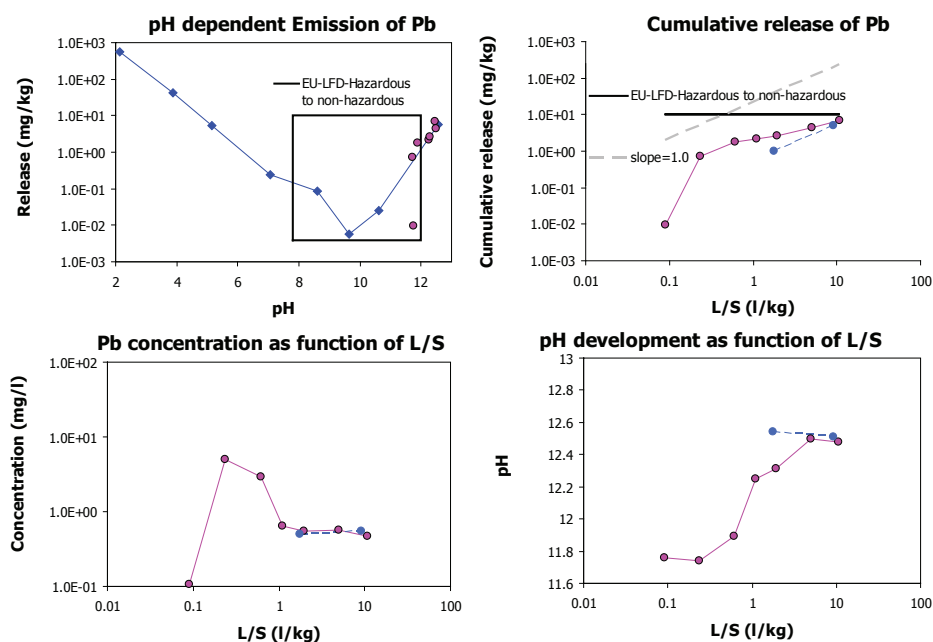


Figure 5. Results of Equilibrium-based Leaching Tests for Lead in A Cement-Stabilized Waste:
a) comparison of pH-dependence and percolation test data as a function of pH,
b) cumulative release from percolation tests as a function of LS ratio, c) concentration data from percolation test, and d) pH evolution in percolation test.

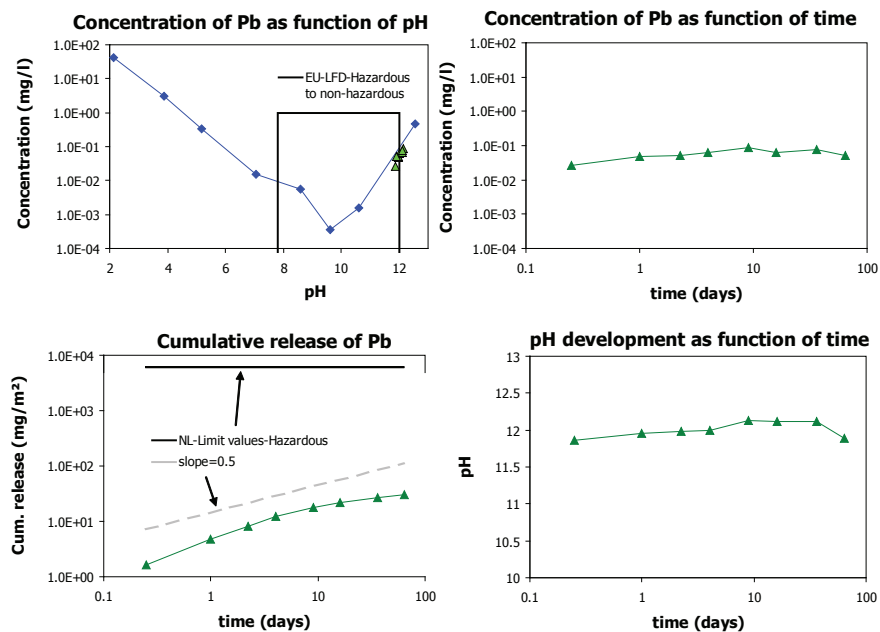


Figure 6. Results of Kinetics-based Leaching Tests for Lead in a Cement-Stabilized Waste:
a) comparison of tank leaching test and pH-dependence as a function of pH,
b) concentration in tank leach test, c) cumulative release from tank leach test, and
d) pH evolution in tank leach test.

column percolation experiments. In general, the data from the percolation test (pink) correspond well with pH-dependence test at the same pH (blue data). This correspondence implies that, under the assumption of local equilibrium, the release can be predicted based on the average pH in the percolation test provided that the pH changes during the percolation experiment are not too large. However, when pH varies greatly (e.g., through carbonation), Figure 5a shows that a relatively large range of lead concentrations can be observed for the size-reduced stabilized waste. The graph of cumulative release as a function of LS ratio can be used to formulate conclusions on the main release mechanism in the percolation test:

- If the cumulative release data is linear with a slope of 1, release is likely controlled by solubility limitations.
- Depletion of highly soluble species (e.g., Cl, Na) is likely when the release curve is shown to become horizontal with increasing LS (i.e., no further release with increasing LS).
- The constituent concentration observed for low LS ratio provides an indication of the concentrations in the porewater of the monolithic material.

The box in the pH dependence graph can be used to reflect the relevant pH domain for a given application and upper and lower threshold concentrations. In the plot of cumulative release as a function of LS, the same reference criterion has been inserted. For the case of cement-stabilized waste, the relevant pH range for size-reduced material is from the pH of the fresh material (pH ~12.8) to the pH associated with fully carbonated material (pH 7.8). The lower horizontal line denotes the lowest analytical detection limit. The upper horizontal line is used to reflect a comparative threshold (i.e., a regulatory criterion; here conversion from hazardous to non-hazardous waste in the European Union Landfill Directive). Selection of appropriate upper threshold comparisons should be made in accordance with the anticipated release scenario (e.g., comparison to drinking water or

groundwater quality criteria typically is not appropriate for waste disposal scenarios because dilution and attenuation between the source term and the point of compliance is not considered).

Many factors cause changes in the percolate concentrations during their transport through the soil, especially when large transport distances are considered. One important factor to be considered is preferential flow (only a portion of the material is in direct contact with percolating water). Lysimeter and field data point suggest that ~20% of the total volume of material being directly in contact with infiltrating water (van Zomeren & Comans 2007). A second important factor is the change in pH when leachate enters soil, which can result in precipitation/dissolution reactions leading to substantial alterations in the percolate in the soil. Overestimation of release will occur when precipitation of constituents of interest occurs at the interface but not considered in the assessment model. The effect of alkaline leachate on near-field soils is difficult to address without appropriate geochemical representation of the interface between materials (e.g., cementitious barrier and soil). The primary constituents of concern will be those constituents that are mobile in the cement-stabilized waste and remain mobile in the subsoil and groundwater system in spite of pH change and other changes.

In Figure 6, the leaching data for lead from a monolithic stabilized waste are provided in a four-panel format that provides useful insights about leaching information about kinetic-based leaching from monolithic materials. The first two graphs show the relationship between pH-dependent concentrations (from equilibrium-based testing) and eluate concentrations from monolith diffusion tests. The concentrations in the tank test correspond generally well with the appropriate pH conditions in the pH dependence test, implying that solubility controls the release from monolithic waste. Solubility control indicates that the dilute solution boundary condition for estimating diffusion-controlled release from a semi-infinite material

into an infinite bath is not satisfied (i.e., the conditions for estimating a valid observed diffusivity have not been met). The pH-concentration box shown in Figure 6a is the same as that discussed earlier for granular material. For this case of lead release from a cementitious material, the pH change with time and, hence, solubility concentration is more important than transport by diffusion. Neutralization of the matrix associated with aging would be expected to decrease the release rate of lead in accordance with the pH-dependence data. The conclusion can be reached that release in the long term will not exceed a limiting value (e.g., the horizontal line shown in Figure 6c), if that limit is not exceeded in the short term.

3.3.4 Modeling & Simulation

A geochemical speciation/transport modeling framework forms an integrated approach that allows linking together various aspects of materials. Proper thermodynamic stability data and other solubility controlling parameters (Fe-oxide, Al-oxide, dissolved organic carbon and particulate organic matter) are used for modeling of the complex systems indicated above. The modeling code used to illustrate this simulation approach, the Objects Representing CHEmical Speciation and TRANsport model or ORCHESTRA (Meeussen 2003), is one of several geochemical speciation and reactive transport simulation codes that can be applied. Several other geochemical speciation and reactive transport simulation codes are discussed in later in this chapter.

Using a geochemical speciation and reactive transport approach involves the following steps:

- **Characterization of the Material:** Measurement of leaching properties using equilibrium-based and kinetics-based leaching tests following the flowchart shown in Figure 3. Note that for monolithic materials, the first fractions of a percolation test on size reduced material provide a suitable

estimate for the porewater composition of the monolithic material. In addition, direct observation of solid phases (i.e., by x-ray diffraction) should be conducted when available in order to define solid phase chemical speciation.

- **Chemical Speciation Fingerprint of the Material:** Prediction of the pH-dependent release from size-reduced sample based on a selected mineral set, sorption onto Fe- and Al-oxides, interaction with dissolved and particulate organic matter and incorporation in solid solutions, thus establishing a “chemical speciation fingerprint” (CSF).
- **Simulation/Verification of Percolation Release:** The CSF is used in combination with a percolation transport scenario using a dual porosity model to describe the outcome of laboratory percolation tests. Comparison of predicted release to laboratory data is used to verify CSF mineral selection.
- **Simulation/Verification of Mass Transport Release:** The CSF is used in combination with transport in a dissolution-diffusion scenario to simulate release from a monolithic material, taking into account refresh or leachant renewal cycles, continuous renewal, and estimated product tortuosity (measured for porosity and pore structure). Comparison of predicted release and laboratory data verify that all transport phenomena and chemical interactions are accounted for in the simulation scenario.
- **Scenario- or Site-specific Simulation:** When a satisfactory prediction is obtained for the CSF over time- or LS-dependent release, the material can be assumed to be well characterized over a wide range of pH and time or L/S conditions relevant for long term behavior. The chemical speciation fingerprint of the material in conjunction with obtained mass transfer parameters can then be used as the basis for reactive transport modeling to predict release under well-defined field scenarios with external influencing factors (e.g., carbonation, redox change, degree and variation in water contact, and varying degrees of preferential flow).

3.4 Chemical Reaction Transport Modeling for Monolithic Wastes

The release from monolithic waste materials is governed by chemical reactions and by transport processes inside the material. As has been observed in recent years (Tiruta-Barna, Barna & Moszkowicz 2001; van der Sloot et al. 2007b), release from monolithic products is not only controlled by diffusion from the interior of the product, but to a large extent also governed by solubility limitations. Major efforts have been made in recent years to find means to establish under what circumstances solubility control governs and when diffusion is the main release controlling mechanism (Piantone et al. 2006; van der Sloot et al. 2007b; van Zomeren et al. 2007).

Under landfill conditions, most trace constituents are found to be solubility-controlled, while soluble salts are dominated by diffusion-controlled release (Aarnink, Bleijerveld & van der Sloot 2007; van der Sloot et al. 2007b). The tank leaching test can be used to determine the apparent tortuosity of the material in its original physical state. This information is important input for chemical reaction transport models that allow transport by diffusion to be taken into account. Diffusion is driven by a concentration gradient with limited external solution rather than by an assumption of an infinite bath. The leachant renewal cycles as applied in the DMLT (CEN PrEN-15863 2009) have been modeled for some major, minor and trace elements. In modeling, the first step is to ensure that the proper tortuosity is used by matching release of soluble salts like Na, K and Cl with observed release in a laboratory experiment. The CSF is applied and the initial pH is adjusted to obtain a proper pH and electrical conductivity model description. It is important to obtain a good match for the major elements, since these to a large extent control the release behavior of trace constituents. Also, use of sufficiently small spatial cells is important in order to allow a good description of the pH gradient

3.5 Modeling Leaching Processes

Leaching rates of substances from monolithic porous material can conceptually be assumed to be governed by different processes. The release can be expressed in a leaching rate [mg/kg of material/day], cumulative release [mg/m²] at a given time, or concentration [mg/L] in time and space. Radionuclide release often is expressed as fractional release per unit time; however, fractional release assumes that the total concentration of the radionuclide is available for release which is not realistic in most cases. Many publications address release modeling from cement-based materials (Aarnink, Bleijerveld & van der Sloot 2007; Černý & Rovnaníková 2002; Garrabrants & Kosson 2005; Garrabrants, Sanchez & Kosson 2003; Jones & Serne 1995; Marchand & Samson 2009 in press; Samson, Marchand & Beaudoin 2000; Nguyen et al. 2008; Tiruta-Barna, Barna & Moszkowicz 2001; van der Sloot et al. 2007b; Garrabrants, Kosson & DeLapp 2007; Sanchez et al. 2003), with governing equations ranging from empirical (e.g., simple, 1-dimensional diffusion) to almost fully mechanistic (e.g., transport by diffusion coupled with full chemistry). Common assumptions and simplifications are used to describe constituent release mechanisms and release rates.

3.5.1 Solubility-controlled Release

Under this assumption, the dissolved concentration of a substance is in equilibrium with a solid phase which buffers the dissolved concentration to a constant value as long as a solid phase exists. This assumption implies that leaching rates are independent of external conditions and remain constant over time until the solid component is depleted. Leaching rates would not be affected by surface area (i.e., larger surface area would not increase leached concentrations). However, cumulative leaching rates in a leaching test would be affected by the amount of water in contact with the sample.

3.5.2 Diffusion-controlled Release

Under this assumption, leaching rates are controlled by individual component diffusion rates and concentration profiles in the solid matrix. For 1-dimensional (1-D) systems the leaching rates as a function of time can be described with closed form, mathematical analytical solution. In that case there would be a linear relationship with a slope of $\frac{1}{2}$ between cumulative leached concentrations and log time, implying that leaching rates decrease logarithmically over time. Fitting of linear partitioning (K_d approach) and/or tortuosity can be used to calibrate the model. This model can only describe mono-component, linearly adsorbing species in a 1-D infinite media system.

3.5.3 Multi-component Diffusion-controlled Release

Under this assumption, diffusion rates of substances are determined by local concentrations in pore solutions and resulting local concentration gradients. In turn, these local concentrations are assumed to be governed by multi-component interaction processes between solutes and solid phase via precipitation and adsorption reactions. The multi-component nature of these interactions implies that the behavior of a substance is dependent on the behavior of other substances and, therefore, cannot be isolated from the rest of the system. For example, the pH dependent dissolution of calcium, aluminum, iron, lead and zinc in concrete are all interdependent. Porewater concentrations of the species are dependent on localized pH and can increase or decrease as a function of pH changes according to the LSP curves. Generally, cationic species become more soluble at low pH, but the solubility of amphoteric species (e.g., lead and aluminum) also increases at the very alkaline conditions that exist in cementitious materials. For such constituents, long-term leaching rates may actually become higher over time.

Depending on chemical conditions, leaching rates even can become negative (i.e., the material takes up constituents from the surrounding environment). This behavior can be observed under tank test conditions for substances such as magnesium, which after a refresh of solution initially leaches from the solid material, but re-precipitates if pH increases during the test. It shows that leaching behavior is not an intrinsic material property that can be measured in a simple test, but is determined by understanding the interaction processes between the material and the contacting environment.

In light of the complexity described above, release behavior often cannot be expressed by simple solubility, linear partitioning (K_d), or purely diffusion-controlled processes and a more mechanistic approach is required to achieve more accurate release estimates. In order to use results of short term leaching tests for estimation of long term leaching rates under field conditions, mechanistic models are necessary that predict changes over time in effective diffusion rates. However, even though mechanistic models can take into account the effect of changing chemical conditions on effective leaching/diffusion rates, these models only provide a “best estimate” based on the current level of understanding of the processes involved. Validating the predictive capabilities of these models over longer time scales is very difficult.

3.5.4 Dual Porosity Regimes

In a number of cases, zones with different flow rates, connected with concentration gradient driven mass exchange (diffusion analog), are important to properly describe release. This conceptual model is for systems that consist of a combination of distinct zones where convective transport dominates, and zones where diffusive transport dominates. Examples are cracked concrete, heterogeneous soils, and systems exposed to natural infiltration and, thus, subject to preferential flow

paths. For concrete materials, this situation occurs between the cement paste and the aggregates. If the aggregates are relatively porous, the total mass transport simulation may require separate descriptions of the transport through the paste and mass release from relatively porous aggregates (Sanchez et al. 2003). In the case of essentially non-porous aggregates, only the space occupied by aggregate affects the tortuosity of the material; however, transport through the interfacial transition zone in the cement paste around aggregates can play an important role.

3.5.5 Orthogonal Diffusion with Convection

This conceptual model can be considered as an extension of the dual porosity model, in which the stagnant zone is subdivided in a series of cells so as to calculate diffusion and concentration gradients within the stagnant zone. Mass exchange is in that case controlled by the concentration gradient over diffusion convection boundary (Schaefer et al. 1995).

3.5.6 Unsaturated Flow (Richards equation) Coupling

For transport of solutes in unsaturated systems (pores partially filled with water), it is necessary to calculate the unsaturated water flow, and to use this information in combination with dissolved ion concentrations for calculating the resulting mass transport by convection. Unsaturated conditions also greatly affect diffusion rates, as ions need to travel longer distances and the cross-section for diffusion processes is reduced. This is reflected in the increase in tortuosity with decreasing saturation.

3.5.7 Release from Structures Intermittently Wetted by Rain or Spray Water

Utilization of concrete in surface structures (all forms of building on land) is characterized by intermittent wetting and drying. Drying of the porous network

greatly facilitates formation of calcite as uptake of CO_2 from the air, via gas diffusion, is five orders of magnitude faster than through liquid phase diffusion under saturated conditions. In carbonation cases, the release can be estimated based on the progression of the neutralization front. Modern concretes have a rather low connected porosity, which delays ingress of substances as well as release of substances. In Roman cements, which at the time of placement were considerably more porous, full carbonation is observed after 2,000 years (van der Sloot et al. 2008b). This process may even have been enhanced by the higher porosity and the uptake of moisture in the structure, which would thus effectively act as a CO_2 pump.

3.5.8 Multi-phase Equilibrium vs. Kinetic Controls

In considering transport processes over long time scales, interactions amongst elements potentially are important. For reactive elements and substances, single substance calculations that do not account for multi-species interactions (e.g., as a function of pH and porewater composition) often will not provide good estimation of actual system behavior. Thus, multi-element modeling that can account for the competitive effects and multiple factors affecting solid-liquid partitioning over different chemical forms is recommended. While local thermodynamic equilibrium is an appropriate assumption for most reactions over long time scales, some chemical reactions proceed at very slow rates, especially some precipitation/dissolution reactions. For these cases, the progress of reactions is kinetically controlled, and should be taken into account accordingly in modeling the system. In laboratory studies, such kinetic effects have been identified for Ca, Mg, Al, SO_4 , Mo, Pb, Ni, Cd, Cu and Zn in MSWI bottom ash leaching (Dijkstra, van der Sloot & Comans 2002).

3.5.9 Mechanistic Chemical Retention vs. Linear Sorption

Prediction of leaching rates of elements from porous solid samples is often done with an empirical, linear sorption model (K_d approach). In this model, it is assumed that the mobility of the element of interest in the porous matrix is a constant fraction of the mobility of this element in free water:

$$K_d = \frac{S_i}{C_i} \quad (17)$$

where: K_d is the linear partitioning coefficient of species i [L/kg], S_i is the concentration of species i bound to the solid phase [mg/kg], and C_i is the concentration of species i in the liquid phase [mg/L]. In several transport models, the partition coefficient, K_d , is used as a mass ratio between adsorbed and free masses [mg_{solid}/mg_{liquid}]; however, the mass ratio form is both sensitive to variations in LS ratio as well as changes in chemical conditions (e.g., pH, redox, etc).

Often, this fraction applied as a constant over time and being independent of changing chemical conditions or interactions with other substances. Under the K_d approach, it is possible to measure the leach rate in a short term experiment, and the resulting calculated K_d is then used to predict leaching rates over long times. When large changes in chemical conditions are anticipated, the K_d value for a particular species may be varied in response to chemical conditions when supporting data is available. Under the assumption that linear sorption describes all chemical reactions $R(C_i)$, the 1-D diffusion-reaction equation becomes:

$$\frac{\partial C_i}{\partial t} = \frac{\phi_d D_{eff}}{\left[1 + \frac{\rho_b \cdot K_d}{\phi}\right]} \frac{\partial^2 C_i}{\partial x^2} = \frac{\phi_d D_{eff}}{R_d} \frac{\partial^2 C_i}{\partial x^2} \quad (18)$$

where: ϕ_d is the "diffusion through" porosity [m³_{pore}/m³], ϕ is the total porosity of the porous material [m³_{pore}/m³], ρ_b is the bulk solid phase density [kg_{solid}/m³_{solid}] and R_d is the chemical retention term [-].

The K_d approach is easy to implement and adequately approximates liquid-solid partitioning dilute species in groundwater. Many USDOE performance assessments, as well as PAs by USNRC licensees, represent very complex systems incorporating data and conceptual model uncertainties such that errors in release models may represent a small fraction of the uncertainty of the total assessment. If the chemical conditions of the disposal unit can be expected to remain constant over some long period, and if the K_d values were determined under similar and representative conditions, then this approach may be appropriate within the uncertainty of the leaching assessment. This is particularly so when the K_d value is high and releases are a small fraction of the inventory.

However, the simple partitioning approaches (e.g., linear, Langmuir and Freundlich isotherms) are well known to be insufficient for describing complex geochemical reaction that control partitioning in subsurface environments (Zhu 2003). For these systems, a more sophisticated model can improve the accuracy of predictions for understanding the evolution of chemical conditions within a system where (1) the behavior of primary matrix constituents is controlled by dissolution-precipitation phenomena, (2) mobility of trace constituents is known to change under the chemical conditions that are likely to evolve over time. In cementitious materials, major parameters that can lead to enhanced mobility of radionuclides include decreases in pH, oxidation of initially reduced wasteforms, and complexation with components of water entering the system (e.g., CO₂). Since the "effective K_d " depends strongly on local chemical conditions which can vary over time and location, leaching estimates based on initial release rates can lead to inaccurate predictions of long term leaching behavior.

As an illustration of the differences between K_d and mechanistic approaches, the simulation of leaching test data for sodium representing a non-reactive constituent and calcium as a reactive constituent are shown in Figure 7, 8, and 9, respectively (Meeussen,

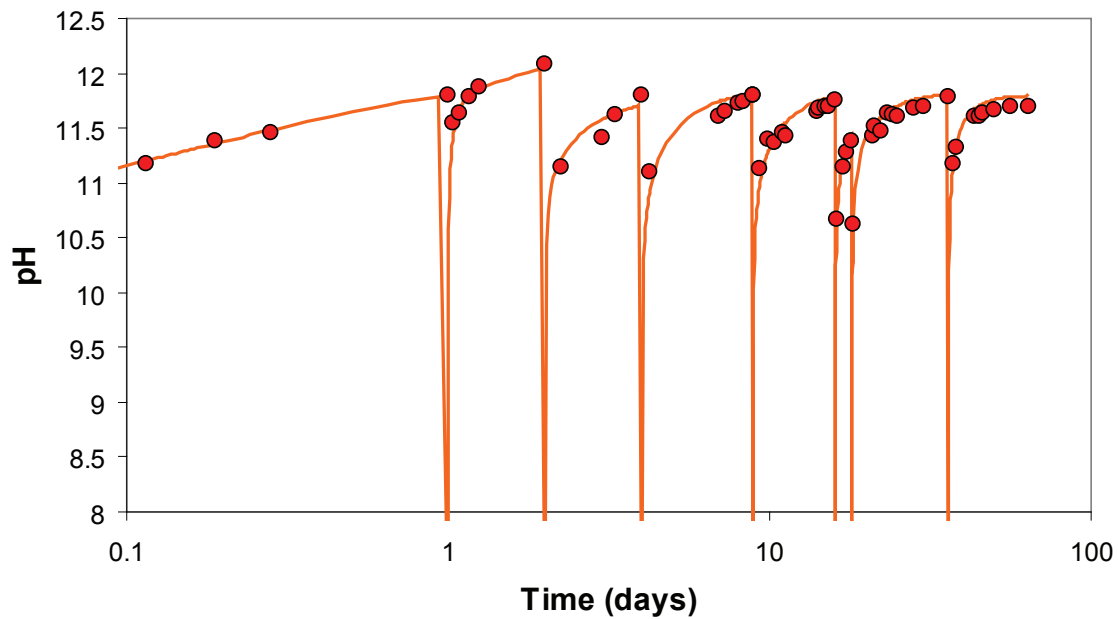


Figure 7. pH Development in A Tank Leach Test with Leachant Renewal
(Red Data Points) for a Cement-stabilized Waste in Comparison with Results from Mechanistic Modeling Taking A Mineral Assemblage into Account.

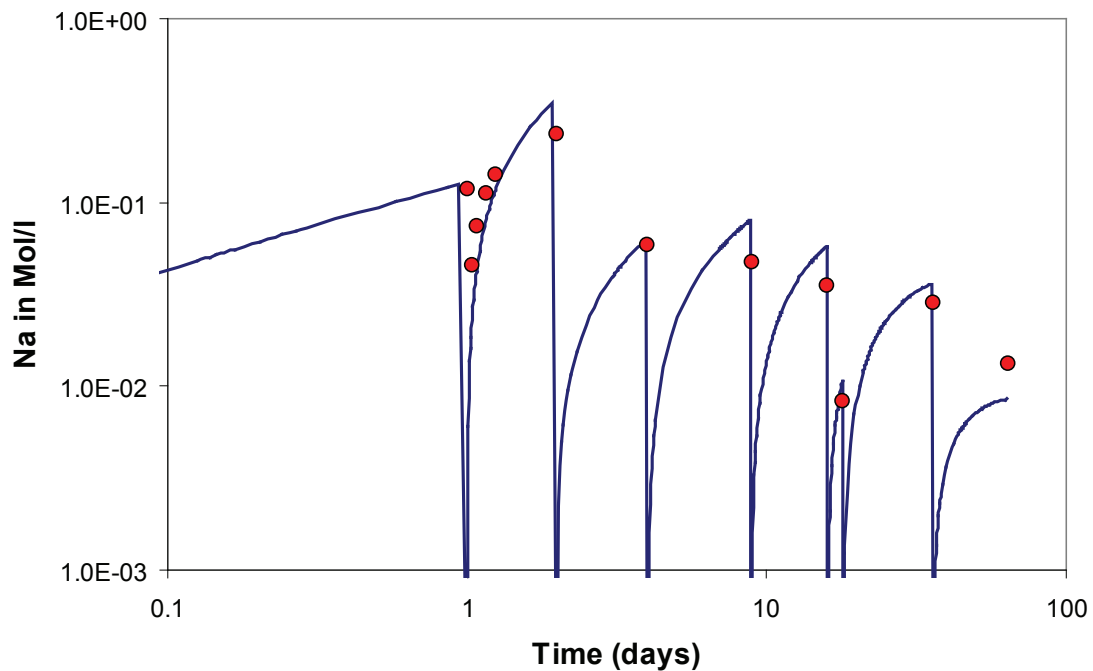


Figure 8. Na Development in A Tank Leach Test with Leachant Renewal
Red Points Represent Lab Data, Predicted Concentration Using Linear Sorption (K_d) and Predicted Concentration Using Multiphase Thermodynamic Approach) Overlap.

