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Mathematical modeling of heavy metals diffusion and removal from cylindrical cement forms coated with bio-film

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ABSTRACT

MATHEMATICAL MODELING OF HEAVY METALS DIFFUSION AND REMOVAL FROM CYLINDRICAL CEMENT FORMS COATED WITH BIO-FILM

by
Mojdeh Tabatabaie

A mathematical model is developed to predict bioleaching of heavy metals from long cylindrical shape cementitious samples. In this model, the metal concentration difference within the solid and its surface is considered as the main driving force for transport of metals to the surface of a sample at a given temperature and pressure. Fick's first and second law are applied to explain the motion of contaminants in a long and uniform cylindrical solid. In addition, the model considers Michaelis-Menten type kinetics, a special case of the widely accepted Langmuir-Hinshelwood reaction mechanism, at the surface of the encapsulating cylinder. The resulting model is solved analytically by applying regular perturbation techniques and Laplace transform.

Specifically, the mathematical model consisting of a partial differential equation describing the mass transfer of the targeted species as it moves through the encapsulating cylinder toward the surroundings. The nature of the species interaction at the surface of the cylinder renders an otherwise linear problem to be nonlinear. However, by applying a boundary perturbation technique, a series of linear problems are generated that can then be solved using traditional methods such as the Laplace Transform. The Residue Theorem is used to carry out the inversions yielding closed form solutions of the targeted species concentration profile.

The model was benchmarked by using effective diffusivities and specific surface bio-reaction rate constants within published ranges. Values of the mass concentrations

generated by the model for bioleaching of a number of metals namely cobalt, calcium, and chromium, from encapsulated cementitious cylindrical matrices are in reasonable agreement with those reported in the published literature.

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Mojdeh Tabatabaie

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APPROVAL PAGE

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LIST OF SYMBOLS

A_n, a	Constants
B_n	Constant
C_A	Element concentration (mol/cm^3)
D_{AB}	Diffusion coefficient (cm^2/s)
J	Bessel function notations
$k_0, k_1, and\ k_2$	Specific constants; (cm/s), (cm/s), and (cm^3/g)
r	Cylindrical coordinate (cm)
R	Cylindrical column mean radius (cm)
s	Laplace variable
t	Time (s)
w	Dimensionless group defined in Equation (4.27), $w = \frac{k_0 R}{D_{AB}}$
ψ	Dimensionless concentration defined in Equation (4.17), $\psi(\xi,\tau) = \frac{C_A}{C_{A0}}$
ξ	Dimensionless radius defined in Equation (4.18), $\xi = \frac{r}{R}$
τ	Dimensionless time defined in Equation (4.19), $\tau = \frac{D_{AB} t}{R^2}$
ε	Adjustable parameter between zero and one
λ	Eigen value

CHAPTER 1

INTRODUCTION

1.1 Objective

The objective of this work is to present a mathematical model developed for the prediction of heavy metals leaching from cylindrical shape cementitious bodies. The model uses Laplace Transform with linearization/perturbation techniques to solve the partial differential equation subject to boundary conditions that consider Michaelis-Menten kinetics, a special case of the widely accepted Langmuir-Hinshelwood reaction kinetics, at the surface of the cylinder. The model is then tested against published data and the results of numerical solution.

1.2 Background Information

Heavy metals are classified in a variety of ways such as: specific gravity, relative atomic mass, atomic number, chemical properties, toxicity, and/or those elements included between copper and bismuth on the Periodic Table (Duffus, 2002). Arsenic, cadmium, chromium, copper, lead, mercury, nickel, cobalt, selenium, and zinc (As, Cd, Cr, Cu, Pb, Hg, Ni, Co, Se, and Zn) are generally referred to as heavy metals. They are extensively used in various manufacturing processes, welding and cutting of materials, electroplating, pigment and paints production, photography, plastics, and leather tanning products (Jatkar, 1998; Duclos, 2001), are few examples. They are also used in making of refractory materials (Kurlekar and Bayer, 2001) and as catalyst in production of certain chemicals (Dae-Chul and Son-Ki, 2001). Chromium (VI), for example, is extensively used as corrosion inhibitor in manufacturing different forms of stainless steel.

Trace amounts of heavy metals such as iron, cobalt, copper, manganese, molybdenum, vanadium, strontium, zinc, and chromium are necessary for a wide range of metabolic activities in human body or other living organisms, and are significant components of many consumable products. However, their excessive amounts in the body can be detrimental to human health. For example, a trace amount of chromium (Cr) in human body is known to enhance the action of insulin (Mertz, 1969; 1993; 1998), a hormone critical to the metabolism and storage of carbohydrate, fat, and protein in the body (Porte Jr. et al., 2003). On the other hand, Cr (VI) is listed as a carcinogen by the Environmental Protection Agency (USEPA, 1998). The latter fact has prompted a wide range of studies to contain industrial waste streams contaminated with unacceptable levels of heavy metals.

Over the years, a number of technologies have been used to immobilize and/or remediate wastes contaminated with heavy metals, with cement based solidification-stabilization being the most dominant of such practices. Solidification/stabilization are generic terms given to a host of technologies that utilize physical and/or chemical processes to protect the environment from the harmful impacts of disposed hazardous, radioactive, and mixed wastes (USEPA, 1999). However, environmental factors such as exposure to harsh weather, acidic conditions and presence of certain microbial organisms can instigate the leaching of these encapsulated contaminants into the environment.

Researchers have reported on the factors affecting leaching of heavy metals from their cementitious matrices and developed mathematical models simulating such findings and/or examining different scenarios influencing the process. This research uses Michaelis-Menten kinetics, a special case of the widely accepted Langmuir-Hinshelwood

kinetics (Fogler 2006, Shuler 2002) to develop a mathematical model that predicts diffusion and removal of waste metals encapsulated in solid cylinder due to biofilm surrounding the cylinder.

CHAPTER 2

LITERATURE REVIEW

2.1 Solidification/Stabilization of Heavy Metals

Over the years, substantial amounts of waste contaminated with heavy metals have been generated due to their extensive use in manufacturing of numerous products. Of the methods that are available to treat the staggering amount of waste containing heavy metals, solidification/stabilization has been used the most. U.S. EPA in its publication "A Citizen's Guide to Solidification/Stabilization" defines the process as following: "Solidification/stabilization refers to a group of cleanup methods that prevent or slow the release of harmful chemicals from polluted soil or sludge. These methods usually do not destroy the chemicals—they protect human health and the environment by preventing the chemicals from moving into the environment. Solidification refers to a process that binds the polluted soil or sludge and cements it into a solid form. Stabilization refers to changing the chemicals so they become less harmful or less mobile." (USEPA, 1999-b) These two methods are often used together to prevent exposure to harmful chemicals.

The solidification/stabilization technique uses Portland cement as a binding agent to immobilize contaminants within the treated material; cement is mixed with the waste slurry so that the hydrating properties of cement lower the solubility/mobility of toxic contaminants via chemical bonding or physical entrapment within the microstructure of the cement fabric (Portland Cement Assoc-a, 2011). Malone and Jones (1979), Malone et al (1980), USEPA (1986c) and Roy et al (1992) provide a comprehensive overview of solidification/stabilization practices. Cement minerals can substantially reduce heavy

metal solubility via one or a combination of three mechanisms: precipitation, adsorption to the surfaces and incorporation. While precipitation as hydroxides limits the solubility of a few heavy metal cations, some oxyanions are bounded by the formation of calcium salts. Heavy metal cations may adsorb quite strongly to calcium silicate hydrate (C-S-H) because their ions are sufficiently soluble in basic media. The cations diffuse into the C-S-H particles where they are probably adsorbed to the silicate chains (Johnson, 2004).

Cement solidification/stabilization can be applied to industrial waste prior to disposal in landfills or used on site to treat contaminated soil and sediments (Olmo et al., 2003). Portland cement solidification/stabilization has been successfully applied in remediation of a number of Superfund and Brownfield sites including: New Bedford Harbor, New Bedford, Massachusetts; Yellow Water Road, Baldwin, Florida; Peak Oil/Bay Drum, Tampa, Florida; and 90th South Battery Site, West Jordan, Utah. **(**Portland Cement Assoc-b, 2011)

It is well established that most heavy metals encapsulated in cement remain stable in alkaline (high pH) environment. Deviation from alkaline condition, however, could mobilize the captured heavy metals from their matrices. Moreover, presence of materials such as grease, oil, chlorocarbons, sodium hydroxide, copper, zinc, etc have shown to deteriorate the setting and 'strength development properties' of cement and pozzolan binding agents that are commonly used in solidification/stabilization processes (Bricka and Jones, 1993). Different technologies have been developed to alleviate deficiencies of cement-based solidified wastes to the extent that the heavy metal contaminants are stabilized more effectively. (Chen and Majewski, 1978; Papp, 1996; Cropek et al., 2000; Sylvester et al., 2001; Hachiya et al., 2003; Jianguo et al., 2004)

Farmer et al. (2006) contended that millions of tons of chromite ore ($FeCr_2O_4$) processing residues were land filled in Glasgow, Scotland and Hudson County, New Jersey. They cited previous research (Darrie, 2001) indicating similar situations existing in China, Russia, Kazakhstan, India, and Pakistan. The authors asserted that on some of these sites, chromite residues were deposited for over 130 years (1830-1968). As chromite, Cr(III), chromium is inert and is not soluble in either acid or water. When exposed to basic environment, chromite converts to chromate with Cr(VI) chromium which is water-soluble. The reaction for this process with soda ash can be generalized as follows (Burke et al., 1991):

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

As a result, the amount of Cr(VI) leach out had been so much that the receiving ground waters and streams in the area are still contaminated. Considering the adverse impact of these metals on human health (USEPA, 1998; Zhang and Li, 1987; Saryan and Reedy, 1988), controlling their mobility from depositories into the ground and surface water tables has been of continuous interest to researchers worldwide.

While solidification/stabilization substantially reduces migration of encapsulated contaminants, studies have shown that they leach out of their matrices when exposed to suitable conditions. Because of such observations, the stability of heavy metals solidified in cement forms have been investigated under different physical and chemical conditions (Fernandez et al., 2003; Han et al., 2005). Furthermore, a thorough comparison of different fixation techniques for soil containing arsenic using federal Extraction Procedure--Toxicity (EPTox) test and the Toxicity Characteristic Leaching Procedure

(TCLP), as well as the California Waste Extraction Test (WET) has been conducted by Chu et al. (1991).

2.2 Leaching

Leaching is defined as the removal of materials from solids via dissolving away by "the action of a percolating liquid." (Merriam Webster Dictionary, 2011). Perry's Chemical Engineers' Handbook (Perry and Green, 1997) defines leaching as "the removal of a soluble fraction, in the form of a solution, from an insoluble, permeable solid phase with which it is associated." In this work we employ the definition given in the Chemical Engineers Handbook. Leaching of metals from cement forms has been widely studied with focus on describing parameters that promote the process such as, flow regime, pH variation and microbial activity (Hosoya, 2002). Shi and Kan (2006) have studied the chromium dosage impact on the physical properties of Portland cement in the presence of water reducers such as sulfonic acetone formaldehyde, polycarboxylic and naphthalene series. They reported good cementitious activity of chromium slag and a substantial decrease of Cr(VI) concentration in the leachate when polycarboxilic series was added to the mix.

Examining the leaching behavior and mechanism of Cr(VI) in cement and fly ash cement mortars using standard leachability test under acidic environment and carbonated conditions, Zeng et al. (2006) found that Cr(VI) leaching was reduced significantly after hydration of cement but increased under acidic and carbonated conditions.

Islam et al. (2004) have argued that re-mineralization of heavy metals in stabilized/solidified waste form at pH 4-5, has a negative impact on their release. As a

result of re-mineralization, heavy-metal releases to the leachate were reduced by factors ranging between 3.2 and 6.2 at pH 4 and between 74 and 193 at pH 5. At pH 6 and 7, re-mineralization of Pb and Zn occurred closer to the surface of the particles. They concluded that the amount of heavy-metal release depend on both the leachate pH and the re-mineralization factor. Yu et al (2005) demonstrated that leachability of Zn, Cr, Cu, Mn, Cd, and Pb depended on pH and testing method. Lower pH resulted in higher leaching of heavy metals tested.

While technologies have been developed to counter flow regime impact on mobilizing solidified contaminants (Fleming and Cullinane, 1992; Bobrowski and Gawlicki, 1997; Pagilla and Canter, 1999), restraining leaching in acidic environments, usually created by acid forming bacteria thiobacillus thiooxidans and/or thiobacillus ferrooxidans, continues to be a challenge (Löser, Zehnsdorf, and Seidel, 2005).

2.3 Bioleaching

Use of microorganisms to extract metals from low concentration waste streams is of interest to industry (mining, metal manufacturing, etc.) due to the low cost and high efficiency of bio-extraction compared to conventional methods. Two microorganisms, sulfur and iron oxidizing bacteria, *Thiobacillus thiooxidans* and *Thiobacillus ferrooxidans* are known to be the most effective microorganisms as they remove more than 50% of the metals from contaminated matrices (Gehrke et al. 1998; Gomez and Boserker, 1999).

Using thin section analysis Mahoney and Edwards (1966) described *Thiobacillus thiooxidans* structures comparable to gram negative heterotrophic bacteria that oxidize

elemental sulfur for energy, use carbon dioxide as source of carbon and can withstand a pH of less than one. These bacteria are usually isolated from anaerobically digested/dewatered sewage sludge or soil (Ryu et al, 2003). Liu et al (2004) identified the optimum composition of the growth medium for *Thiobacillus thiooxidans* to achieve optimal production of sulfuric acid. Furthermore, they noted low cost, mild process conditions and therefore low energy demand when compared to conventional technologies, as few advantages of bioleaching (Liu et al. 2004).

Dees and Shively (1982) describe *Thiobacillus thiooxidans* as chemilithotsophilic (rock eating) acidophilic bacterium. This bacterium uses elemental sulfur as energy source and is important in microbial catalysis of sulfide oxidation. They contend that *Thiobacillus thiooxidans* oxidize both sulfur and sulfide to sulfuric acid. The optimal pH range for *Thiobacillus thiooxidans* growth is determined to be about 3. It was proposed that *Thiobacillus thiooxidans* resist high acidic environment due to existence of ornithine (an amino acid) lipid in their membrane that protects them from strong acid environment (Dees & Shively, 1982). Liu et al. (2003, 2004) have reported similar observations.

The sulfur-oxidizing bacteria *Thiobacillus thiooxidans* have shown high activity in environments containing substantial heavy metal concentrations, and sulfate with pH 1.5-2.5 (Cho 2000). When the chemical and physical effects of microbial-influenced degradation (MID) using an active culture of *Thiobacillus thiooxidans* on ordinary cement pastes with water: cement (w:c) ratios ranging from 0.2 to 0.5 were compared to the effects of sterile media containing H_2SO_4 using an intermittent immersion technique, Knight et al. (2002) observed no significant difference between the two monitoring Ca, Al, and Fe releases. Using *Thiobacillus thiooxidans* culture, Bae et al (2001) have shown

that 94% of 3500 mg/kg Zn, 70% of 420 mg/kg Cu, 54% of 105 mg/kg Pb, and 46% of 8.5 mg/kg Cd were removed from the sediment in 8 days.

Studying the kinetics of bio-dissolution of metals from Indian Ocean nodules, Mehta et al. (2003) suggested that the bacterial oxidation using *Thiobacillus thiooxidans* and *Thiobacillus ferrooxidans* in the presence of pyrite and sulfur, produced ferrous sulfate and sulphurous acid respectively, which in turn reduced Mn(IV) in the nodules to Mn(II), thereby dissolving the metal through an indirect mechanism following the shrinking core kinetic model.

Removal of copper, nickel, and cobalt via bioleaching from ocean manganese ore nodules has been successfully tested using 'autotrophic microorganisms' – *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* in particular - in the presence of pyrite and sucrose. The process compared Cu, Ni, and Co acidic leaching from the nodules using H_2SO_4 at pH of 2 in 8 days. This bioleaching process recovered 37% Ni, 43% Cu, and 9% Co from the nodules. The recovery was significantly enhanced when pyrite and a reducing agent was added to the system, resulting in complete dissolution of the impurity metals in about 20 hours (Kumari and Natarajan, 2001).

In another study, the removal of metals from copper ore waste by flotation was significantly improved when the preliminary mechanical activation was combined with bioleaching using *Thiobacillus thiooxidans*. The maximum degree of extraction of aluminum was achieved in 28 days and its value reached 71% of its total quantity for an industrial waste product that was mechanically activated for 4 hours. Under similar conditions of bioleaching, silicon showed a low degree of extraction, about 2.5% of its total quantity, in the waste (Bojinova and Velkova, 2001). Monitoring copper dissolution

from a sulfide ore in cultures of *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans*, Pogliani and Donati (2000) reported that the copper dissolution from covellite (main copper phase in the ore used) didn't change significantly from one culture to the other. The dissolution of copper is explained using a mechanism proposed by Schippers and Sand (1999).

A number of researchers have shown that mixed cultures of *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* strains perform better than single strain in removing cobalt from pyrite (Borhany et al., 2003) and zinc from marmatite (Qiu et al., 2002). Similarly, Vahabzadeh et al. (2002) have reported that pre-treating gold-bearing sulfide ores using a mixed culture of *Thiobacillus ferrooxidans, Thiobacillus thiooxidans,* and *Leptospirillum ferrooxidans* strains significantly improved leaching of gold compared to conventional cyanidation. They concluded that the rate of bioleaching showed an increase using three bacteria combination over that from *Thiobacillus ferrooxidans* alone.

Furthermore, the highest recovery of Ni, Cu and Co were achieved (95.4%, 48.6% and 82.6%, respectively) in the aeration bioleaching of a low-grade Ni-Cu sulfide ore with mixed *Thiobacillus ferrooxidans* (TF5 strains) and *Thiobacillus thiooxidans* after 20 days (Fang et al., 2001). On the other hand, similar copper dissolution was found in the *Thiobacillus ferrooxidans* and the mixed culture composed of *Thiobacillus thiooxidans* and *Leptospirillum ferrooxidans* (Falco et al., 2001).

Ryu et al. (2003) reached a similar conclusion. They reported that the rate of leaching of metals (Zn, Cu, Cr, Pb, Ni, & Al) was higher at low sludge solid concentration due to lower pH. Dobryn et al. (1986) investigated leaching of zinc and

chromium from geothermal sludge using *Thiobacillus thiooxidans* and *ferrooxidans* by changing sludge and nutrient concentration, agitation rate, air bubbling and sterility, while monitoring the bacterial growth. They contended that *Thiobacillus thiooxidans* was better in removing zinc and *Thiobacillus ferrooxidans* in removing chromium. They also concluded that sludge to medium ratio of over 10% was toxic to microorganisms.

Löser, Zehnsdorf, & Seidel (2005) studied metal extraction from sediments in suspension or solid-bed system. In each case they performed two types of experiments: one was directly adding acid and the other, creating acid for leaching using microorganisms. In each case the sediments were treated by acids or microbial leaching and then washed with fresh water and analyzed for heavy metals. They found that the rate of microbial leaching was faster than acid leaching in a solid-bed set up. The authors associated this outcome to the fact that acid was produced within the bed in a microbial environment rather than being percolated through the bed therefore, the leaching rate was faster.

Using a municipal sludge from the Guilin (China) Sewage Treatment Plant as the cultivating medium and reductive sulfur as the growth substrate for Thiobacillus thiooxidans metabolism, Huang (2005) has reported removal of 70.8% Cu, 80.4% Zn, and 78.9% Cd from a 5 g substrate/L and 15% recirculation ratio of acclimated sludge in a bioleaching test.

Qiu, Xiong, Zhong, & Wang (2005) have compared bioleaching of chalcopyrite (Cu FeS_2) using pure cultures of *acidithiobacillus ferrooxidans* and *acidithiobacillus thiooxidans* and a mixed culture of both of these microorganisms. They concluded that more copper was extracted when a mixed culture was used compared to a pure culture of

either microorganism.

Salari et al. (2006) demonstrated that adding equal amounts of *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* culture solutions to mine ores containing copper, *Thiobacillus ferrooxidans* released more Cu than *Thiobacillus thiooxidans* in 60 days. Using mixed cultures consisting of five different strains for bioleaching of sulfidic Cu ores, Farshidy et al. (2004) were able to bioleach low grade copper ore by 26% in 17 days and do the same for chalcopyrite ore in 27 days.

Microorganisms have been extensively used to extract metals from ores. Acid-rock drainage (ARD) is generated from almost all hard-rock mining operations that deal with sulfide mineralization and pyrite (FeS_2). *Thiobacillus ferrooxidans*, gram-negative, acidophilic and rod-shaped, are natural bacteria in these environments and use sulfur for food/energy. As they proliferate on the surface of the sulfide rocks and particles, they contribute to a rapid change of the environment in which acid is formed and pH declines to 2.5–3. Under these conditions, heavy metals such as copper, lead, zinc, cobalt, nickel, and iron are leached into solution leading to serious metallic ion pollution which can kill fish and other living organisms. This process is a complex set of interactions between microbiology, mineralogy, microbial ecology and hydrologyical features (Meech and Curtis, 2006)

2.4 Bioleaching from Solidified/Stabilized Formations

The wealth of knowledge from microbial dissolution of toxic metals in mine wastes (Francis et al., 1989; Vachon et al., 1994; Wang and Chen, 2009) has led to studies on the effect of microorganisms on stability of heavy metals in solidified waste matrices.