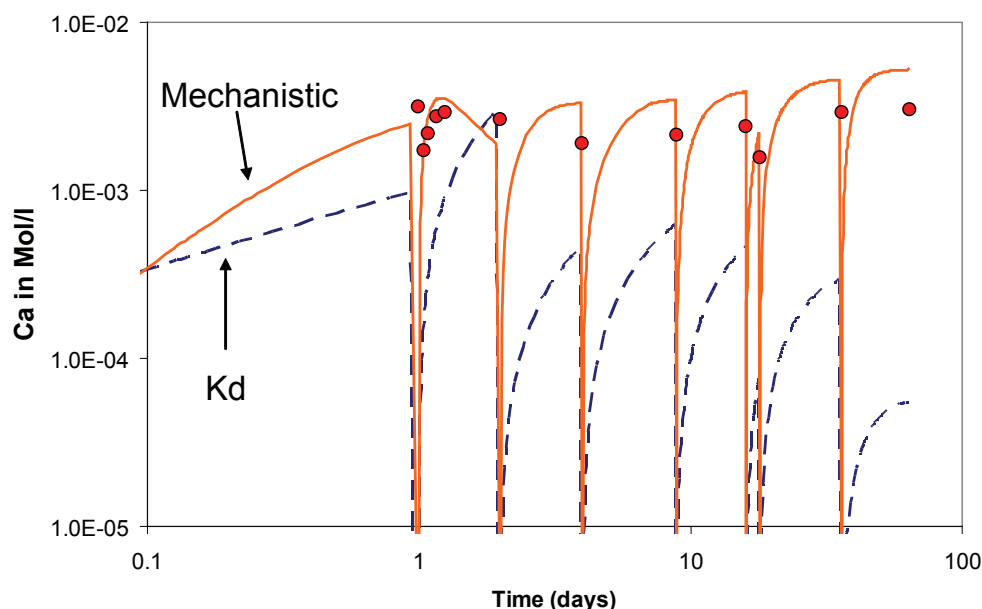


Figure 9. Simulation of Calcium Leaching Data from A Tank Leach Test of Cement-stabilized Waste Red Points Represent Lab Data, Blue Line Indicates Predicted Concentration Using Linear Sorption (K_d) and Orange Line Indicates Predicted Concentration Using Multiphase Thermodynamic Approach).

2009). The K_d values used were estimated from initial leaching rates during the first two days of leaching. For non-reactive substances such as Na or Cl, the K_d model is sufficient and the diffusion model adequately simulates leaching data. However, applying the K_d approach to substances that have a pH-dependent solubility (e.g., Ca, Mg, Al) can lead to significant over- or under-prediction of long term leaching rates.

3.6 Transport and Thermodynamic Codes

Several well-known computer codes exist that can calculate chemical speciation and reactive transport³. The capabilities of these models in terms of chemical and physical processes are compared in Table 2.

3.6.1 PHREEQC

PHREEQC (http://www.brr.cr.usgs.gov/projects/GWC_coupled/phreeqc) is probably the most widely-used, general-purpose chemical speciation software (Parkhurst & Appelo 1999) to the point that it has become the de-facto standard for chemical speciation calculations in aqueous or soil systems. In addition to standard aqueous complexation, ion activity, and precipitation models, PHREEQC contains a number of surface complexation models. The greatest drawbacks of this model are (1) a dated approach to ionic interaction with organic matter and (2) limited transport capabilities which cannot be extended.

3.6.2 MINTEQA2

MINTEQA2 (<http://www.epa.gov/ceampubl/mmedia/minteq/index.html>) is an older generation speciation

³STADIUM (<http://www.sem.qc.ca/en/slm/software.html>) is another chemo-physical transport code primarily focused on durability assessments in structural cement-based materials. Therefore, description and application of this code is discussed in another chapter.

program that comes with an extended database of chemical equilibrium constants. Although it can handle precipitation reactions, MINTEQA2 includes only limited surface complexation models and does not contain a transport module. In addition, all MINTEQA2 (sub)models are available within PHREEQC, which offers more functionality.

3.6.3 Geochemists Workbench

The focus of Geochemist Workbench (<http://www.rockware.com>) is inorganic systems. The model contains extended graphical options (e.g., predominance diagrams), but only limited surface complexation options. Neither organic matter adsorption models

Table 2. Comparison of Chemical and Physical Processes of Several Thermodynamic Programs

	PHREEQC	MINTEQA2	HYDRUS	Geochemist Workbench	GEMS	HYTEC-CHESS	LeachXS™-ORCHESTRA	STOMP	PORFLOW
Aqueous Complexation	✓	✓		✓	✓	✓	✓		
Ion Activity Correction	✓	✓		✓	✓	✓	✓	✓	
Precipitation	✓	✓		✓	✓	✓	✓	✓	✓
Solid Solutions	✓				✓		✓		
Ion Exchange	✓	✓	✓	✓		✓	✓		
Surface Complexation (Fe/Al oxides)	✓	✓	✓	✓		✓	✓		
Organic Matter Complexation							✓		
Colloids							✓		
Diffusion	✓		✓			✓	✓	✓	✓
Electro-neutral Diffusion	✓						✓	✓	✓
Ion-specific Diffusion	✓						✓	✓	
Gas Diffusion	✓						✓	✓	✓
Convection	✓		✓			✓	✓	✓	✓
Colloid Transport						✓	✓		
Unsaturated Water Flow			✓				✓	✓	✓
Porosity/Permeability Feedback								✓	
Cracked Material Feedback									

nor unsaturated transport modeling capabilities are embedded into Geochemist Workbench.

3.6.4 HYDRUS

HYDRUS (<http://www.pc-progress.com>) is primarily a model for describing water flow in the vadose soil zone and it describes unsaturated water flow in combination with transport of a small number of predefined ions. The model does not contain full speciation, or multi-component interactions with solid soil phase. Therefore, this model is of limited use for describing the mass transport of ions in highly reactive porous media such as cementitious barriers. Hybrid models combining HYDRUS and PHREEQC chemical speciation are in use in Europe (Jacques et al. 2003).

3.6.5 GEMS

The GEMS (<http://gems.web.psi.ch>) chemical speciation code was developed by Dimetri Kulik at the Paul Scherrer Institute (PSI) in Switzerland. The model uses Gibbs free energy minimization as the numerical approach rather than the standard way of solving the set of non-linear equations formatted by the mass-action, mass balance relationships. Thermodynamic data is supplied by the PSI thermodynamic database and de Cement 2007 database of Lothenbach et al. (Lothenbach et al. 2008; Lothenbach & Wieland 2006; Lothenbach & Winnefeld 2006; Matschei, Lothenbach & Glasser 2007). The GEMS code addresses temperature/pressure dependency and high ionic strength effects on multi-component, non-ideal solid solutions. However, the model does not contain adsorption models for organic matter.

3.6.6 HYTEC-CHESS

CHESS is a geochemical speciation module developed by Jacques van der Lee at the Ecole des Mines in Paris (www.cig.enscm.fr/chess). The CHESS geochemical module can calculate chemical speciation

taking into account standard chemical reaction types (e.g., aqueous complexation, precipitation, ion exchange, surface complexation according to the GTLM), but does not contain adsorption models for organic matter.

HYTEC is a transport algorithm that combines the CHESS geochemical module with a model for convection/diffusion. There is only limited feedback possible between chemical and physical processes (i.e., changes in speciation, such as leaching of calcium mineral or precipitation, which would be expected to change the porosity and, hence, physical transport, are not linked).

3.6.7 LeachXS™-ORCHESTRA

LeachXS™-ORCHESTRA is more a modeling framework than a specific model itself. LeachXS™ has several databases, among which a database with leaching data in unified format to facilitate comparison of test results from various sources (van der Sloot et al. 2008a). ORCHESTRA is used as a calculation engine with a number of predefined model systems, within the expert system LeachXS™. The combination is a uniquely open system, where chemical and physical model components can be extended by users. Extended model databases include parameters for surface complexation and solid solution models and all chemical models can be used in combination with mass transport to calculate diffusion and convection in systems of arbitrary lay out (e.g., 1-D diffusion, dual porosity, diffusion-convection, radial diffusion, and multi-flow domains like cracked matrices). The program can take into account system phases with different diffusion-convection properties (dissolved, solid, gas, colloidal phase). The LeachXS™ shell creates the necessary input information from stored experimental data, and conveniently presents the calculated output in graphical form which greatly facilitates the use of advanced geochemical and transport models by non-specialists.

3.6.8 STOMP

The Subsurface Transport Over MultiPhases (STOMP) code developed by the Pacific Northwest National Laboratory (PNNL) calculates the time-dependent thermal and hydrogeologic flow and contaminant transport, including volatile and non-volatile organic compounds, in variably saturated subsurface aqueous and vapor phase environments (White & Oostrom 1996; White, Oostrom & Lenhard 1995). The code can be run in one, two, or three dimensional modes and has been used by the Hanford Groundwater Remediation Project and by the team preparing the Hanford Tank Closure and Waste Management Environmental Impact Statement.

3.6.9 PORFLOW

PORFLOW is developed and marketed by Analytic & Computational Research, Inc. (ACRI) to solve problems involving transient and steady-state fluid flow, heat and mass transport processes in multi-phase, variably saturated, porous or fractured media with dynamic phase change. The porous/fractured media may be anisotropic and heterogeneous, arbitrary sources may be present and, chemical reactions or radioactive decay may occur. PORFLOW accommodates alternate fluid and media property relations and complex and arbitrary boundary conditions. The geometry may be 2-D or 3-D and the mesh may be structured or unstructured, giving flexibility to the user. PORFLOW has been widely used at the Savannah River Site (SRS) and in the USDOE complex to address major issues related to the groundwater and nuclear waste management.

4.0 BEHAVIOR OF TYPICAL CEMENTITIOUS MATRIXES

The CBP reference cases include a range of concretes, grouts, and stabilized wastes with binders based on tertiary and quaternary blends of portland cement,

blast furnace slag, coal fly ash, and silica fume (Langton 2009). The release from cement mortars, concrete, and cement-stabilized waste with different waste loading have some common aspects due to the common factor of cement. Comparisons will be made in the following to illustrate relationships and discrepancies between the different cement-based materials.

4.1 Cement Mortars and Concretes

The leaching behavior of a wide range of some 60 cement mortars and concretes from worldwide origin have been tested using the combination of pH-dependence leaching test (TS14429) and tank leaching test (NEN 7345) similar to the integrated leaching assessment approach. The leaching test results, shown in its entirety in Appendix A and for a selected range of major and minor elements in Figure 10 and Figure 11 show systematic leaching behavior for a wide range of constituents as a function of pH and leaching time. In the pH dependence leaching test, concentrations are dictated by the chemical speciation in the cement matrix where as systematic release from monolithic materials is largely controlled by the tortuosity of the matrix and by the release levels governed by pH. The bandwidth of leaching of major elements for all mortars irrespective of its type or origin falls within relatively narrow ranges (van der Sloot et al. 2008b). This implies that the same mineral phases are controlling release. One important to note is that the matrix mineralogy as obtained from X-Ray Diffraction (XRD) and other techniques does not necessarily reflect the phases controlling release.

In fact, the exposure of products to the atmosphere results in significant changes in surface mineralogy as pH and redox conditions change in a thin surface layer. If the pH in the surface of a cement mortar changes from pH > 12 to a pH around 10 or even lower, then several elements show a significantly altered leachability (e.g., SO₄, V, Cr, Ca) over sometimes orders of magnitude. This is reflected in the release

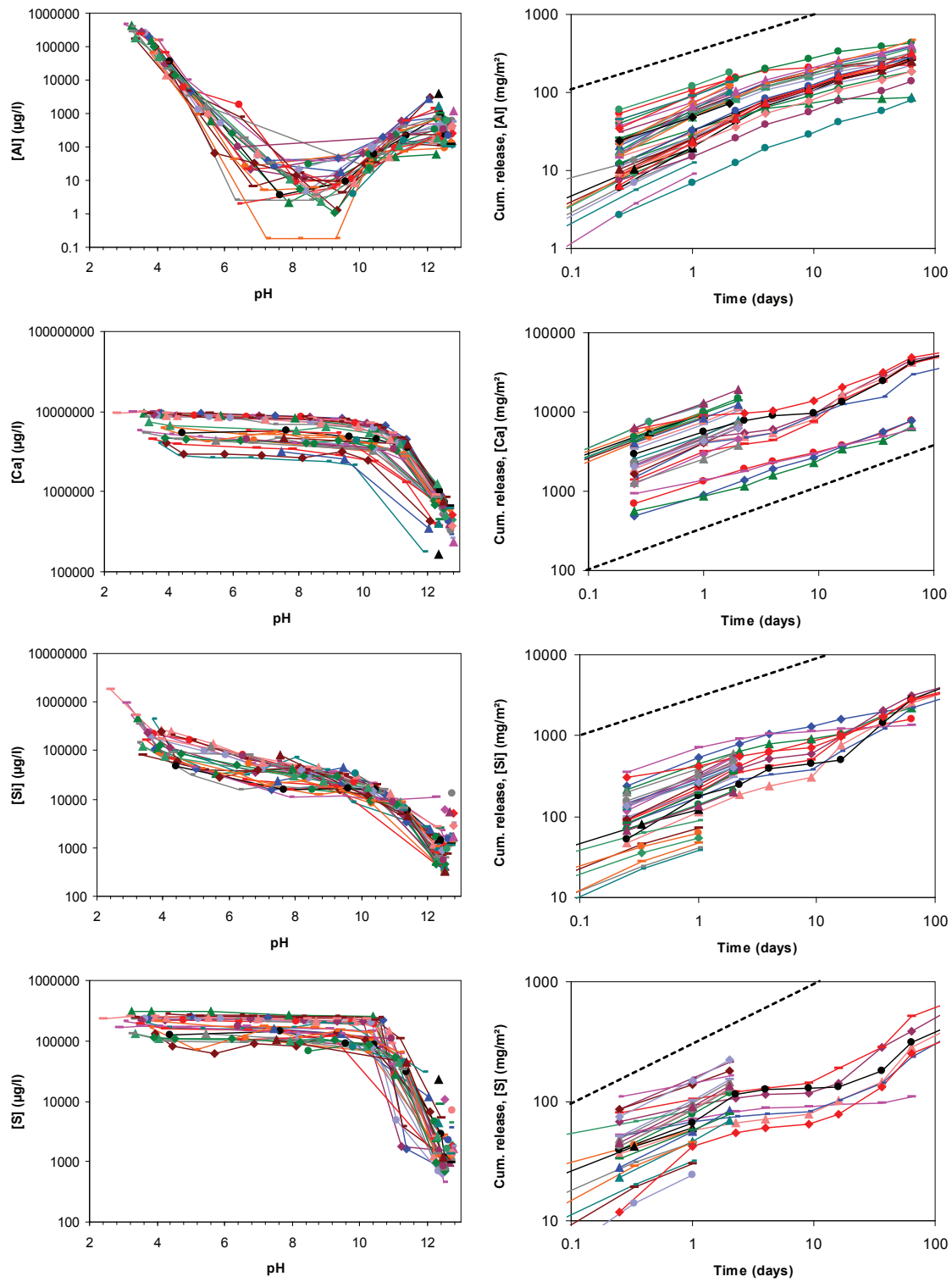


Figure 10. pH Dependence and Tank Leaching Test Behavior of Al, Ca, Si and SO₄ (Shown as Total S) from Cement Mortars of Worldwide Origin

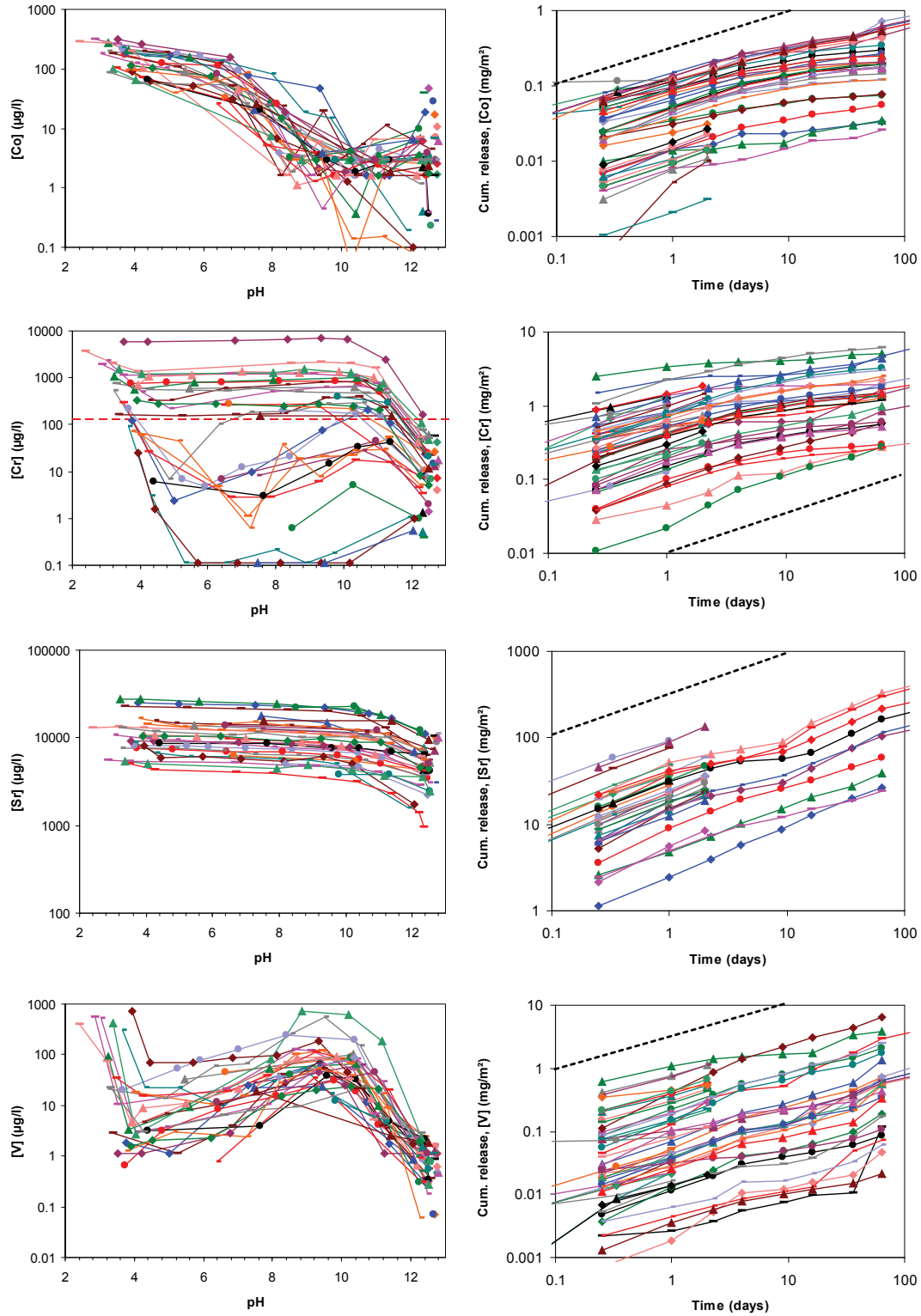


Figure 11. pH Dependence and Tank Leaching Test Behavior of Co, Cr, Sr and V from Cement Mortars of Worldwide Origin

from a monolith leach test. The larger bandwidth in the monolith leach test is associated with the elements that show the largest sensitivity to pH change in the domain pH 12-9.

A consequence of the release behavior of oxyanions as a function of pH is that upon carbonation oxyanions are readily released. As a simplified assumption, one can model the progression of the carbonation front and use the neutralized layer to quantify the oxyanion release by assuming complete release of the mobile fraction of the oxyanion from this layer (van der Sloot et al. 2008b).

4.1.1 Roman Cement Analog

In Figure 12, a comparison of major, minor and trace elements is given for Portland cement (CEM I), blended cements (different blends of Portland cement with blast furnace slag cement and fly ash), Roman cement (2000 years old from an aqueduct in Germany) and cement-stabilized hazardous waste (MSWI fly ash). The leaching behavior as a function of pH in the cement-based materials is mostly very similar, which indicates that the same mineral and sorptive phases control release. The structure of the Roman cement is fully carbonated throughout which has consequences for the leaching behavior of Ca, Ba, Mg and Sr as these species are directly or indirectly affected by carbonation. The leaching of sulfate, Se and Cr is lower than in the other cement mortars, but since the original composition of the Roman cement is not known, it is hard to link the decreased release to leaching and a more likely explanation would seem that these trace constituents are incorporated in less soluble phases. The oxyanion leaching from Roman cement at high pH (e.g., Cr and V) does not show the decrease that is characteristic of substitution into ettringite, indicating the absence of ettringite in the fully carbonated matrix. In the cement-stabilized waste, the leaching behavior of metals show an increase towards low pH

that is related to the higher contamination level in the waste as compared to the commercial cements. Salts (Na, K) and some anions (Mo, B, Sb) are also increased relative to the commercial cements. The distinction between the blended cements containing blast furnace slag and regular Portland cements is the reducing nature of these blends, which is reflected in the leaching behavior of Fe (leachability edge shifted to higher pH), and Cr (low leachability due to conversion of Cr VI to Cr III).

In Appendix B, results of chemical speciation modeling of cement mortars is given. Information on major elements, minor element and a range of trace elements is available. Information of this type is currently lacking for radionuclides. From the stable element chemistry, insight in the chemical behavior of specific radionuclides can be inferred (e.g., Pb, Mo, Sr, Cs, Rb).

4.2 Cement-Stabilized Wastes

In Appendix C results of different types of cement-stabilized waste are compared. This relates to cement-stabilized MSWI fly ash (a material with a high concentration level of trace elements and a high salt load) and stabilization recipes as simulant for grouts to be used in conjunction with waste liquids. It follows that for some elements the release behavior is rather similar between the different mixes. For some constituents, however, the release behavior is significantly different.

In spite of such differences, elements with comparable release behavior can be identified, e.g., metals behave a certain way with low leachability at mild alkaline conditions. On the other hand oxyanions may consistently show a maximum release at pH between 8 and 11. Depending on the sulfate loading, oxyanion substitution in ettringite type phases may be limited by competition between the trace constituents and the abundantly present sulfate.

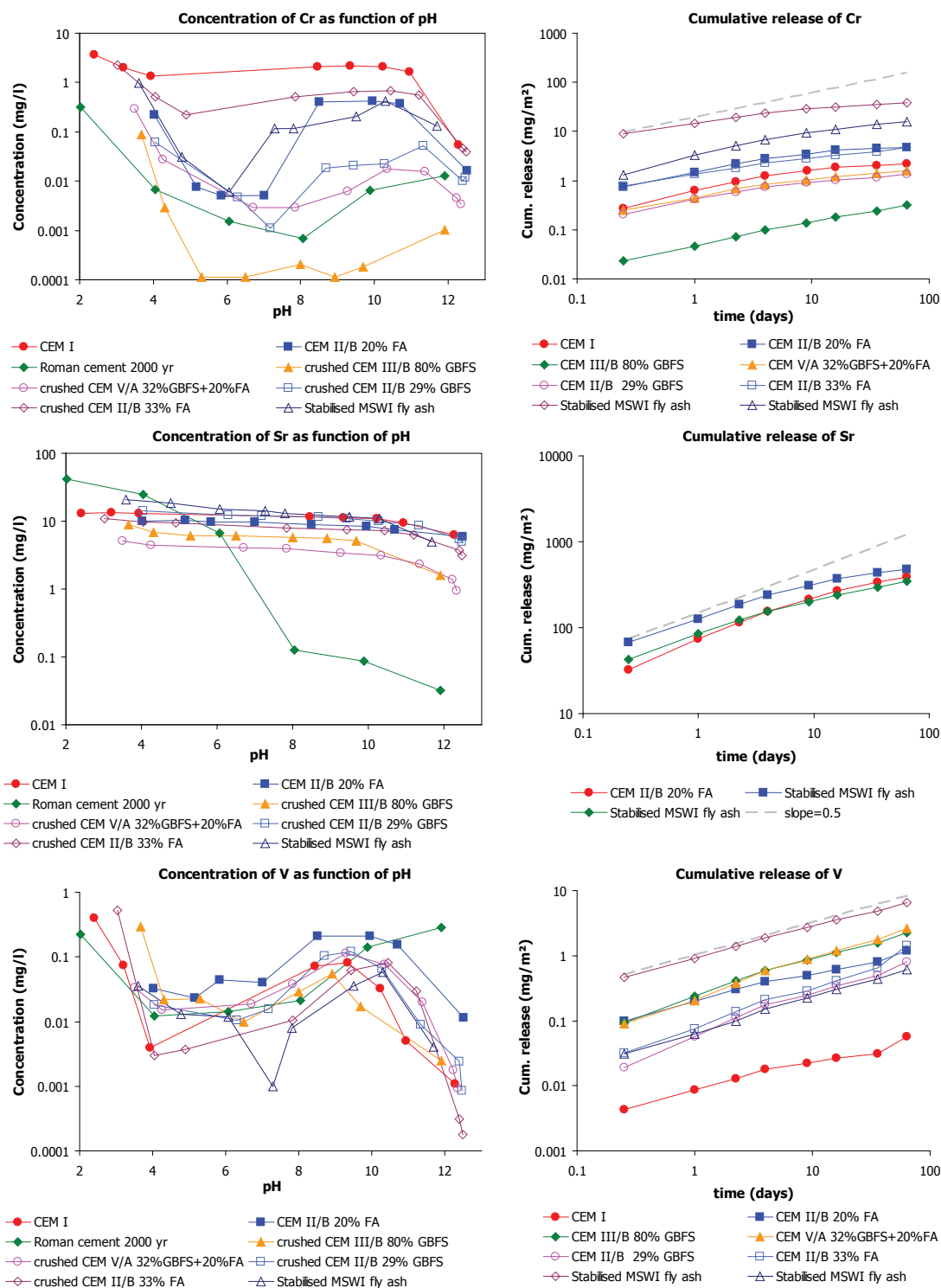


Figure 12. Comparison of Leaching Behavior of Cr, Sr, and V from Portland Cement and Selected Blended Cements, Roman Cement, and Cement Stabilized Waste Using pH Dependence and Tank Leaching Tests

In works by Aarnink et al. (2007) and van der Sloot et al. (2007b), the low LS ratio fraction of column tests could be used to optimize the chemical speciation fingerprint for the sample as a function of LS ratio. If at low LS ratio (0.2-0.3), the same concentration is observed (deviation less than 50%), diffusion is not likely to be the main controlling release mechanism but rather solubility control is the controlling mechanism.

In terms of leaching behavior, the release of a wide range of major, minor and trace elements from stabilized waste is very similar. Differences in release level, which are related to the loading of a particular constituent, may be evident as shown for the sample series (MBD, SWD and AMD) with increasing of relevant constituents (Garrabrants, Kosson & DeLapp 2007). This series represents a solidified matrix similar in recipe to saltstone or caststone with no salt loading (MBD), salt solution at 2.5 M sodium with trace I and Re (SWD), and salt loading with enhance levels of I and Re along with several heavy metals (AMD). The absence of ettringite in the highly-loaded stabilized hazardous waste (NL) is indicated in Appendix C figures as the release at high pH not showing the characteristic decrease between pH 11.5 and 12.5. In contrast, this reduction in release is obvious for several oxyanions in the hazardous stabilized waste (UK).

For the cement-stabilized MSWI fly ash, laboratory leaching data have been compared with data obtained from leaching studies on core samples taken from a test bed for studying hazardous waste disposal and from the full scale operation (field). In Figure 13, the comparison at the different levels of testing is given.

For all matrices, information is available on a wide range of major, minor and trace elements. As indicated before, for several the stable elements release behavior may be indicative for radionuclides of interest. This applies in particular for Sr, Cs and Sb. In Figure 14, a comparison is given between stable element

leaching and radionuclide leaching from cement-stabilized radioactive waste solution. In the case of the stabilized radioactive waste solution (containing in a first solution Cs-137, Ce-144 and U-234 and in a second solution Ru-103 and Ru-106) illite was added to increase the retention capabilities of the mix.

Experimental data on a stabilized radioactive waste solution using cement and tested according to a tank test protocol is given in Figure 14. The composition of the mixes was: BFS cement, silica fume waste solution and a retarder in the ratio 8:2:7:0.08 and BFS cement, silica fume, illite, waste solution and a retarder in the ratio 8:1.6:0.4:7:0.1)

In the mix, illite was used under the assumption that Cs would interact with the illite to stabilize it and reduce its leaching behavior. In this figure a comparison is made of stable elements and the radioactive species for similar grout formulations.

4.3 Soils

Both clay barriers (e.g., bentonite type clays, Boom clay) and natural soil behavior is of relevance in judging release behavior in the scenarios to be evaluated. Release behavior is available on a range of natural soils and contaminated soils. Although the behavior is rather variable, release behavior from soil is largely dictated by sorption for which interaction with hydrated iron-oxides and both particulate and dissolved organic matter play a major role. When the proper interaction parameters are known, there is good agreement between model and observed release behavior (Dijkstra et al. 2008; Dijkstra, van der Sloot & Comans 2006).

The neutralization of alkalinity released from cementitious matrices by a clay backfill, clay liner or natural soil is important for the release of substances from cementitious barriers, as the changes in soil due to alkalinity changes have significant influence on mobility of various substances. The neutralization is

significantly influenced by the degree of saturation, as carbon dioxide may contribute to the neutralization. Modeling of oxidation/carbonation of a steel slag as sub-base of a parking lot (H.A. van der Sloot et al. 2007) has shown the magnitude of such influences. Both clay barriers (e.g., bentonite type clays,

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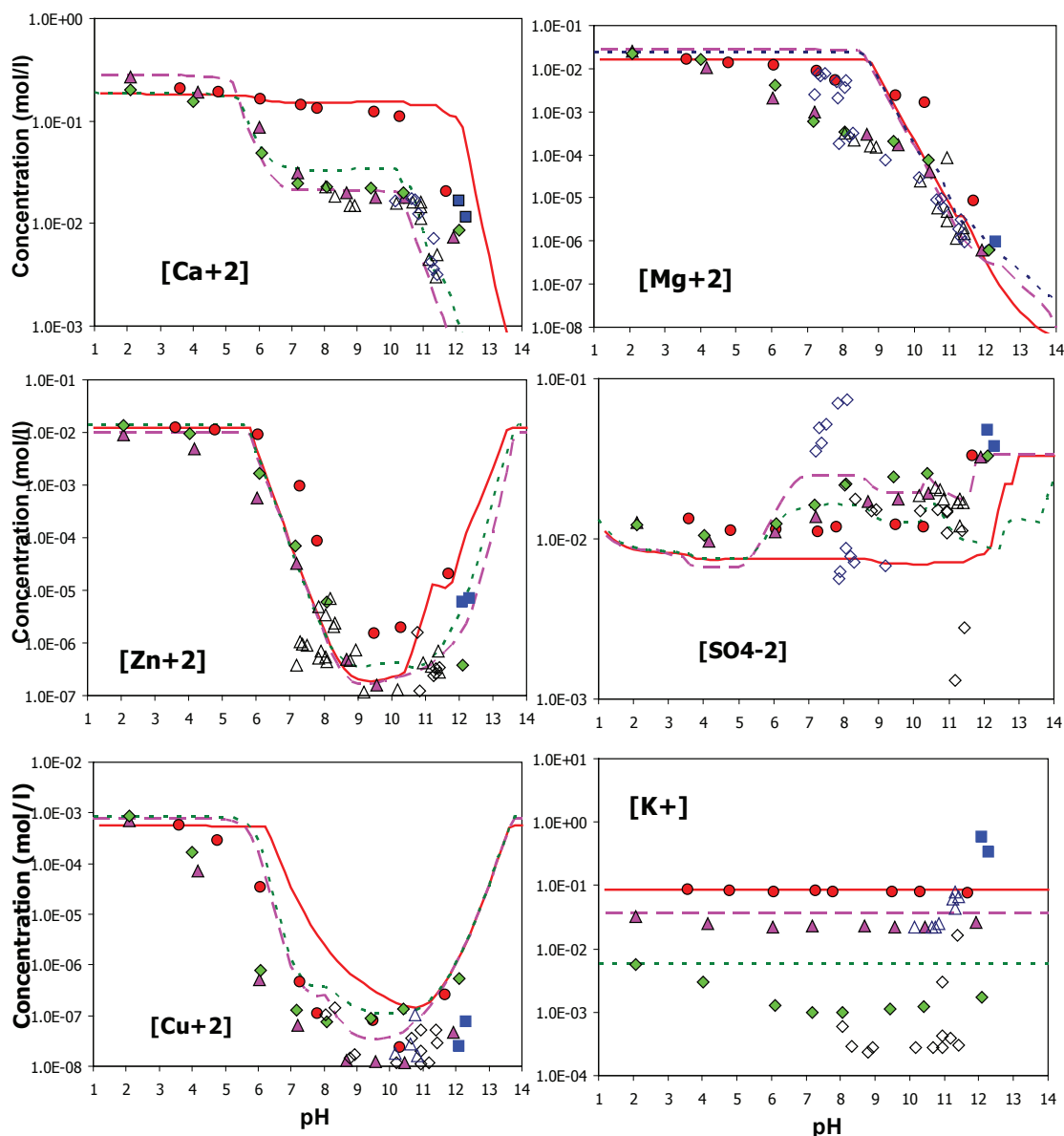


Figure 13. Geochemical Speciation Modeling Of pH-Dependence Data Using LeachXS™-ORCHESTRA for Several Cement-stabilized Wastes Including Freshly-stabilized Waste (Red Points), Cored Samples from A Stabilized Waste Cell (Green Diamonds and Pink Triangles), and Field Leachate Data (Open Diamonds).

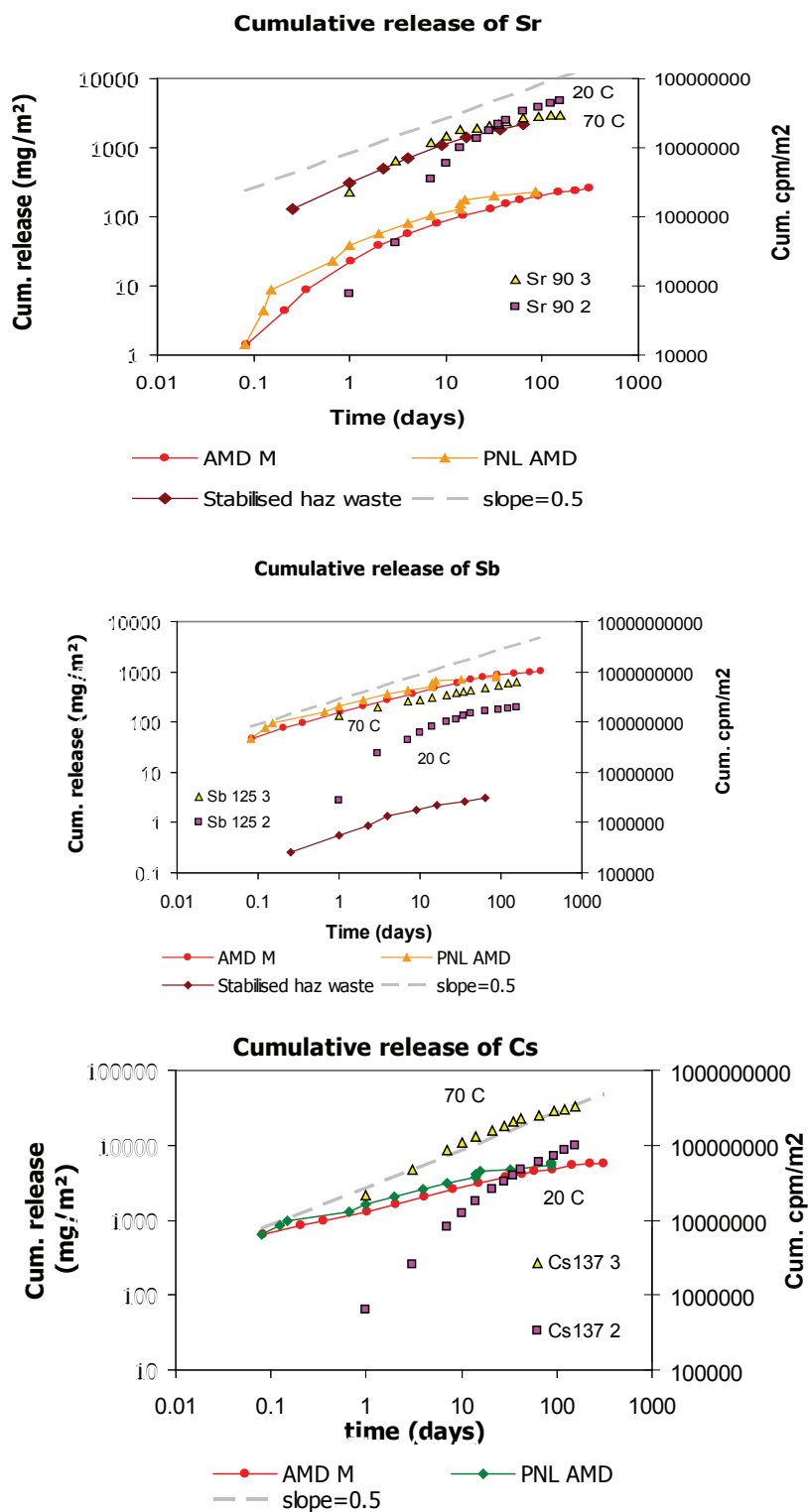


Figure 14. Comparison of Release of Cement-stabilized Waste Grout and Cement-stabilized Radioactive Waste Solution with Illite Addition Containing ^{137}Cs , ^{90}Sr and ^{125}Sb Using A Tank Leach Test

with hydrated iron-oxides and both particulate and dissolved organic matter play a major role. When the proper interaction parameters are known, there is good agreement between model and observed release behavior (Dijkstra et al. 2008; Dijkstra, van der Sloot & Comans 2006).

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5.0 LEACHING ASSESSMENT IN CBP REFERENCE CASES

The transport of constituents across interfaces plays a large role in the assessment of leaching, both in the short-term (e.g., precipitation leading to boundary layer formation) and long-term (e.g., CO₂ or O₂ ingress and associated effects). Therefore, it is important to relevant interfaces of CBP reference cases into context with leaching processes and aging effects.

5.1 Interface Identification in CBP Reference cases

The CBP has identified reference cases in which cementitious media are relied upon to retard the release of constituents: (1) a spent fuel pool scenario, (2) waste tank closure scenario, and (3) low-level radioactive waste vault scenario (Langton 2009). The interfaces associated with each of these cases can be expressed as a one-dimensional abstraction of a conceptualized multi-layer system.

5.1.1 Spent Fuel Pool

In Figure 15, a prototypical spent fuel pool is depicted with a break out to show the main release scenario related to this reference case. Interaction of pool water with a concrete pool wall will show a very slow carbonation progression. As pool water is maintained with low concentrations in critical salts (e.g., Cl⁻, SO₄²⁻ and Mg²⁺) the effects on rebar will be less severe than attack from the outside in case of aggressive groundwater containing higher levels of these potentially critical components. In the long-term pool scenario, the development of a crack or fissure is more serious threat to long term containment. Once a through thickness crack or fissure develops, the interior hydraulic head (up to ca. 6 m) will force water to start flowing facilitating transport. The flowing water may further erode the crack serving as the flow conduit. It is unlikely that species dissolving from the matrix will have a chance to precipitate and clog the pores in spite of the fact that under stagnant conditions such sealing might occur or might even be stimulated. The water containing dissolved radionuclides will enter into the second barrier, if any, and enter the surrounding soil system, where depending on the outflow rate soil erosion may occur. The interaction of released substances with soil will proceed and can be described provided the interaction parameters are known.

5.1.2 Tank Closure

In Figure 16, tank closure is depicted with a break out to show the main long-term release issues indicated. For tank closure, a grout formulation is used to fill the tank and the annulus between the tank liner and tank wall in order to reduce direct emission by restricting water flow and to provide the chemical conditions (pH, redox) which enhance constituent retention. In this case, a range of conditions are relevant: (1) the degree to which the waste is adequately mixed with grout or remains as sludge in the bottom of the tank;

(2) the degree to which the grout interacts with the steel lining, and (3) the extent of contact with CO_2 from the atmosphere and the ingress of water. The interactions at the different material interfaces forms a first step in evaluating long term processes. In a second step, the quantification of carbonation and oxidation fronts is important because they determine to a large extent the potential mobilization of radionuclides of concern. The formation of cracks in the grout enhances these processes.

5.1.3 Low-level Radioactive Waste Vault

In Figure 17, a low level radioactive waste vault is depicted with a break out to show the main long-term release interfaces. This case has many similarities with the tank closure in that the development of carbonation and oxidation fronts are important to determine the release behavior of many radionuclides. Evaluation of the interaction at interfaces with or without air space between them is an important first step to quantify the potential release, which may be further augmented by further deterioration of the matrix. Sulfate attack from the waste form into concrete is important in case where sulfate concentrations are elevated in the residual waste or soil.

The most important chemical gradients within and at the boundaries of a cementitious material are with respect to pH, redox, salt (total dissolved ionic content) and, obviously, radionuclide concentrations within cement-stabilized grout and waste forms. The reactions at interfaces are quite complex with the possibility of very substantial changes in pore solution composition and solubility controlling conditions occurring over a relatively small distance. Understanding the processes and conditions at interfaces between dissimilar materials is helpful in deciding whether such reactive zones play an active role in the transport of substances across an interface. Several material interfaces relevant to cementitious materials in nuclear applications are discussed below.

5.1.4 Cementitious Wasteforms and Grouts-Concrete

The interface between cement-stabilized waste and concrete is characterized by a gradient in soluble salts and depending on the nature of the cement used (i.e., reducing waste forms, grouts and concretes), a redox gradient. Different pore structures amongst the two materials can also result in capillary suction between materials across the interface. Cement-stabilized waste forms and grouts may contain substances that can have a detrimental effect on concrete (like sulfates) or chlorides. If there is a void between the concrete and the waste form or grout, then carbonation and oxidation will likely proceed faster in the waste form or grout than in the concrete because porosity is usually lower in concrete. The rate of front movement (especially in pH, carbonation and sulfate) will likely significantly influence the mobility of different elements.

5.1.5 Concrete-Soil Interface

The interface between concrete and a clay barrier, soil or backfill typically is characterized by a large pH gradient. The consequences are re-mineralization reactions which, depending on the nature of the soil, can have surface effects on the concrete (Viani, Torretto & Matzen 1997). Organic matter from soil interacts with the concrete and can potentially mobilize constituents. As long as the monolithic product remains intact, the affected layer is generally limited. Concrete exposed to a moist soil atmosphere will carbonate faster than when exposed to the atmosphere, as the CO_2 concentration in the soil gas phase is generally higher than the CO_2 level in the atmosphere as a consequence of biodegradation of organic matter in soil systems. Modern concretes exposed to soil and other environmental conditions are only slowly carbonated, unlike the much more porous Roman cements used to construct aqueducts. The ancient pozzolans, e.g., volcanic tuff or trass, have rather high porosity, which allows drying to occur more

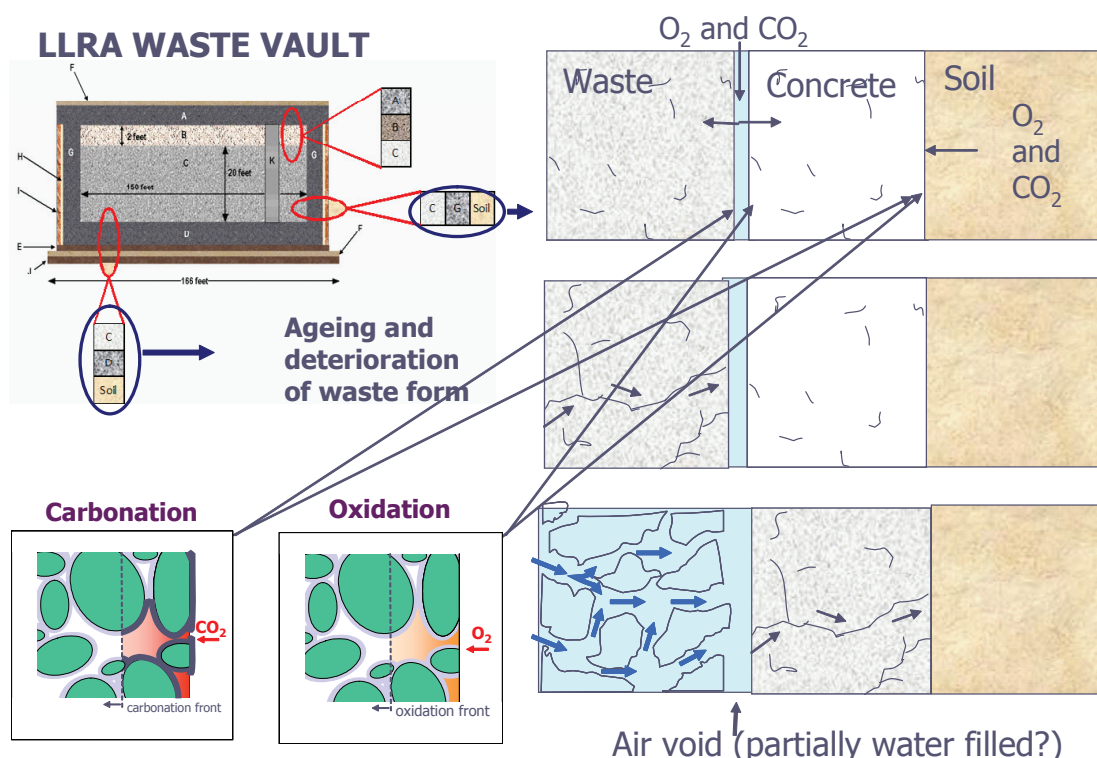


Figure 17. Low-level Waste Vault Scenario with Breakout of Multilayer System Abstraction

rapidly and carbonation to penetrate deeper. Lumps of Roman cement, sampled from ancient German aqueducts, were tested for trace element behavior and found to be fully carbonated to the depth of the core (~10 cm) after approximately 2,000 years (van der Sloot et al. 2008b).

5.1.6 Additional Barriers

Additional barriers between grout and surroundings may be steel linings or other additional barriers like high density polyethylene. These will form an effective barrier, until the lining fails, which is likely at a time scale of 1,000s of years. Corrosion of the barrier will be dependent on the interfacial chemistry. The modeling must assume failure at some point in time.

5.2 Multilayer Systems Modeling

The above sections highlight the importance of material interfaces within the CBP reference cases. The chemical interactions between the materials layers in a multilayer system can be studied by applying a saturated system of granular materials of all of these matrices using diffusion as the only transport process (tortuosity of mortar about 10 times higher than stabilized waste and soil). This type of system can elucidate the chemical interactions occurring at interfaces (mobilization and precipitation). The full CSF as derived from modeling the pH-dependence test results for the individual materials of this multilayer system are used as starting point.

In Figure 18 and Figure 19, an example of the modeling is given. Each figure represents the concentrations of speciated solid and liquid phases as a function of depth through a 3-layered system comprising a stabilized waste, a cement mortar and a soil. In order to be able to simulate a response with relative short computational duration, the layers are kept relatively thin (3-cm). The concentrations are shown on both linear (left) and logarithmic (right) scales.

The composition of the stabilized waste (increased sulfate and imposed reducing conditions) and the soil have been modified to force a response to sulfate and Mg from the soil on the cement mortar. In the model run with LeachXS™-ORCHESTRA the distribution

over dissolved and solid phases is calculated. Interactions at the interface between the cement matrix and the soil are of particular interest due to the large gradient in pH between the two matrices. To some degree, the soil buffering capacity will neutralize the alkalinity released from the cement-based matrix; however, the buffer capacity of most mortars will exceed that of the soil, implying movement of an alkaline pH front. Since soil organic matter is mobilized at high pH, progression of an alkaline front into the soil may affect transport of species. When an ettringite front develops at the soil-cement interface, species may be incorporated into precipitated ettringite by substitution.

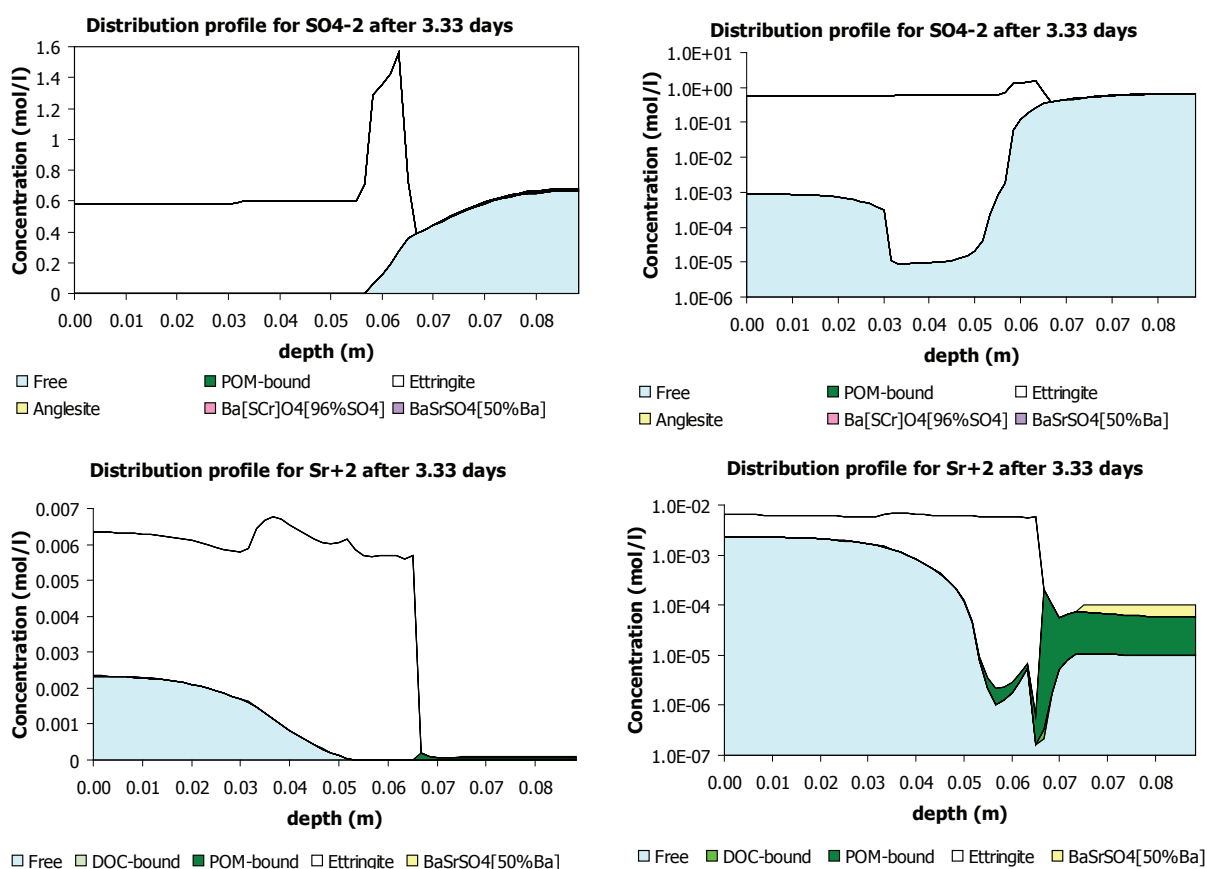


Figure 18. LeachXS™-ORCHESTRA Simulation of SO₄ and Sr Transport by Diffusion in A 3-layer System of Stabilized Waste/cement Mortar/soil with 3-cm Layers.

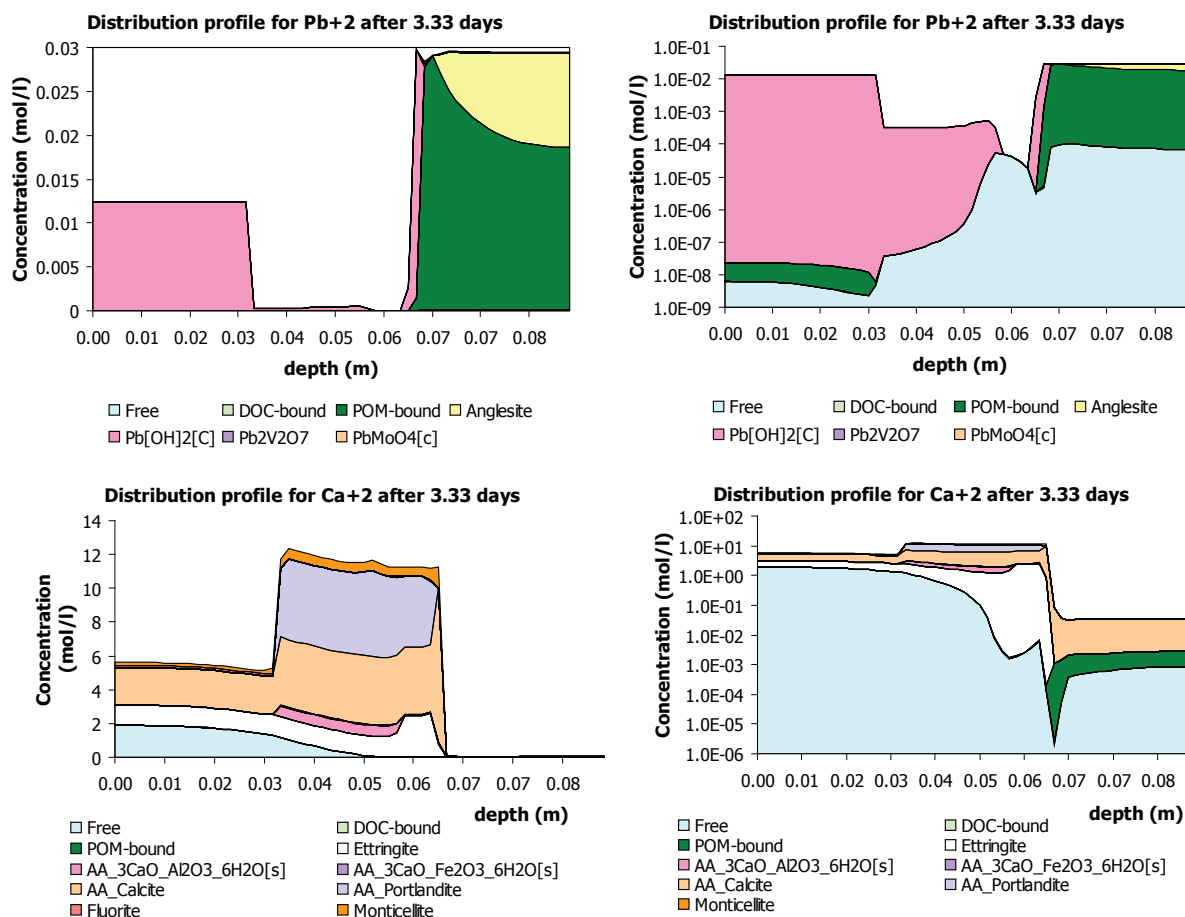


Figure 19. LeachXST™-ORCHESTRA Simulation of Pb and Ca Transport by Diffusion in A 3-layer System of Stabilized Waste/cement Mortar/soil with 3-cm Layers

In future work, unsaturated conditions with gas interaction will be taken into account. When air can penetrate at the stabilized waste-cement interface then due to carbonation, a substantial gradient may develop at this interface as well.