Thiobacillus thiooxidans and *Thiobacillus ferrooxidans* are of value in selective and efficient removal of metals from certain waste streams, their activities can transform solidified/stabilized heavy metals into soluble forms, hence, cause their leaching into soil and/or water bodies. This has triggered research in understanding the mechanism of heavy metals release from such matrices.

Idachaba et al. (2001) used current Nuclear Regulatory Commission's (NRC) protocol to evaluate the stability of Tuskegee cement/$CoCl_2$ waste form in the presence of *Thiobacillus thiooxidans*. Exposure to *Thiobacillus thiooxidans* significantly enhanced Tuskegee cement/$CoCl_2$ waste forms instability degradation as measured by enhanced physical deterioration and increased leaching of Ca and Co. Instability of the waste was intensified with increased levels of $CoCl_2$ content in the leachate. Also, the degradative capability of *Thiobacillus thiooxidans* closely followed its ability to significantly decrease the pH of its environment.

Evaluating the leaching of chromium from cement waste forms, Idachaba et al. (2004) have compared a controlled sample with one having a refined biofilm formation on outer surface. Approximately 50% of the total chromium was leached from the experimental sample exposed to the bacterial broth of pH~ 2.00 within the first 24 hours of evaluation while no chromium leaching from the control sample (acidified to give pH of comparable to that of bacterial broth) was detected within the same time period. These experiments showed similar concentrations for leached calcium from both samples (control and one with biofilm on the outer surface) during the same time period.

Theoretical understanding of these observations and developing models that accurately predicts bioleaching have become of growing interest to scientists in the field.

In the work described below, the Michaelis-Menten kinetics is used to model microbial leaching of metals encapsulated in cylindrical shape solids.

2.5 Mathematical Modeling of Heavy Metal Leaching

A number of mathematical models explaining mechanical and/or physiochemical leaching of heavy metals from non-stabilized and/or stabilized forms are available in literature. Bishop (1986) studied the long term potential of heavy metals leaching from solidified/stabilized matrices. Using diffusion based model shown below, the author successfully simulated a series of up-flow column leaching tests.

$$\left(\frac{\sum a_n}{A_0}\right)\left(\frac{V}{S}\right) = 2\left(\frac{D_e}{\pi}\right)^{0.5} t_n^{0.5} \tag{2.1}$$

Where:

a_n = contaminant loss during nth leaching period (mg)

A_0 = initial amount of contaminant present in the specimen (mg)

V = volume of specimen (cm^3)

S = surface area of specimen (cm^2)

t_n = time to end of nth leaching period (sec)

D_e = effective diffusion coefficient (cm^2/sec)

For a linear leaching rate over the leaching period, Bishop (1986) suggested the following equations to determine the effective diffusion coefficient D_e :

$$D_e = \pi\left(\frac{a_n}{A_0}\right)^2\left(\frac{V}{S}\right)^2\left(\frac{1}{\Delta t}\right)^2\left(t_n - \frac{\Delta t_n}{2}\right) \tag{2.2}$$

Where

Δt_n = duration of nth leaching period (sec)

$(t_n - 0.5\ \Delta t_n)$ = elapsed time at the middle of leachant nth renewal period (sec)

and the leachability index, LX :

$$LX = \frac{1}{7}\sum_{n=1}^{7} \log\left(\frac{1}{D_e}\right) \tag{2.3}$$

The leachability index was used to compare the relative mobility of different contaminants on a 'uniform scale that varies from 5 (D_e = 10^{-5} cm^2/s, very mobile) to 15 (D_e = 10^{-15}, immobile)'. Simulation results indicated that the diffusion coefficients did not stay constant and changed with time as the speciation of the metals changed to more soluble forms. Other important factors affecting the leaching rate included: particle size (surface-to-volume-ratio in particular) leachant velocity and acidity.

Cheng and Bishop (1990) have argued that leaching mechanism in the pozzolanic-based solid matrices is controlled by the free H^+ available in the leachant. Measuring alkalinity of leachate, they suggest that hydrogen ions penetrate into the solid matrix and neutralize the alkalinity provided by the binder in the leach front. As the pH drops due to H^+ penetration, the metals precipitated at high pH environment dissolve and diffuse away into the leachate. Considering early stages of leaching, an 'unsteady diffusion with fast chemical reaction', authors developed a kinetic leaching model to be used for prediction of the acid penetration in the pozzolanic-based paste. Diffusion from a solid with constant surface concentration into a semi-infinite medium having initial zero concentration, was shown to be proportional to the square root of time (Crank, 1975) and involves a single dimensionless parameter: $z / \sqrt{4D_e t}$, where z is penetration

distance and D_e the effective diffusion coefficient. The concentration of diffusing substance $C(z,t)$ and the flux of diffusion $J(z,t)$ are given by:

$$C(z,t)=C_o\left[1-erf\left(z/\sqrt{4D_e t}\right)\right] \tag{2.4}$$

$$J(z,t)=C_o\left(\sqrt{D_e/\pi t}\right)\exp(-z^2/4D_e t) \tag{2.5}$$

The mass balance of H^+ in a small shell within the solid can be written as:

$$\begin{pmatrix}Hydrogen\,ion\\ accumulation\end{pmatrix}=\begin{pmatrix}H^+ diffusion\ in\\ -out\end{pmatrix}+\begin{pmatrix}amount\,H^+\ produced\\ by\,chemical\,reactions\end{pmatrix} \tag{2.6}$$

In differential form:

$$\frac{\partial C_H}{\partial t}=\frac{\partial}{\partial z}\left(D_e\frac{\partial C_H}{\partial z}\right)-\frac{\partial\theta f(C_H)}{\partial t} \tag{2.7}$$

where θ is the density of the sample with mass/volume unit and $f(C_H)$ is acid neutralization capacity (ANC). Assuming constant D_e and θ, with $f(C_H) = KC_H$, and using the boundary conditions:

$$\begin{aligned} &C_H(z,\ 0)\approx 0 \quad \text{for all z}\\ &C_H(0,\ t)=C_o \quad \text{for t}>0\\ &C_H(z,\ t)\approx 0 \quad \text{for z}=\infty \end{aligned} \tag{2.8}$$

The solution was given as:

$$C_H(z,t)=C_o\left[1-erf\left(z\sqrt{(1+\theta K)}/\sqrt{4D_e t}\right)\right] \tag{2.9}$$

$$J(z,t)=C_o\left(\sqrt{D_e(1+\theta K)/\pi t}\right)\exp(-z^2(1+\theta K)/4D_e t) \tag{2.10}$$

Equation (2.9) was used to find the H^+ concentration at any given distance and given time.

Batchelor (1992) developed a 'numerical leaching' model which considered interactions between calcium (as a measure of the alkalinity of the treated waste), hydrogen ion, lead (as the contaminant that can precipitate as hydroxide) and acetate (as a measure of acidity of the leaching solution). The model was applied to a rectangular solid of finite thickness containing contaminant, held in an acidic bath of finite volume. The diffusion path for the molecules through the solid was assumed on the order of half of the pore radius and that for the molecules in the liquid was taken on the order of half of the pore length. The model assumed presence of two solids ($Ca(OH)_2$, $Pb(OH)_2$), six soluble species (Ca^{+2}, H^+, Ac^-, Pb^{+2}, OH^-, HAc) and reactions between them (providing the equilibrium constant for each reaction):

$$H_2O \longleftrightarrow H^+ + OH^- \qquad Log\ K_w = -14.0 \qquad (2.11)$$

$$H^+ + Ac^- \longleftrightarrow HAc \qquad Log\ K_{HAc} = 4.76 \qquad (2.12)$$

$$Ca^{2+} + 2H_2O \longleftrightarrow Ca(OH)_2 + 2H^+ \qquad Log\ K_{Ca(OH)_2} = -\mathbf{22.675} \qquad (2.13)$$

$$Pb^{2+} + 2H_2O \longleftrightarrow Pb(OH)_2 + 2H^+ \qquad Log\ K_{Pb(OH)_2} = -\mathbf{8.15} \qquad (2.14)$$

Writing a material balances relating the total concentration of each species per unit volume (T_{ss}) to the concentration of contaminant in mobile phase and assuming the Fickian diffusion with local chemical equilibrium, resulted in Equation (2.15).

$$\frac{\partial T_{ss}}{\partial t} = D_e \frac{\partial^2 C_m}{\partial X^2} \qquad (2.15)$$

To simplify solving this equation, Batchelor (1992) defined the concentration in mobile phase in terms of total concentration of each species using a factor G, representing mobile fraction of the species.

$$\frac{\partial T_{ss}}{\partial t} = D_e \frac{\partial^2 (G T_{ss})}{\partial X^2} \tag{2.16}$$

A modified Crank-Nicholson algorithm was employed to solve the dimensionless form of Equation (2.16) numerically. The model predictions agreed with those obtained analytically for infinite bath conditions.

Hinsenvel and Bishop (1994) used Fick's bulk diffusion model to determine contaminant leaching out of solid form:

$$\frac{\partial C}{\partial t} = D_e \frac{(\partial^2 C)}{(\partial x^2)} \tag{2.17}$$

where:

D_e : effective diffusion coefficient, corrected for porosity and tortuosity ($cm^2 s^{-1}$)

C : concentration of the contaminant (g cm^{-3})

t : time (s)

x : distance (cm).

Equation (2.17) was solved for contaminant concentration profile in a specimen as a function of dimensionless time, which can be used to determine leaching rate:

$$C(x,t) = 3C_0 \, erf\left[\frac{x}{4D_e t}\right] \tag{2.18}$$

where:

C_0 : initial contaminant concentration in the solid

erf : standard error function

x : distance into the solid

t : leaching time.

Baker and Bishop (1997), based on research that showed leaching of contaminants is a result of the dissolution of the outer shell of the waste form which then results in a solubilization and release of contaminants from the leached shell, modeled contaminants release using shrinking unreacted core (SUC). They used acid exposure, rather than time, as the key variable in evaluating leaching behavior. Acid exposure is defined as 'the amount of acid a specimen is exposed to under acidic conditions' which is equivalent to the acid concentration X time/volume (mol min l^{-1}). To compensate for the change in acid concentration over time, the authors define the exposure integral, $I(t)$, as:

$$I(t)=\int_0^t \overline{C_r}\, dt \tag{2.19}$$

where $\overline{C_r}$ is the average acid concentration. They also define conversion, ζ, relating the amount of leached shell to the original amount of material. For flat specimens, this is simply the acid penetration depth (APD) and for cylindrical or spherical shape specimens, conversion is a dimensionless number relating the original specimen radius to the core radius. Under the leached shell diffusion limitation, the conversion, as measured by acid penetration depth (cm), has been shown to follow the relationship:

$$\zeta=\sqrt{\frac{2D_{e,s}(c_{H,i}-c_{H,c})}{\beta_c}t} \tag{2.20}$$

where:

$D_{e,s}$: effective diffusion coefficient (for acid species)(cm^2s^{-1})

$c_{H,i}$: hydrogen ion concentration at the liquid interface (kmole m^{-3})

$c_{H,c}$: hydrogen ion concentration at the core boundry (kmole m^{-3})

β_c : acid neutralization capacity (ANC), the quantitative capacity of cement to react with a strong acid to a pre-determined pH, (kmol eq m^{-3}).

Assuming the H^+ concentration at the leaching front is much less than that in the bulk liquid, the exposure integral , Equation (2.19), can be substituted into Equation (2.20) to give:

$$\zeta = \sqrt{\frac{2D_{e,s}I(t)}{\beta_c}} \tag{2.21}$$

The authors corroborate validity of their formulation studying 'the behavior of real-world' solidified wastes.

Brouwers (1997) developed models to study leaching from immersed materials and from granular materials flushed in a column. A semi-infinite medium diffusion model was used for immersed materials in which mass transfer from the material to leachate was inversely proportional to √t. The same proportionality (√t) was assumed for unsteady leaching process from granular materials flushed in a column. From solving the system of differential equations developed and comparing the leaching expressions to those obtained by Godbee and Joy (1974), Brouwers concluded that the resulting equations can be used for determining an effective diffusion coefficient and/or comparing immobilization yields.

Li and Wu (1999) used a multi-component reactive solute-transport model to study the migration of dissolved heavy metals (Cd^{2+}, Pb^{2+}, Cu^{2+}, and Zn^{2+}) in a kaolinite landfill liner subject to different pH environments. This model has the capability of simulating water flow, advective-dispersive-solute transport, and chemical reactions

processes, simultaneously. Using concentration values of the four studied metals close to ones found in real leachate, the model calculated the concentration profiles of these metals in the simulated clay barrier and predicted the leachate pH effects on their mobilities. It was found that in a nearly neutral leachate, the heavy metals mobility changed as: Cd^{2+}< Pb^{2+}<Cu^{2+}<Zn^{2+}. However, in an acidic environment the order changes to Pb^{2+}< Cu^{2+}< Zn^{2+}<Cd^{2+}. It was also identified that the mobility of $Cd^{2+}$and Pb^{2+} were very sensitive to pH where the mobility of Cu^{2+} and Zn^{2+} were not affected as much.

Camacho and McGee (2001) developed and tested a combined statistical model to quantify the amount of three heavy metals (Cr, Cd, and Al) released from fly ash solidified/stabilized waste and compared the results to data obtained using the US-EPA's toxicity characteristic leaching procedure (TCLP). TCLP is a procedure used by the Environmental Protection Agency to corroborate the acceptability of the solidified/stabilized waste for land disposal (USEPA, 2008). The model is developed based on 'a simplex-centroid and a 26-3 fractional factorial experimental design.' Taking appropriate process conditions of the solidified waste formation, the model evaluates parameters for minimum release of the metals. Curve fitting of the results to find the maximum metal release to the leaching solution, a linear polynomial equation was found for Cr and Cd release, where a third degree polynomial fitted Al data.

Understanding that the immobilization of heavy metals in the solidified waste needs a steady alkaline environment, Catalan and Wetteskind (2002) developed an alkalinity depletion model for solidified/stabilized zinc contaminated wastes to predict the growth of leachate pH with time for various infiltration situations. The model

parameters include: the initial effective alkalinity of the treated waste, the alkalinity depletion rate, the infiltration rate, and the height of the solidified block. Comparing the model prediction with experimental results, it was found that for a typical full-scale disposal situation, the leachate alkalinity stays unchanged hence the heavy metals stay immobilized in the solidified waste for a long period of time.

Among researchers, contribution of Tiruta-Barna's group to understand and model leaching of chemical elements from solid forms is noteworthy. They have studied "distributed mass transfer rate for modeling the leaching of porous granular materials containing soluble pollutants" (Tiruta-Barna et al, 2000), "modeling of solid/liquid/gas mass transfer for environmental evaluation of cement-based solidified waste" (Tiruta-Barna et al., 2001), and "release dynamic in various process identification for a cement based material in various leaching conditions" (2005), to name a few. Tiruta-Barna et al (2004, 2005) conducted an extensive study of release dynamic under several leaching conditions for cement based materials and developed a coupled chemical-mass transfer model to describe the leaching behavior.

Assuming diffusion as the main mechanism of mass transfer in the solid/porous phase and dispersive convection in the leachate, Tiruta-Barna et al. (2005) developed a model that was applied to four leaching scenarios namely: diffusion, convection, late dissolution, and surface dissolution. They concluded that the hydrodynamic dispersion and the residence time had no effect on the leaching behavior of alkaline, which is controlled by diffusion, whereas the behavior of calcium was strongly influenced by these factors. The latter had significant impact on pH values, hence, on the concentration of Pb in the leachate, the monitored pollutant.

Halim et al. (2005) simulated the leaching of Pb, Cd, As, and Cr from cementitious wastes using the United States Geological Survey public domain PHREEQC geochemical package. Four different matrices were examined namely calcite, portlandite, calcium-silicate-hydrate (C-S-H) matrix, and the free metal compounds. The model used the following equation to describe the dissolution rates of these matrices:

$$\frac{dM}{dt} = 50x10^4 k_{system} A\left(c_1 a_{H^+} + c_2 a_{H_2CO_3} + c_3 a_{OH^-} - c_4 a_{Ca^{2+}} a_{CO_3^{2-}} + c_5\right) \quad (2.22)$$

Where:

dM / dt = dissolution rate of each matrix

k_{system} = constant

A = surface area of the matrix (in m^2 g^{-1} of waste)

$a_{H^+}, a_{H_2CO_3}, a_{OH^-}, a_{Ca^{2+}}, a_{CO_3^{2-}}$ = *activities of* $H^+, H_2CO_3, OH^-, Ca^{2+}$, *and* CO_3^{2-}

Using both kinetic terms and equilibrium thermodynamics of key compounds, the model provided information on leachate and precipitate speciation. The model predicted leaching of Pb, Cd, As, and Cr from cement and indicated that Pb and As were predominantly incorporated within the calcium-silicate-hydrate matrix while a greater portion of Cd was seen to exist as discrete particles in the cement pores and Cr (VI) existed mostly as free CrO_4^{2-} ions.

Malviya and Chaudhary (2006) studied the leaching behavior and immobilization characteristics of solidified/stabilized heavy metals from steel processing plant waste. They reported that the mechanical strength of the samples decreased with increase in waste content. Using the geochemical modeling to predict speciation, they found that the

dominant leaching mechanism was surface wash off in the initial stages followed by diffusion for Pb, Zn, Cu, Re, and Mn. They reported a diffusion coefficient of 11.5, an indication of a low mobility in the cement matrix.

Yalcin and Unlu (2006) have mathematically modeled the dissolution kinetics of chromium during leaching of chromite ore processing residue (COPR). Using a sequence of batch (dissolution) and mass flushing (leaching) operational modes, the model provided the effectiveness of intermittent leaching. The model indicated that the difference between aqueous phase concentration and saturation concentration (effective solubility), the mass fraction of dissolvable chromium remaining in the solid phase and the steady-state tailing behavior of COPR control the chromium dissolution.

Hall (2006) developed a model to estimate the timescale necessary to achieve equilibrium concentration of heavy metals in landfill wastes. The base for analysis was a raw municipal solid waste (MSW) for which only cadmium failed to reach equilibrium. The program was tested for a range of pre-filling treatment for non-flushed and flushed sites with active management. Testing the model for concentrations of heavy metals at or below UK requirements, the study revealed that stabilization time for metals such as arsenic and chromium can take more than 1000 years before stabilization under different scenarios. When testing the model for mechanical and biological treatment scenarios, the model indicated possibility of achieving equilibrium under minimal flushing.

Farmer et al. (2006) conducted an integrated assessment and modeling research to identify mineral phases and processes responsible for the retention and release of Cr(VI) under different field condition. It was found that both, the nature of mineral phase retention and the buffered high pH of the sites influence mobility of Cr(VI) in waste.

Slack et al. (2007) modeled leachate migration from municipal solid waste using LandSim (UK EA, 2006) program. The model predicted that heavy metals such as arsenic and chromium could migrate beneath a model landfill site over a 20,000 year period in excess of European Union and US-EPA drinking water standards at the unsaturated zone/aquifer interface, with levels of mercury and cadmium exceeding minimum reporting values (MRVs).

In their recent publication (Schiopu et al., 2009) they used PHREEQC, coupled with the Lawrence Livermore National Laboratory (LLNL) thermodynamic data base, to model and simulate leaching from concrete under outdoor exposure conditions. The model intended to combine 'chemical-transport' effect on leaching of toxic compounds from 'concrete based construction products' exposed to rain water under outdoor exposure conditions. The model was tested using experimental data. Assuming that in a porous monolith like the concrete slabs, diffusion is the main transport mechanism in the solid, for each chemical element α of concentration C_{α}^{Pores} in the pores water, the mass balance equation is:

$$\frac{\partial C_{\alpha}^{Pores}}{\partial t} = D_e \frac{\partial^2 C_{\alpha}^{Pores}}{\partial z^2} - \sum_{n=1}^{N} \frac{\partial S_{\alpha,n}^{Pores}}{\partial t} \tag{2.23}$$

$$\begin{cases} if\ S_{\alpha,n}^{Pores} \geq 0\ and\ C_{\alpha}^{Pores} > C_{\alpha}^{sat-Pores}\ then \dfrac{\partial S_{\alpha,n}^{Pores}}{\partial t} = R_{\alpha,n} \\ else: \dfrac{\partial S_{\alpha,n}^{Pores}}{\partial t} = 0 \end{cases} \tag{2.24}$$

where $S_{\alpha,n}^{Pores}$ is the concentration in the pore water of the element α in a solid phase n, involved in a chemical reaction with kinetic constant k_r, $C_{\alpha}^{sat-Pores}$ is the saturation

concentration in pore water, and D_e is the effective diffusion coefficient. Equation (2.23) is solved subject to boundary conditions:

$$\left.\frac{\partial C_\alpha^{Pores}}{\partial t}\right|_{z=0} = 0 \tag{2.25}$$

at the bottom face, $z = 0$ and:

$$D_e \left.\frac{\partial C_\alpha^{\text{int}\,erface}}{\partial t}\right|_{z=h} = k_{SL}\left(C_\alpha^{leachate} - C_\alpha^{\text{int}\,erface}\right) \tag{2. 26}$$

at monolith/leachate interface, $z = h$.

Schiopu et al. (2009) further considered presence of gases, CO_2 in particular, in pores of the solid and their possible interaction with chemical species. The model results compared with experimental data demonstrating its viability to be used in assessment of concrete type construction material leaching behavior.