6.0 LYSIMETER STUDIES FOR RADIOACTIVE WASTE

The use of field lysimeter systems provides the realistic experimental conditions to assess the leachability and durability of radioactive waste. Field lysimeters are devices that are designed to contain waste, soil,

and a means of sampling water in a sump at the bottom of the lysimeter. Often pore water samplers are installed, as well as other instrumentation to monitor percolate properties.

Typically, lysimeters are installed in the field with the intention of collecting long-term data on leachability of waste under natural precipitation conditions. Thus, the systems are open to precipitation (and generally plant growth), but are isolated from the subsurface to prevent loss of leachates. Although lysimeters may provide credible field conditions, the leachate results may be difficult to interpret because of limited experimental control of the system. In addition, the

process of setting up, monitoring, and decommissioning lysimeters can be costly, especially when radioactive species are present. Several projects that used lysimeters to examine the behavior of radionuclides in waste are discussed below.

6.1 Special Waste Forms Lysimeter Project

Starting in 1982, the USDOE sponsored the Special Waste Forms Lysimeter Project, with two sets of lysimeters; one set at an arid site (at Hanford) and another at a humid site (at SRS). Each set of lysimeters consisted of a series of 1.8-m diameter by 3-m deep cylinders, arrayed around an instrument caisson. The wastes were full-size (210 liters) commercial nuclear power plant wastes, solidified in Portland cement, bitumen, or a polymer. Replicate waste forms, of both small and full scale, were leached in laboratory experiments (Arnold et al. 1983) allowing for comparison of field data to lab data at various scales.

Interim results (Skaggs & Walter 1989) of arid site lysimeters at Hanford showed water balance data as well as leaching information after three years of exposure (1984-1987). All the lysimeters contained boiling water reactor wastes, in most cases, solidified with cement. Five of the lysimeters showed breakthrough of ^{60}Co , but no release of other radionuclides. Between 1 and 6 μCi of ^{60}Co were detected in percolation waters over about 720 days. Although only a small fraction of the total ^{60}Co inventory was leached, it was not sorbed onto the lysimeter soil, presumably because the ^{60}Co was complexed with a chelating agent. By 1992 (eight years of exposure), results indicated that about 27% of the precipitation had percolated through the lysimeters, removing 71-76% of the wastes tritium inventory. Much lower fractional releases ($<0.1\%$) of ^{60}Co and ^{137}Cs were also observed (Jones & Serne 1995). Laboratory leach tests conducted on replicate waste forms using a modified ANS 16.1 test showed that large quantities of ^{137}Cs (80%) leached from the waste in 35 days, while only 0.5% of the ^{60}Co was released.

Substantially more activity was observed in the leachate from the humid site than the arid site (McIntyre 1987). An anionic form of ^{60}Co was found in concentrations as high as 1,120 pCi/L in leachates of cement waste forms and 11.1 pCi/L in polymer solidified waste leachates. The polymer waste form released more ^{90}Sr (up to 6.6 pCi/L) than the cement waste forms. ^{137}Cs was also observed in leachate from one of the cement waste form lysimeters.

Radial soil cores were taken below the waste forms that showed the distribution of radionuclides in the soil of the lysimeter. In both the arid and humid sites, ^{60}Co was found to be the most mobile radionuclide, especially from cement waste forms, because a fraction of it was complexed and in an anionic form which was not retained by lysimeter soils. The implication of this study for cement-like waste forms was that anionic radionuclides (e.g., Tc, I, and complexed transition metals) will be difficult to sequester.

6.2 Other Lysimeter Studies

At SRS, 115 lysimeters of various designs were installed, many to investigate leaching of defense wastes. Of these, 12 were small 52 liter lysimeters (upside down plastic carboys with the bottoms cut off) used to study leaching and geochemistry of Pu in SRS soil (Kaplan et al. 2003). The key finding from these studies was that regardless of its original oxidation state, the Pu converted within 33 days to less mobile Pu(IV) form. Pu (VI), a mobile form that was placed in a lysimeter, moved 5 cm over 2 years, implying that it converted to a less soluble form.

Three lysimeters at Savannah River were put in place in 1983-4 containing 9,500 liter saltstone waste-form. One lysimeter had a gravel cap, one a clay cap, and the third was uncapped. Leaching of ^{99}Tc and nitrate from the uncapped lysimeter was greatest with the highest activity in leachate being 11.9 nCi/L. Leachates of the other lysimeters were consistent with background concentrations (McIntyre, Oblath & Whilite 1989).

Thirteen years of experimental results from field tests in Russia provide information on leaching and waste-form integrity under simulated repository conditions and more open, subsurface conditions (Ojovan et al. 2002). The materials were sodium nitrate reactor wastes that were incorporated into glass, bitumen and cement waste forms. The cement waste form lost 2.02% of its activity in 13 years while bitumen lost 0.65% and glass 0.007%. Under repository-like conditions, releases were much lower, 0.04, 0.002, and 0.001% for cement, bitumen and glass, respectively. Under these conditions, leach rates appear to reach steady state after about ten years. There was little change in glass waste forms, with the exception of a thin weathering layer detected by x-ray analysis. The cement waste forms were fragile with compressive strengths around 1 MPa and appeared to have undergone deterioration and recrystallization. Bitumen waste forms had become harder and more thermostable over time with the leach rate also decreasing over time.

The USNRC funded a series of lysimeter studies to develop information on low-level waste form behavior (McConnell et al. 1998; Rogers et al. 1989). Epicor-II resin used to decontaminate water from the Three-Mile Island accident was solidified in portland cement and vinyl ester styrene polymer. These experiments ran for ten years and consisted of field tests at Oak Ridge and Argonne National Laboratories. Comparisons were made to two computer models. Cement waste forms retained ^{90}Sr better than VES but on average 65% of ^{90}Sr was leached. An average of 37% of ^{137}Cs was leached. $^{134/137}\text{Cs}$ and ^{90}Sr were detected at the surface of one lysimeter in which unidentified plants had grown and drawn activity up through the roots. Comparison of lysimeter leaching with leach test results indicate that lysimeter releases of ^{90}Sr were at least 100 times lower than leach tests, while for ^{137}Cs releases were 5 orders of magnitude less. These differences include limited contact with percolating water as well as retention of radionuclides on the soil of the lysimeters. Most of the activity

remained bound to soil within the first 10-20 cm under the waste forms.

7.0 KNOWLEDGE GAPS AND NEEDS

The most important “gaps” in our knowledge which, when understood in more detail, would lead to greater understanding of long term release from cementitious barriers used in radioactive waste management are summarized below.

7.1 Aging of Cementitious Materials

The chemical and physical aging phenomena for cementitious materials, not uniformly taken into account in most leaching evaluations, may be deleterious or beneficial to long-term performance of cementitious barriers. Enhanced understanding of aging phenomena for cementitious material under credible release scenario conditions will improve prediction of constituent release over extended performance periods.

Aging and leaching evaluation of cementitious materials should take advantage of natural analogues and studies conducted on historical materials. Further investigations are needed to assess the rate of carbonation and oxidation processes and the effect of these aging mechanisms on constituent release. Descriptions of historical situations like the 2000-year-old Roman aqueducts cement and analogues from the waste management field (e.g., radionuclides in waste) or from long-term technical performance studies on concrete in Germany and Sweden also can provide valuable information.

7.2 Chemical Retention of Radionuclides

The thermodynamic data required to properly predict radionuclide behavior under defined chemical conditions in cementitious materials is either lacking or not compiled in a concise, readily available form. This data includes thermodynamic constants for

precipitation, aqueous complexation, sorption to solid phases of cementitious materials and soils, interactions with mobile colloidal organic material and reduction/oxidation. Testing should provide data on pH-dependence, redox capacity, metal (hydr)oxide sorption and organic carbon (total organic carbon and DOC). The use of stable isotope data where radionuclides data is lacking might be feasible. Radioactive decay constants and decay series need to be including in the presented leaching assessment approaches.

7.3 Uniform Testing and Interpretation

The process of leaching assessment would benefit from a uniform approach in terms of guidance documents, a battery of integrated leaching tests, interpretation methodologies, and integrated database of leaching data for relevant materials. Cementitious materials and other radionuclide containing wastes may be assessed by the same set of leaching tests (e.g., pH dependence test, percolation leaching test, and mass transfer test, with redox capacity test where appropriate). Formation of an integrated database of release and chemical retention data for soils and cementitious materials would benefit leaching assessment by providing the ability to directly compare different leaching tests, test conditions and field scale results. Information should include as many constituents as possible (e.g., radionuclides, metals, and primary constituents).

7.4 Systematic Leaching Behavior

Evaluating of the potential sensitivities of systematic leaching behavior to perceived heterogeneities between cementitious material formulations and contaminants can simplify the assessment process considerably. Mixed municipal solid wastes have been found to behave in a remarkably constituent, systematic matter in spite of obvious macroscopic heterogeneities. Similar characteristic behavior is likely for cementitious barrier materials, especially cement-treated wastes, in that the conditions created by the stabilization process tend

to make these materials behave more systematically, thereby making the release process more predictable.

7.5 Predominance Diagrams

The use of predominance diagrams developed using thermodynamic data of the major, minor and trace constituents that control conditions in cementitious systems can be integrated with the thermodynamic data of radionuclides to the extent available. Predominance diagrams not only allow assessment of pH-pe fields, but also put focus on changes in other chemical retention factors like carbonate, organic matter, and iron oxide. Such insights would be beneficial for defining anticipated initial, intermediate and end point conditions of disposal scenarios without knowing precisely at what time scale such changes may occur.

7.6 Kinetically-Controlled Processes

Investigation of the role of kinetically-controlled reactions would enhance current descriptions of chemical retention for species and conditions where the local equilibrium assuming is not valid. For example, conducting pH-dependence tests at extended contact times, within the practical limitations of maintaining experimental conditions, would improve the understanding of slow chemical reactions.

7.7 Transport in Unsaturated Materials

Using a multi-element mechanistic model to describe transport by solely diffusion processes can be monitored and combined with verification experiments in the laboratory by applying the diffusion tube principle (Schaefer et al. 1995). In the case of reducing materials, experience has already been gained on how to avoid oxidation during the diffusion experiment from work on sediments. The model to describe the multi-element transport behavior of this type is operational in LeachXS™.

The modeling and experimental work needs to be expanded for different material combinations (grout-cement, cement mortar–bentonite clay, cement mortar–natural soil). Basic information on pH dependent behavior of bentonite and clay used as barrier is currently lacking and needs to be developed. In this modeling, the electrochemical potential is likely to be consideration. This appears to be important, not only in case an electrical potentials is applied, but also for high concentration electrolytic solutions. It would be valuable to compare the effects of Nernst equation methodologies to the traditional diffusion-based approach.

7.8 Comparative Evaluations

Comparative studies, conducted by interpreting model methodologies (e.g., linear sorption vs.

mechanistic chemical retention), conceptual models (e.g., cracked vs. uncracked materials), and parameters appear to be a useful tool in development of mechanistic leaching simulation approaches. Good understanding of the limitations and possibilities of various modeling approaches (e.g., K_d approach versus a mechanistic approach) is mandatory. Model runs on the same test data with different model approaches can provide insight in this aspect. In addition, to what extent derived parameters (from analogy in behavior with stable elements) can be used to describe release under a range of experimental test conditions needs to be determined. To date, these derived parameters have not been individually verified by adequate chemical and physical characterization (e.g., ettringite substitution, iron-oxide sorption, organic matter interaction). understanding of slow chemical reactions.

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APPENDIX A. Comparison of Leaching Results from Cement Mortars

Cement mortars studied in ECRICEM I and II (2001 and 2008) are presented in Table A.1.

Table A.1. Cementitious materials studied.

Material Type	Material Components
Commercial Portland Cement	
CEM I	Clinker, gypsum, filler
CEM I	Clinker, gypsum
CEM I	Clinker, gypsum, filler
CEM II-L	Clinker, gypsum, limestone (14 %)
CEM I	Clinker, gypsum
CEM I	Clinker, gypsum, filler
CEM I	Clinker, gypsum, filler
CEM I	Clinker, gypsum, filler
CEM I	Clinker, gypsum, filler
CEM I-HS	Clinker, gypsum
Slag Cement	
CEM III/B	80% GBFS
CEM III/B 32.5 N	66% GBFS
CEM II/B-S 32.5 R	29% GBFS
CEM II/B-S 32.5 R	29% GBFS
CEM II/A-S 32.5 R	20% GBFS
CEM III/A 32.5	69% GBFS + 5% LS
CEM II/A-S 32.5 R	
CEM II/B-S 32.5 R	
Composite Cement (with one component)	
CEM II/B-V 32.5 N	33% FA
CEM II/A-V 42.5 N	10% FA
CEM II/A-V	with chromate reduction and 17 % FA
CEM II/B-Q	32% P
CEM II/B-P 32.5 R	26 % Trass (P)
CEM II/B-L	28% LS
CEM II/A-L 32.5 R	13% LS
CEM II/A-LL 32.5 R	13 % LS
Composite Cements (with more than one component)	
CEM V/A 32.5 N	32% GBFS+20% FA
CEM V/A 32.5 N	23% GBFS+22% FA
CEM II/B-M 32.5 R	33% GBFS+9% LS
CEM IV/A 32.5 R	15% FA+17% P
CEM II/B-M 32.5 R	14% GBFS+12% LS+5% FA
CEM II/B-T 42.5 R	Burnt Oil Shale
Portland Cements	
CEM I	without LD slag in raw mix
CEM I	with LD slag in raw mix
CEM I 42.5 R	with chromate reduction

Notes:

GBFS = granulated blast furnace slag

FA = fly ash

LD = Linz-Donawitz

LS = limestone

P = pozzolan

APPENDIX B. Comparison of Leaching Test Results from Portland Cement Mortar, Blended Cement Mortar, Stabilized Waste and Roman Cement Mortar.

In the graphs shown below the leaching behavior as a function of pH (pH dependence test) and as a function of time (monolith leach test) for the following materials are given:

- CEM I cement mortar
- CEM II/B 20% FA
- Roman cement 2000 year (fully carbonated)
- CEM III/B 80% GBFS
- CEM V/A 32%GBFS+20%FA
- CEM II/B 29% GBFS
- CEM II/B 33% FA
- Cement stabilized MSWI fly ash

Graphs for the following elements are given in the figures indicated:

Fig. B.1.	Al, As, B
Fig. B.2.	Ba, Ca, Cd
Fig. B.3.	Cl, Co, Cr
Fig. B.4.	Cu, Fe, K
Fig. B.5.	Li, Mg, Mn
Fig. B.6.	Mo, Na, Pb
Fig. B.7.	SO ₄ as S, Sb, Se
Fig. B.8.	Si, Sn, SO ₄
Fig. B.9.	Sr, V, Zn
Fig. B.10.	DOC

The first graph gives the release as a function of pH, the second graph shows the concentration in eluates from the monolith leach test as a function of time. The third graph shows the cumulative release expressed in mg/m² as a function of time and the fourth graph shows the pH as a function of time (days).

The Roman is fully carbonated, which is reflected in the behavior of many elements, but in particular in Ca, Mg, and Sr.

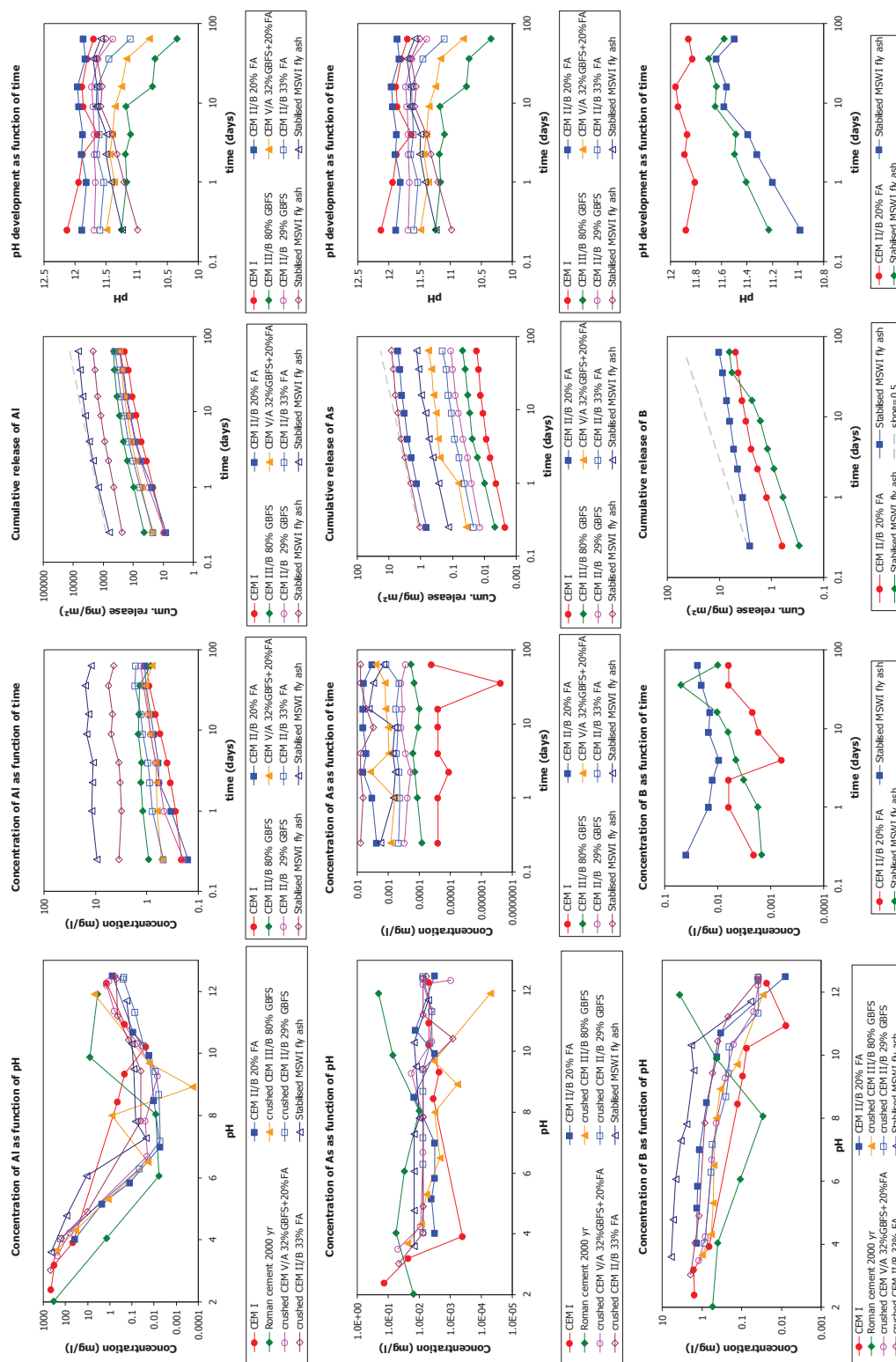


Figure B.1. Aluminum, arsenic and boron leaching results from several cementitious materials.

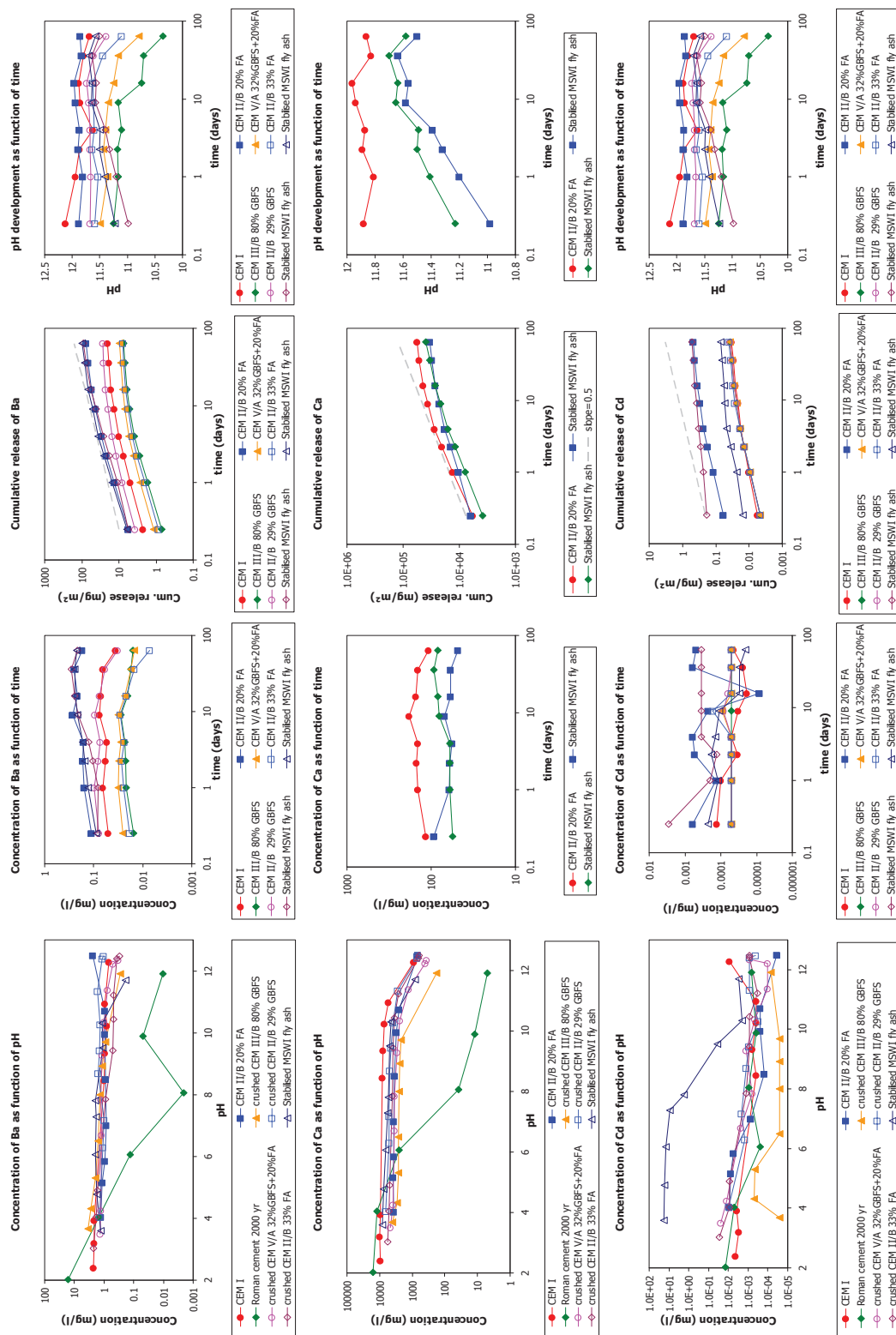


Figure B.2. Barium, calcium and cadmium leaching results from several cementitious materials.

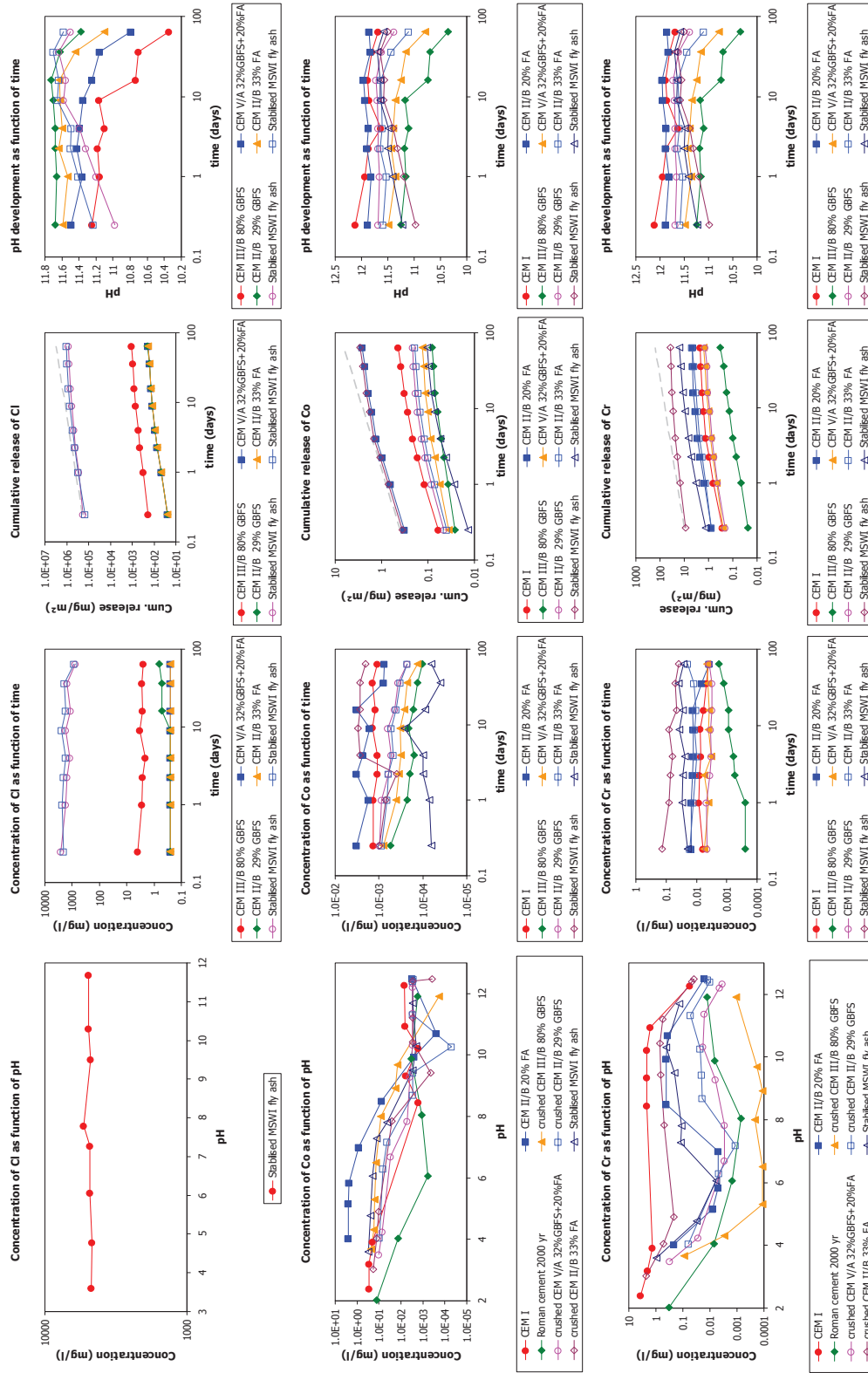


Figure B.3. Chloride, cobalt, and chromium leaching results from several cementitious materials.

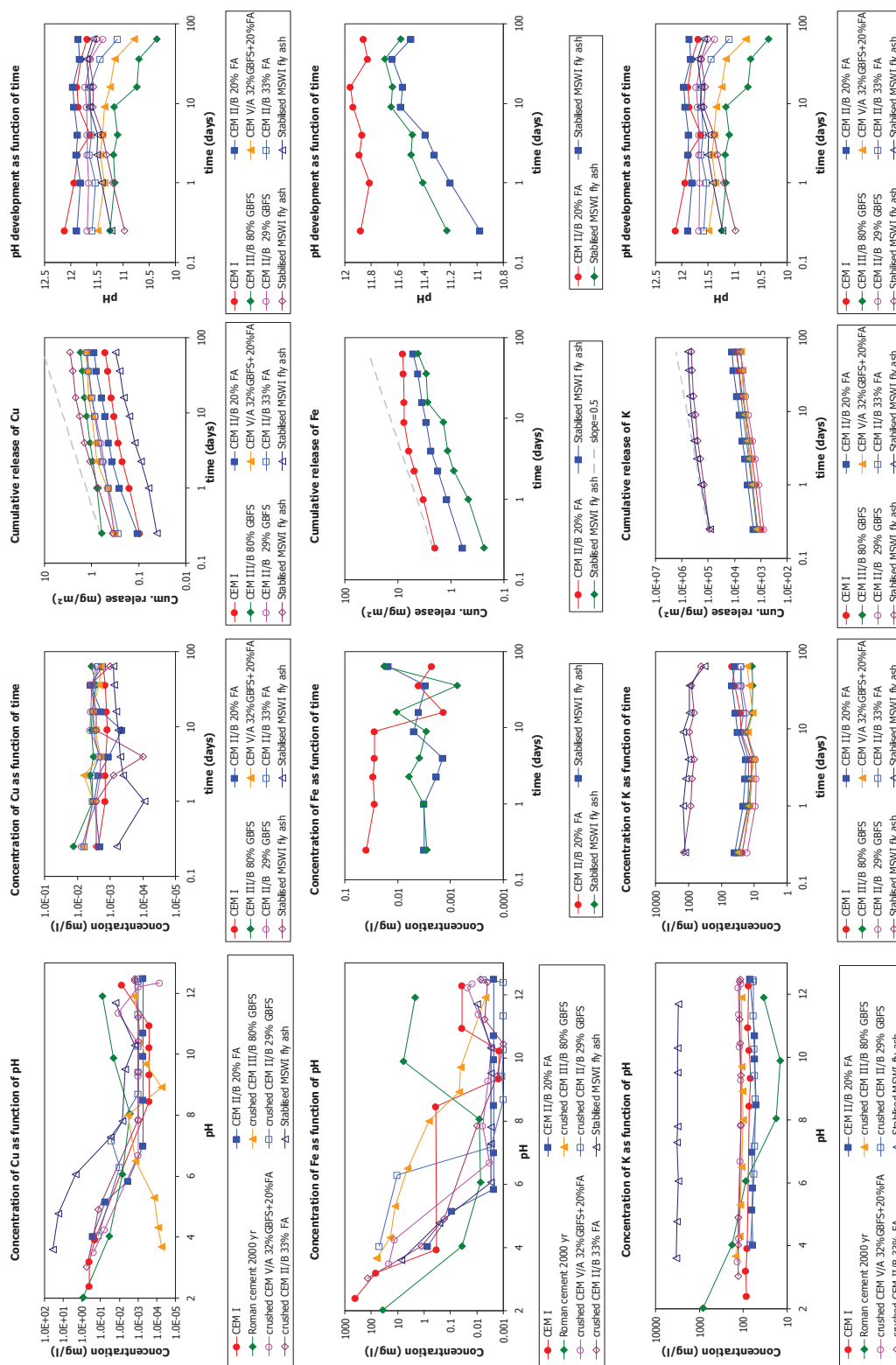


Figure B.4. Copper, iron and potassium leaching results from several cementitious materials.

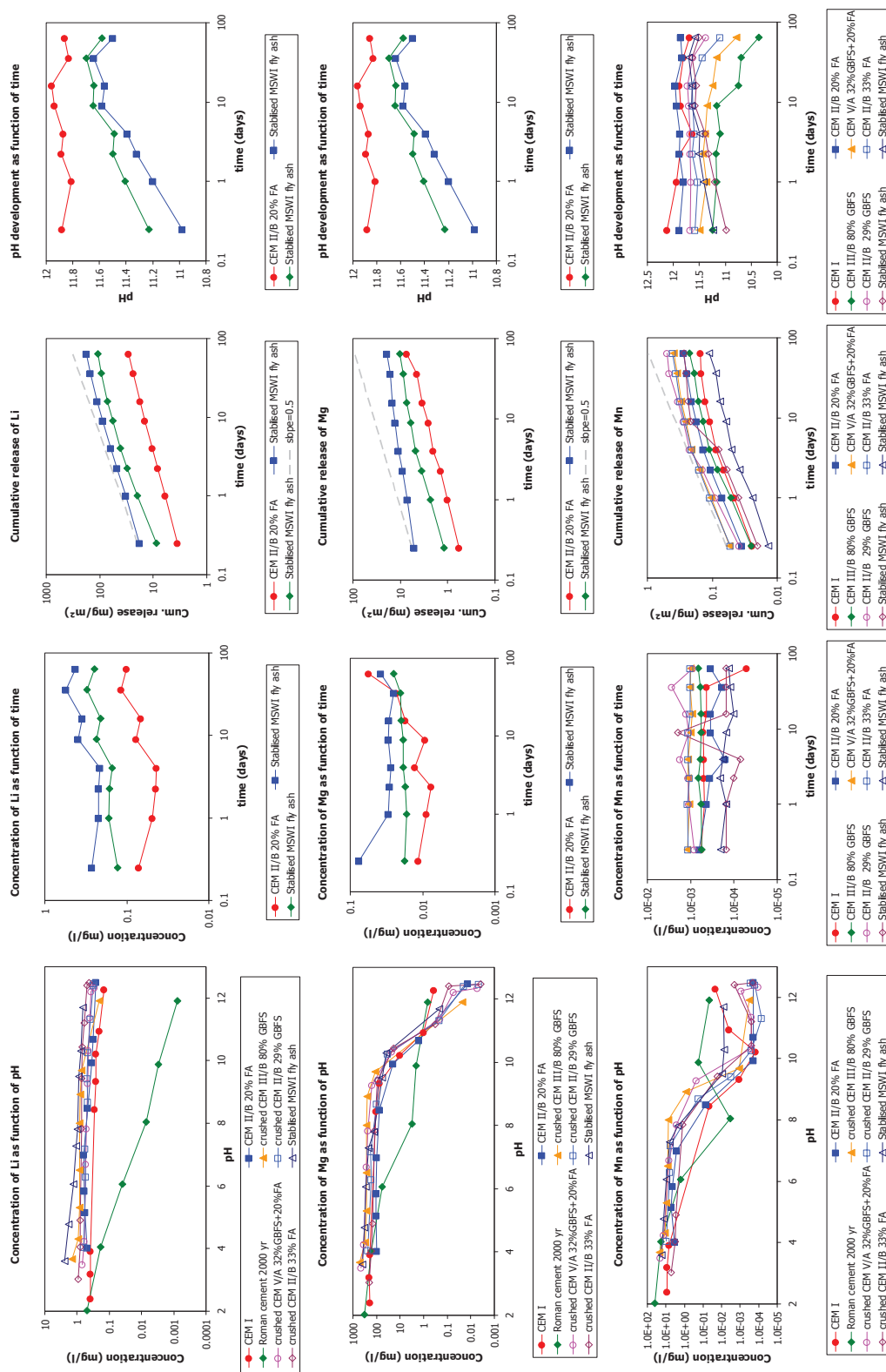


Figure B.5. Lithium, magnesium and manganese leaching results from several cementitious materials.

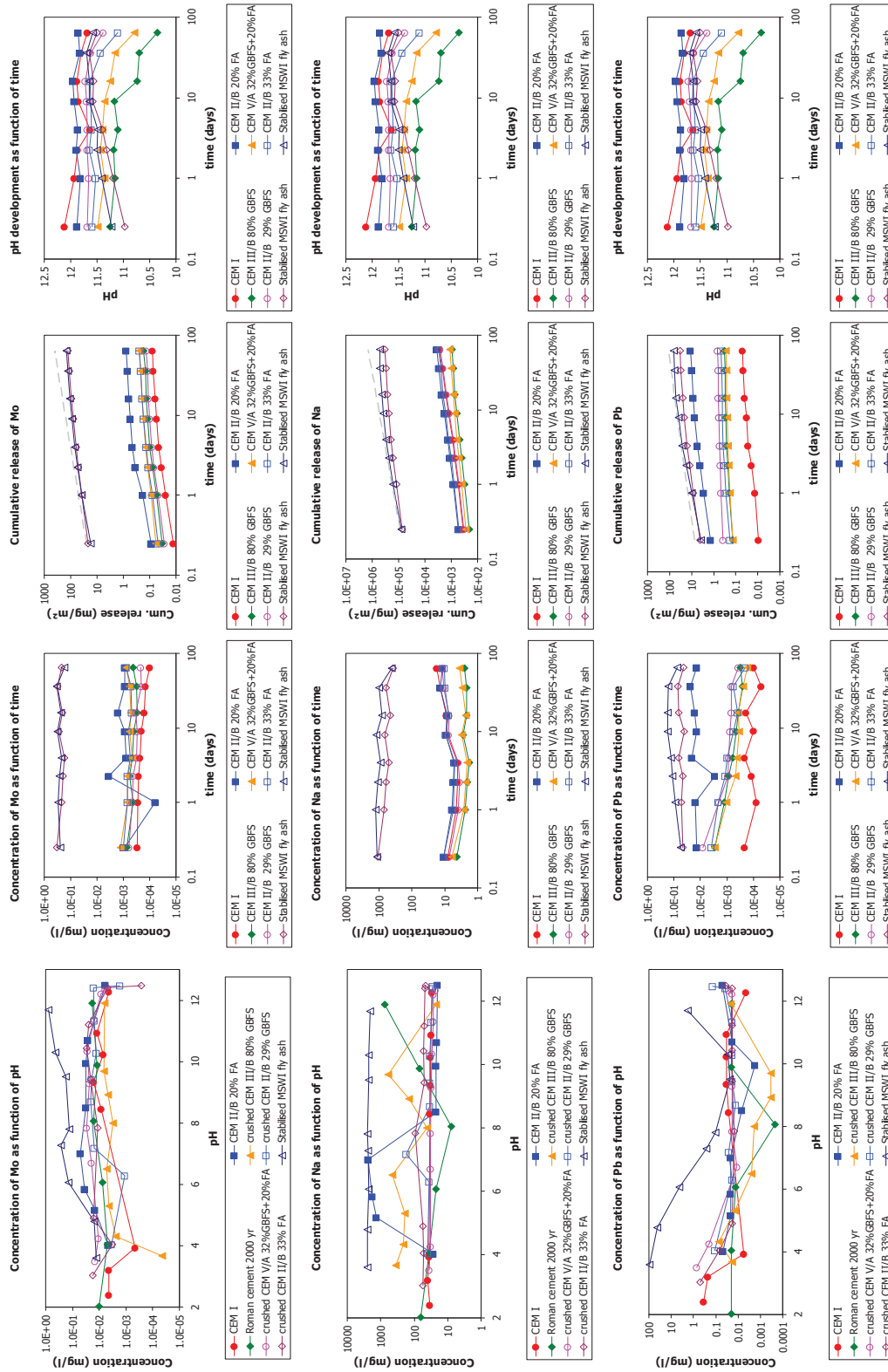


Figure B.6. Molybdenum, sodium and lead leaching results from several cementitious materials.

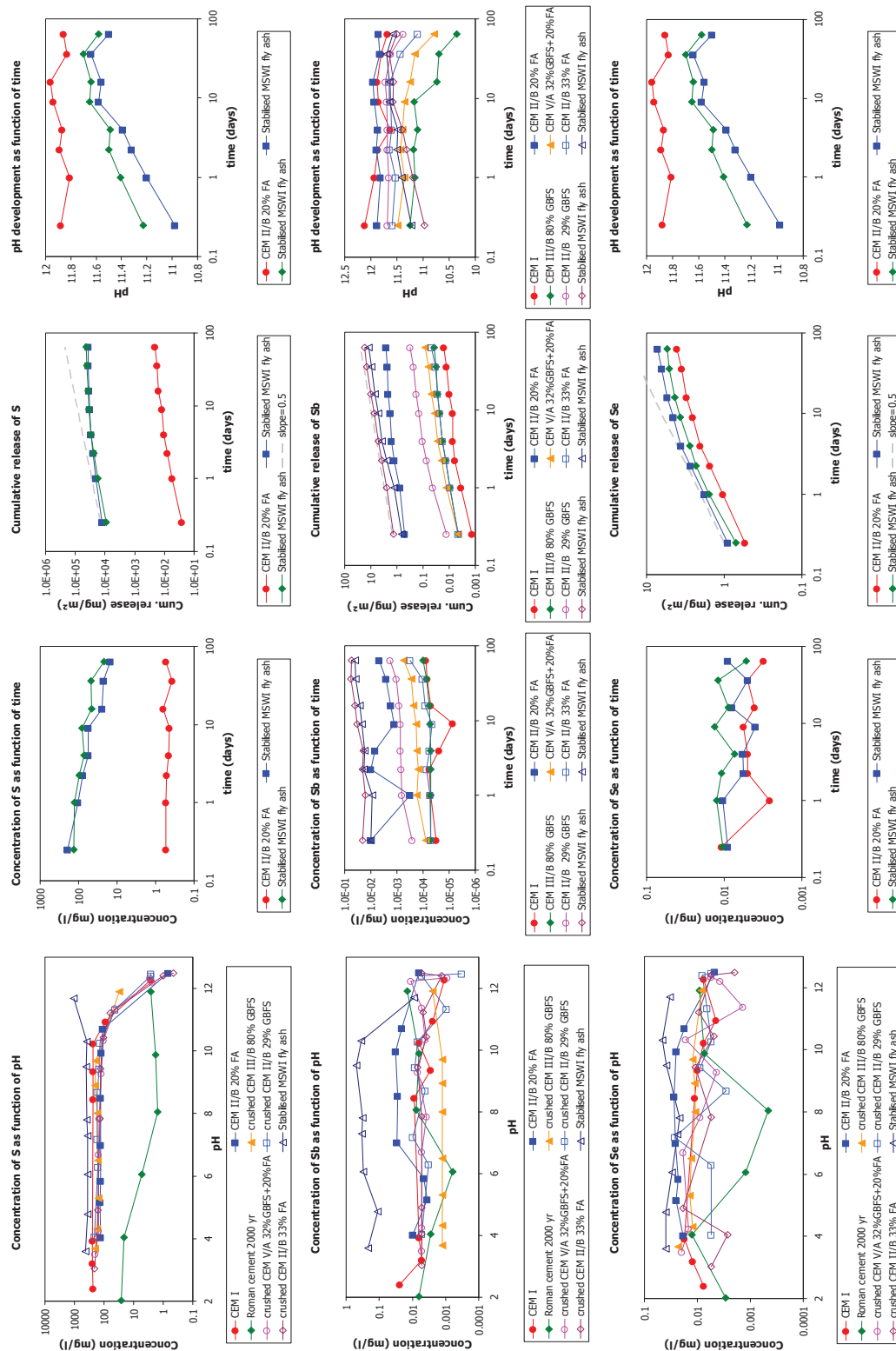


Figure B.7. Sulfur, antimony and selenium leaching results from several cementitious materials.

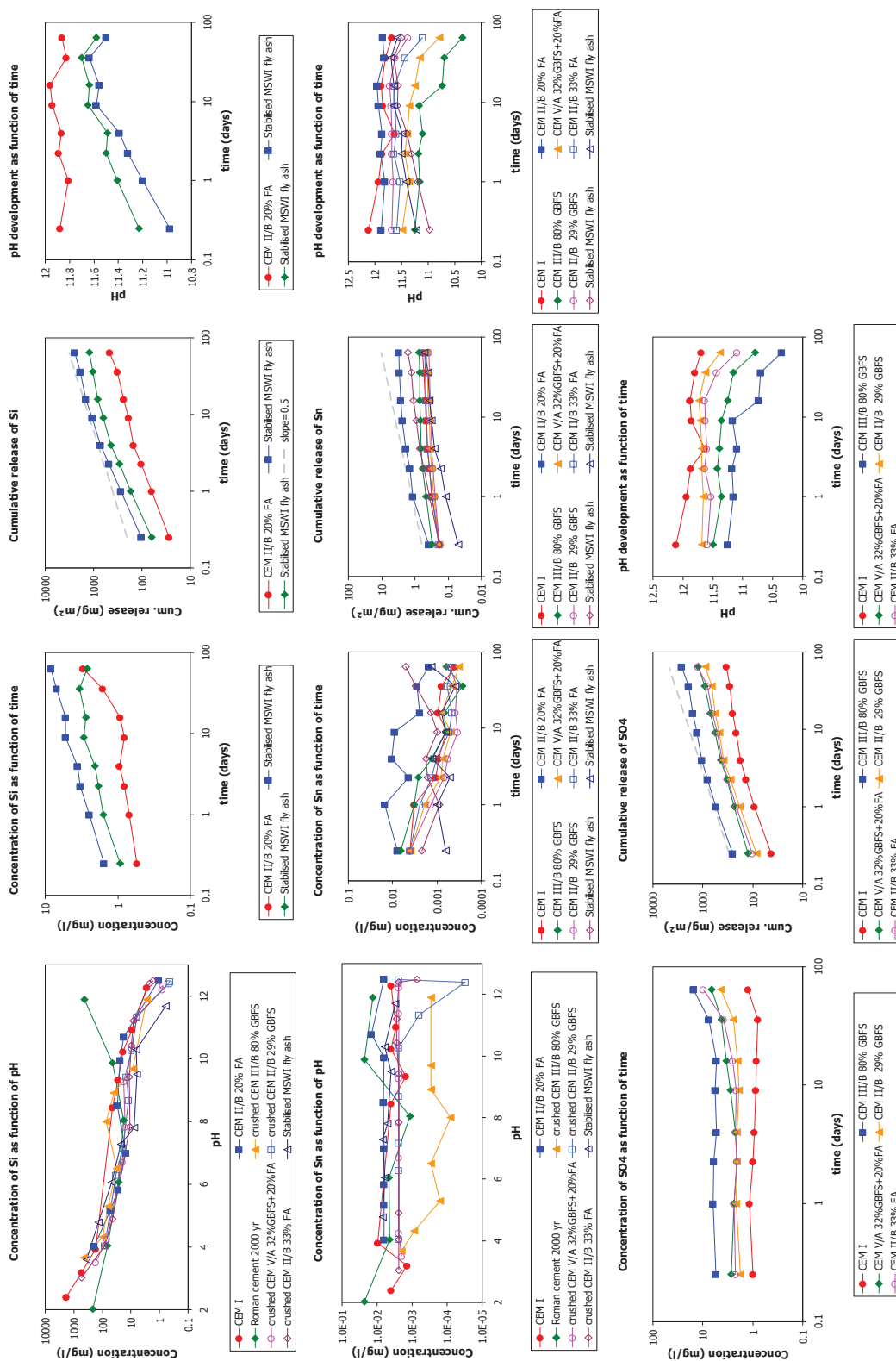


Figure B.8. Silicon, tin and sulfate leaching results from several cementitious materials.

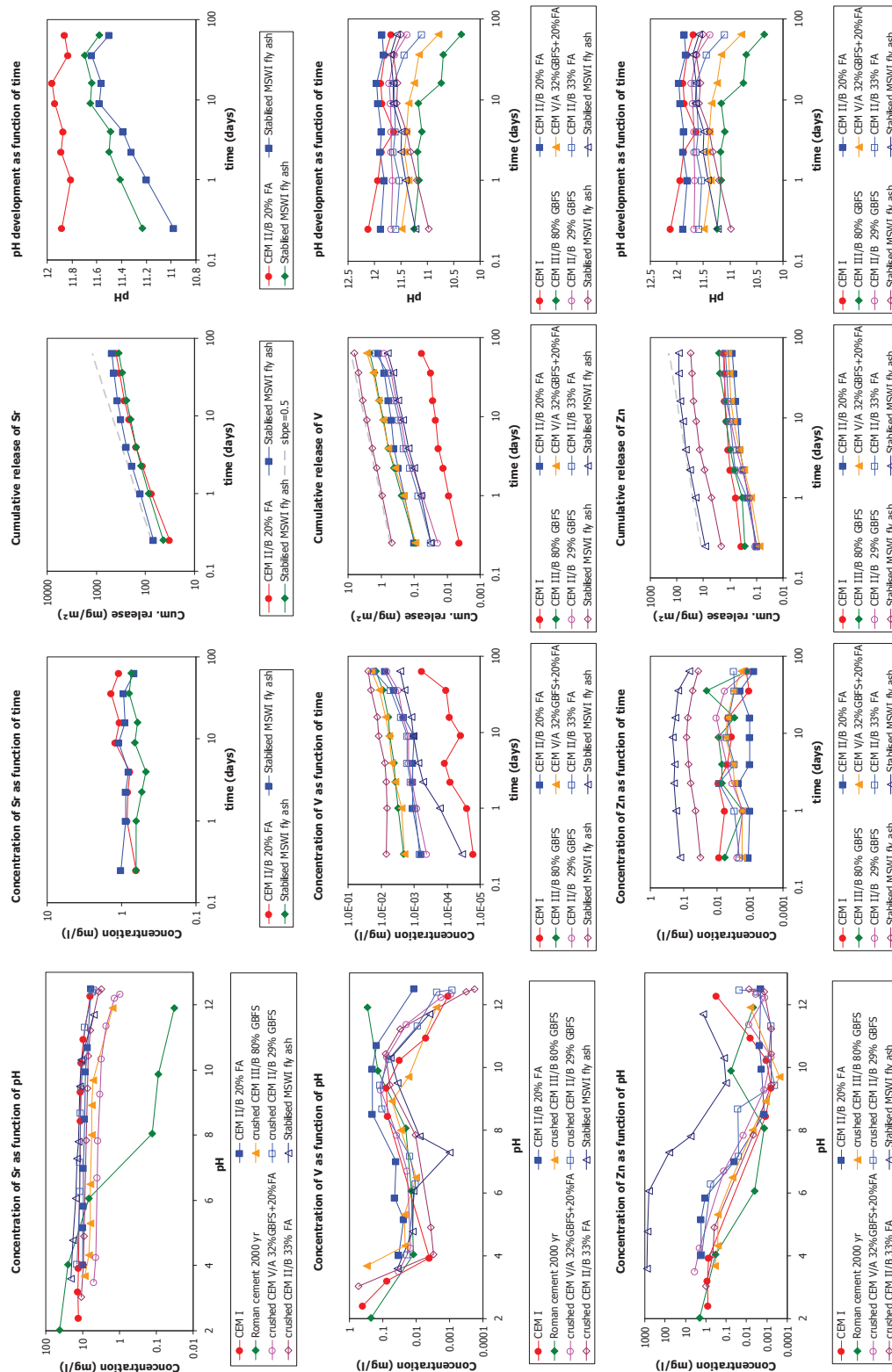


Figure B.9. Strontium, vanadium and zinc leaching results from several cementitious materials.

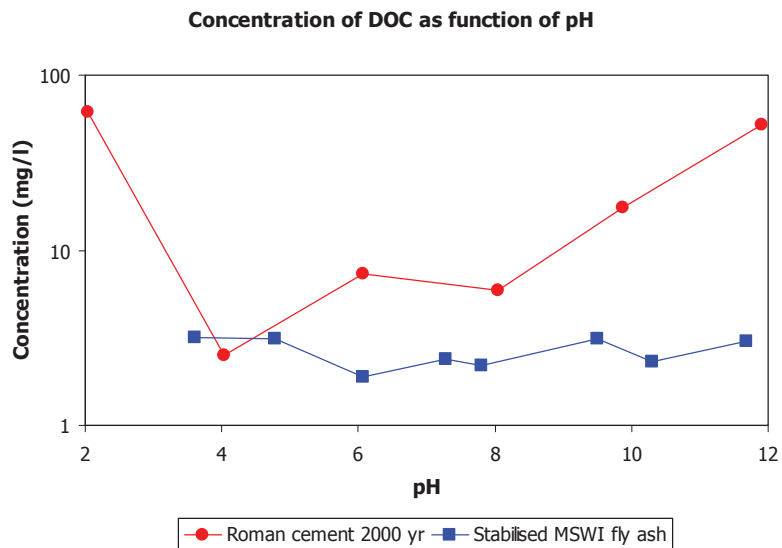


Figure B.10. Acid neutralization capacity of stabilized MSWI fly ash and roman cement.

APPENDIX C. Acid Neutralization Capacity.

The acid neutralization capacity (ANC) in combination with field exposure properties like acidification, carbonation and other sources of neutralization dictate how long it takes for the surface of the specimen to be neutralized. This will in turn lead to another leaching characteristic than the fresh product.

The pH dependence test provides a very valuable means of evaluating environmental behavior of cement mortar than any other test. The pH dependence test data cover a wide range of potential exposure conditions – service life (own pH and externally imposed pH), recycling stage as aggregate and end-of-life conditions after full carbonation.

The results derived from the pH dependence test for the cements studied in ECRICEM I and II are given to indicate generic behavior in Figure C.1. Blended cements generally show a lower ANC than regular Portland cements.

The ANC of cement-based products is high (Figure C.1). Therefore only the surface of cement-based products can be neutralized and thus shows leaching characteristics corresponding to the neutral pH. Element solubility is controlled by different conditions within the mortar and on the surface of a carbonated specimen. Since the surface is in direct contact with the surrounding environment, this condition is more determining for the release than the highly alkaline interior of the material.

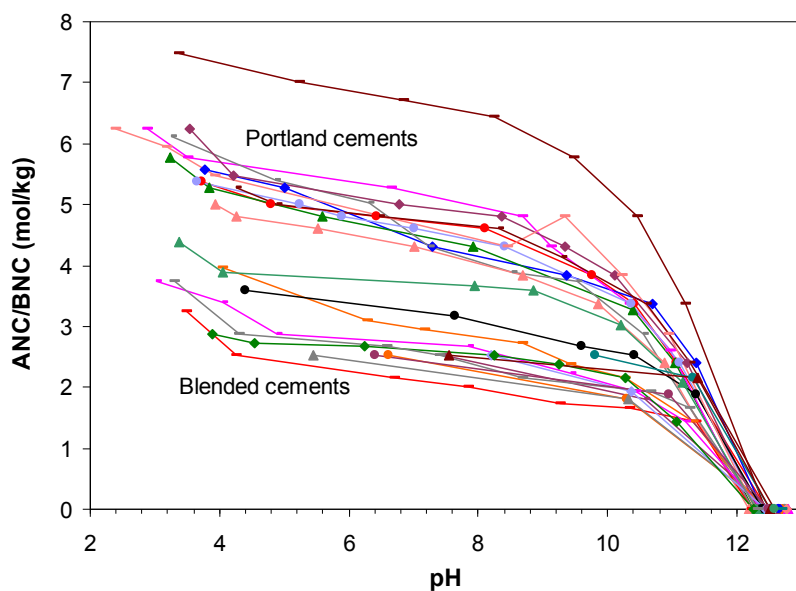


Figure C.1. Acid neutralization capacity of cement mortars from the pH dependence leaching test.

APPENDIX D. Chemical Speciation Modeling.