Bayar et al. (2009) have used regression method and neural networks (NNs) to predict behavior of solidified/stabilized industrial sludge containing toxic heavy metals. NNs is a statistical tool for data analysis that can be used to analyze the relations between variables depending on the predictive variables used by means of a mechanism known as training or learning. Upon a training process, NNs become able to produce estimation by using the relationship developed during the learning phase. The use of neural network technique, authors claim, gives a better understanding of impacts different component in a mix impart on each other, and therefore, helps with selecting an ‘optimum’ solidification/stabilization technology. The paper reports reasonably good results when the technique was applied to species made by Portland cement as binder to solidify the

tested waste and using EPA approved leaching test methods (DIN 38414-S4 Test and EPTox Test) for their analyses.

Applying Geochemical speciation modeling on the concentrations of Cu, Cr, Mo and Ni in the leachates released from different recycled concrete aggregate samples. Engelsen et al. (2010) reproduced the characteristic pH dependent release patterns for these elements and found reasonable matches between the predicted and measured concentrations. Binding of Mo and Cr as oxyanions (MoO_4^{2-} and CrO_4^{2-}) to ettringite was modeled with fair agreement for Cr only. For Cu and Ni, the predicted and measured concentrations agreed well for the partly carbonated sample at high alkaline pH (11–13).

2.6 Mathematical Modeling of Heavy Metal Bioleaching

Bioleaching of heavy metals from mining and municipal waste streams has been extensively studied. Also, researchers have related the deterioration of solidified/stabilized heavy metal waste in cementitious forms to the activities of microorganisms. While experimental studies in the field are abundant, models simulating bioleaching of solidified/stabilized heavy metal wastes from cementitious materials are limited (Hall, 2006; Löser et al., 2005; Xu and Ting, 2009). Löser et al. (2005) developed several models to explain their experimental results on removal of heavy metals from polluted sediments with bioleaching. Elemental sulfur was used as the leaching agent. They proposed that the leaching is a two-step process: the microbial oxidation of sulfur to form sulfuric acid followed by the reaction of the acid formed with the sediment. The models differed on the degree of complexity to describe S^0 oxidation, assuming S^0 particles having uniform size (Model I), a measured particle size distribution

(Model II), or applying an adapted Rosin-Rammler-Sperling-Bennett (RRSB) distribution (Model III). Comparing data from these simulations runs with experimental data they had obtained, authors reported that Model I, though simple, slightly deviated from the measured data, Model II simulated the data best, and Model III performed in between.

Saddawi et al. (2005) have developed a formula to calculate the rate of biooxidation of elemental sulfur by Thiobacillus thiooxidans bacteria. The formula prediction of biooxidation rate in an oxygen and carbon dioxide rich environment, for a varying pH (0.35 – 4.5) and temperature (288 – 321 K) ranges was confirmed by experimental data. The authors concluded that physical form of sulfur (tabulated sulfur powder or pastilles sulfur) has no effect on the rate of biooxidation. In another study, Xu and Ting (2009) investigated bioleaching kinetics of heavy metal ions by the Aspergillus Niger fungus from municipal solid waste incineration fly ash at various pulp densities (1 – 6%) in batch system.

Olivera-Nappa et al. (2010) have proposed a two-dimensional non-homogeneous biofilm model to study chemical and biochemical reactions applied to biological metal leaching from mineral ores. Bouffarda and Dixonb(2009) employed HeapSim to evaluate unknown parameters and to identify the rate-controlling steps governing a simple leach system consisting of only pyrite under isothermal conditions. The temperature at which the column tests were performed encompassed the range of the mesophilic cells (15–40 °C), moderate thermophilic cells (30–55 °C), and extreme thermophilic cells (50–80 °C). Using experimental values for the ore-, geometry-, and hydrology-related parameters characteristic of the column tests, the model provided biological parameters

of iron- and sulfur-oxidizing cells and the oxygen gas–liquid mass transfer rate by trial and error from simultaneous best fits of five leach data sets: extent of sulfide oxidation, effluent solution potential, iron concentration, cell numbers, and sulfur grade.

Considering the different reactions for the system and the fact that many occurrences (sphere, disk, vein) of pyrite in the ore were shown to be oxidized electrochemically with ferric ions to produce ferrous ions, sulfate, and elemental sulfur, the rate of pyrite oxidation was recommended as:

$$r_{FeS_2} = G_{FeS_2}\frac{dx}{dt} = G_{FeS_2}k_0 \exp\left[\frac{E_a}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right]\sqrt{\frac{C_{Fe(III)}}{C_{Fe(II)}}}\left(1-x\right)^{\varphi}, \quad \frac{\text{mole FeS}_2}{\text{kg ore.h}} \qquad (2.27)$$

with diffusion equation:

$$\left(1+\frac{1}{\rho\varepsilon_s}\frac{S_i}{C_{s_i}}\right)\frac{\partial C_{s_i}}{\partial t} = \left\{\frac{D_i}{\left(\tau X\right)^2}\right\}\left[\frac{1}{\xi^n}\frac{\partial}{\partial\xi}\left(\xi^n\frac{\partial C_{s_i}}{\partial\xi}\right)\right] + \sum_j v_{ij}r_j, \qquad \frac{\text{mol}}{\text{m}^3\text{stagnant.h}} \qquad (2.28)$$

subject to boundary conditions:

$$C_{s_i}\left(\xi,0\right) = C_{s_i,0}$$

$$C_{s_i}\left(\xi=1,t\right) = C_{f_i} \qquad (2.29)$$

$$\left.\frac{\partial C_{S_i}}{\partial\xi}\right|_{\xi=0} = 0$$

where:

S = the adsorbed concentration of species on the ore, taking a value of zero for all species but microbes

C = the concentration in solution

ε_S = the proportion of the stagnant phase in the heap

D = the diffusivity

τ = the tortuosity of the stagnant solution pathway

X = the length of the stagnant solution pathway

n = a geometric factor (0 for linear, 1 for cylindrical, and 2 for spherical; in this work only the value n = 2 is used)

ξ = the normalized position in the stagnant solution pathway

ν = the stoichiometric coefficient of species i in reaction j

r = the rate of reaction j

The subscript s stands for stagnant solution.

The model showed that increasing temperature, increasing proportion of fine pyrite grains, and higher pyrite head grades were the rate-limiting steps to shift from particle kinetics to oxygen gas–liquid mass transfer. Competition for oxygen between sulfur- and iron-oxidizing microorganisms lowered potentials and retarded pyrite oxidation.

De Windta and Devillersb (2010) used a reactive transport model to assess biodegradation of cement-based materials for a long-term exposure. Using HYTEC they modeled a bioleaching test (with Aspergillus niger fungi) applied to ordinary Portland cement pastes over 15 months. Their calculations indicated that the biogenic organic acids (acetic, butyric, lactic and oxalic) strongly accelerated hydrate dissolution by acidic hydrolysis. It was reported that the deepest degradation front corresponded to portlandite dissolution and decalcification of calcium silicate hydrates. A complex pattern of sulfate phases dissolution and precipitation took place in an intermediate zone. The outermost degraded zone consisted of alumina and silica gels. The modeling accurateness of calcium leaching, pH increase and degradation thickness was consistently enhanced

while considering increased diffusivity in the degraded zones. Precipitation of calcium oxalate was predicted by the model but was hindered in the bioleaching reactor.

In summary, review of literature indicates that available models mainly consider diffusion of heavy metals from a solid matrix to the surface and dissolution from the surface to surrounding medium via simple mass transfer derived by concentration gradient between the surface (higher concentration) and the medium (lower concentration). Furthermore, research has shown that the presence of microbial species on the surface of the solid object is key to the removal of solidified/stabilized heavy metals (Idachaba, 2004; Meech and Curtis, 2006). While a number of mathematical models have been developed to explain bioleaching phenomena of heavy metal from contaminated cementitious waste forms (Löser et al., 2005; Saddawi et al., 2005; Hall, 2006; Xu and Ting, 2009; Olivera-Nappa et al., 2010; De Windta and Devillersb, 2010), none have addressed the scenario where Michaelis-Menten reaction kinetics is applied at the surface of cementitious solid body encapsulating heavy metals. In this study we have modelled diffusion of heavy metals from encapsulated solid matrices to the surface and their biological removal from the surface to the surronding environmnet via Michaelis-Menten kinetics.

CHAPTER 3

PROBLEM STATEMENT

Solidification/stabilization processes have been used to immobilize heavy toxic metals in contaminated wastes for decades. These processes are designed to protect the environment from harmful impacts of disposed hazardous wastes. Cement based solidification/stabilization of wastes containing heavy metals has been widely practiced. The stability of the captured metals in cementitious forms has been investigated under different physical, chemical and biological conditions. Experimental research has shown that under certain acidic conditions produced by microbial activities, metals leach from cement based encapsulations. These studies demonstrated that in the presence of microbial species such as Thiobacillus thiooxidans, metals did leach out and as a result, not only metals were exposed to the environment, but strength of the cement was decreased.

While a number of mathematical models have been developed to explain bioleaching phenomena of metals from contaminated cementitious waste forms, none have addressed the scenario where Michaelis-Menten reaction kinetics is applied at the surface of solid body encapsulating heavy metals. It is the objective of this study to develop a mathematical model that combines fundamentals of diffusion in solids and Michaelis-Menten kinetics of reactions in the biofilm region formed on the solid surface, to describe the leaching of metals from solidified wastes. This model should provide a correlation for bioleaching that can be used to predict viability of a process under

conditions beyond the range of available data and help with strategizing predictive measures and developing better remediation practices.

The model was developed for diffusion of metals out of a solid with cylindrical geometry. The primary mechanism controlling the bioleaching process on the surface of the sample would be Michaelis-Menten type kinetics, which is a special case of Langmuir-Hinshelwood model. The primary species concentration profiles will be derived analytically by solving the partial differential equations using boundary perturbation technique to linearize the equations and Laplace transform to solve the partial differential equation utilizing the initial and boundary values. The resulting concentration profiles produced by the analytical and numerical solutions of the model are then compared with the available experimental data in literature.

CHAPTER 4

MODEL FORMULATION

In this chapter the theoretical background for the proposed model is briefly explained. The primary objective is to develop a mathematical model that adequately describes the bioleaching of heavy metals from encapsulated cylindrical shape concrete. The boundary condition of proposed model is nonlinear. The mathematical model is solved both analytically and numerically. Analytical solution follows linearization of the nonlinear equations which leads to an infinite series of differential equations that can be solved using Laplace transform. Details of proposed mathematical approach and solutions are presented in appendices A and B, respectively. A program written in MATLAB provided numerical solution of the model.

4.1 Diffusion in Solids

4.1.1 General Background

Diffusion is defined as the process by which atoms and/or molecules in a matter is transported from one part of a system to another as a result of random molecular motions (Crank, 1975 ; Glicksman, 2000; Mehrer, 2007). The driving force for this process at a given temperature and pressure is concentration difference between the two parts within the system**.** Fick's first law of diffusion for any binary solid, liquid, or gas solution defines the molecular mass flux J_A (mass flow rate per unit area for species A) as:

$$\overrightarrow{J_A} = -\rho D_{AB} \nabla \omega_A \tag{4.1}$$

where ρ is density, D_{AB} is diffusivity, and ω_A is mass fraction of species A, respectively. For a binary system with no velocity, constant density, and no chemical reaction, Fick's second law of diffusion is expressed as (Sherwood et al., 1975; Treybal, 1980):

$$\frac{\partial C_A}{\partial t} = D_{AB}\nabla^2 C_A \tag{4.2}$$

Following Bird et al. (2002) the equation of continuity for species A in terms of ω_A for constant ρ *and* D_{AB} in cylindrical coordinates is:

$$\rho\left(\frac{\partial \omega_A}{\partial t} + v_r\frac{\partial \omega_A}{\partial r} + \frac{v_\theta}{r}\frac{\partial \omega_A}{\partial \theta} + v_z\frac{\partial \omega_A}{\partial z}\right) = \rho D_{AB}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial \omega_A}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2 \omega_A}{\partial \theta^2} + \frac{\partial^2 \omega_A}{\partial z^2}\right] + r_A \tag{4.3}$$

where ω_A is the mass fraction of species A (encapsulated metal in this model), ρ *and* D_{AB} are the mass density and diffusion coefficient respectively.

By making the following observations:

- The diffusion process is occurring in a solid which means velocity terms are zero.
- There is a chemical reaction indicated in this process but that occurs at the interface between the waste form and its environment, therefore no generation or consumption of species A ($r_A \equiv 0$) occurs within the solid phase.

Equation (4.3) can be reduced to

$$\rho\left(\frac{\partial \omega_A}{\partial t}\right) = \rho D_{AB}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial \omega_A}{\partial r}\right) + + \frac{1}{r^2}\frac{\partial^2 \omega_A}{\partial \theta^2} + \frac{\partial^2 \omega_A}{\partial z^2}\right] \tag{4.4}$$

- Assuming a long cylinder, we anticipate that the diffusion contribution in the z-direction will be much less than the diffusion contribution in the r-direction, that is: $D_{AB}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial \omega_A}{\partial r}\right) >> D_{AB}\frac{\partial^2 \omega_A}{\partial z^2}$.

- Uniform distribution throughout the cylinder suggests that: $\frac{\partial \omega_A}{\partial \theta} \approx 0$.

Therefore, the equation of continuity for species A in this system reduces to:

$$\rho\left(\frac{\partial \omega_A}{\partial t}\right) = \rho D_{AB}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial \omega_A}{\partial r}\right)\right] \tag{4.5}$$

Finally if ρ is moved inside the derivatives and divide each term by the molecular weight of species A and observe that:

$$\frac{\rho \omega_A}{M_A} = \frac{\rho_A}{M_A} = C_A \tag{4.6}$$

Where C_A is the concentration of species A which results in:

$$\frac{\partial C_A}{\partial t} = D_{AB}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_A}{\partial r}\right) \tag{4.7}$$

where:

t = time

r = cylindrical coordinates

D_{AB} = diffusion coefficient

Considering initial condition:

$$C(r,0)=C_0 \tag{4.8}$$

which states that the initial value is fixed. The boundary conditions are given as:

$$C(0,t) = \text{finite} \quad \text{or} \quad \frac{\partial C}{\partial r} = 0 \qquad \text{at} \qquad r = 0 \text{ for all t} \tag{4.9}$$

$$-D_{AB}\frac{\partial C}{\partial r} \cong \frac{k_1 C}{1 + k_2 C} \qquad \text{at} \qquad r = R \tag{4.10}$$

It is expected the targeted species to be well distributed within the encapsulated cylinder and to be a finite amount at the center. However, at the surface we anticipate the Michaelis-Menten type kinetics to account for the transfer of species from the cylinder to the surroundings as represented by Equation (4.10). Equation (4.10) dictates units of k_1 and k_2 to be (cm/sec) and (cm^3/g), respectively.

4.1.2 Surface Kinetics

Equation (4.10) demonstrates the typical bio-reaction kinetics of species on the surface of a cylindrical solid covered with microorganisms (in this case Thiobacillus-thiooxidan). The reaction steps can be written as (Fogler, 2006):

$$\text{Tt} + \text{S} \xrightarrow{k_1} \text{Tt.S} \tag{i}$$

$$\text{Tt.S} \xrightarrow{k_2} \text{Tt} + \text{S} \tag{ii}$$

$$\text{Tt.S} + \text{W} \xrightarrow{k_3} \text{P} + \text{Tt} \tag{iii}$$

Letting Tt, S, Tt.S, W, and P represent the microorganism, substrate, microorganism-substrate complex, water and product of bio-reaction, respectively, one can apply pseudo steady state hypothesis (PSSH) to these reactions (Fogler, 2006) and show that the rate of consumption of substrate, or formation of products, is given by the Michaelis-Menten kinetics formulated as:

$$r_P = -r_S = \frac{V_{max} C_S}{K_M + C_S} \tag{4.11}$$

Equation (4.11) is an established rate equation for biological reaction systems (Missen et al., 1999, Tzafriri, 2003; Norton et al., 2004; Fogler, 2006); V_{max} and K_M are Michaelis-Menten constants. Equation (4.11) can be modified to the more convenient form:

$$r = \frac{k_1 C}{1 + k_2 C} \tag{4.12}$$

where k_1 and k_2 represent experimentally derivable constants.

The boundary condition given in Equation (4.10) assumes a uniform diffusion of heavy metals to the surface of a long, cylinder of radius R and continuous disappearance of them at the surface via the kinetics represented in Equation (4.12).

4.2 Mathematical Approach

General equation for diffusion in a long solid cylinder is given by Equation (4.13) (Crank, 1975; Bird et al., 2002):

$$\frac{\partial C_A}{\partial t} = D_{AB}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_A}{\partial r}\right) = D_{AB}\left(\frac{\partial^2 C_A}{\partial r^2}+\frac{1}{r}\frac{\partial C_A}{\partial r}\right) \tag{4.13}$$

In our model, the following initial and boundary conditions apply:

$$C_A(r,0) = C_{A0} \tag{4.14}$$

$$C_A(0,t) \ \ is \ \ finite \tag{4.15}$$

$$-D_{AB}\frac{\partial C_A}{\partial r} \cong \frac{k_1 C_A}{1+k_2 C_A} \quad (\text{mol/cm}^2\text{s}) \qquad at \ r = R \tag{4.16}$$

4.2.1 Non-dimensionalizing

Dimensionless parameters given in Equations (4.17) to (4.19) can be used to change Equations (4.13) to (4.16) into dimensionless form.

$$\Psi(\xi,\tau) = \frac{C_A}{C_{A0}} \tag{4.17}$$

$$\xi = \frac{r}{R} \tag{4.18}$$

$$\tau = \frac{D_{AB}\,t}{R^2} \tag{4.19}$$

Substituting into equations (4.13) – (4.16) results in equations (4.20) – (4.23):

$$\frac{\partial \Psi}{\partial \tau} = \frac{\partial^2 \Psi}{\partial \xi^2} + \frac{1}{\xi}\frac{\partial \Psi}{\partial \xi} \tag{4.20}$$

$$\Psi(\xi,0) = 1 \tag{4.21}$$

$$\Psi(0,\tau) \text{ is finite} \tag{4.22}$$

$$-D_{AB}\, C_{A_0}\, \frac{\partial \psi}{\partial \xi} = \frac{k_1 C_{A_0} \psi}{1 + k_2 C_{A_0} \psi} \qquad at \qquad \xi = 1 \tag{4.23}$$

Rearranging Equation (4.23):

$$-\frac{\partial \psi}{\partial \xi} = \frac{R}{D_{AB} C_{A_0}} \left[\frac{k_1 C_{A_0} \psi}{1 + k_2 C_{A_0} \psi} \right] = \frac{R}{D_{AB} C_{A_0}} \left[\frac{k_1 C_{A_0} \psi}{1 + k_2 C_{A_0} \psi} \right] = \frac{R}{D_{AB} C_{A_0}} \left[\frac{\frac{k_1 C_{A_0} \psi}{k_2 C_{A_0} \psi}}{\frac{1}{k_2 C_{A_0} \psi} + 1} \right]$$

$$= \frac{R}{D_{AB} C_{A_0}} \left[\frac{\frac{k_1}{k_2}}{1 + \frac{1}{k_2 C_{A_0} \psi}} \right] = \frac{\frac{k_1}{k_2} R}{D_{AB} C_{A_0}} \left[\frac{1}{\frac{1}{k_2 C_{A_0} \psi} + 1} \right] \tag{4.24}$$

Substituting $k_0 = \frac{k_1 / k_2}{C_{A_0}}$ changes Equation (4.24) to:

$$-\frac{\partial \psi}{\partial \xi} = \frac{k_0 R}{D_{AB}} \left[\frac{1}{1 + \frac{1}{k_2 C_{A_0} \psi}} \right] \tag{4.25}$$

Equation (4.25) can be written as:

$$-\frac{\partial \psi}{\partial \xi} = w \left[1 + \frac{1}{k_2 C_{A_0} \psi} \right]^{-1} \tag{4.26}$$

Where:

$$w = \frac{k_0 R}{D_{AB}} \tag{4.27}$$

Using Taylor series expansion, the rational fraction in Equation (4.26) can be expanded as:

$$-\frac{\partial \psi}{\partial \xi} = w\left[1 - \left[\frac{1}{k_2 C_{A_0} \psi}\right]^{-1} + \left[\frac{1}{k_2 C_{A_0} \psi}\right]^{-2} - \left[\frac{1}{k_2 C_{A_0} \psi}\right]^{-3} + \ldots \right] \tag{4.28}$$

Or:

$$-\frac{\partial \psi}{\partial \xi} = w\left[1 - k_2 C_{A_0} \psi + \left(k_2 C_{A_0} \psi\right)^2 - \ldots\right] = w\left[1 - \varepsilon\psi + \varepsilon^2 \psi^2 \ldots\right] \tag{4.29}$$

Where: $\varepsilon = k_2 C_{A_0}$ and the heterogeneous reaction rate expression can be restated in the following form:

$$Rxn\ rate = w\left[1 - \varepsilon\Psi + \varepsilon^2 \Psi^2 - \ldots\right] \tag{4.30}$$

Series converges if $|\varepsilon|$ <1 or $\left|k_2 C_{A_0}\right| < 1$.

In Equation (4.27) w is Damköhler number (Fogler, 2005; Bird, Stewart and Lightfoot, 2002).