In this appendix, the results of multi-element modeling of pH dependence test data are provided using LeachXS-ORCHESTRA. The starting point for the modeling is the determination of the available content (i.e., the maximum concentration as observed in the pH dependence leaching test) and some additional parameters like pH , LS ratio, solid organic matter content, dissolved organic matter content, reactive iron-oxide phases and a selection of minerals.

An example, input specification is given in Figure D.1.:

Prediction case	D2 CEM I	DOC/DHA data	pH>DOC] (kg/l)	DHA fraction JHA] (kg/l)	Polynomial coefficients	
Speciation session	CEM I D2		1.00 1.000E-06	0.50 5.000E-07	C0	-6.134E+00
Material	Cement mortar CEM I D2		3.76 1.000E-06	0.30 3.000E-07	C1	-1.554E-01
			5.00 1.000E-06	0.25 2.500E-07	C2	1.116E-02
Solved fraction DOC			7.28 1.000E-06	0.20 2.000E-07	C3	0.000E+00
Sum of pH and pe			9.36 1.000E-06	0.20 2.000E-07	C4	0.000E+00
L/S	0.2		10.70 1.000E-06	0.30 3.000E-07	C5	0.000E+00
Clay	13.00		11.37 1.000E-06	0.40 4.000E-07		
HFO	0.000E+00 kg/kg		12.40 1.000E-06	0.50 5.000E-07		
SHA	1.000E-04 kg/kg		14.00 1.000E-06	0.70 7.000E-07		
2.500E-04 kg/kg						
Reactant concentrations	Reactant	mg/kg	Reactant	mg/kg	Selected Minerals	
Ag+	not measured	Mg+2	4.308E+03	AA_2CaO_Al2O3_8H2O[s]	AA_Jennite	PbMoO4[c]
Al+3	2.017E+03	Mn+2	6.155E+01	AA_2CaO_Al2O3_SiO2_8H2O[s]	AA_Magnesite	Rhodochrosite
H3AsO4	5.781E-01	MoO4-2	2.793E-01	AA_2CaO_Fe2O3_8H2O[s]	AA_Portlandite	Strontianite
H3BO3	3.061E+01	Na+	2.717E+02	AA_2CaO_Fe2O3_SiO2_8H2O[s]	AA_Syngenite	Tenorite
Ba+2	2.771E+01	NH4+	not measured	AA_3CaO_Al2O3_6H2O[s]	AA_Tobermorite-I	Wairakite
Br-	not measured	Ni+2	2.211E+02	AA_3CaO_Fe2O3_6H2O[s]	AA_Tobermorite-II	Willemite
Ca+2	9.798E+04	NO3-	not measured	AA_3CaO_Fe2O3_CaCO3_11H2O[s]	AA_Tricarboaluminate	
Cd+2	5.057E-03	PO4-3	1.183E+00	AA_4CaO_Fe2O3_13H2O[s]	Analbite	
Cl-	5.000E+01	Pb+2	2.538E+00	AA_4CaO_Fe2O3_13H2O[s]	Cd[OH]2[A]	
CrO4-2	2.166E+00	SO4-2	2.586E+03	AA_4CaO_Fe2O3_13H2O[s]	Cr[OH]3[C]	
Cu+2	4.991E+00	Sb[OH]6-	3.489E-01	AA_Al[OH]3[am]	Fe_Vanadate	
F-	5.000E+01	SeO4-2	4.196E-01	AA_Anhydrite	Ferrihydrite	
Fe+3	1.591E+02	H4SiO4	1.153E+03	AA_Brucite	Magnesite	
H2CO3	8.000E+03	Sr+2	2.620E+02	AA_Calcite	Manganite	
Hg+2	not measured	Th+4	not measured	AA_CaO_Al2O3_10H2O[s]	Ni[OH]2[s]	
I-	not measured	UO2+	not measured	AA_CO3-hydroxalite	Pb[OH]2[C]	
K+	2.455E+03	VO2+	7.206E-01	AA_Fe[OH]3[microcr]	Pb2VO7	
Li+	4.880E+00	Zn+2	2.188E+01	AA_Gibbsite	Pb3[VO4]2	
				AA_Gypsum	PbCrO4	

Figure D.1. Example input specification for speciation modeling of cement mortars using LeachXS-ORCHESTRA.

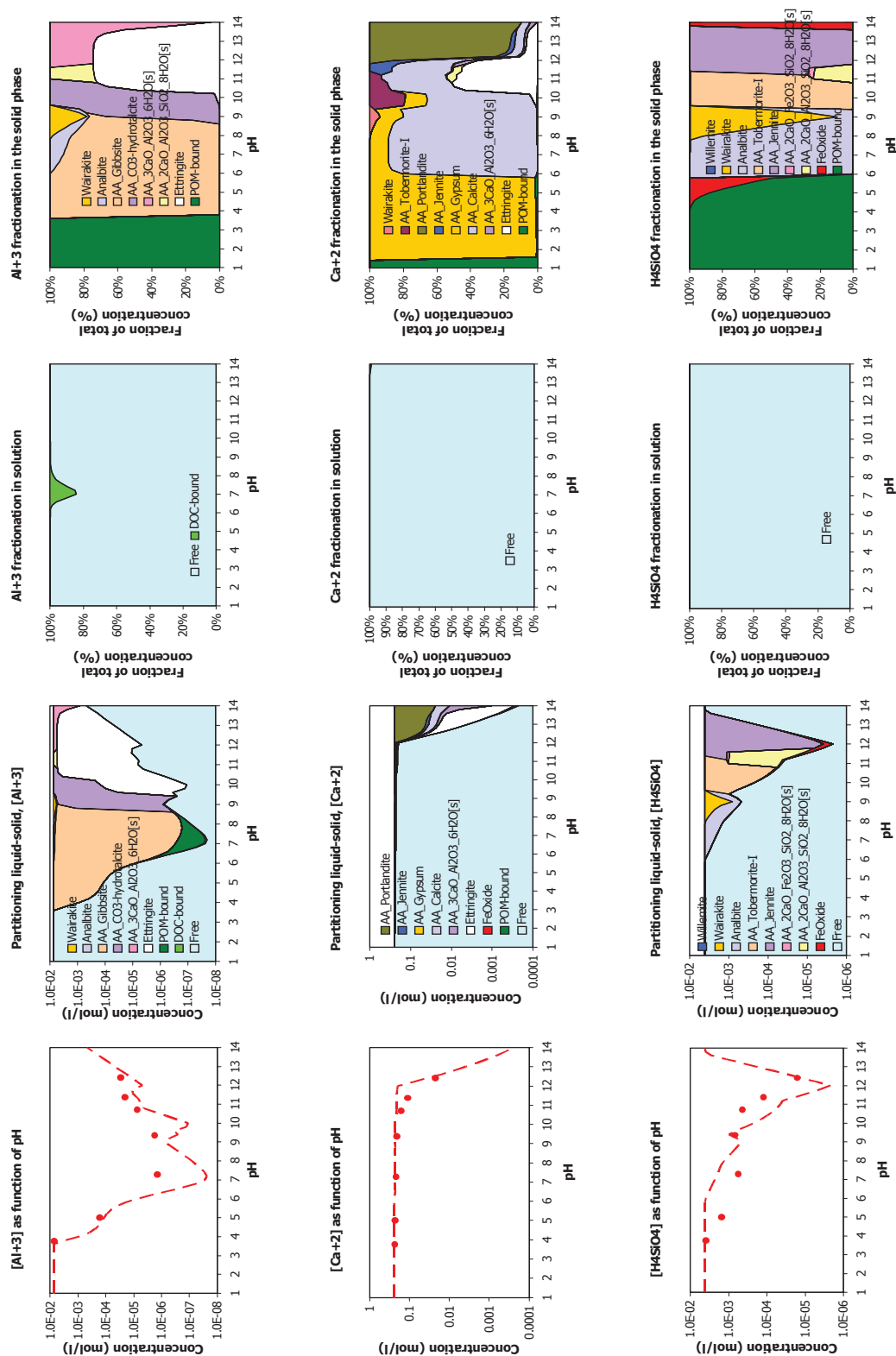


Figure D.2. Aluminum, calcium and silicon speciation modeling results for a cementitious mortar.

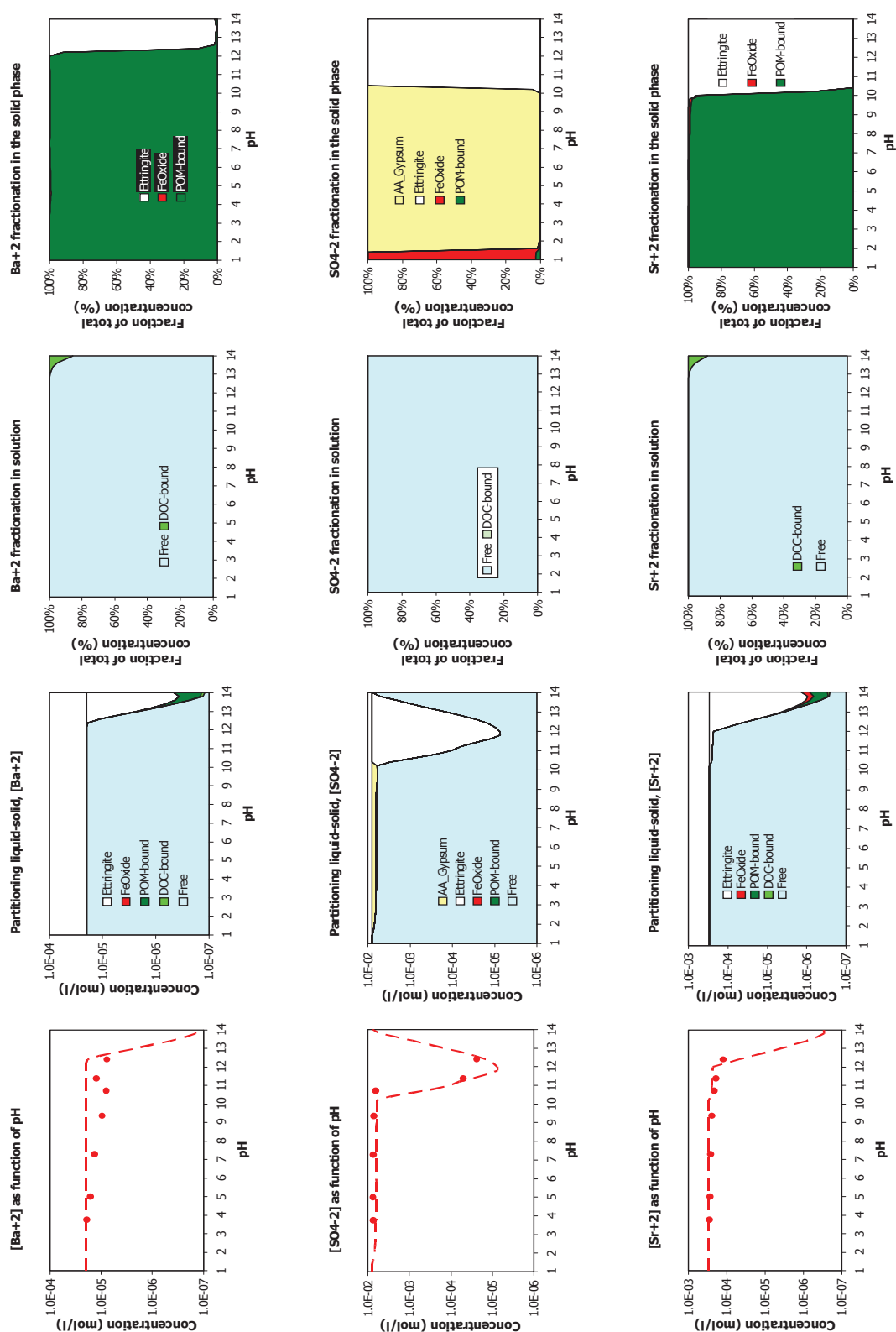


Figure D.3. Barium, sulfate and strontium speciation modeling results for a cementitious mortar.

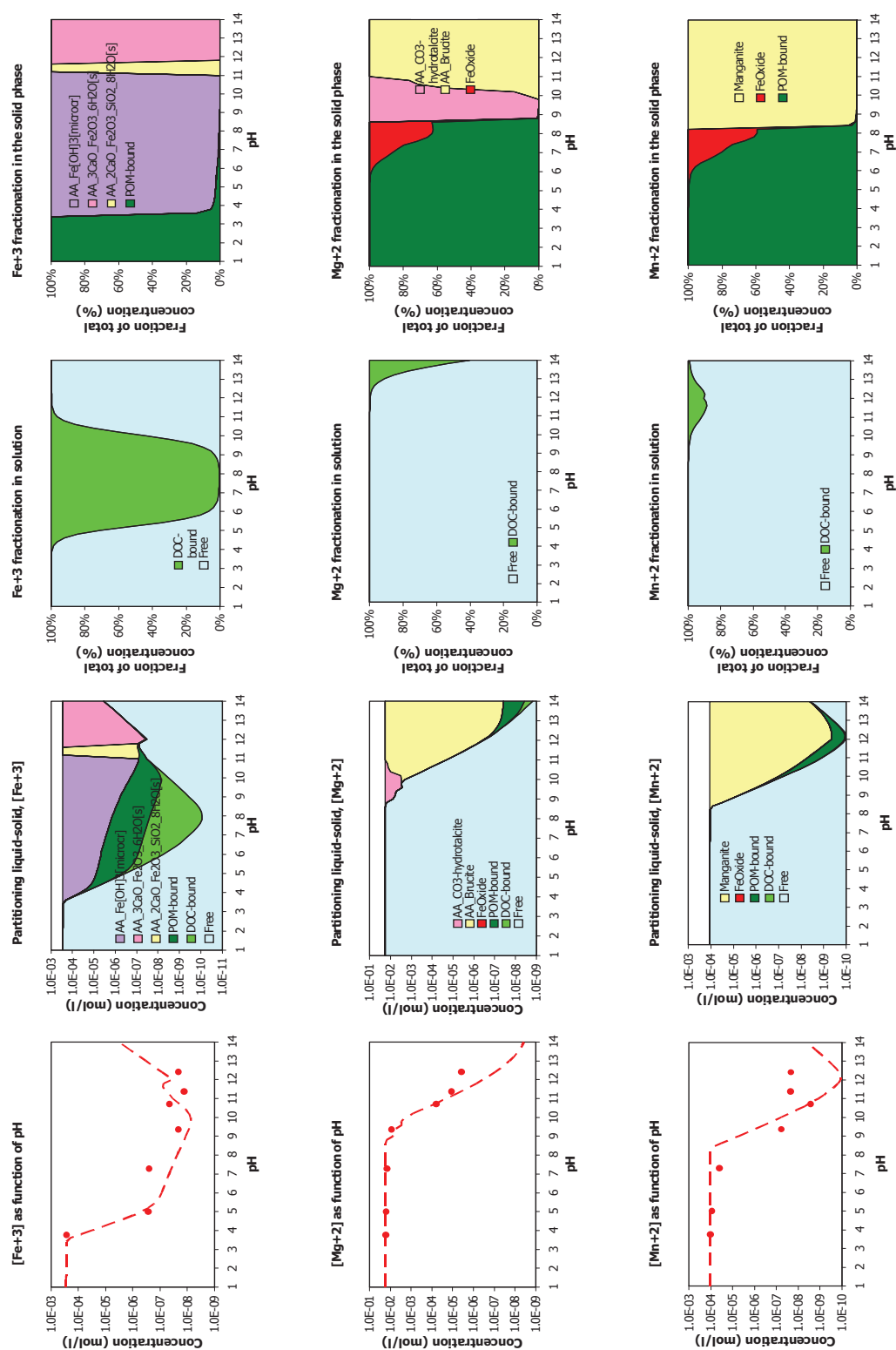


Figure D.4. Iron, magnesium and manganese speciation modeling results for a cementitious mortar.

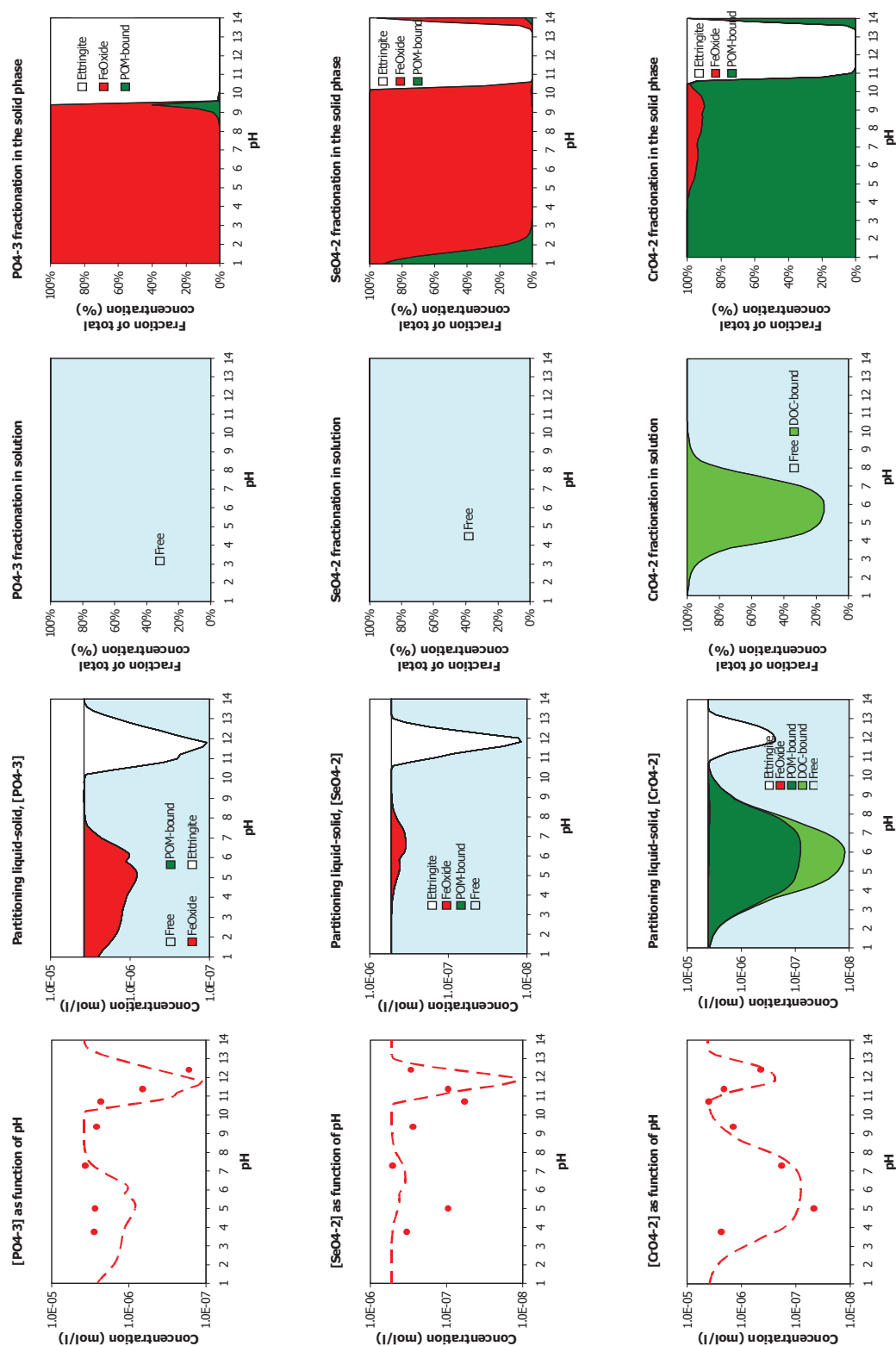


Figure D.5. Phosphate, selenate and chromate speciation modeling results for a cementitious mortar.

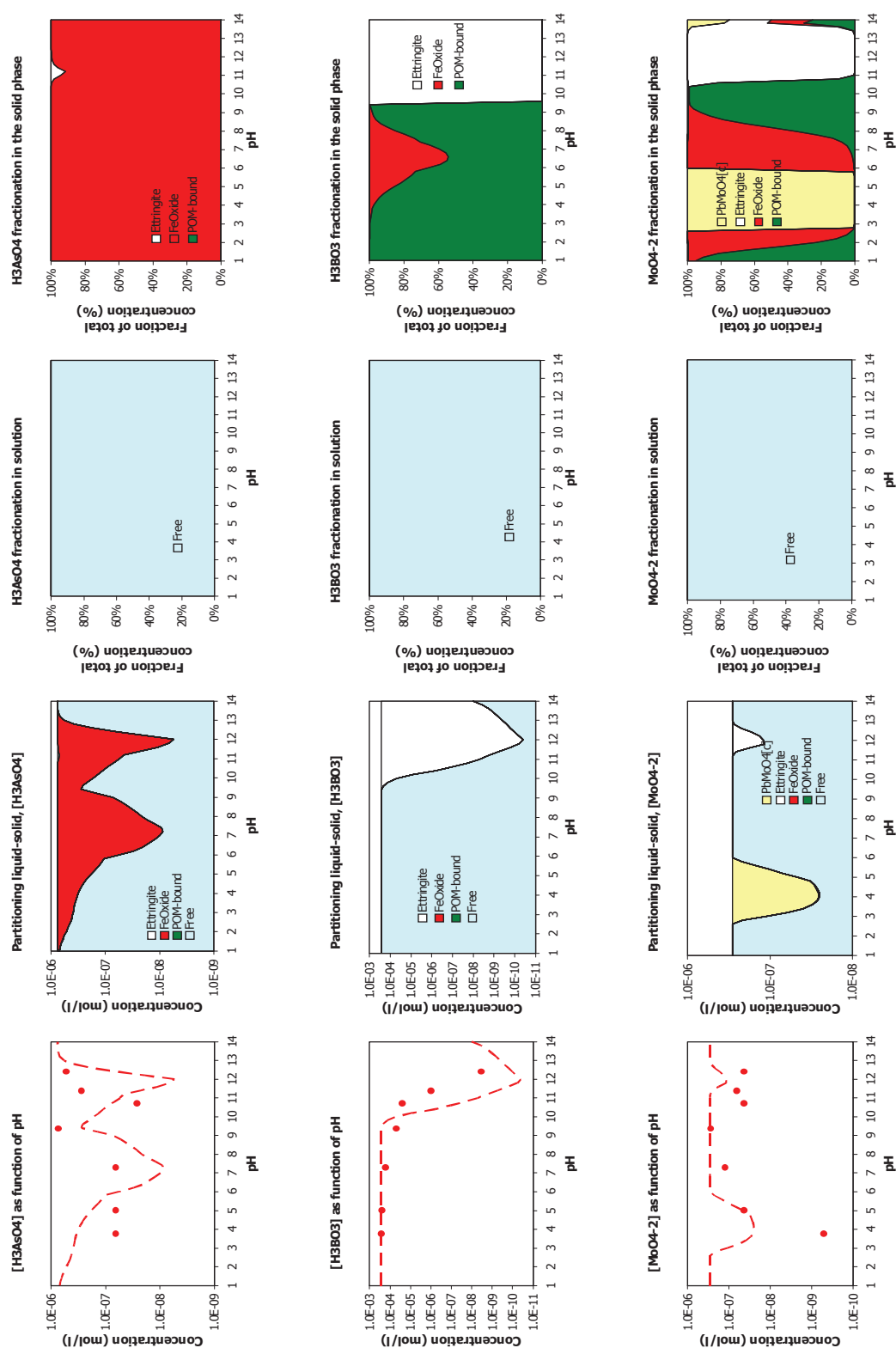


Figure D.6. Arsenate, borate and molybdate speciation modeling results for a cementitious mortar.

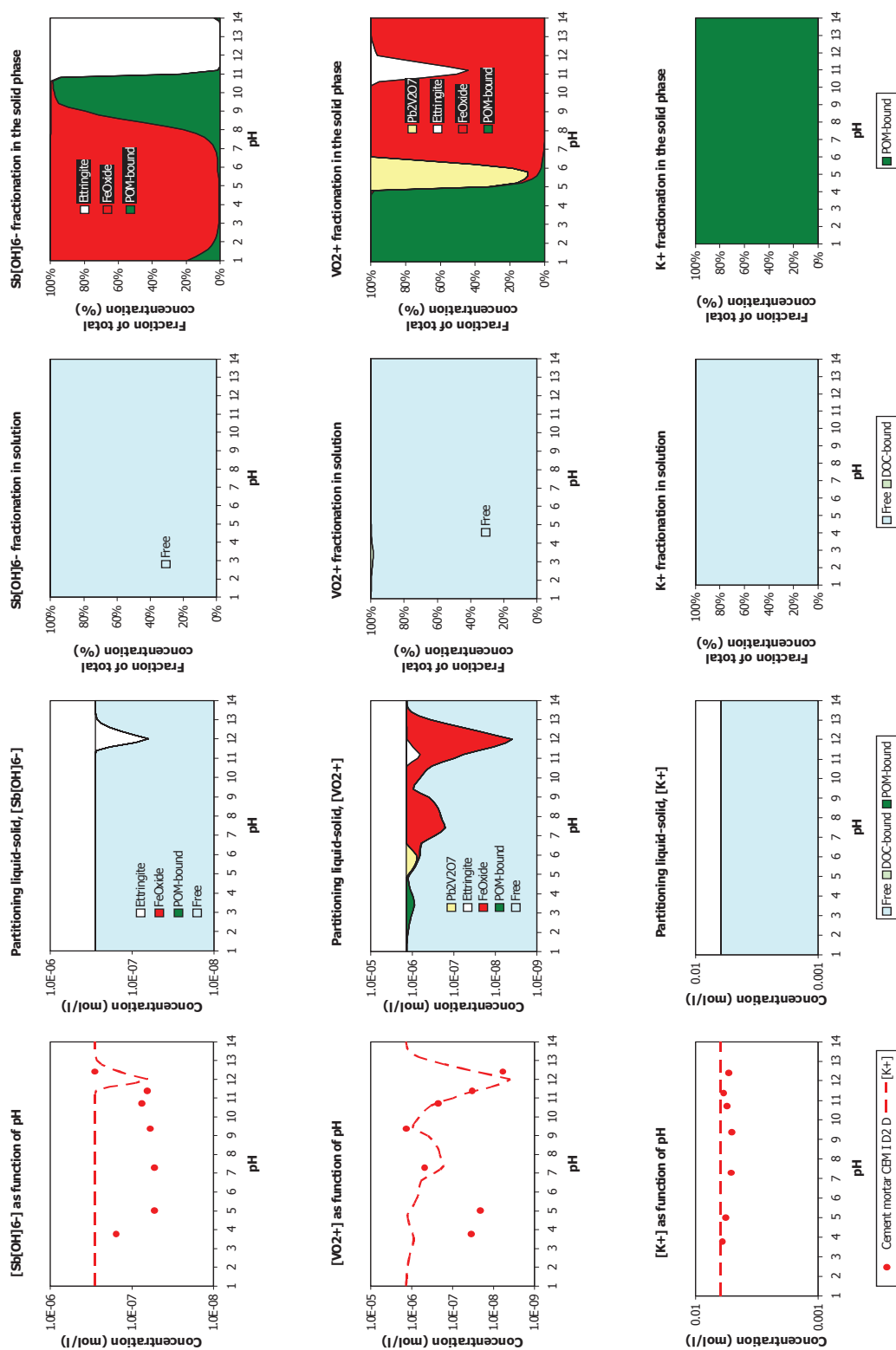


Figure D.7. Antimony, vanadium and potassium speciation modeling results for a cementitious mortar.