The motivation for expanding Equation (4.16) or Equation (4.23) in the form of a converging series, Equation (4.29), comes from the observation that the quantity $1/(1+x)$ is a rational function and expandable in a converging series form within an appropriate region (Loney, 1996-a; Loney, 1996-b; Loney and Huang, 1993) where the denominator is non-zero for real physical systems. Also it is important to note that the problem described by Equations (4.13)–(4.16) would be linear except for Equation (4.16). Therefore a boundary perturbation around the condition at the surface of the cylinder is appropriate strategy to linearize the problem.

In order to linearize this problem, we start by restating the dimensionless concentration profile as:

$$\Psi = \Psi_0 + \varepsilon\Psi_1 + \varepsilon^2 \Psi_2 + \ldots \tag{4.31}$$

Substituting Equation (4.31) in Equations (4.20) and (4.21) results in:

$$\frac{\partial \Psi_0}{\partial \tau}+\varepsilon\frac{\partial \Psi_1}{\partial \tau}+\varepsilon^2\frac{\partial \Psi_2}{\partial \tau}+\ldots=\frac{\partial^2 \Psi_0}{\partial \xi^2}+\varepsilon\frac{\partial^2 \Psi_1}{\partial \xi^2}+\varepsilon^2\frac{\partial^2 \Psi_2}{\partial \xi^2}+\varepsilon^3\frac{\partial^2 \Psi_3}{\partial \xi^2}+\ldots + \frac{1}{\xi}\left[\frac{\partial \Psi_0}{\partial \xi}+\varepsilon\frac{\partial \Psi_1}{\partial \xi}+\varepsilon^2\frac{\partial \Psi_2}{\partial \xi}+\ldots\right] \tag{4.32}$$

where:

$$\Psi_0+\varepsilon\Psi_1+\varepsilon^2\Psi_2+\varepsilon^3\Psi_3+\ldots=1 \qquad at \quad \tau=0 \tag{4.33}$$

Similarly, the conditions given by Equations (4.22) and (4.29) become:

$$\Psi \text{ is finite } \Rightarrow \Psi_i \quad is \quad finite; \qquad i=0,1,2,\ldots \quad at \quad \xi=0 \tag{4.34}$$

and:

$$-\frac{\partial}{\partial \xi}\left[\Psi_0+\varepsilon\Psi_1+\varepsilon^2\Psi_2+\varepsilon^3\Psi_3+\cdots\right]= w\left[\begin{array}{c}1-\varepsilon(\Psi_0+\varepsilon\Psi_1+\cdots)+\varepsilon^2(\Psi_0+\varepsilon\Psi_1+\cdots)^2 \\ -\varepsilon^3(\Psi_0+\varepsilon\Psi_1+\cdots)^3+\cdots\end{array}\right], \quad at \quad \xi=1 \tag{4.35}$$

Equating powers of ε results in a series of linear problems as follows:

ε^0 :

$$\left\{\begin{array}{l}\dfrac{\partial \Psi_0}{\partial \tau}=\dfrac{\partial^2 \Psi_0}{\partial \xi^2}+\dfrac{1}{\xi}\dfrac{\partial \Psi_0}{\partial \xi} \\ \Psi_0=1 \quad at \quad \tau=0 \\ \Psi_0 \quad is \quad finite \quad at \quad \xi=0 \\ -\dfrac{\partial \Psi_0}{\partial \xi}=w \quad at \quad \xi=1\end{array}\right\} (I)$$

ε^1 :

$$\left\{\begin{array}{l} \dfrac{\partial \Psi_1}{\partial \tau} = \dfrac{\partial^2 \Psi_1}{\partial \xi^2} + \dfrac{1}{\xi}\dfrac{\partial \Psi_1}{\partial \xi} \\ \Psi_1 = 0 \quad at \;\; \tau = 0 \\ \Psi_1 \;\; is \;\; finite \;\; at \;\; \xi = 0 \\ \dfrac{\partial \Psi_1}{\partial \xi} = w\Psi_0 \;\; at \;\; \xi = 1 \end{array}\right\} \; (II)$$

etc.

4.2.2 Solution

Problems (I) and (II) can be solved by method of Laplace Transform as shown in Appendix (A) and Appendix (B). The solution for the first estimate, ε^0, is:

$$\boxed{\Psi_0(\xi,\tau) = 1 + \frac{w}{2}\left(\frac{1}{2} - \xi^2\right) - 2w\tau + \sum_{n=1}^{\infty} \frac{2wJ_0(\lambda_n \xi)}{{\lambda_n}^2 J_0(\lambda_n)} e^{-{\lambda_n}^2 \tau}} \tag{4.36}$$

and the solution for the second estimate, ε^1, is:

$$\begin{aligned} &\Psi_1(\xi,\tau) = \frac{w(4-w)}{2}\left[\left(\frac{1}{4.2} - \frac{\xi^2}{2^2}\right) - \tau\right] + \sum_{n=1}^{\infty} \frac{w(4-w)}{2} \frac{J_0(\lambda_n \xi)}{{\lambda_n}^2 J_0(\lambda_n)} e^{-{\lambda_n}^2 \tau} - \\ &w^2\left[\frac{1}{4^2.3} - \frac{1}{4}\left(\frac{1}{4} - \frac{\xi^2}{2}\right) - \frac{\xi^4}{4^2} + \left(\frac{1}{2} - \xi^2\right)\tau - 2\tau^2\right] + 4w^2 \sum_{n=1}^{\infty} \frac{J_0(\lambda_n \xi)}{{\lambda_n}^4 J_0(\lambda_n)} e^{-{\lambda_n}^2 \tau} \\ &+2w^2 \frac{{\lambda_2}^4 \ldots {\lambda_n}^4 + {\lambda_1}^4 {\lambda_3}^4 \ldots {\lambda_n}^4 + \ldots + {\lambda_1}^4 \ldots {\lambda_{n-1}}^4}{{\lambda_1}^4 {\lambda_2}^4 \ldots {\lambda_n}^4} + \\ &\sum_{i=1}^{n} \left\{ \frac{2w^2}{{\lambda_1}^2 {\lambda_2}^2 \ldots {\lambda_i}^2 \ldots {\lambda_n}^2} \left[\left(K_{1i} \frac{-\xi}{2{\lambda_i}^2} J_1(\lambda_i \xi) + (K_{2i} - K_{3i}) J_0(\lambda_i \xi) \right) + \tau K_{1i} J_0(\lambda_i \xi) \right] e^{-{\lambda_i}^2 \tau} \right\} \end{aligned} \tag{4.37}$$

For this work we decide to use the first two estimates on Ψ_0 and Ψ_1 which is:

$$\Psi = \Psi_0 + \varepsilon\Psi_1 \tag{4.38}$$

$$\Psi(\xi,\tau) = \Psi_0(\xi,\tau) + \varepsilon\Psi_1(\xi,\tau) = 1 + \frac{w}{2}\left(\frac{1}{2} - \xi^2\right) - 2w\tau + \sum_{n=1}^{\infty} \frac{2wJ_0(\lambda_n\xi)}{{\lambda_n}^2 J_0(\lambda_n)} e^{-{\lambda_n}^2\tau} +$$
$$\varepsilon\left[\begin{array}{l} \dfrac{w(4-w)}{2}\left[\left(\dfrac{1}{4.2} - \dfrac{\xi^2}{2^2}\right) - \tau\right] + \sum_{n=1}^{\infty} \dfrac{w(4-w)}{2} \dfrac{J_0(\lambda_n\xi)}{{\lambda_n}^2 J_0(\lambda_n)} e^{-{\lambda_n}^2\tau} - \\ w^2\left[\dfrac{1}{4^2.3} - \dfrac{1}{4}\left(\dfrac{1}{4} - \dfrac{\xi^2}{2}\right) - \dfrac{\xi^4}{4^2} + \left(\dfrac{1}{2} - \xi^2\right)\tau - 2\tau^2\right] + 4w^2 \sum_{n=1}^{\infty} \dfrac{J_0(\lambda_n\xi)}{{\lambda_n}^4 J_0(\lambda_n)} e^{-{\lambda_n}^2\tau} \\ +2w^2 \dfrac{{\lambda_2}^4 \ldots {\lambda_n}^4 + {\lambda_1}^4 {\lambda_3}^4 \ldots {\lambda_n}^4 + \ldots + {\lambda_1}^4 \ldots {\lambda_{n-1}}^4}{{\lambda_1}^4 {\lambda_2}^4 \ldots {\lambda_n}^4} + \\ \sum_{i=1}^{n}\left\{\dfrac{2w^2}{{\lambda_1}^2 {\lambda_2}^2 \ldots {\lambda_i}^2 \ldots {\lambda_n}^2}\left[\begin{array}{l}\left(K_{1i}\dfrac{-\xi}{2{\lambda_i}^2} J_1(\lambda_i\xi) + (K_{2i} - K_{3i}) J_0(\lambda_i\xi)\right) + \\ \tau K_{1i} J_0(\lambda_i\xi)\end{array}\right] e^{-{\lambda_i}^2\tau}\right\} \end{array}\right] \tag{4.39}$$

Where:

$$J_1(i\sqrt{s}) = 0 \Rightarrow\ i\sqrt{s} = \lambda_i \Rightarrow\ \{\lambda_1 = 3.8317, \lambda_2 = 7.0156, \lambda_3 = 10.1735 \ldots \lambda_n\} \tag{4.40}$$

Substituting for dimensionless parameters in Ψ_0 and Ψ_1 terms and solving for $C_A(r,t)$:

$$
\begin{aligned}
&C_A(r,t) = C_{A_0}(r,0) \\
&\left\{ 1 + \frac{Rk_0}{2D_{AB}}\left(\frac{1}{2} - \left(\frac{r}{R}\right)^2\right) - \frac{2k_0}{R}t + \sum_{n=1}^{\infty} \frac{2Rk_0 J_0(\lambda_n \frac{r}{R})}{D_{AB}{\lambda_n}^2 J_0(\lambda_n)} e^{-{\lambda_n}^2 \frac{D_{AB}t}{R^2}} + \right. \\
&\left[\frac{Rk_0\left(4D_{AB} - Rk_0\right)}{2\left(D_{AB}\right)^2}\left[\left(\frac{1}{4.2} - \frac{r^2}{2^2R^2}\right) - \frac{D_{AB}}{R^2}t\right] + \sum_{n=1}^{\infty} \frac{Rk_0\left(4D_{AB} - Rk_0\right)}{2\left(D_{AB}\right)^2} \frac{J_0(\lambda_n \frac{r}{R})}{{\lambda_n}^2 J_0(\lambda_n)} e^{-{\lambda_n}^2 \frac{D_{AB}t}{R^2}} - \right. \\
&\left(\frac{Rk_0}{D_{AB}}\right)^2\left[\frac{1}{4^2.3} - \frac{1}{4}\left(\frac{1}{4} - \frac{r^2}{2R^2}\right) - \frac{r^4}{4^2R^4} + \left(\frac{1}{2} - \left(\frac{r}{R}\right)^2\right)\frac{D_{AB}}{R^2}t - 2\left(\frac{D_{AB}}{R^2}t\right)^2\right] + 4\left(\frac{Rk_0}{D_{AB}}\right)^2 \\
&\varepsilon \left. \left. \sum_{n=1}^{\infty} \frac{J_0(\lambda_n \frac{r}{R})}{{\lambda_n}^4 J_0(\lambda_n)} e^{-{\lambda_n}^2 \frac{D_{AB}}{R^2}t} + 2\left(\frac{Rk_0}{D_{AB}}\right)^2 \frac{{\lambda_2}^4 \ldots {\lambda_n}^4 + {\lambda_1}^4 {\lambda_3}^4 \ldots {\lambda_n}^4 + \ldots + {\lambda_1}^4 \ldots {\lambda_{n-1}}^4}{{\lambda_1}^4 {\lambda_2}^4 \ldots {\lambda_n}^4} + \right. \right. \\
&\left. \left. \sum_{i=1}^{n} \left\{ \frac{2\left(\frac{Rk_0}{D_{AB}}\right)^2}{{\lambda_1}^2 {\lambda_2}^2 \ldots {\lambda_i}^2 \ldots {\lambda_n}^2} \left[\left(K_{1i} \frac{-\left(\frac{r}{R}\right)}{2{\lambda_i}^2} J_1(\lambda_i \frac{r}{R}) + (K_{2i} - K_{3i}) J_0(\lambda_i \frac{r}{R}) \right) + \frac{D_{AB}}{R^2} t\, K_{1i} J_0(\lambda_i \frac{r}{R}) \right] e^{-{\lambda_i}^2 \frac{D_{AB}}{R^2}t} \right\} \right] \right\}
\end{aligned}
\tag{4.41}
$$

Subject to:

$$
J_1(\lambda_i) = 0, \quad \lambda_i \Rightarrow \left\{\lambda_1 = 3.8317, \lambda_2 = 7.0156, \lambda_3 = 10.1735 \ldots \lambda_n\right\} \tag{4.42}
$$

CHAPTER 5

TESTING THE MODEL

In this chapter, model's results are compared to reported data in literature (Idachaba et al., 2001; Idachaba et al., 2004). Concentration profile generated by the model using Equation (4.41) and experimental data from literature are graphed in Sections 5.1 and 5.2 for cobalt/calcium and chromium/calcium, respectively. The model was numerically solved using experimental values reported by Idachaba et al. (2001). The results for this approach are presented in Section 5.3 for cobalt/calcium.

In calculating the dimensionless parameter, $w = Rk_0 / D_{AB}$, values used for k_0, specific constant (cm/sec), and D_{AB}, effective diffusivity (cm^2/sec), are within the range of values given in literature (Löser et al., 2005); ε is chosen between zero and one to improve model prediction of the reported experimental data.

Reported values for specific constant k_o, range from 0.23 – 0.48 μm/day (Löser et al., 2005) or 2.66E-10 – 5.55E-10 cm/sec. Values reported for effective diffusivity vary from 1E-5 cm^2/s, for very mobile, to 1E-15 cm^2/s, for immobile species (Bishop, 1986). In this study values predicted by the model for metal leachates from solidified/stabilized waste forms when exposed to microbially induced degradation (MID) in presence of Thiobacillus thiooxidans, are compared to those reported by Idachaba et al. (2001, 2004).

5.1 Leaching of Cobalt – Concentration Profile

5.1.1 Material and Methods Used for Testing Stability of Cylindrical Cementitious Cobalt Containing Samples

Idachaba et al. (2001) have reported on the stability of cement based solidified waste containing cobalt chloride when exposed to a microbially induced degradation environment, Thiobacillus thiooxidans bacteria in particular. They studied two combinations of Portland type 1cement and cobalt chloride mixtures:

1. 21% cobalt chloride/79% cement with cobalt chloride:water:cement ratios of 1:2.76:3.76.
2. 49% cobalt chloride/51% cement with cobalt chloride:water:cement ratios of 1.86:1:1.91.

Mixtures were solidified in 5 ml plastic vials and then shaped in cylindrical forms with dimensions of 2.0 cm height and 1.5 cm in diameter.

Using the approach subscribed by Nuclear Regulatory Commission (NRC), experimental waste samples were immersed in Thiobucillus thiooxidans broth and few others in a sterile growth medium as control. Thiobacillus thiooxidans broth was pumped from a continuously operated bioreactor over experimental waste samples placed in soxhlet tubes and sterile growth medium was pumped over control samples also contained in soxhlet tubes, both at flow rate of 100 ml d^{-1}. Soxhlet tubes were filled and drained at nearly 7 hour intervals. The pH of the broth was 1.7 – 1.9 and that of the growth medium about 4.0. The authors have reported on the cumulative leaching of both, cobalt and calcium.

5.1.2 Comparison of Model Predictions and Experimentally Measured Metal Concentrations in Leachates from Stability Studies of Cobalt Containing Solidified Waste Samples

The experimental data reported by Idachaba et al. (2001) as well as those predicted by the model, on the cumulative amounts of cobalt and calcium leached from cobalt chloride containing cementitious waste forms for samples of 49% cobalt chloride /51% cement mix, are tabulated in Table 5.1. Based on data provided by the report on cumulative amounts of leached cobalt (503.1 mg) and calcium (711.1 mg) that constituted 38.5% of initial cobalt and 29.3% of initial calcium, respectively, in the samples tested, the initial quantity of each metal in the samples was calculated. This amounted to 1306.75 mg cobalt and 2427 mg calcium in each sample used. Figure 5.1 shows model's prediction of declining trends for both, cobalt and calcium, due to the microbial degradation, on the surface of samples studied.

Figures 5.2 and 5.3 compare the trends of experimental values reported by Idachaba et al. (2001) and model predictions for cumulative cobalt and calcium leached from samples containing 49% cobalt chloride/51% cement, respectively. It is evident from these figures that the model predicts experimental data within the acceptable range. Table 5.3 lists the values of parameters k_o and D_{AB} used in the model to calculate amount of cobalt and calcium diffused to the sample surface at any given time. The value of ε was taken as 0.1 for both cobalt and calcium.

The model prediction for cumulative cobalt and calcium leached out of cylindrical solid samples formed with 21% cobalt chloride/79% cement mix, as well as experimental data reported by Idachaba et al. (2001) are listed in Table 5.2. Initial quantities of cobalt and calcium in the samples studied were calculated to be 4722 mg and 3182 mg, respectively. The trends of data for cobalt and calcium are shown in Figures 5.4 and 5.5.

These figures indicate a close agreement between the reported findings and the proposed model predictions.

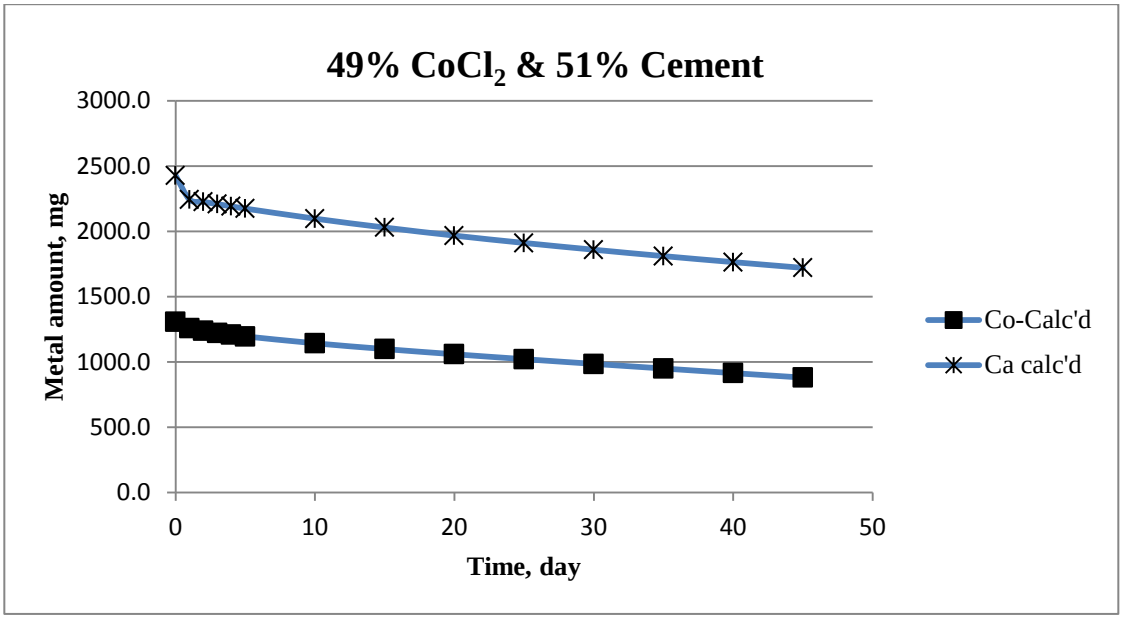


Figure 5.1 Cobalt and calcium concentrations profiles for 49% cobalt chloride and 51% cement sample (Idachaba et al., 2001) on the surface of a cementitious cylinder as predicted by the model.

Table 5.1 Values of Model Prediction and Idachaba et al. (2001) Data for Cumulative Amounts of Cobalt and Calcium Leached from Cementitious Cylindrical Solids Containing 49% $CoCl_2$ & 51% Cement

Time	mg Co on surface	mg Co Leached	mg Co leached	mg Ca on surface	mg Ca leached	mg Ca leached
Day	calc'd	Calc'd	Idachaba	calc'd	Calc'd	Idachaba
0	1306.8	0.0	0	2427.0	0.0	0
1	1257.7	49.1	10	2244.4	182.6	100
2	1238.4	68.3	30	2226.2	200.8	140
3	1222.3	84.4	40	2208.5	218.5	170
4	1208.2	98.6	50	2191.3	235.7	190
5	1195.4	111.4	60	2174.7	252.3	200
10	1142.4	164.3	120	2097.7	329.3	400
15	1098.4	208.4	150	2029.4	397.6	490
20	1058.5	248.2	250	1967.8	459.2	510
25	1020.9	285.8	290	1911.4	515.6	580
30	984.7	322.1	330	1859.2	567.8	600
35	949.2	357.6	380	1810.4	616.6	650
40	914.2	392.6	400	1764.3	662.7	690
45	879.5	427.3	450	1720.5	706.5	700

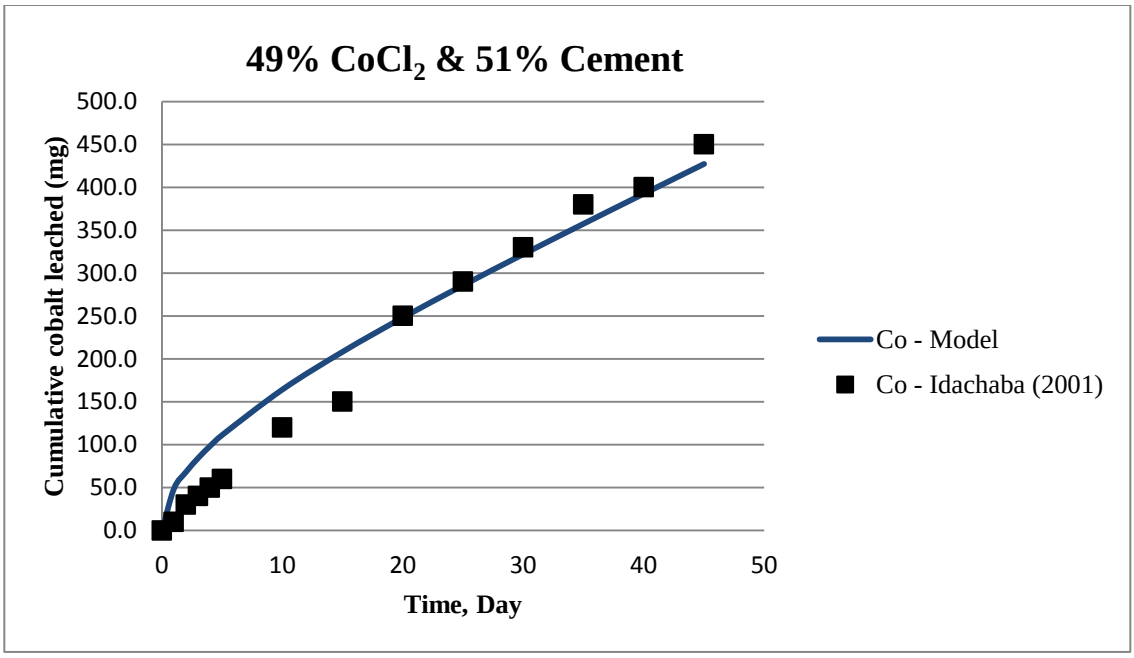


Figure 5.2 Model prediction compared to experimental results of Idachaba et al. (2001) for cumulative amount of cobalt leached from a cementitious solid cylinder exposed to MID containing 49% cobalt chloride and 51% cement.

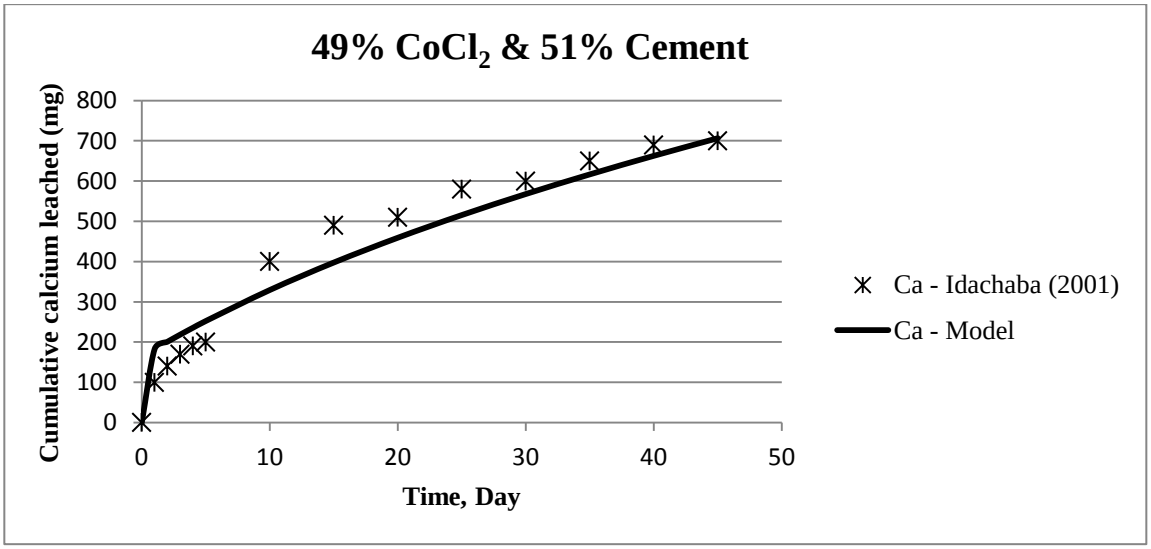


Figure 5.3 Model prediction compared to experimental results of Idachaba et al. (2001) for cumulative calcium leaching from a cementitious solid cylinder containing 49% cobalt chloride and 51% cement exposed to MID.

Table 5.2 Values of Model Prediction and Idachaba et al. (2001) Data for Cumulative Amounts of Cobalt and Calcium Leached from Cementitious Cylindrical Solids Containing 21% $CoCl_2$ & 79% Cement

Time	mg Co on surface	mg Co leached	mg Co leached	mg Ca on surface	mg Ca leached	mg Ca leached
Day	Model	Model	Idachaba	Model	Model	Idachaba
0	4722.0	0.0	0	3182.0	0.0	0
1	4703.6	18.4	8	3006.5	175.5	40
2	4701.4	20.6	13	2991.3	190.7	80
3	4699.2	22.8	17	2976.5	205.5	100
4	4697.1	24.9	23	2962.1	219.9	150
8	4689.5	32.5	45	2948.1	233.9	270
10	4686.0	36.0	50	2882.6	299.4	330
15	4678.0	44.0	52	2823.7	358.3	420
20	4671.0	51.0	57	2770.1	411.9	475
25	4664.6	57.4	62	2720.7	461.3	510
30	4658.6	63.4	68	2674.7	507.3	525
35	4653.1	68.9	70	2631.6	550.4	550
40	4647.8	74.2	77	2590.8	591.2	570
45	4642.8	79.2	80	2552.1	629.9	610

Table 5.3 Values of K_o and D_{AB} Used in Model Prediction of Metals Leached out of Cementitious Solid Waste Samples Containing Cobalt Chloride

		Metal	**K_o** (cm/sec)	**D_{AB}** (cm^2/sec)	**ε**
1	Idachaba et al. (2001) (49%$CoCl_2$/51% cement)	Cobalt	2.15E-08	5.00E-08	0.1
2		Calcium	8.00E-09	5.00E-09	0.1
3	Idachaba et al. (2001) (21%$CoCl_2$/79% cement)	Cobalt	5.00E-10	6.5E-09	0.1
4		Calcium	5.00E-09	4.25E-09	0.1

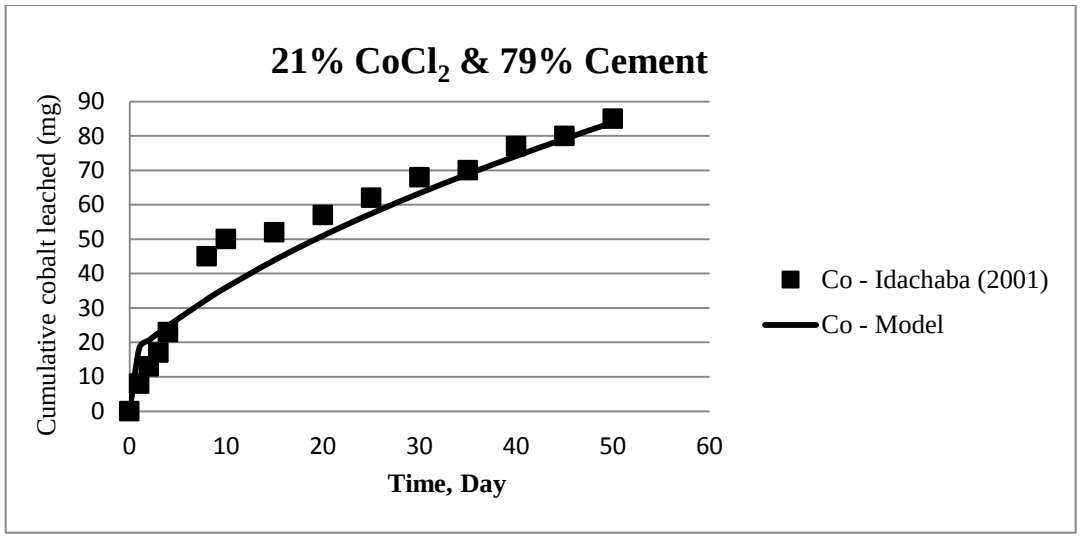


Figure 5.4 Model prediction compared to experimental results of Idachaba et al. (2001) for cumulative cobalt leached from a cementitious solid cylinder containing 21% cobalt chloride and 79% cement exposed to MID.

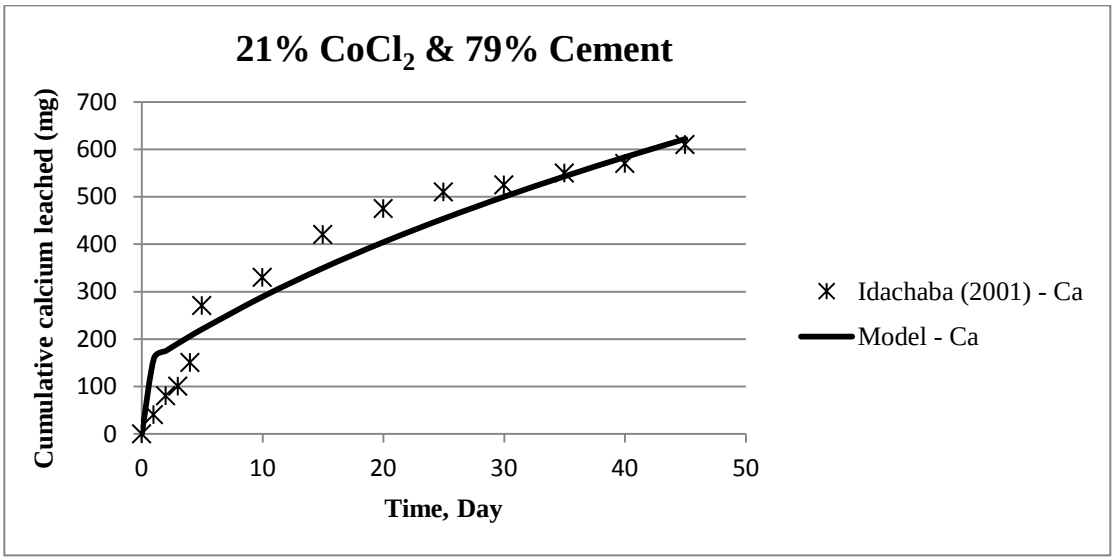


Figure 5.5 Model prediction compared to experimental results of Idachaba et al. (2001) for cumulative calcium leached from a cementitious solid cylinder containing 21% cobalt chloride and 79% cement exposed to MID.

5.2 Leaching of Chromium – Concentration Profile

5.2.1 Material and Methods Used for Testing Stability of Cylindrical Cementitious Chromium Containing Samples

The model predictions for chromium and calcium leaching from solidified waste containing chromium (III) nitrate were compared to experimental data reported by Idachaba et al. (2004).

Samples with two different compositions of chromium (III) nitrate, both prepared with 100% Portland type 1, cement (Tuskegee cement) were studied. The first group of samples contained 17% chromium (III) nitrate and 83% cement; the second group had a mix of metallic compounds including 4% chromium (III) nitrate, 4% cobalt chloride, 4% manganese (II) chloride, 4% lead nitrate, 4% nickel sulfate and 80% cement (Idachaba et al., 2004). Appropriate portions of each waste were mixed with cement and water and were allowed to set in 5 ml plastic vials. The samples were then cylindrically shaped with 2.0 cm height and 1.5 cm in diameter. Authors reported that no curing procedure was applied in production of samples tested. It should be noted that at any given time, model calculates the concentration of metal on the surface of the solid cylinder and not what has leached out. The value of metal in the leachate is calculated from the difference between surface concentrations in consecutive time intervals.

5.2.2 Comparison of Model Predictions and Experimentally Measured Metal Concentrations in Leachates from Stability Studies of Chromium Containing Solidified Waste Samples

The model predictions of chromium and calcium leached are compared to chromium and calcium leached out of solidified samples covered with biofilm in Idachaba et al. (2004) study. The pre-fabricated cylindrical shape cementitious waste samples containing chromium (III) nitrate that were tested for bioleaching by Idachaba et al. (2004), were

covered with a biofilm layer of Thiobacillus thiooxidans that was grown over the samples by a prescribed method elsewhere (Idachaba et al., 2001). Authors compared stability of these samples against similar ones without biofilm layer on them which were used as control.

Quantities of cumulative chromium and calcium leached from a solidified cylindrical chromium (III) nitrate waste calculated by the model, as well as experimental values reported by Idachaba et al. (2004) from samples subjected to microbially induced degradation (MID) are listed in Table 5.4. Values used for k_o and D_{AB} in these calculations are shown in Table 5.5.

Figure 5.6 shows the experimental results reported by Idachaba et al. (2004) for cumulative chromium leached from a solidified 17% chromium (III) nitrate subject to MID as well as the model prediction. The calculated cumulative quantities for chromium and experimental data follow similar trend.

Table 5.4 Values of Model Prediction and Idachaba et al. (2004) Experimental Data for Chromium and Calcium Leached from Cementitious Cylindrical Solid Samples Containing 17% $Cr(NO_3)_3$ and 83% Cement Covered with Biofilm

Time Day	% cummulative Cr leached, Model	% cummulative Cr leached, Idachaba et al (2004)	% cummulative Ca leached, Model	% cummulative Cr leached, Idachaba et al (2004)
0	0	0	0.00	0
1	2.23	2.8	1.31	1.3
2	2.47	2.8	2.47	1.3
3	2.70	2.8	3.59	1.3
4	2.93	3.00	4.68	2.0
5	3.14	3.2	5.74	4.5
10	4.14	3.8	10.43	10.
15	5.01	4.1	14.78	13.
20	5.80	4.9	18.70	18.
25	6.52	6	22.28	24.
30	7.18	7.2	25.58	28.0

Table 5.5 Values of K_o and D_{AB} Used in Prediction of Metals Leached out of Cementitious Solid Waste Forms

		Metal	**K_o** (cm/sec)	**D_{AB}** (cm^2/sec)	**ε**
1	Idachaba et al. (2004) (17% $Cr(NO_3)_3$)	Chromium	2.50E-09	5.5E-09	0.1
2		Calcium	1.25E-08	5.00E-09	0.1
3	Idachaba et al. (2001) (4% $Cr(NO_3)_3$)	Chromium	2.50E-09	2.00E-09	0.1
4		Calcium	8.500E-09	3.50E-09	0.01

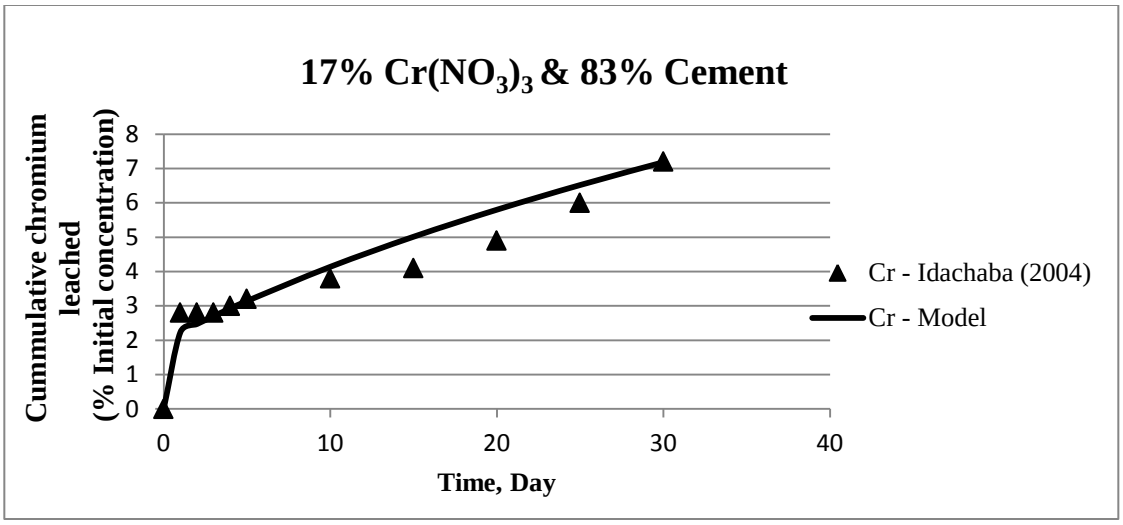


Figure 5.6 Model prediction compared to experimental results of Idachaba et al. (2004) for cumulative chromium leached from a cementitious solid cylinder containing 17% chromium (III) nitrate and 83% cement exposed to MID.

Figure 5.7 shows the model prediction and values reported by Idachaba et al. (2004) for cumulative calcium in leachate from a solidified, cementitious, cylindrical waste containing 17% chromium (III) nitrate and 83% cement. Figure 5.8 indicates a close model prediction of the experimental values reported for calcium from the samples studied.

Experimental data reported by Idachaba et al. (2004), as well as values predicted by the model, for chromium and calcium leached from cylindrical cementitious samples containing 4% chromium (III) nitrate, 80% cement, and balance of other metal compounds are tabulated in Table 5.6 and graphically presented in Figures 5.8 and 5.9. While the model falls short of close chromium leach estimation at the early exposure of samples to MID (Figure 5.8) its prediction of calcium leached from the samples is in scientifically acceptable range (Figure 5.9).

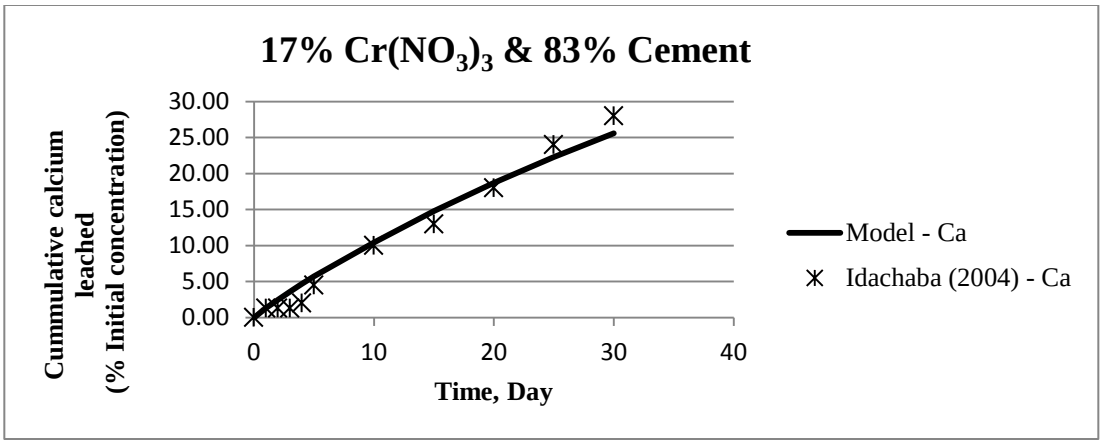


Figure 5.7 Model prediction and experimental results of Idachaba et al. (2004) for cumulative calcium leached from a cementitious solid cylinder containing 17% chromium (III) nitrate and 83% cement exposed to MID.

Table 5.6 Values of Mmodel Prediction and Idachaba et al. (2004) Experimental Data for chromium and Calcium Leached from Cementitious Cylindrical Solid Samples Containing 4% Chromium (III) Nitrate, 80% Cement and Balance of Other Metal Compounds Covered with Biofilm Layer

Time, Day	% Cummulative Cr leached-Model	% Cummulative Cr leached Idachaba (2004)	% Cummulative Ca leached - Model	% Cummulative Ca leached Idachaba (2004)
0	0.0	0	0.0	0
1	5.6	7.7	1.0	1.40
2	5.8	7.7	1.7	1.75
3	6.1	7.7	2.4	2.00
4	6.3	7.7	3.2	2.50
5	6.5	7.7	3.9	3.00
10	7.7	8	7.1	7.00
15	8.7	9	10.1	10.00
20	9.7	10	12.9	12.
25	10.7	10.5	15.5	15.
30	11.6	11	17.9	17.