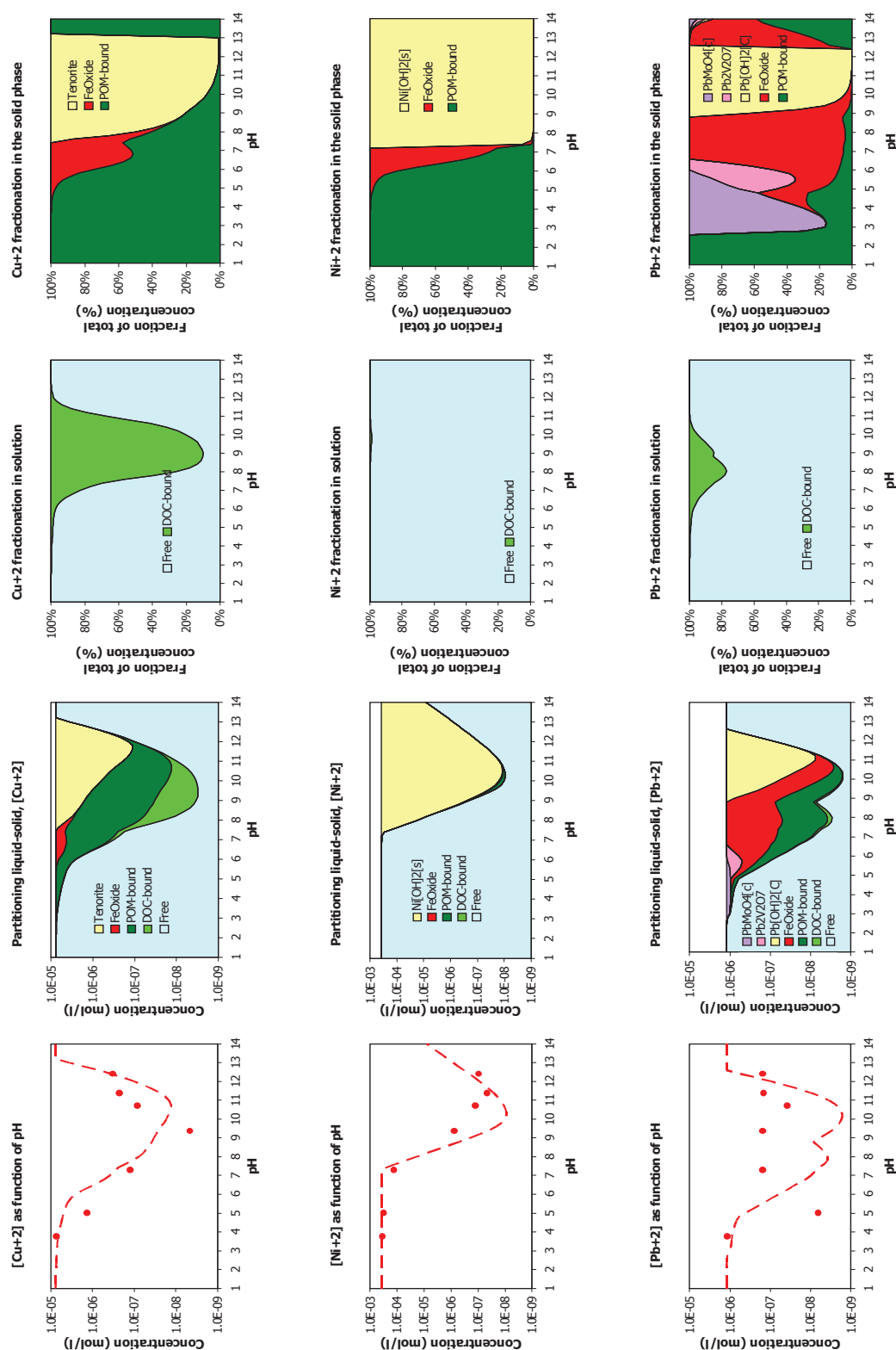


Figure D.8. Copper, nickel and lead speciation modeling results for a cementitious mortar.

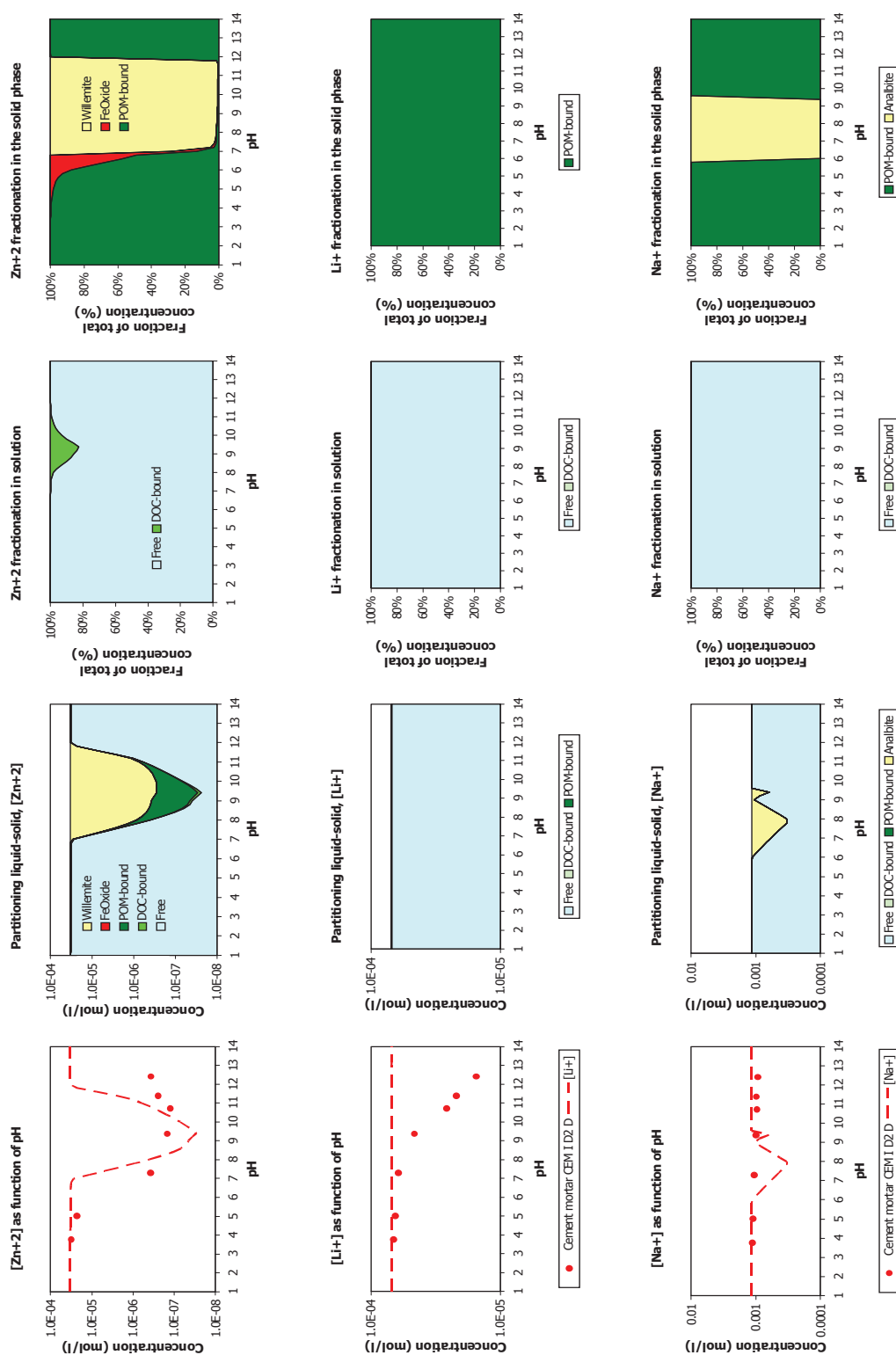


Figure D.9. Zinc, lithium and sodium speciation modeling results for a cementitious mortar.

Appendix E. Comparison of Stabilized Hazardous Waste and Simulation Grout.

In the graphs shown below, the leaching behavior as a function of pH (pH dependence test) and as a function of time (monolith leach test) for the following materials is given:

- Material blank (MBD)
- Stabilized waste mix (SWD)
- Academic mix (AMD)
- Cement stabilized MSWI fly ash NL
- Cement stabilized MSWI fly ash NL
- Cement stabilized MSWI fly ash UK
- Cement stabilized MSWI fly ash UK

Graphs for the following elements are given in the figures indicated:

Fig. E.1.	Al, As, B
Fig. E.2.	Ba, Ca, Cd
Fig. E.3.	CN total, CN volatile, Co
Fig. E.4.	Cr, Cs, Cu
Fig. E.5.	F, Fe, Hg
Fig. E.6.	I, K, Li
Fig. E.7.	Mg, Mn, Mo
Fig. E.8.	Na, Ni, P
Fig. E.9.	Pb, Rb, Re
Fig. E.10.	SO ₄ as S, Sb, Se
Fig. E.11	Si, Sn, Sr
Fig. E.12.	U, V, Zn

The first graph gives the release as a function of pH, the second graph shows the concentration in eluates from the monolith leach test as a function of time. The third graph shows the cumulative release expressed in mg/m² as a function of time and the fourth graph shows the pH as a function of time (days).

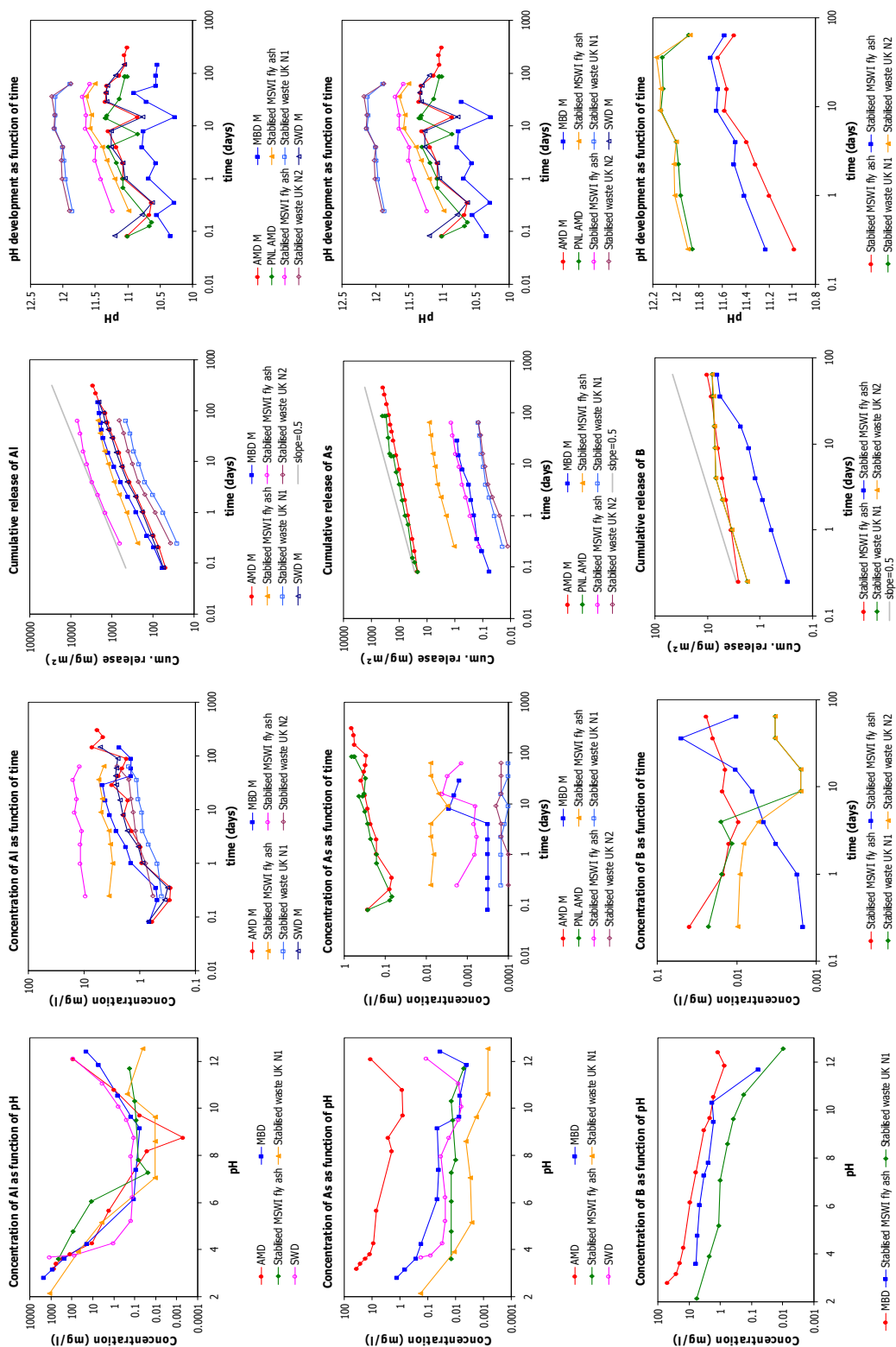


Figure E.1. Aluminum, arsenic and boron leaching results.

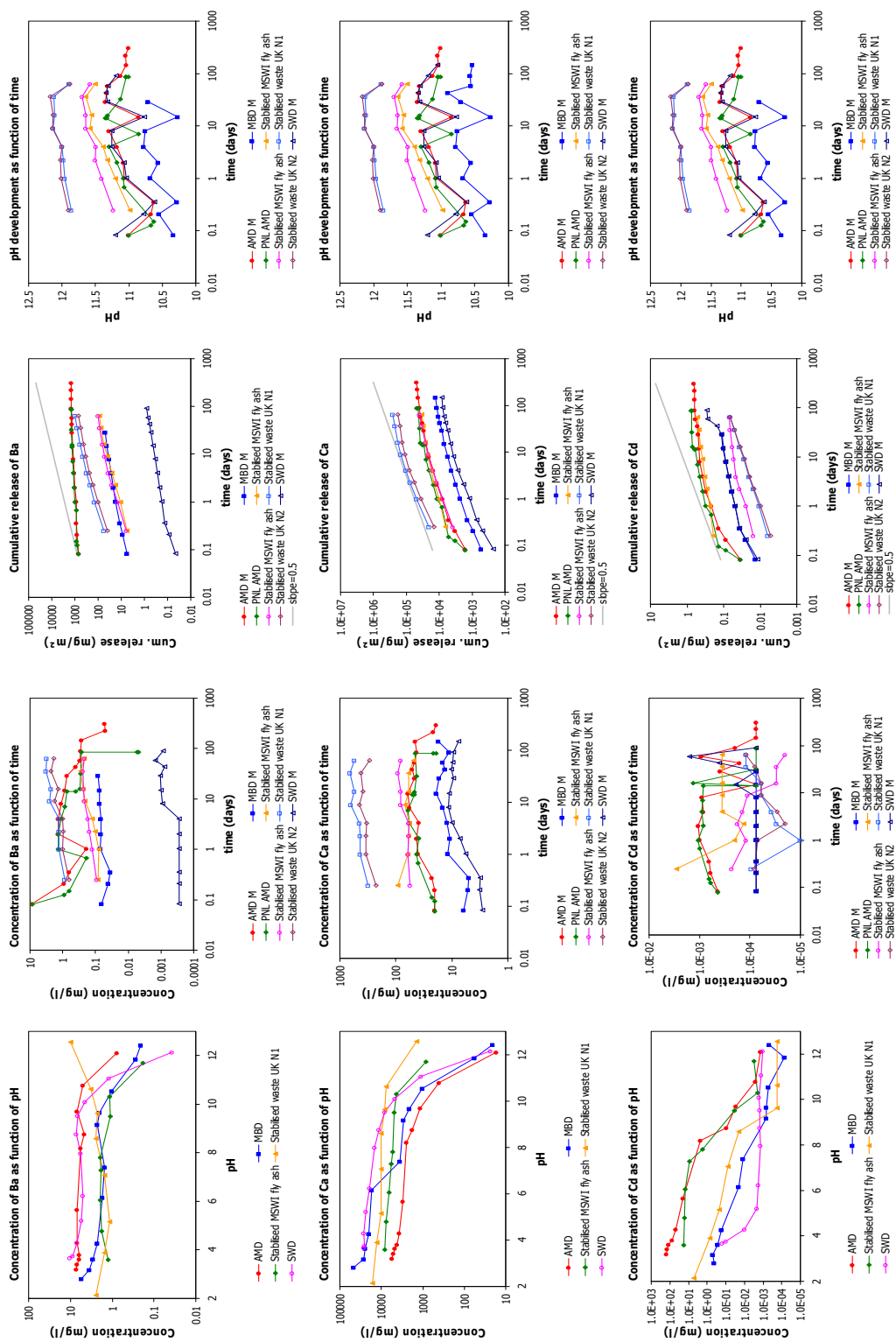


Figure E.2. Barium, calcium and cadmium leaching results.

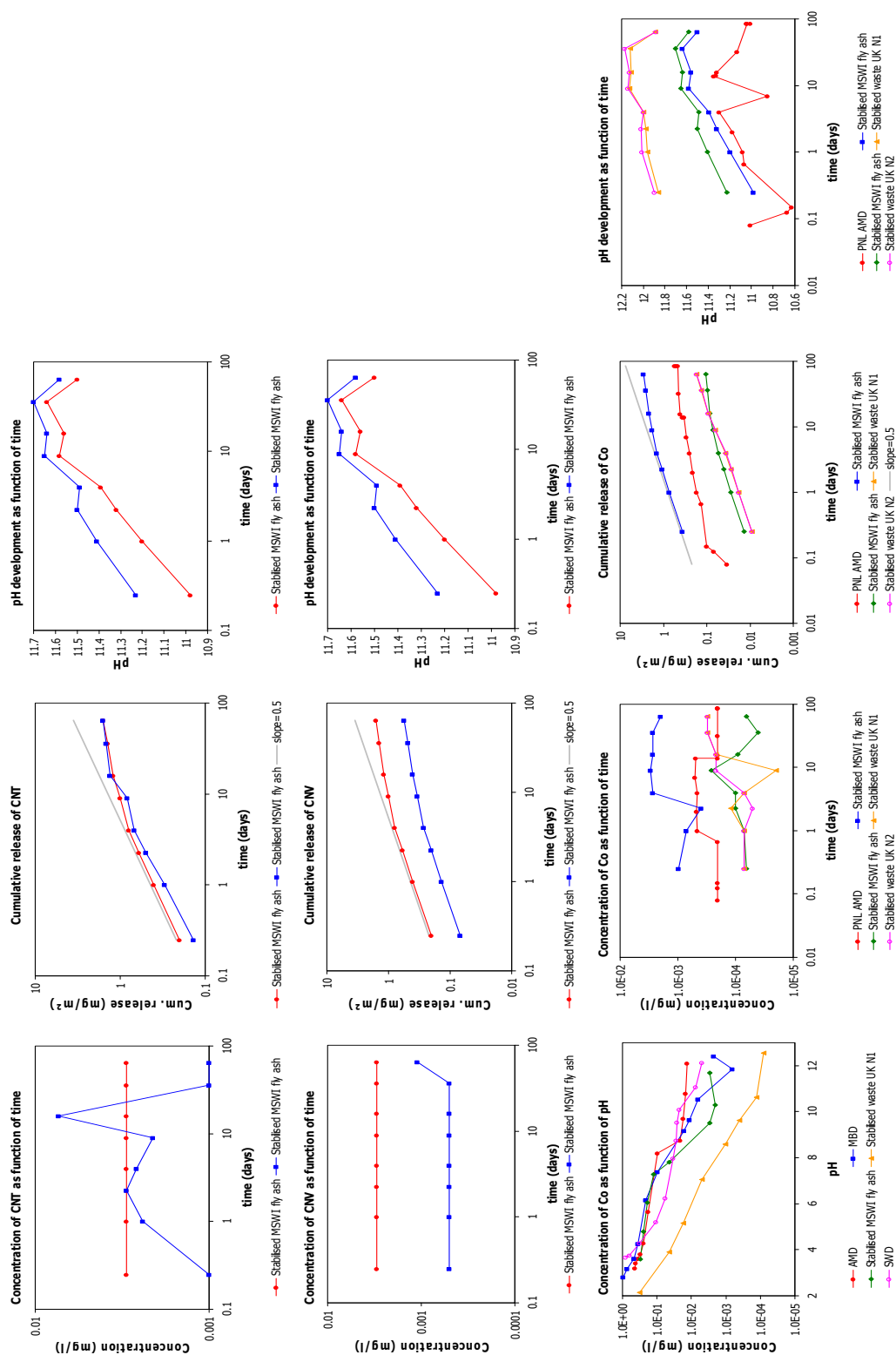


Figure E.3. Total cyanide, volatile cyanide and cobalt leaching results.

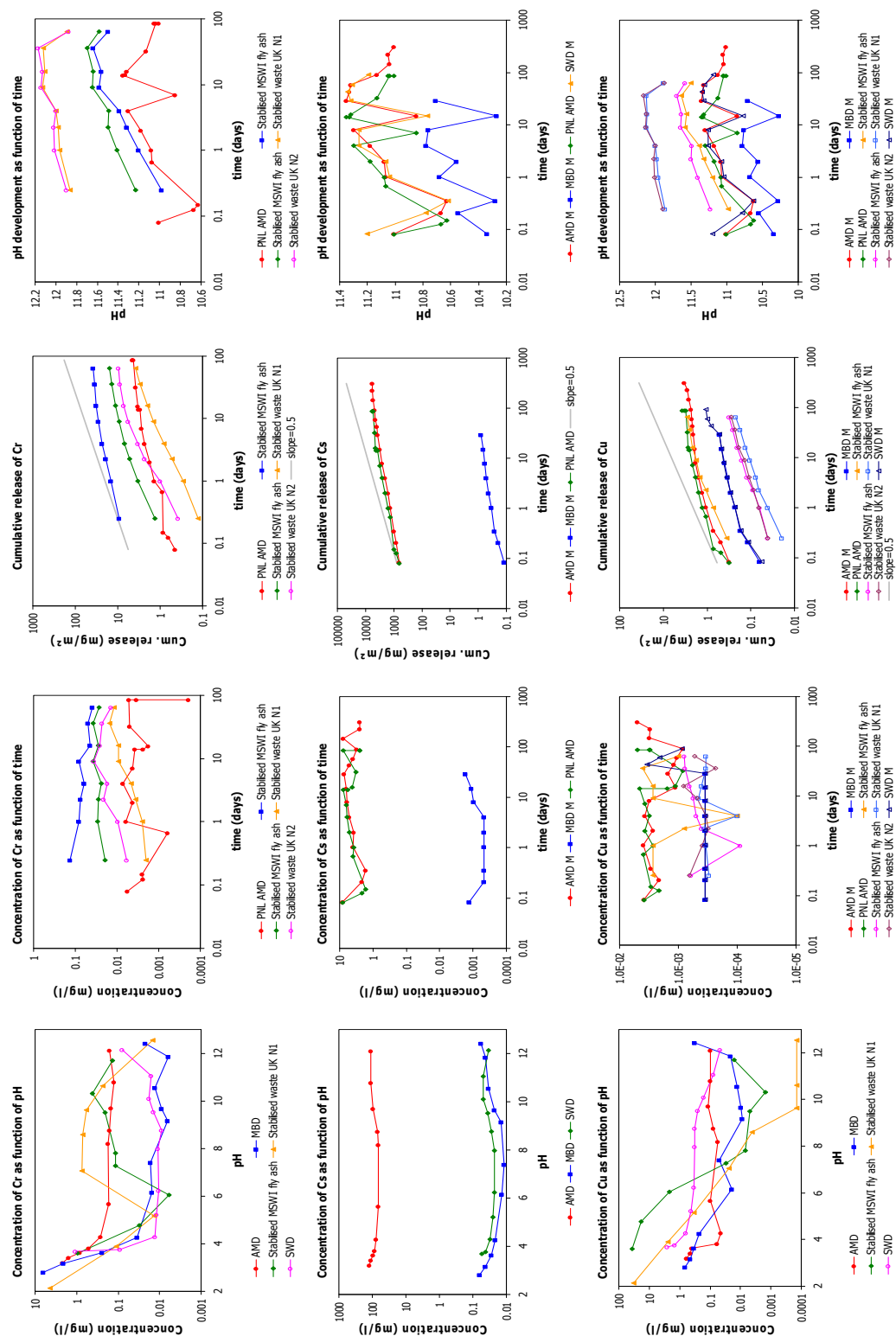


Figure E.4. Chromium, cesium and copper leaching results.

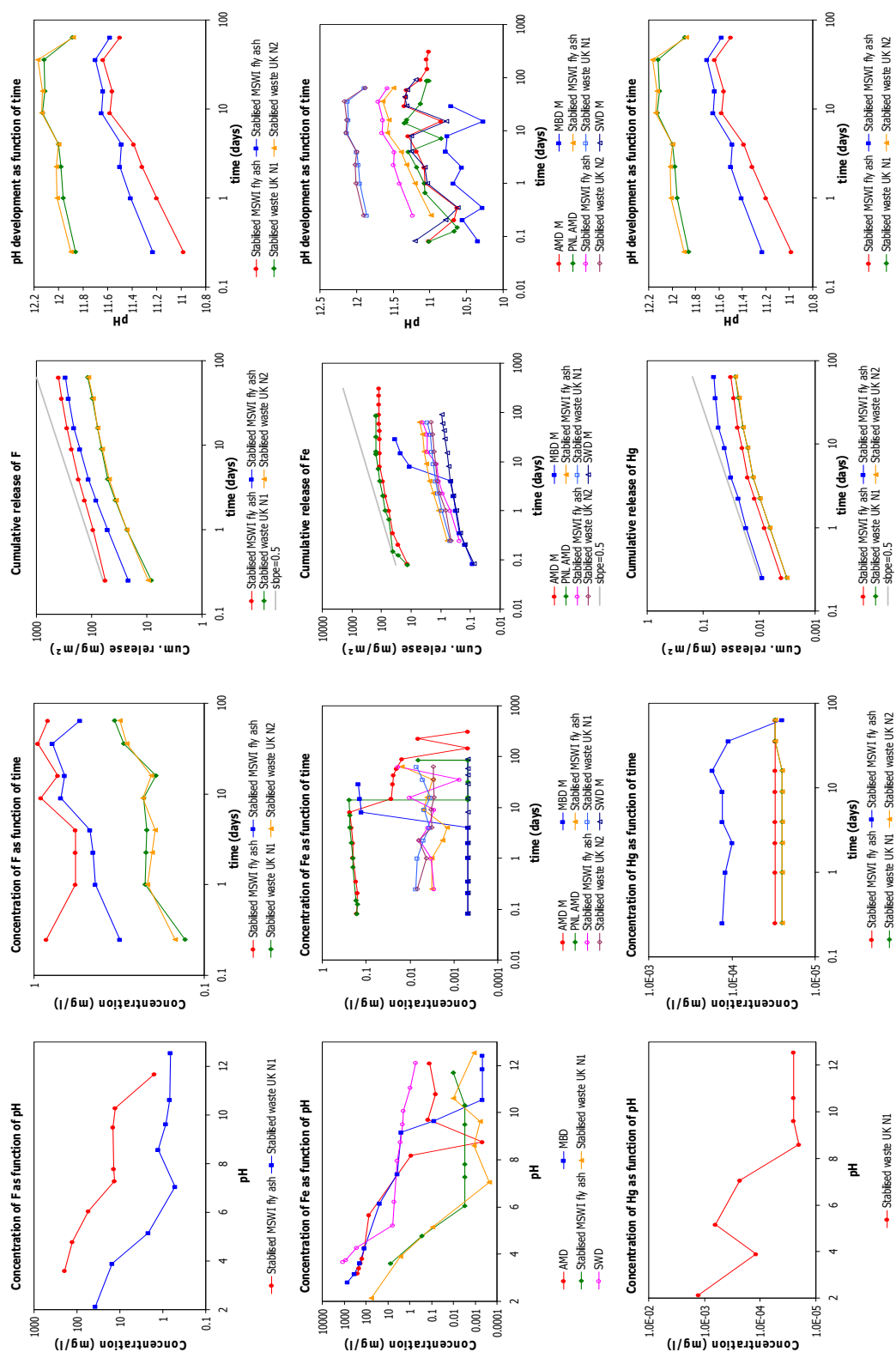


Figure E.5. Fluoride, iron and mercury leaching results.