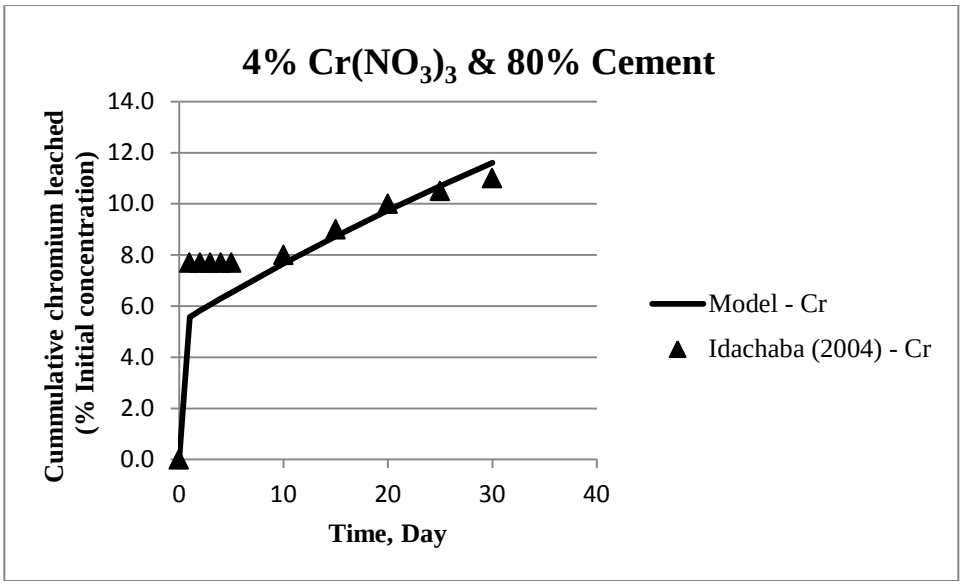
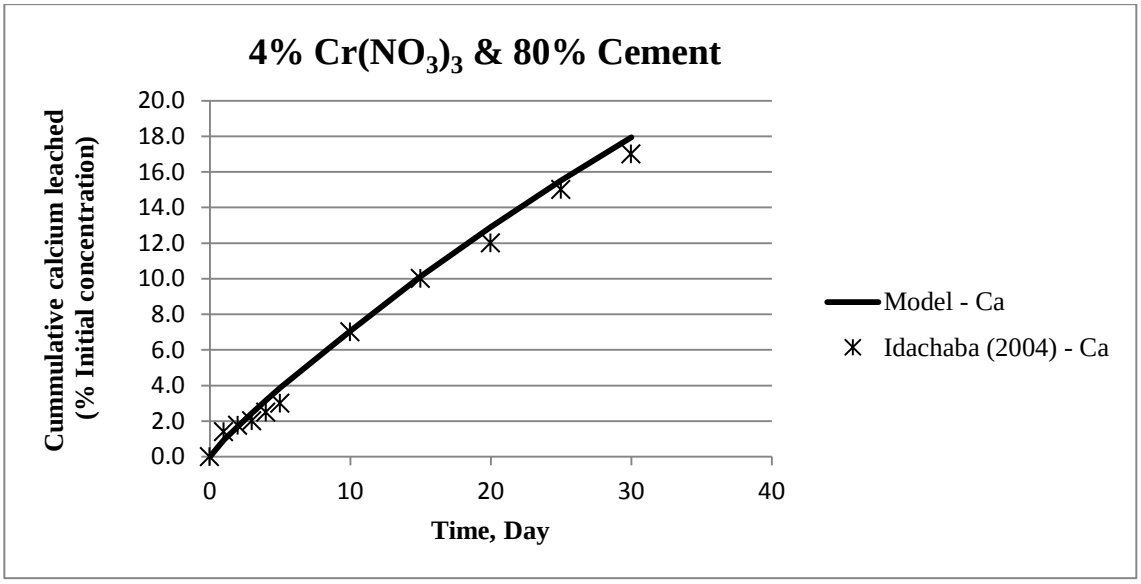


Figure 5.8 Model prediction and experimental results of Idachaba et al. (2004) for cumulative chromium leached from a cementitious solid cylinder containing 4% chromium (III) nitrate, 80% cement, and balance of other metal compounds exposed to MID.



.

Figure 5.9 Model prediction and experimental results of Idachaba et al. (2004) for cumulative calcium leached from a cementitious solid cylinder containing 4% chromium (III) nitrate, 80% cement, and balance of other metal compounds exposed to MID.

5.3 Numerical Solution

The partial differential equation with initial value and boundary conditions developed for the physical situration under study was solved numerically using MATLAB's PDEPE subroutine (Constantinides and Mostoufi, 2000). This subrouting solves differential equations having the general form of (5.1):

$$c\left(x,t,u,\frac{\partial u}{\partial x}\right)\frac{\partial u}{\partial t}=x^{-m}\frac{\partial}{\partial x}\left(x^{m}f\left(x,t,u,\frac{\partial u}{\partial x}\right)\right)+s\left(x,t,u,\frac{\partial u}{\partial x}\right) \qquad (5.1)$$

Where:

m= 0 for Cartesian, 1 for cylindrical, 2 for spherical

$u(x,t_0)=u_0(x)$ is initial condition. (5.2)

$p(x,t,u)+q(x,t)f\left(x,t,u,\frac{\partial u}{\partial x}\right)=0$ is boundary conditions (5.3)

S = source

Our model formulation developed in chapter 4 resulted in following equations:

$$\frac{\partial C_A}{\partial t}=D_{AB}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_A}{\partial r}\right) \quad \text{or} \quad \frac{\partial C_A}{\partial t}=\frac{1}{r}\frac{\partial}{\partial r}\left[r\left(D_{AB}\frac{\partial C_A}{\partial r}\right)\right] \qquad (4.7)$$

with initial condition:

$$C(r,0)=C_0 \qquad (4.8)$$

and boundary conditions:

$$C(0,t)=\text{finite} \quad \text{or} \quad \frac{\partial C}{\partial r}=0 \quad \text{at} \quad r=0 \text{ for all t} \qquad (4.9)$$

$$-D_{AB}\frac{\partial C}{\partial r}\cong\frac{k_1 C}{1+k_2 C} \quad \text{or} \quad \frac{k_1 C}{1+k_2 C}+\left(D_{AB}\frac{\partial C}{\partial r}\right)=0 \quad \text{at} \quad r=R \qquad (4.10)$$

Comparing the two formulations, the PDEPE parameters for our model will be:

$$m = 1 \tag{5.4}$$

$$c\left(x, t, u, \frac{\partial u}{\partial x}\right) = 1 \tag{5.5}$$

$$f\left(x, t, u, \frac{\partial u}{\partial x}\right) = D_{AB}\frac{\partial C_A}{\partial r} \tag{5.6}$$

$$s\left(x, t, u, \frac{\partial u}{\partial x}\right) = 0 \tag{5.7}$$

$$u\left(x, t_0\right) = C_{A0} \tag{5.8}$$

$$p_a\left(x, t, u\right) = 0 \tag{5.9}$$

$$q_a\left(x, t\right) = 0 \tag{5.10}$$

$$p_b\left(x, t, u\right) = \frac{k_1 C_A}{1 + k_2 C_A} \tag{5.11}$$

$$q_b\left(x, t\right) = 1 \tag{5.12}$$

Where pa and qa are parameters for boundry conditions at r = 0 and, pb and qb are the same at r = R.

Based on these parameters, a MATLAB program shown on the next page was developed and executed.

```
function DPC
%  DPC   Diffusion Problem in a
%  Cylinder
%  Solving PDE equation for radial
%  diffusion in a long cylinder
%  dC/dt = (1/r)(d/dr)(r(Dab(dC/dr))
%  C(r,0): C_Ao = 1306.8 (mg)
%  C(0,t) = finite OR dC(0,t)/dr = 0
%  C(R,t):
%  (1/Dab){[(k1*C/(1+k2*C))]+dC/dr}=0
%   u = C; x = r; t = t;

global Dab R
Dab=5*10^(-7);
%  Diffusivity coefficient (cm^2/sec)
R=0.75;     % cm - Radius of cylinder
tend=45;    % Days
m=1;
xmesh = linspace(0,R,200);
tspan = linspace(0,tend,10);

sol =
pdepe(m,@DPCpde,@icDPC,@bcDPC,xmesh,tspan,[]);
u = sol(:,:,1);
mesh(xmesh,tspan,u)
 xlabel('R','FontSize',12)
 ylabel('t','FontSize',12)
 zlabel('C','FontSize',12,'Rotation',0)
 figure, plot(x,u(end,:)
% ------------------------------------------------------
% Subfunctions
% ------------------------------------------------------
  function[c,f,s] = DPCpde(x,t,u,DuDx)
  global Dab
  Dab=5*10^(-7);
  c=1;
  f=Dab*DuDx;
  s=0;
% ------------------------------------------------------
% Initial Condition
% ------------------------------------------------------
   function u0 = DPCic(x)
% Initial condition at t=0
   u0=1306.8;
% ------------------------------------------------------
```

```
function[pa,qa,pb,qb]=DPCbc(xa,ua,xb,ub,t)
% Boundary conditions at r=0 and r=R
global Dab k1 k2 R
% Diffusivity coefficient (cm^2/day)
Dab=5*10^(-7);
% Rate constants
k1=0.0606;  % Rate constant (cm/day)
k2=0.0165;   % Rate constant (cm^3/mg)
R=0.75;       % cm - Radius of cylinder
pa=0;
qa=0;
pb=(k1*ub/(1+k2*ub));
qb=1;
```

Running the program for 49% cobalt chloride and 51% cement resulted in a reasonable distribution of cobalt diffusing out ot the cylindrical saple reported by Idachaba et al (2001) as shown in Figures 5.10 and 5.11. Figure 5.12 shows that the results of analytical and numerical prediction of cobalt leached from a cylindrical cementitious cobalt chloride sample compare well.

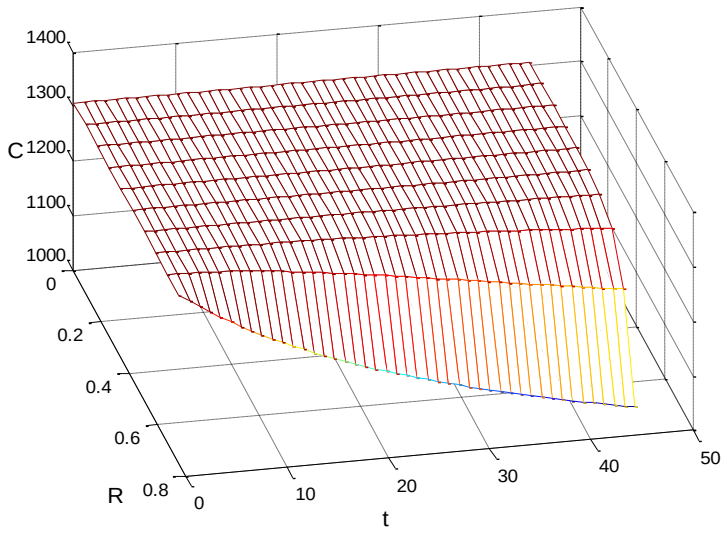


Figure 5.10 3D (C, R, t) change in cobalt concentration in a cementitious cylindrical sample covered with a layer of *Thiobacillus thiooxidans*.

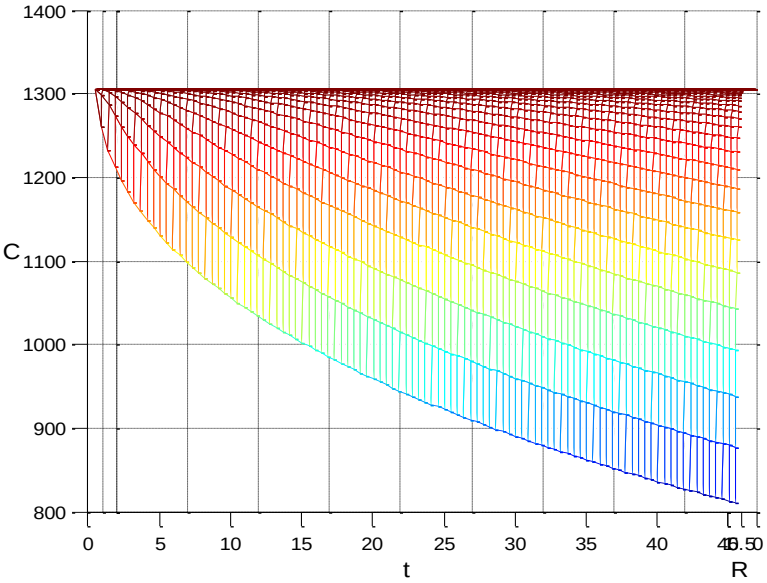


Figure 5.11 Cobalt concentration change at the surface of a cementitious cylindrical sample covered with *Thiobacillus thiooxidans*.

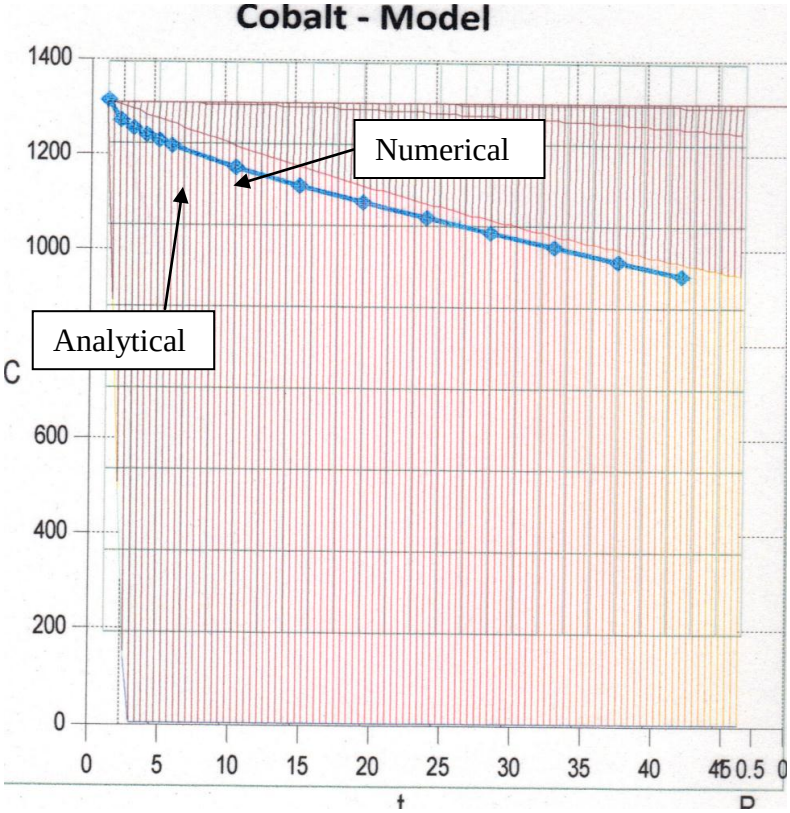


Figure 5.12 Analytical and numerical prediction of cobalt leached from a cylindrical cementitious cobalt chloride sample.

It should be noted that the specific rate constants, k_1 and k_2, used in the program were found based on experimental data provided by Idachaba et al. (2001). Starting with Michaelis-Menten rate law (Fogler, 2006):

$$-\text{rate} = -\frac{dC_A}{dt} = \frac{k_1 C_A}{1 + k_2 C_A} \tag{5.13}$$

Inversing both sides of (5.13) and rearrnging:

$$\frac{dt}{-dC_A} = \frac{1 + k_2 C_A}{k_1 C_A} = \frac{1}{k_1 C_A} + \frac{k_2}{k_1} \tag{5.14}$$

Plotting (-dt/dC) versus (1/C) provides values for (1/k1), slope of the line, and (k2/k1), the intercept. Table 5.12 lists the values used to perform this analysis.

Table 5.7 Values of Cobalt Diffused out of Cylindrical Solidified Samples Reported by Idachaba et al. (2001)

t , Day	**Idachaba mg/cc leached**	**C_A-Out**	**C_A @ Surf**	**Δt**	**ΔC**	**$\Delta t/-\Delta C_A$**	**$1/C_A$**
0	0	0.00	373.14				
5	60	17.14	356.00	5	-17.14	0.29	0.0028
10	120	34.29	338.86	5	-17.14	0.29	0.0030
15	180	51.43	321.71	5	-17.14	0.29	0.0031
20	250	71.43	301.71	5	-20.00	0.25	0.0033
25	290	82.86	290.29	5	-11.43	0.44	0.0034
30	330	94.29	278.86	5	-11.43	0.44	0.0036
35	380	108.57	264.57	5	-14.29	0.35	0.0038
40	425	121.43	251.71	5	-12.86	0.39	0.0040
45	500	142.86	230.29	5	-21.43	0.23	0.0043

These values were determined to be: $k_1 = 0.0606$ 1/day , $k_2 = 0.0165$ cm^3/mg

Using these constant and the initial concentration of cobalt in solidified cobalt samples (1306.8 mg/L) reported by Idachaba et al. (2001) the value of k_o can be calculated.

CHAPTER 6

CONCLUSIONS

A mathematical model is proposed to predict diffusion and removal of heavy metals from cementitious solidified/stabilized cylindrical forms covered with biofilm of Thiobacillus thiooxidans and/or Thiobacillus ferrooxidans within the reliability of experimental data (chapters 4-5). The model applies Fick's law to a long, cylindrical shape solid containing heavy metals with the assumption that the metal is uniformly distributed throughout the cylinder at all times. Furthermore, the model incorporated Michaelis-Menten kinetics to count for the role of biofilm formed on the surface of the cylinder by Thiobacillus microorganisms. The developed system of differential equations for the model was solved both anatically as well as numerically. To solve analytically, the dimensionless form of the differential equations for the model was linearized using perturbation technique and solved using Laplace transform.

This model assumes that the concentration difference within the solid is the main driving force for diffusion of captured metals to the surface of the solid and that the biofilm facilitates its transfer from the surface to the surrounding environment, either by consuming and releasing the metal to the environment or by dissolving it in the strong acid the microorganisms form on the surface of the solid.

In present work, a model is proposed that for the first time incorporates biofilm influence in removal of heavy metals from cementitious solidified/stabilized forms. The key variables in the model developed are specific constant, k_o, and effective diffusivity, D_e. These variables were calculated from published experimental data or

taken within the range of reported values in literature for the metals studied in this project. Given the values for k_o and D_e, the model calculates concentration of encapsulated metal at the surface of a cylindrical solid at a given time.

The predictions of model's analytical solution were compared with experimental data reported in the literature on cobalt chloride, chromium nitrate, and calcium release from encapsulated cementitious solid cylinders. For cobalt and calcium the model successfully reproduced the reported diffusion and removal data. For chromium, the trends predicted by the model and those experimentally reported were in good agreement. Furthermore, predictions of numerical solutions compared well with data available on colbalt leaching out of cement-based waste form via a predominantly biological mechanism.

CHAPTER 7

RECOMMENDATIONS

Following recommendations could further improve applicability of the proposed model to specific situations.

- The model proposed is a global model that can be applied to all types of heavy metals encapsulated in cementitious solid forms with less attention to structural formation of these metals in their solidified/stabilized forms. Relating values for specific rate constant, k_o, and effective diffusivity, D_e, for leaching of metals that a relative understanding of their chemical/physical structures are available would enhance applicability of this model to more specific situations.
- The proposed model is tested for available data on leaching of single heavy metals, namely cobalt and chromium, from encapsulated cylindrical solid. For practical purposes, it would be advantageous to test the model against mixture of heavy metals leaching out of solidified/stabilized cementitious samples.
- The model uses Michaelis-Menten kinetics to account for predominantly biological removal of metals diffused to the surface of a cylindrical solid form. The commonly reported microorganisms reported to form on such formations are Thiobacillus thiooxidans and Thiobacillus ferrooxidans. A kinetic study of the growth rate of these microorganisms could provide valuable data on metals removal from these solid surfaces to the surrounding environments.

APPENDIX A

DETAILED MATHEMATICAL SOLUTION FOR Ψ_0 THE FIRST ESTIMATE OF Ψ

Calculation of first estimate using Laplace Transform, and Residue Theorem

ε^0 :

$$\left\{\begin{array}{l} \dfrac{\partial \Psi_0}{\partial \tau} = \dfrac{\partial^2 \Psi_0}{\partial \xi^2} + \dfrac{1}{\xi}\dfrac{\partial \Psi_0}{\partial \xi} \\ \\ \Psi_0 = 1 \quad at \;\; \tau = 0 \\ \\ \Psi_0 \;\; is \;\; finite \;\; at \;\; \xi = 0 \\ \\ -\dfrac{\partial \Psi_0}{\partial \xi} = w \;\; at \;\; \xi = 1 \end{array}\right\} \; (I)$$

Let $$L\left\{\Psi_0(\xi,\tau)\right\} = u(\xi,s) \tag{A.1}$$

Then

$$s\,u(\xi,s) - 1 = \frac{d^2u}{d\xi^2} + \frac{1}{\xi}\frac{du}{d\xi} \tag{A.2}$$

subject to:

$$u(\xi,s) \; is \;\; finite \; at \;\; \xi = 0 \tag{A.3}$$

$$-\frac{du}{d\xi} = \frac{w}{s} \;\; at \;\; \xi = 1. \tag{A.4}$$

Resulting in a general solution:

$$u(\xi,s) = a_1 J_0\left(i\sqrt{s}\xi\right) + a_2 Y_0\left(i\sqrt{s}\xi\right) + \frac{1}{s} \tag{A.5}$$

It should be noted that $Y_0\left(i\sqrt{s}\xi\right)$ is unbounded as $\xi \to 0$, hence a_2 must be zero. This reduces Equation (A.5) to:

$$u(\xi, s) = a_1 J_0\left(i\sqrt{s}\xi\right) + \frac{1}{s} \tag{A.6}$$

From Equation (A.4):

$$-\frac{du}{d\xi} = \frac{w}{s} \Rightarrow a_1 = \frac{w}{s i\sqrt{s} J_1\left(i\sqrt{s}\right)} \tag{A.7}$$

Therefore Equation (A.6) can be written as:

$$u(\xi, s) = \frac{w J_0\left(i\sqrt{s}\xi\right)}{s i\sqrt{s} J_1\left(i\sqrt{s}\right)} + \frac{1}{s} \tag{A.8}$$

The inverse Laplace transform would have the following form:

$$\Psi_0(\xi, \tau) = 1 + L^{-1}\left\{\frac{w J_0\left(i\sqrt{s}\xi\right)}{s i\sqrt{s} J_1\left(i\sqrt{s}\right)}\right\} \tag{A.9}$$

To complete the solution, the ratio is first simplified and then Residue theorem (Jenson and Jeffreys, 1981; Loney, 2001) used to complete inverting Laplace transform. Rewriting Bessel functions in series format, the fraction in Equation (A.9) results in (A.10):

$$\frac{wJ_0(i\sqrt{s\xi})}{si\sqrt{s}J_1(i\sqrt{s})} = \frac{w[1+\frac{s\xi^2}{2^2}+\frac{s^2\xi^4}{2^2 4^2}+\frac{s^3\xi^6}{2^2 4^2 6^2}+...]}{-s[\frac{s}{2}+\frac{s^2}{2^2 4}+\frac{s^3}{2^2 4^2 6}+...]} = \frac{w[1+\frac{s\xi^2}{2^2}+\frac{s^2\xi^4}{2^2 4^2}+\frac{s^3\xi^6}{2^2 4^2 6^2}+...]}{-s^2[\frac{1}{2}+\frac{s}{2^2 4}+\frac{s^2}{2^2 4^2 6}+...]} \tag{A.10}$$

The fraction can be written as:

$$\frac{\left[1+\frac{s\xi^2}{2^2}+\frac{s^2\xi^4}{2^2 4^2}+\frac{s^3\xi^6}{2^2 4^2 6^2}+\ldots\right]}{-\left[\frac{1}{2}+\frac{s}{2^2 4}+\frac{s^2}{2^2 4^2 6}+\ldots\right]}=A_0+A_1 s+A_2 s^2+\ldots \qquad \text{(A.11)}$$

Or:

$$\left[1+\frac{s\xi^2}{2^2}+\frac{s^2\xi^4}{2^2 4^2}+\frac{s^3\xi^6}{2^2 4^2 6^2}+\ldots\right]=\left[-\frac{1}{2}-\frac{s}{2^2 4}-\frac{s^2}{2^2 4^2 6}-\ldots\right]$$

$$\left(A_0+A_1 s+A_2 s^2+\ldots\right)=A_0\left[-\frac{1}{2}-\frac{s}{2^2 4}-\frac{s^2}{2^2 4^2 6}-\ldots\right]+ \qquad \text{(A.12)}$$

$$A_1 s\left[-\frac{1}{2}-\frac{s}{2^2 4}-\frac{s^2}{2^2 4^2 6}-\ldots\right]+A_2 s^2\left[-\frac{1}{2}-\frac{s}{2^2 4}-\frac{s^2}{2^2 4^2 6}-\ldots\right]+\ldots$$

Equating the coefficients of both sides result:

$$-\frac{A_0}{2}=1, \qquad A_0=-2 \qquad \text{(A.13)}$$

$$-\frac{A_0}{2^2\bullet 4}-\frac{A_1}{2}=\frac{\xi^2}{2}, \qquad A_1=\frac{1}{2}\left(\frac{1}{2}-\xi^2\right) \qquad \text{(A.14)}$$

$$\frac{A_0}{2^2\bullet 4^2\bullet 6}-\frac{A_1}{2^2\bullet 4}-\frac{A_2}{2}=\frac{\xi^4}{2^2\bullet 4^2}, \qquad A_2=\left[\frac{1}{4^2 6}-\frac{\left(\frac{1}{2}-\xi^2\right)}{2^2 4}-\frac{\xi^4}{2^2 4}\right] \qquad \text{(A.15)}$$

Therefore,

$$\frac{wJ_0(i\sqrt{s}\xi)}{si\sqrt{s}J_1(i\sqrt{s})}=\frac{P(s)}{Q(s)}=\frac{w\left[-2+\frac{s}{2}\left(\frac{1}{2}-\xi^2\right)+s^2\left(\frac{1}{4^2 6}-\frac{1}{2^2 4}\left(\frac{1}{2}-\xi^2\right)-\frac{\xi^4}{2^2 4^2}\right)+\ldots\right]}{-s^2} \tag{A.16}$$

The Residue theorem (Loney, 2001) can now be applied to find the inverse Laplace transform. In general, the inverse Laplace transform of function *F(s)* can be written as:

$$f(t)=L^{-1}\left[F(s)\right]=\sum_{1}^{\infty}\rho_n(t) \tag{A.17}$$

Where $\rho_n(t)$ is called the *residue* of function *F*(*s*) at the singularities s_n. The residues of *F*(*s*) can be determined as following:

$$\rho_n(t)=\frac{P(s_n)}{Q'(s_n)}e^{s_n t} \tag{A.18}$$

where $Q'(s_n)$ is the value of $\frac{dQ}{ds}$ evaluated at the singular point of interest. Noting that:

$$\frac{P(s_n)}{Q'(s_n)}=\lim_{s\to s_n}\frac{P(s)}{\left[\frac{Q(s)-Q(s_n)}{s-s_n}\right]}=\lim_{s\to s_n}(s-s_n)\frac{P(s)}{Q(s)} \tag{A.19}$$

When s_n is a multiple pole of order m of *F*(*s*), then:

$$\rho_n(t)=e^{s_n t}\left[\beta_1+\beta_2 t+\beta_3\frac{t^2}{2!}+\ldots+\frac{\beta_m t^{m-1}}{(m-1)!}\right] \tag{A.20}$$

where

$$\beta_i = \lim_{s \to s_n} \frac{1}{(m-i)!} \frac{d^{m-i}}{ds^{m-i}} \left[(s - s_n)^m F(s) \right] \tag{A.21}$$

Applying Equation (A.20) to Equation (A.16) at singularities, when $s = 0$:

$$\rho_0(\tau) = e^{0\tau} \left[\beta_1 + \tau \beta_2 \right] \tag{A.22}$$

$$\beta_1 = \lim_{s->0} \frac{d}{ds} \left[\frac{s^2 w J_0(i\sqrt{s}\xi}{s i \sqrt{s} J_1(i\sqrt{s})} \right] =$$

$$\lim_{s->0} \frac{d}{ds} \left\{ s^2 \frac{w\left[-2 + \frac{s}{2}\left(\frac{1}{2} - \xi^2 \right) + s^2 \left(\frac{1}{4^2 6} - \frac{1}{2^2 4}\left(\frac{1}{2} - \xi^2 \right) - \frac{\xi^4}{2^2 4^2} \right) + \ldots \right]}{s^2} \right\} \tag{A.23}$$

$$= \frac{w}{2}\left(\frac{1}{2} - \xi^2 \right)$$

$$\beta_2 = \lim_{s->0} \left[\frac{s^2 w J_0(i\sqrt{s}\xi}{s i \sqrt{s} J_1(i\sqrt{s})} \right] =$$

$$\lim_{s->0} \left\{ s^2 \frac{w\left[-2 + \frac{s}{2}\left(\frac{1}{2} - \xi^2 \right) + s^2 \left(\frac{1}{4^2 6} - \frac{1}{2^2 4}\left(\frac{1}{2} - \xi^2 \right) - \frac{\xi^4}{2^2 4^2} \right) + \ldots \right]}{s^2} \right\} \tag{A.24}$$

$$= -2w$$

The Laplace inverse at $s = 0$ is:

$$\boxed{\rho_0(\tau) = e^{0\tau}\left(\beta_1 + \tau\beta_2\right) = \frac{w}{2}\left(\frac{1}{2} - \xi^2 \right) - 2w\tau} \tag{A.25}$$

For the case $s \neq 0$:

$$\frac{w J_0\left(i\sqrt{s}\xi\right)}{s i\sqrt{s} J_1\left(i\sqrt{s}\right)} = \frac{P(\xi, s)}{Q(s)} \tag{A.26}$$

$$Q(s) = s i\sqrt{s} J_1\left(i\sqrt{s}\right) = 0 \tag{A.27}$$

Hence:

$$J_1\left(i\sqrt{s}\right) = 0 \tag{A.28}$$

Substituting:

$$i\sqrt{s} = \lambda \;\Rightarrow s = -\lambda^2 \tag{A.29}$$

Therefore,

$$J_1\left(\lambda_n\right) = 0, \;\; n = 1, 2, 3, \cdots \tag{A.30}$$

Also,

$$Q(s) = s i\sqrt{s} J_1\left(i\sqrt{s}\right) \tag{A.31}$$

$$\begin{aligned} Q'(s) = & \frac{d}{ds}\left[s i\sqrt{s} J_1\left(i\sqrt{s}\right)\right] = \\ & \frac{3}{2} i\sqrt{s} J_1\left(i\sqrt{s}\right) + i s^{3/2} \frac{1}{2} s^{-1/2} \frac{d}{ds}\left[J_1\left(i\sqrt{s}\right)\right] \end{aligned} \tag{A.32}$$

And (Spiegel, 1971),

$$J_1'(x) = \frac{1}{2}\left[J_0(x) - J_2(x)\right] \tag{A.33}$$

$$J_2(x) = \frac{2}{x} J_1(x) - J_0(x) \tag{A.34}$$

$$J_1'(x) = J_0(x) - \frac{1}{x} J_1(x) \tag{A.35}$$

Therefore,

$$Q'(s) = \frac{d}{ds}\left[s i\sqrt{s} J_1\left(i\sqrt{s}\right)\right] = \frac{3}{2} i\sqrt{s} J_1\left(i\sqrt{s}\right) - \frac{s}{2}\left[J_0\left(i\sqrt{s}\right) - \frac{1}{i\sqrt{s}} J_1\left(i\sqrt{s}\right)\right] \quad (A.36)$$
$$= \frac{s}{2} J_0\left(i\sqrt{s}\right) \equiv \frac{\lambda^2}{2} J_0(\lambda)$$

Combining Equations (A.18), (A.25), and (A.36):

$$L^{-1}\left\{ \frac{w J_0\left(i\sqrt{s}\xi\right)}{s i\sqrt{s} J_1\left(i\sqrt{s}\right)}\right\} = \frac{w}{2}\left(\frac{1}{2} - \xi^2\right) - 2w\tau + \sum_{n=1}^{\infty} \frac{w J_0\left(\lambda_n \xi\right)}{\frac{\lambda_n^2}{2} J_0\left(\lambda_n\right)} e^{-\lambda_n^2 \tau} \quad (A.31)$$

And, solution for the first estimate will be:

$$\psi_0(\xi,\tau) = 1 + \frac{w}{2}\left(\frac{1}{2} - \xi^2\right) - 2w\tau + \sum_{n=1}^{\infty} \frac{w J_0(\lambda_n \xi)}{\frac{\lambda_n^{\,2}}{2} J_0(\lambda_n)} e^{-\lambda_n^{\,2}\tau} \quad (A.32)$$

APPENDIX B

DETAILED MATHEMATICAL SOLUTION FOR Ψ_1 SECOND ESTIMATE OF Ψ

Laplace transform purterbation and Residue Theorem are used to solve equation set (II).

$$\left\{\begin{array}{l} \dfrac{\partial \psi_1}{\partial \tau} = \dfrac{\partial^2 \psi_1}{\partial \xi^2} + \dfrac{1}{\xi}\dfrac{\partial \psi_1}{\partial \xi} \\ \psi_1 = 0 @ \tau = 0 \\ \psi_1 \text{ is finite at } \xi = 0 \\ \dfrac{\partial \psi_1}{\partial \xi} = w\psi_0 \ \ at \ \xi = 1 \end{array}\right\} \qquad (II)$$

Let

$$L\{\psi_1(\xi,\tau)\} = v(\xi,s) \qquad \text{(B.1)}$$

Then

$$L\left\{\frac{\partial \psi_1}{\partial \tau}\right\} = L\left\{\frac{\partial^2 \psi_1}{\partial \xi^2} + \frac{1}{\xi}\frac{\partial \psi_1}{\partial \xi}\right\} \qquad \text{(B.2)}$$

$$sv(\xi,s) - \psi_1(\xi,0) = \frac{d^2 v(\xi,s)}{d\xi^2} + \frac{1}{\xi}\frac{dv(\xi,s)}{d\xi} \qquad \text{(B.3)}$$

with initial condition:

$$\psi_1(\xi,0) = 0 \qquad \text{(B.4)}$$

and boundary conditions:

$$v(0,s) \text{ is finite} \qquad \text{(B.5)}$$

$$\frac{dv(1,s)}{d\xi} = L\left[w\left(1 + \frac{w}{2}\left(\frac{1}{2} - 1^2\right) - 2w\tau + \sum_{n=1}^{\infty} \frac{wJ_0(\lambda_n 1)}{\frac{\lambda_n^2}{2} J_0(\lambda_n)} e^{-\lambda_n^2 \tau} \right) \right] \qquad \text{(B.6)}$$

$$L\{w\} = \frac{w}{s} \tag{B.7}$$

$$L\{-2w^2\tau\} = \frac{-2w^2}{s^2} \tag{B.8}$$

$$L\left\{ w\sum_{n=1}^{\infty} \frac{wJ_0(\lambda_n)}{\frac{\lambda_n^{\,2}}{2} J_0(\lambda_n)} e^{-\lambda_n^{\,2}\tau} \right\} = 2w^2 \sum_{n=1}^{\infty} \frac{1}{\lambda_n^{\,2}(s+\lambda_n^{\,2})} \tag{B.9}$$

Substituting into Equation (B.6):

$$\frac{dv(1,s)}{d\xi} = w\left(\frac{1}{s} - \frac{w}{4s} - \frac{2w}{s^2}\right) + 2w^2\left(\sum_{n=1}^{\infty} \frac{1}{\lambda_n^{\,2}(s+\lambda_n^{\,2})}\right) \tag{B.10}$$

Equation (B.3) can be written as:

$$\frac{d^2v(\xi,s)}{d\xi^2} + \frac{1}{\xi}\frac{dv(\xi,s)}{d\xi} - sv(\xi,s) = 0 \tag{B.11}$$

Comparing to Bessels's general equation:

$$y'' - \left(\frac{2a-1}{x}\right)y' + \left(b^2c^2x^{2c-2} + \frac{a^2-\gamma^2c^2}{x^2}\right)y = 0 \tag{B.12}$$

with: $a = 0, \qquad b = i\sqrt{s}, \qquad \gamma = 0, \qquad c = 1$

$$v(\xi,s) = b_1 J_0(i\sqrt{s}\xi) + b_2 Y_0(i\sqrt{s}\xi) \tag{B.13}$$

Because Y_0 is unbounded, $b_2 = 0$ at $\xi = 0$. Therefore:

$$\boxed{v(\xi,s) = b_1 J_0(i\sqrt{s}\xi)} \tag{B.14}$$

Applying Equation (B.14) to (B.10):

$$\frac{dv(1,s)}{d\xi} = b_1 i\sqrt{s} J_1(i\sqrt{s}) \tag{B.15}$$

$$b_1 i\sqrt{s} J_1(i\sqrt{s}) = w\left(\frac{1}{s} - \frac{w}{4s} - \frac{2w^2}{s^2}\right) + 2w^2\left(\sum_{n=1}^{\infty} \frac{1}{\lambda_n{}^2(s+\lambda_n{}^2)}\right) \tag{B.16}$$

$$b_1 = w\left(1-\frac{w}{4}\right)\frac{1}{si\sqrt{s}J_1(i\sqrt{s})} - \frac{2w^2}{s^2 i\sqrt{s}J_1(i\sqrt{s})} + \frac{2w^2}{i\sqrt{s}J_1(i\sqrt{s})}\left(\sum_{n=1}^{\infty}\frac{1}{\lambda_n{}^2(s+\lambda_n{}^2)}\right) \tag{B.17}$$

Then from Equation (B.13):

$$v(\xi,s) = w\left(1-\frac{w}{4}\right)\frac{J_0(i\sqrt{s}\xi)}{si\sqrt{s}J_1(i\sqrt{s})} - \frac{2w^2 J_0(i\sqrt{s}\xi)}{s^2 i\sqrt{s}J_1(i\sqrt{s})} + \frac{2w^2 J_0(i\sqrt{s}\xi)}{i\sqrt{s}J_1(i\sqrt{s})}\left(\sum_{n=1}^{\infty}\frac{1}{\lambda_n{}^2(s+\lambda_n{}^2)}\right) \tag{B.18}$$

Inverse Laplace of (B.18):

$$\psi_1(\xi,\tau) = L^{-1}\left\{\begin{array}{l} w\left(1-\frac{w}{4}\right)\frac{J_0(i\sqrt{s}\xi)}{si\sqrt{s}J_1(i\sqrt{s})} - \frac{2w^2 J_0(i\sqrt{s}\xi)}{s^2 i\sqrt{s}J_1(i\sqrt{s})} + \\ \frac{2w^2 J_0(i\sqrt{s}\xi)}{i\sqrt{s}J_1(i\sqrt{s})}\left(\sum_{n=1}^{\infty}\frac{1}{\lambda_n{}^2(s+\lambda_n{}^2)}\right) \end{array}\right\} \tag{B.19}$$

The three terms in Equation (B.19) will be evaluated separately:

$$\psi_1(\xi,\tau) = L^{-1}\left\{ \overbrace{\frac{w(4-w)}{4}\frac{J_0(i\sqrt{s}\xi)}{si\sqrt{s}J_1(i\sqrt{s})}}^{FirstTerm} \overbrace{-\frac{2w^2 J_0(i\sqrt{s}\xi)}{s^2 i\sqrt{s}J_1(i\sqrt{s})}}^{SecondTerm} + \overbrace{\frac{2w^2 J_0(i\sqrt{s}\xi)}{i\sqrt{s}J_1(i\sqrt{s})}\left(\sum_{n=1}^{\infty}\frac{1}{\lambda_n{}^2(s+\lambda_n{}^2)}\right)}^{ThirdTerm} \right\} \tag{B.20}$$

First Term

$$L^{-1}\left\{\frac{w(4-w)}{4}\frac{J_0(i\sqrt{s}\xi)}{si\sqrt{s}J_1(i\sqrt{s})}\right\} = ? \tag{B.21}$$

$$= \frac{w(4-w)}{4}\frac{J_0(i\sqrt{s}\xi)}{si\sqrt{s}J_1(i\sqrt{s})} = \frac{w(4-w)}{4}\frac{\left(1+\frac{s\xi^2}{2^2}+\frac{s^2\xi^4}{2^2.4^2}+\ldots\right)}{is\sqrt{s}\left(\frac{i\sqrt{s}}{2}-\frac{\left(i\sqrt{s}\right)^3}{2^2.4}+\frac{\left(i\sqrt{s}\right)^5}{2^2.4^2.6}+\ldots\right)} \tag{B.22}$$

$$= \frac{w(4-w)}{4}\frac{\left(1+\frac{s\xi^2}{2^2}+\frac{s^2\xi^4}{2^2.4^2}+\ldots\right)}{-s^2\left(\frac{1}{2}+\frac{s}{2^2.4}+\frac{s^2}{2^2.4^2.6}+\ldots\right)}$$

Rewriting the ratio:

$$\frac{\left(1+\frac{s\xi^2}{2^2}+\frac{s^2\xi^4}{2^2.4^2}+\ldots\right)}{-\left(\frac{1}{2}+\frac{s}{2^2.4}+\frac{s^2}{2^2.4^2.6}+\ldots\right)} = A_0 + A_1 s + A_2 s^2 + \ldots \tag{B.23}$$

$$\left(1+\frac{s\xi^2}{2^2}+\frac{s^2\xi^4}{2^2.4^2}+...\right)=\left(A_0+A_1s+A_2s^2+...\right)\left(-\frac{1}{2}-\frac{s}{2^2.4}-\frac{s^2}{2^2.4^2.6}-...\right)=$$
$$A_0\left(-\frac{1}{2}-\frac{s}{2^2.4}-\frac{s^2}{2^2.4^2.6}-...\right)+A_1s\left(-\frac{1}{2}-\frac{s}{2^2.4}-\frac{s^2}{2^2.4^2.6}-...\right)+$$
$$A_2s^2\left(-\frac{1}{2}-\frac{s}{2^2.4}-\frac{s^2}{2^2.4^2.6}-...\right)+... \tag{B.24}$$

Equating the coefficients:

$$\frac{-A_0}{2}=1 \tag{B.25}$$

$$\boxed{A_0=-2} \tag{B.26}$$

$$\frac{-A_0}{2^2.4}-\frac{A_1}{2}=\frac{\xi^2}{2^2} \tag{B.27}$$

$$\frac{A_1}{2}=\frac{2}{2^2.4}-\frac{\xi^2}{2^2} \tag{B.28}$$

$$\boxed{A_1=\frac{1}{4}-\frac{\xi^2}{2}} \tag{B.29}$$

$$\frac{-A_0}{2^2.4^2.6}-\frac{A_1}{2^2.4}-\frac{A_2}{2}=\frac{\xi^4}{2^2.4^2} \tag{B.30}$$

$$\boldsymbol{A_2=\frac{2}{2.4^2.6}-\frac{1}{2.4}\left(\frac{1}{4}-\frac{\xi^2}{2}\right)-\frac{\xi^4}{2.4^2}} \tag{B.31}$$

$$\boxed{\boldsymbol{A_2=\frac{1}{4^2.6}-\frac{1}{2.4}\left(\frac{1}{4}-\frac{\xi^2}{2}\right)-\frac{\xi^4}{2.4^2}}} \tag{B.32}$$

Substituting, Equation (B.21) would be:

$$\frac{w(4-w)}{4}\frac{J_0(i\sqrt{s}\xi)}{si\sqrt{s}J_1(i\sqrt{s})}=$$

$$\frac{w(4-w)}{4s^2}\left(\begin{array}{l}-2+\left(\frac{1}{4}-\frac{\xi^2}{2}\right)s+\\ \left(\frac{1}{4^2.6}-\frac{1}{2.4}\left(\frac{1}{4}-\frac{\xi^2}{2}\right)-\frac{\xi^4}{2.4^2}\right)s^2+\ldots\end{array}\right)=\frac{P(s)}{Q(s)} \tag{B.33}$$