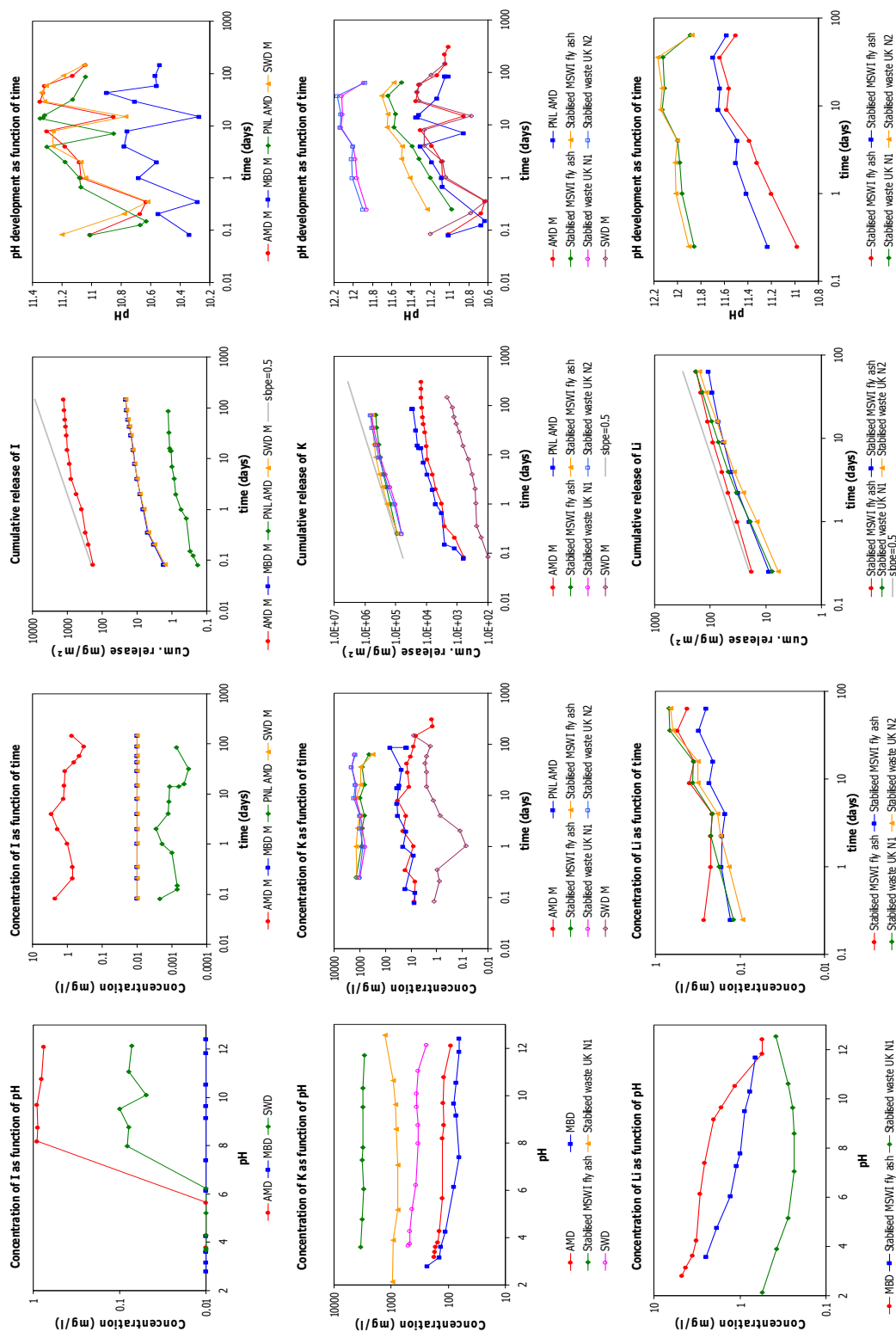


Figure E.6. Iodine, potassium and lithium leaching results.

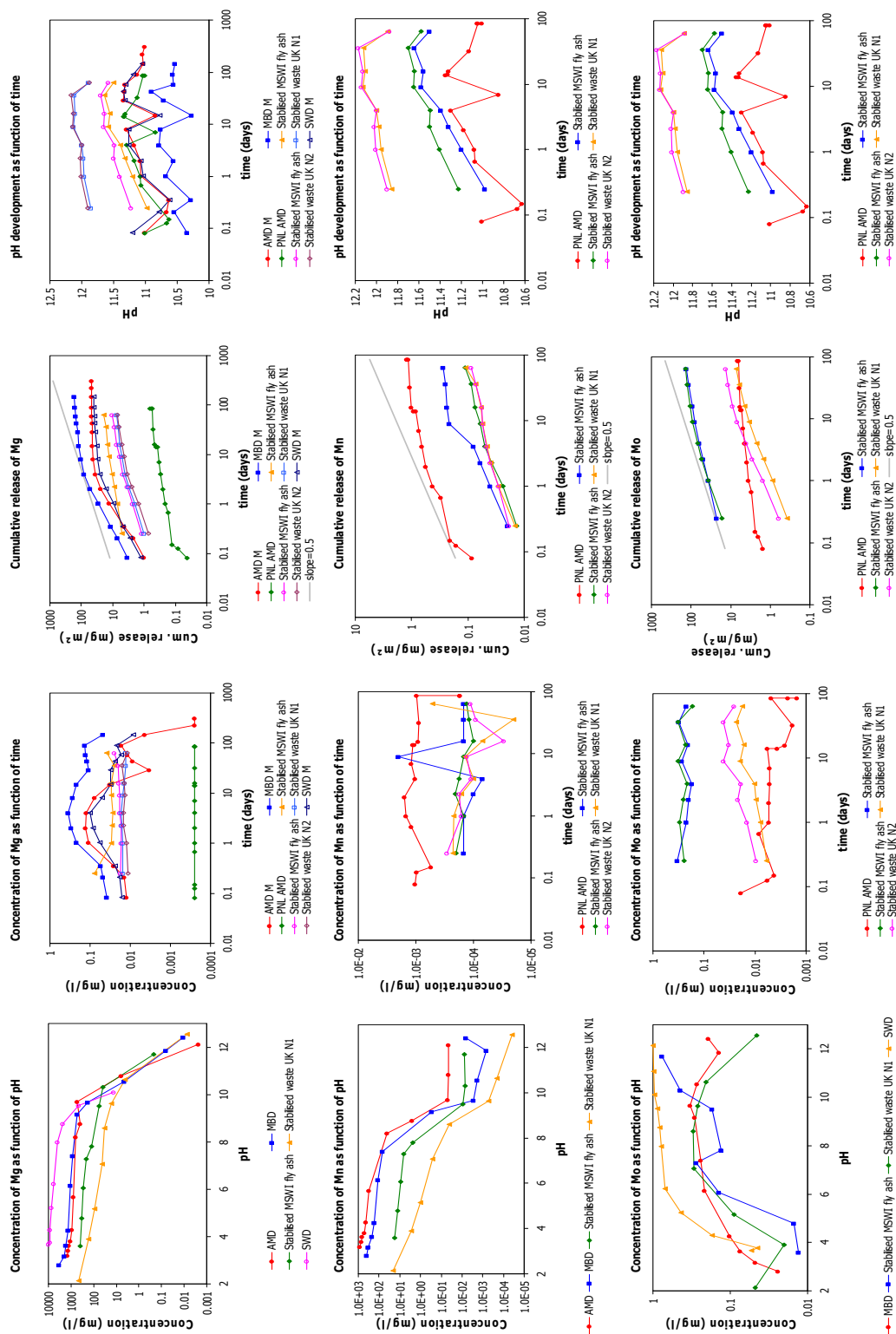


Figure E.7. Magnesium, manganese and molybdenum leaching results.

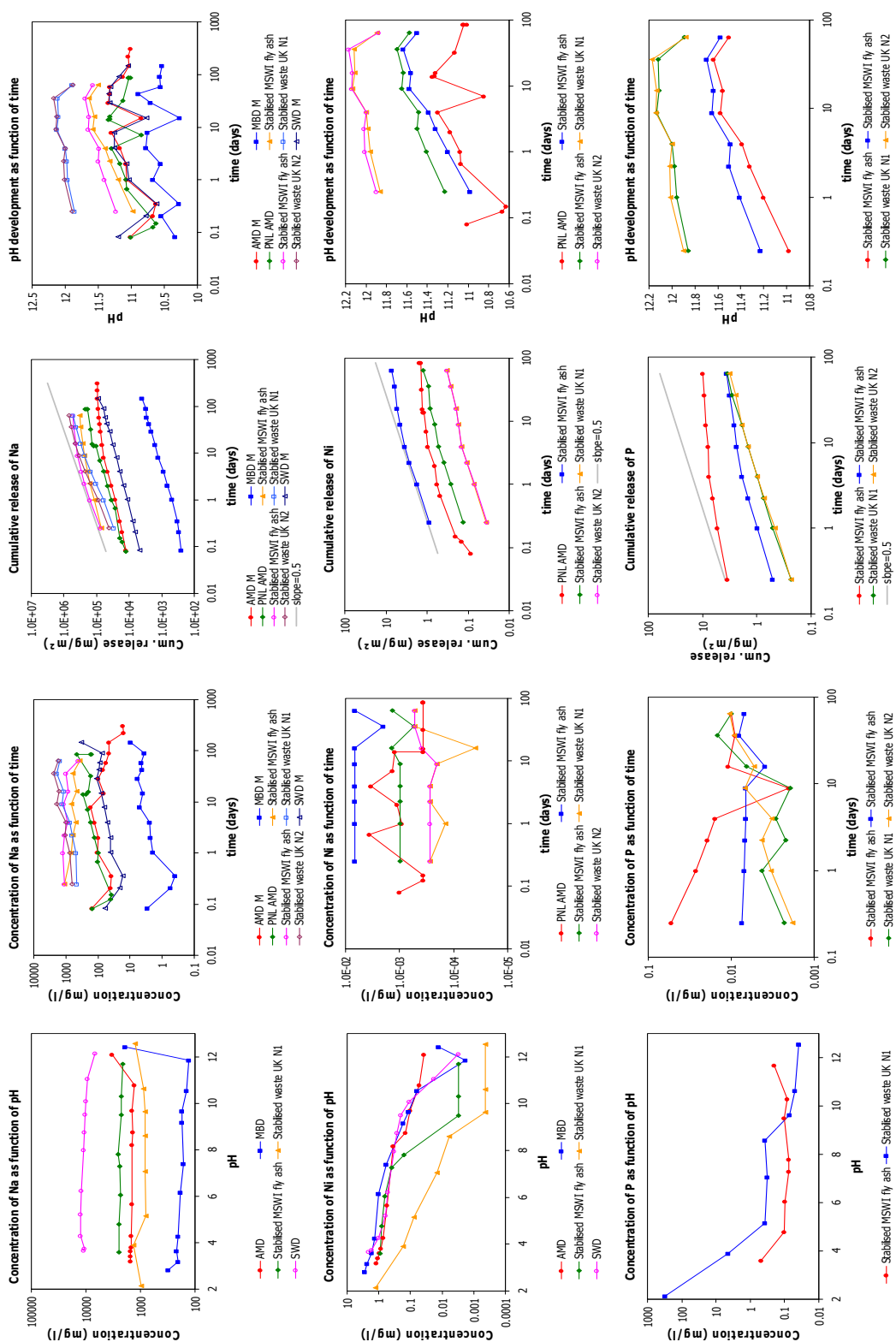


Figure E.8. Sodium, nickel and phosphorus leaching results.

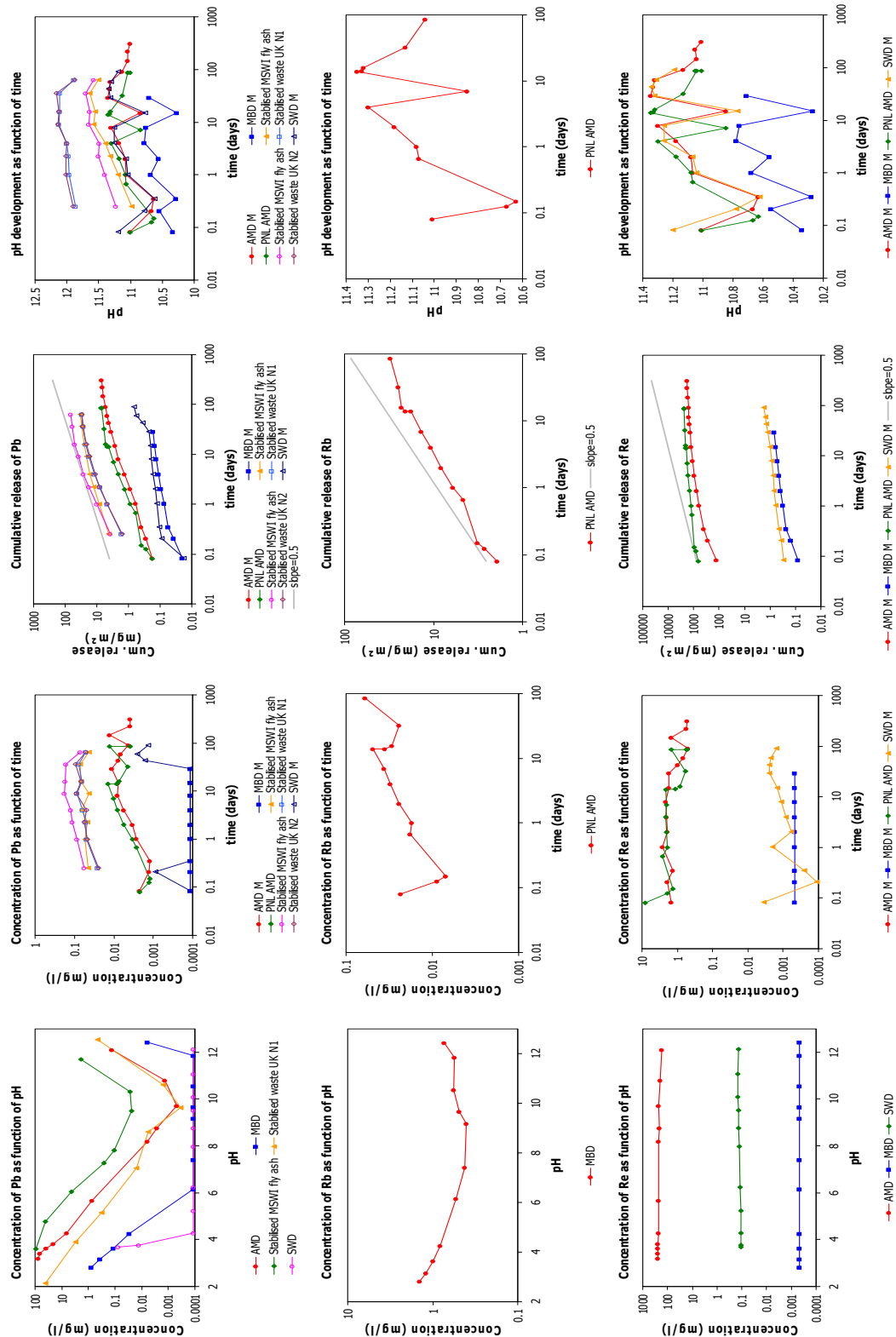


Figure E.9. Lead, rubidium and rhenium leaching results.

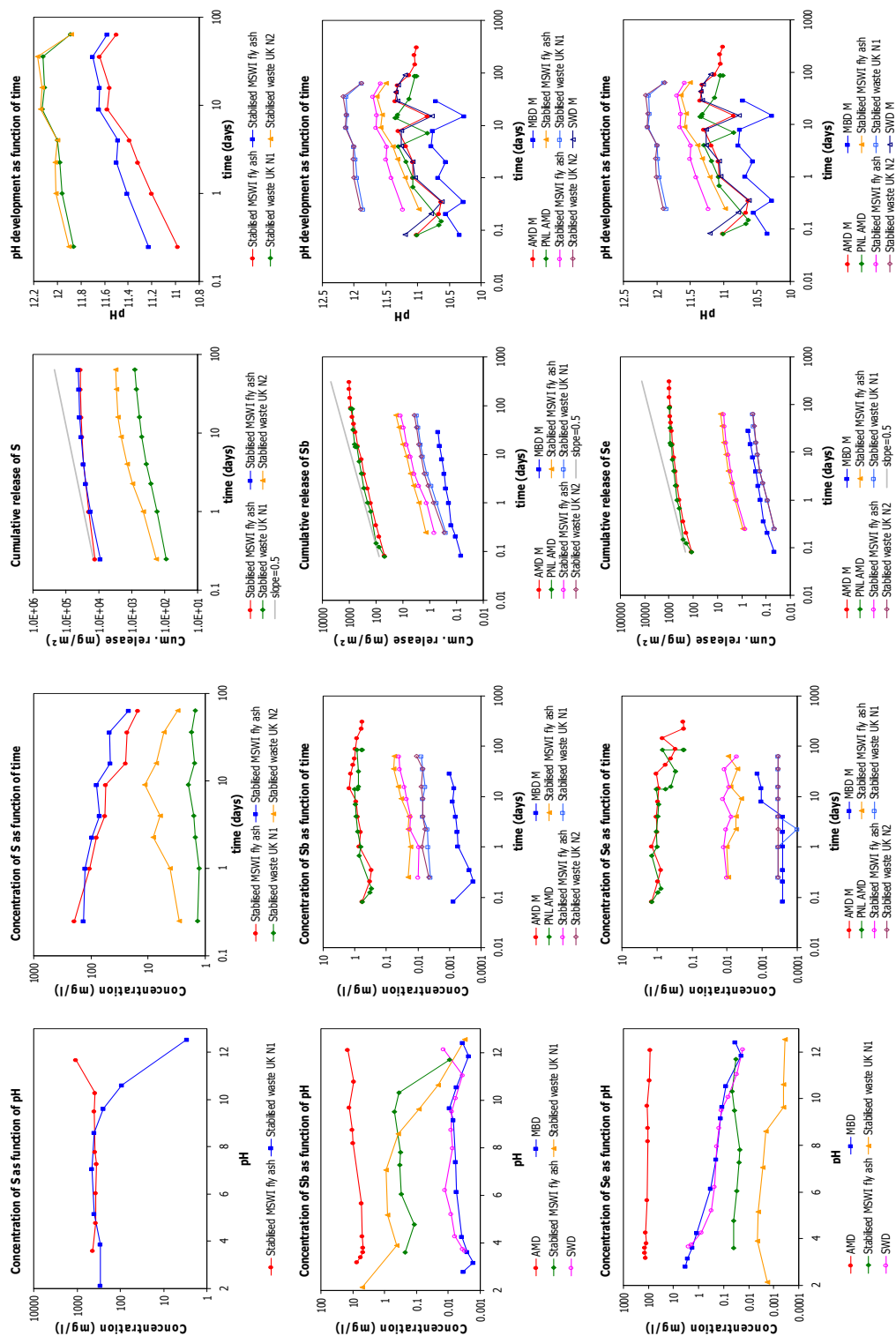


Figure E.10. Sulfur, antimony and selenium leaching results.

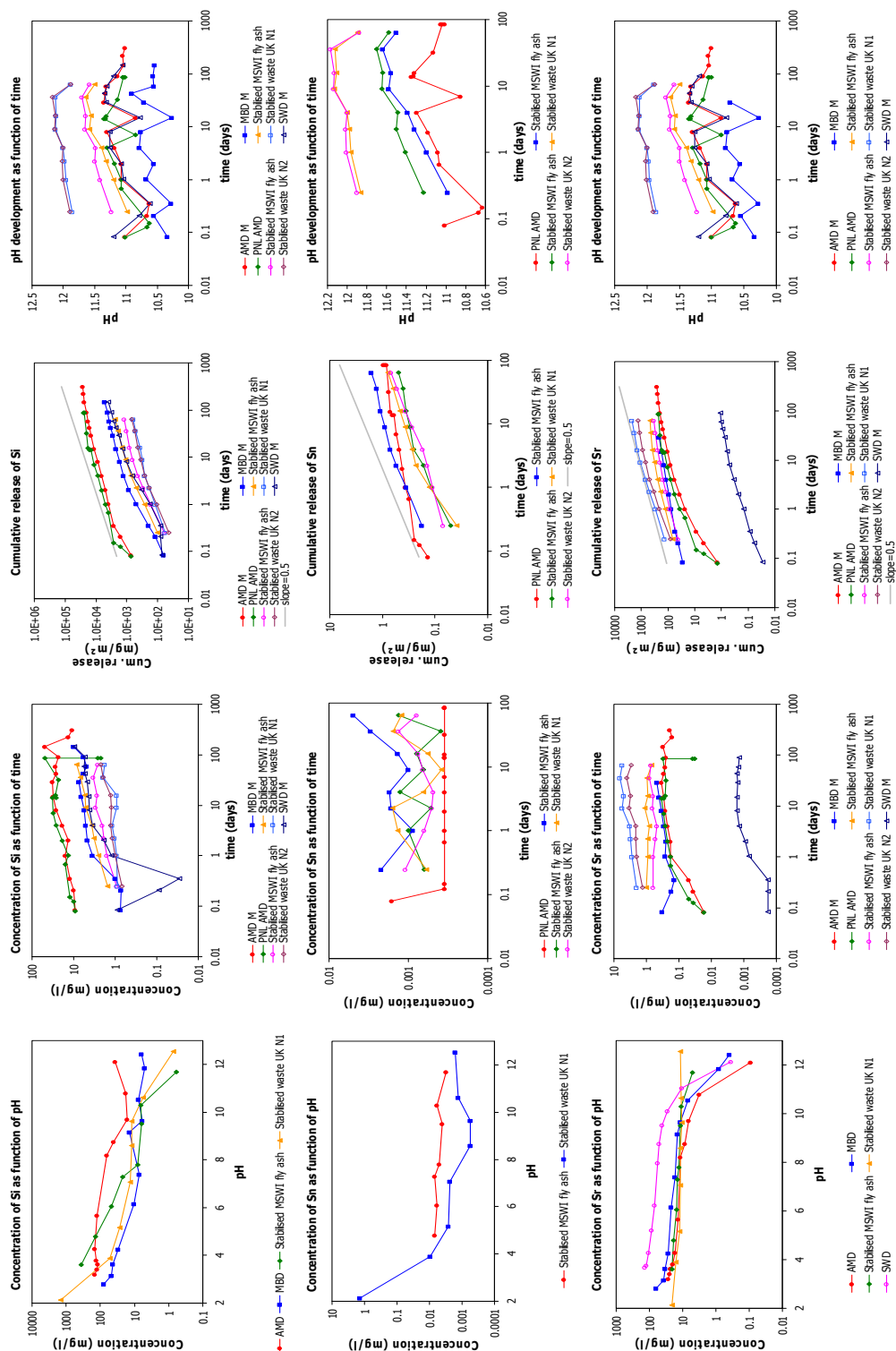


Figure E.11. Silicon, tin and strontium leaching results.

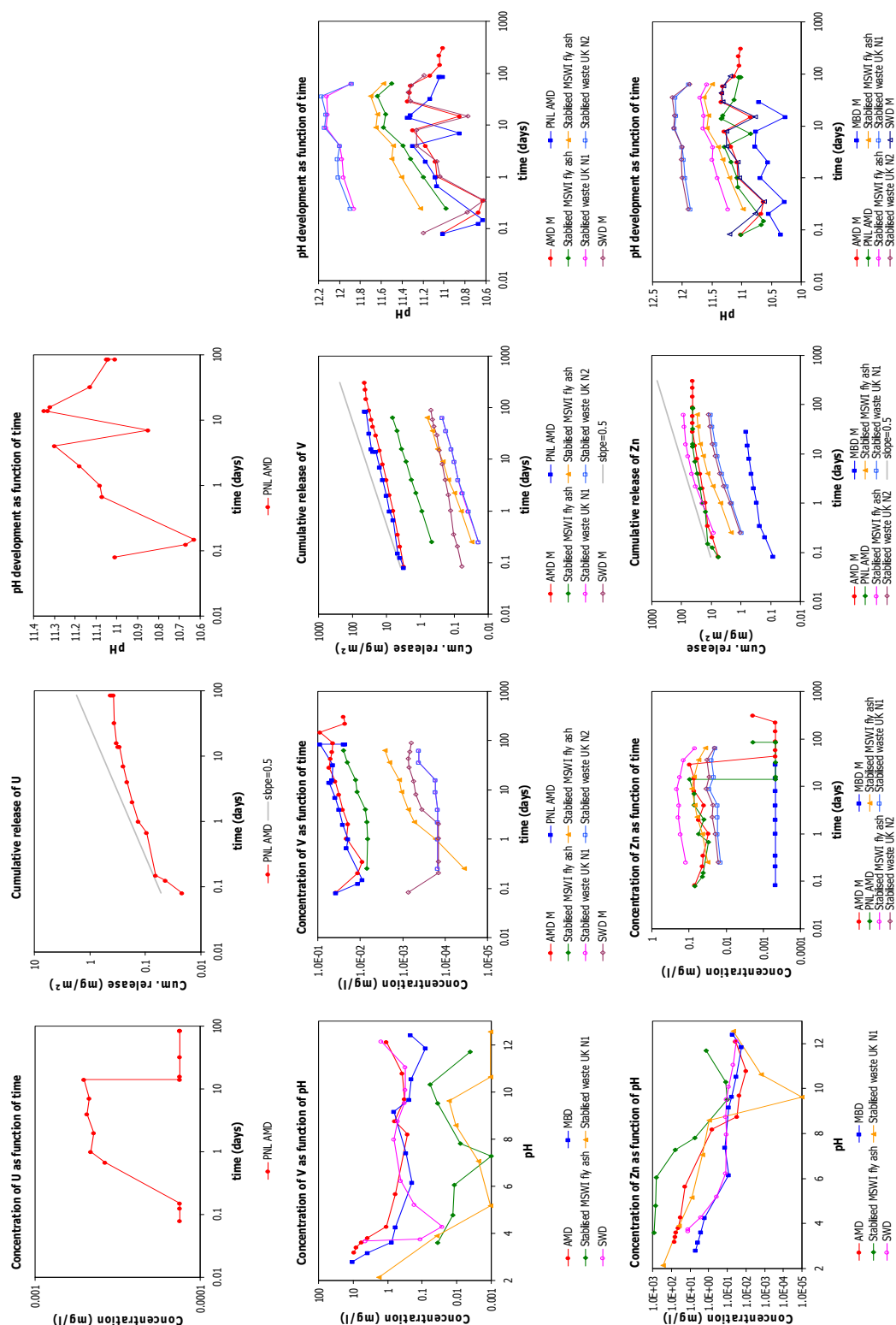


Figure E.12. Uranium, vanadium and zinc leaching results.