Using Residue theorem when s=0,

$$\rho_0(\tau)=e^{0\tau}\left[\beta_1+\tau\beta_2\right] \tag{B.34}$$

$$\beta_1=\lim_{s\to 0}\frac{d}{ds}\left(s^2\frac{w(4-w)}{4}\frac{J_0(i\sqrt{s}\xi)}{si\sqrt{s}J_1(i\sqrt{s})}\right) \tag{B.35}$$

$$\beta_1=\lim_{s\to 0}\frac{d}{ds}\left(s^2\frac{w(4-w)}{4s^2}\left(\begin{array}{l}-2+\left(\frac{1}{4}-\frac{\xi^2}{2}\right)s+\\ \left(\frac{1}{4^2.6}-\frac{1}{2.4}\left(\frac{1}{4}-\frac{\xi^2}{2}\right)-\frac{\xi^4}{2.4^2}\right)s^2+\ldots\end{array}\right)\right) \tag{B.36}$$

$$\boxed{\beta_1=\frac{w(4-w)}{4}\left(\frac{1}{4}-\frac{\xi^2}{2}\right)} \tag{B.37}$$

and:

$$\beta_2=\lim_{s\to 0}\left(s^2\frac{w(4-w)}{4}\frac{J_0(i\sqrt{s}\xi)}{si\sqrt{s}J_1(i\sqrt{s})}\right) \tag{B.38}$$

$$\beta_2=\lim_{s\to 0}\left(s^2\frac{w(4-w)}{4s^2}\left(-2+\left(\frac{1}{4}-\frac{\xi^2}{2}\right)s+\left(\frac{1}{4^2.6}-\frac{1}{2.4}\left(\frac{1}{4}-\frac{\xi^2}{2}\right)-\frac{\xi^4}{2.4^2}\right)s^2+\ldots\right)\right) \tag{B.39}$$

$$\boxed{\beta_2 = \frac{-w(4-w)}{2}} \tag{B.40}$$

Substituting Equations (B.37) and (B.40) into (B.34):

$$\boxed{\rho_0(\tau) = \frac{w(4-w)}{2}\left[\left(\frac{1}{4.2} - \frac{\xi^2}{2^2}\right) - \tau\right]} \tag{B.41}$$

Applying Residue theorem when $s \neq 0$, in Equation (B.33),

$$J_1(i\sqrt{s}) = 0 \tag{B.42}$$

Substituting: $i\sqrt{s} = \lambda.$, $s = -\lambda^2$

$$J_1(\lambda_n) = 0,\ n = 1, 2, 3, . \tag{B.43}$$

The general solution of Equation (B.32) can be written as (Loney, 2001),

$$\rho_n(\tau) = \frac{P(\lambda_n, \xi)}{Q'(\lambda_n)} e^{-\lambda_n{}^2 \tau} \tag{B.44}$$

For:

$$Q(s) = si\sqrt{s}J_1(i\sqrt{s}) \tag{B.45}$$

$$Q'(s) = \frac{3}{2} i\sqrt{s}J_1(i\sqrt{s}) + si\sqrt{s}J'_1(i\sqrt{s}) \tag{B.46}$$

Since (Spiegel, 1971)

$$J'_1(x) = \frac{1}{2}\left[J_0(x) - J_2(x)\right] \xrightarrow{J_2(x) = \frac{2}{x}J_1(x) - J_0(x)} J'_1(x) = J_0(x) - \frac{1}{x}J_1(x) \tag{B.47}$$

$$Q'(s) = \frac{3}{2} i\sqrt{s}J_1(i\sqrt{s}) + \frac{1}{2} is^{-1/2}(si\sqrt{s})\left(J_0(i\sqrt{s}) - \frac{1}{i\sqrt{s}}J_1(i\sqrt{s})\right) \tag{B.48}$$

$$Q'(s) = \frac{3}{2} i\sqrt{s}J_1(i\sqrt{s}) - \frac{1}{2} s\left(J_0(i\sqrt{s}) - \frac{1}{i\sqrt{s}}J_1(i\sqrt{s})\right) \tag{B.49}$$

In terms of λ:

$$\boldsymbol{Q}'(\lambda_n) = \frac{\mathbf{3}}{\mathbf{2}}\lambda_n \boldsymbol{J}_1(\lambda_n) + \frac{\mathbf{1}}{\mathbf{2}}\lambda_n^2\left(\boldsymbol{J}_0(\lambda_n) - \frac{\mathbf{1}}{\lambda_n}\boldsymbol{J}_1(\lambda_n)\right) \tag{B.50}$$

With $\boldsymbol{J}_1(\lambda_n) = \mathbf{0}$, Equation (B.50) reduces to:

$$\boldsymbol{Q}'(\lambda_n) = \frac{\mathbf{1}}{\mathbf{2}}\lambda_n{}^2\boldsymbol{J}_0(\lambda_n) \tag{B.51}$$

Also,

$$\boldsymbol{P}(\xi, \lambda_n) = \frac{\boldsymbol{w}(\mathbf{4}-\boldsymbol{w})}{\mathbf{4}}\boldsymbol{J}_0(\lambda_n\xi) \tag{B.52}$$

Substituting Equations (B.51) and (B.52) into Equation (B.44):

$$\boxed{\rho_n(\tau) = \frac{-\boldsymbol{w}(\mathbf{4}-\boldsymbol{w})}{\mathbf{2}}\frac{\boldsymbol{J}_0(\lambda_n\xi)}{\boldsymbol{s}\boldsymbol{J}_0(\lambda_n)}\boldsymbol{e}^{-\lambda_n{}^2\tau}} \tag{B.53}$$

Therefore, the inverse Laplace for the First Term is given by:

$$\boxed{\boldsymbol{L}^{-1}\left\{\frac{\boldsymbol{w}(\mathbf{4}-\boldsymbol{w})}{\mathbf{4}}\frac{\boldsymbol{J}_0(\boldsymbol{i}\sqrt{\boldsymbol{s}}\xi)}{\boldsymbol{s}\boldsymbol{i}\sqrt{\boldsymbol{s}}\boldsymbol{J}_1(\boldsymbol{i}\sqrt{\boldsymbol{s}})}\right\} = \frac{\boldsymbol{w}(\mathbf{4}-\boldsymbol{w})}{\mathbf{2}}\left[\left(\frac{\mathbf{1}}{\mathbf{4.2}} - \frac{\xi^2}{\mathbf{2}^2}\right) - \tau\right] + \sum_{n=1}^{\infty}\frac{\boldsymbol{w}(\mathbf{4}-\boldsymbol{w})}{\mathbf{2}}\frac{\boldsymbol{J}_0(\lambda_n\xi)}{\lambda_n{}^2\boldsymbol{J}_0(\lambda_n)}\boldsymbol{e}^{-\lambda_n{}^2\tau}} \tag{B.54}$$

Second Term

$$L^{-1}\left\{\frac{2w^2 J_0(i\sqrt{s}\xi)}{s^2 i\sqrt{s} J_1(i\sqrt{s})}\right\} = ? \tag{B.55}$$

$$= \frac{2w^2 J_0(i\sqrt{s}\xi)}{s^2 i\sqrt{s} J_1(i\sqrt{s})} = 2w^2 \frac{\left(1+\frac{s\xi^2}{2^2}+\frac{s^2\xi^4}{2^2.4^2}+\ldots\right)}{is^2\sqrt{s}\left(\frac{i\sqrt{s}}{2}-\frac{\left(i\sqrt{s}\right)^3}{2^2.4}+\frac{\left(i\sqrt{s}\right)^5}{2^2.4^2.6}+\ldots\right)}$$
$$= 2w^2 \frac{\left(1+\frac{s\xi^2}{2^2}+\frac{s^2\xi^4}{2^2.4^2}+\ldots\right)}{-s^3\left(\frac{1}{2}+\frac{s}{2^2.4}+\frac{s^2}{2^2.4^2.6}+\ldots\right)} \tag{B.56}$$

Solving for the ratio:

$$\frac{\left(1+\frac{s\xi^2}{2^2}+\frac{s^2\xi^4}{2^2.4^2}+\ldots\right)}{-\left(\frac{1}{2}+\frac{s}{2^2.4}+\frac{s^2}{2^2.4^2.6}+\ldots\right)} = A_0 + A_1 s + A_2 s^2 + \ldots \tag{B.57}$$

$$\left(1+\frac{s\xi^2}{2^2}+\frac{s^2\xi^4}{2^2.4^2}+\ldots\right) = \left(A_0 + A_1 s + A_2 s^2 + \ldots\right)\left(-\frac{1}{2}-\frac{s}{2^2.4}-\frac{s^2}{2^2.4^2.6}-\ldots\right)$$
$$= A_0\left(-\frac{1}{2}-\frac{s}{2^2.4}-\frac{s^2}{2^2.4^2.6}-\ldots\right) + A_1 s\left(-\frac{1}{2}-\frac{s}{2^2.4}-\frac{s^2}{2^2.4^2.6}-\ldots\right) +$$
$$A_2 s^2\left(-\frac{1}{2}-\frac{s}{2^2.4}-\frac{s^2}{2^2.4^2.6}-\ldots\right)+\ldots \tag{B.58}$$

Equating coefficients:

$$\frac{-A_0}{2} = 1 \tag{B.59}$$

$$\boxed{A_0 = -2} \tag{B.60}$$

$$\frac{-A_0}{2^2.4} - \frac{A_1}{2} = \frac{\xi^2}{2^2} \tag{B.61}$$

$$\frac{A_1}{2} = \frac{2}{2^2.4} - \frac{\xi^2}{2^2} \tag{B.62}$$

$$\boxed{A_1 = \frac{1}{4} - \frac{\xi^2}{2}} \tag{B.63}$$

$$\frac{-A_0}{2^2.4^2.6} - \frac{A_1}{2^2.4} - \frac{A_2}{2} = \frac{\xi^4}{2^2.4^2} \tag{B.64}$$

$$A_2 = \frac{2}{2.4^2.6} - \frac{1}{2.4}\left(\frac{1}{4} - \frac{\xi^2}{2}\right) - \frac{\xi^4}{2.4^2} \tag{B.65}$$

$$\boxed{A_2 = \frac{1}{4^2.6} - \frac{1}{2.4}\left(\frac{1}{4} - \frac{\xi^2}{2}\right) - \frac{\xi^4}{2.4^2}} \tag{B.66}$$

Equation (B.56) can be rewritten as:

$$\frac{2w^2 J_0(i\sqrt{s}\xi)}{s^2 i\sqrt{s} J_1(i\sqrt{s})} = \frac{2w^2}{s^3}\left(\begin{array}{l} -2 + \left(\frac{1}{4} - \frac{\xi^2}{2}\right)s + \\ \left(\frac{1}{4^2.6} - \frac{1}{2.4}\left(\frac{1}{4} - \frac{\xi^2}{2}\right) - \frac{\xi^4}{2.4^2}\right)s^2 + \ldots \end{array}\right) = \frac{P(s)}{Q(s)} \tag{B.67}$$

Using Residue theorem when s=0,

$$\rho_0(\tau) = e^{0\tau}\left[\beta_1 + \beta_2\tau + \frac{\beta_3}{2}\tau^2\right] \tag{B.68}$$

$$\beta_1 = \lim_{s\to 0}\frac{1}{2}\frac{d^2}{ds^2}\left(s^3\,\frac{2w^2}{s^3}\left(\begin{array}{l} -2 + \left(\frac{1}{4} - \frac{\xi^2}{2}\right)s + \\ \left(\frac{1}{4^2.6} - \frac{1}{2.4}\left(\frac{1}{4} - \frac{\xi^2}{2}\right) - \frac{\xi^4}{2.4^2}\right)s^2 + \ldots \end{array}\right)\right) \tag{B.69}$$

$$\boxed{\beta_1 = w^2\left(\frac{1}{4^2.3} - \frac{1}{4}\left(\frac{1}{4} - \frac{\xi^2}{2}\right) - \frac{\xi^4}{4^2}\right)} \tag{B.70}$$

$$\beta_2 = \lim_{s\to 0}\frac{d}{ds}\left(s^3\,\frac{2w^2}{s^3}\left(\begin{array}{l}-2 + \left(\frac{1}{4} - \frac{\xi^2}{2}\right)s + \\ \left(\frac{1}{4^2.6} - \frac{1}{2.4}\left(\frac{1}{4} - \frac{\xi^2}{2}\right) - \frac{\xi^4}{2.4^2}\right)s^2 + \ldots\end{array}\right)\right) \tag{B.71}$$

$$\boxed{\beta_2 = w^2\left(\frac{1}{2} - \xi^2\right)} \tag{B.72}$$

$$\beta_3 = \lim_{s\to 0}\left(s^3\,\frac{2w^2}{s^3}\left(\begin{array}{l}-2 + \left(\frac{1}{4} - \frac{\xi^2}{2}\right)s + \\ \left(\frac{1}{4^2.6} - \frac{1}{2.4}\left(\frac{1}{4} - \frac{\xi^2}{2}\right) - \frac{\xi^4}{2.4^2}\right)s^2 + \ldots\end{array}\right)\right) \tag{B.73}$$

$$\boxed{\beta_3 = -4w^2} \tag{B.74}$$

Equation (B.68) can be written as:

$$\boxed{\rho_0(\tau) = w^2\left[\frac{1}{4^2.3} - \frac{1}{4}\left(\frac{1}{4} - \frac{\xi^2}{2}\right) - \frac{\xi^4}{4^2} + \left(\frac{1}{2} - \xi^2\right)\tau - 2\tau^2\right]} \tag{B.75}$$

Applying Residue theorem when $s \neq 0$, in Equation (B.56):

$$J_1(i\sqrt{s}) = 0 \tag{B.76}$$

Substituting: $i\sqrt{s} = \lambda.$, $s = -\lambda^2$

$$J_1(\lambda_n) = 0,\ n = 1, 2, 3, . \tag{B.77}$$

The general solution of Equation (B.56) can be written as (Loney, 2001):

$$\rho_n(\tau) = \frac{P(\lambda_n, \xi)}{Q'(\lambda_n)} e^{-\lambda_n{}^2 \tau} \tag{B.78}$$

$$Q(s) = s^2 i\sqrt{s} J_1(i\sqrt{s}) \tag{B.79}$$

$$Q'(s) = \frac{5}{2} i s^{\frac{3}{2}} J_1(i\sqrt{s}) + s^2 i\sqrt{s} J'_1(i\sqrt{s}) \tag{B.80}$$

Substituting for $J'_1(i\sqrt{s})$ from (Spiegel, 1971):

$$J'_1(x) = \frac{1}{2}\left[J_0(x) - J_2(x)\right] \xrightarrow{J_2(x)=\frac{2}{x}J_1(x)-J_0(x)} J'_1(x) = J_0(x) - \frac{1}{x} J_1(x) \tag{B.81}$$

$$Q'(s) = \frac{5}{2} i s^{\frac{3}{2}} J_1(i\sqrt{s}) - \frac{1}{2} s^2 \left(J_0(i\sqrt{s}) - \frac{1}{i\sqrt{s}} J_1(i\sqrt{s})\right) \tag{B.82}$$

$$Q'(\lambda_n) = -\frac{1}{2} \lambda_n{}^4 J_0(\lambda_n) \tag{B.83}$$

$$P(\xi, \lambda_n) = 2w^2 J_0(\lambda_n \xi) \tag{B.84}$$

$$\boxed{\rho_n(\tau) = -\frac{4w^2 J_0(\lambda_n \xi)}{\lambda_n{}^4 J_0(\lambda_n)} e^{-\lambda_n^2 \tau}} \tag{B.85}$$

Substituting Equations (B.75) and (B.85) into Equation (B.55):

$$\boxed{L^{-1}\left\{\frac{2w^2 J_0(i\sqrt{s}\xi)}{s^2 i\sqrt{s} J_1(i\sqrt{s})}\right\} = w^2\left[\frac{1}{4^2.3} - \frac{1}{4}\left(\frac{1}{4} - \frac{\xi^2}{2}\right) - \frac{\xi^4}{4^2} + \left(\frac{1}{2} - \xi^2\right)\tau - 2\tau^2\right] - 4w^2 \sum_{n=1}^{\infty} \frac{J_0(\lambda_n \xi)}{\lambda_n{}^4 J_0(\lambda_n)} e^{-\lambda_n{}^2 \tau}} \tag{B.86}$$

Third Term

$$L^{-1}\left\{\frac{2w^2 J_0(i\sqrt{s}\xi)}{i\sqrt{s}J_1(i\sqrt{s})}\left(\sum_{n=1}^{\infty}\frac{1}{\lambda_n^{\,2}(s+\lambda_n^{\,2})}\right)\right\} = ? \tag{B.87}$$

$$\frac{2w^2 J_0(i\sqrt{s}\xi)}{i\sqrt{s}J_1(i\sqrt{s})}\left(\sum_{n=1}^{\infty}\frac{1}{\lambda_n^{\,2}(s+\lambda_n^{\,2})}\right) = \frac{2w^2\left(1+\frac{s\xi^2}{2^2}+\frac{s^2\xi^4}{2^2.4^2}+\ldots\right)}{i\sqrt{s}\left(\frac{i\sqrt{s}}{2}-\frac{\left(i\sqrt{s}\right)^3}{2^2.4}+\frac{\left(i\sqrt{s}\right)^5}{2^2.4^2.6}+\ldots\right)}\left(\sum_{n=1}^{\infty}\frac{1}{\lambda_n^{\,2}(s+\lambda_n^{\,2})}\right)$$

$$= \frac{2w^2\left(1+\frac{s\xi^2}{2^2}+\frac{s^2\xi^4}{2^2.4^2}+\ldots\right)}{\left(-\frac{s}{2}-\frac{s^2}{2^2.4}-\frac{s^3}{2^2.4^2.6}-\ldots\right)}\left(\sum_{n=1}^{\infty}\frac{1}{\lambda_n^{\,2}(s+\lambda_n^{\,2})}\right) \tag{B.88}$$

$$= \frac{2w^2\left(1+\frac{s\xi^2}{2^2}+\frac{s^2\xi^4}{2^2.4^2}+\ldots\right)}{-\left(\frac{s}{2}+\frac{s^2}{2^2.4}+\frac{s^3}{2^2.4^2.6}+\ldots\right)}\left(\frac{1}{\lambda_1^{\,2}(s+\lambda_1^{\,2})}+\frac{1}{\lambda_2^{\,2}(s+\lambda_2^{\,2})}+\ldots\right)$$

$$= \frac{2w^2\left(1+\frac{s\xi^2}{2^2}+\frac{s^2\xi^4}{2^2.4^2}+\ldots\right)\left(\lambda_2^{\,2}(s+\lambda_2^{\,2})\lambda_3^{\,2}(s+\lambda_3^{\,2})\ldots+\lambda_1^{\,2}(s+\lambda_1^{\,2})\lambda_3^{\,2}(s+\lambda_3^{\,2})\ldots+\ldots\right)}{-s\left(\frac{1}{2}+\frac{s}{2^2.4}+\frac{s^2}{2^2.4^2.6}+\ldots\right)\left(\lambda_1^{\,2}(s+\lambda_1^{\,2})\lambda_2^{\,2}(s+\lambda_2^{\,2})\lambda_3^{\,2}(s+\lambda_3^{\,2})\ldots\right)}$$

Rewriting the ratio as:

$$\frac{\left(1+\frac{s\xi^2}{2^2}+\frac{s^2\xi^4}{2^2.4^2}+\ldots\right)\left(\lambda_2^{\,2}(s+\lambda_2^{\,2})\lambda_3^{\,2}(s+\lambda_3^{\,2})\ldots+\lambda_1^{\,2}(s+\lambda_1^{\,2})\lambda_3^{\,2}(s+\lambda_3^{\,2})\ldots+\ldots\right)}{-\left(\frac{1}{2}+\frac{s}{2^2.4}+\frac{s^2}{2^2.4^2.6}+\ldots\right)\left(\lambda_1^{\,2}(s+\lambda_1^{\,2})\lambda_2^{\,2}(s+\lambda_2^{\,2})\lambda_3^{\,2}(s+\lambda_3^{\,2})\ldots\right)} = \tag{B.89}$$

$$= A_0 + A_1 s + A_2 s^2 + \ldots$$

$$\left(1+\frac{s\xi^2}{2^2}+\frac{s^2\xi^4}{2^2.4^2}+\ldots\right)*$$
$$\left(\lambda_2{}^2(s+\lambda_2{}^2)\lambda_3{}^2(s+\lambda_3{}^2)\ldots+\lambda_1{}^2(s+\lambda_1{}^2)\lambda_3{}^2(s+\lambda_3{}^2)\ldots+\ldots\right)= \quad \text{(B.90)}$$
$$\left(A_0+A_1s+A_2s^2+\ldots\right)\left(-\frac{1}{2}-\frac{s}{2^2.4}-\frac{s^2}{2^2.4^2.6}-\ldots\right)*$$
$$\left(\lambda_1{}^2(s+\lambda_1{}^2)\lambda_2{}^2(s+\lambda_2{}^2)\lambda_3{}^2(s+\lambda_3{}^2)\ldots\right)$$

Rearranging the terms in Equation (B.91), one can solve for constants of similar powers of S namely A_0, A_1, A_2, etc. (Motamedvaziri, 2008).

$$\left(\lambda_1{}^2(s+\lambda_1{}^2)\lambda_2{}^2(s+\lambda_2{}^2)\lambda_3{}^2(s+\lambda_3{}^2)\ldots\right)=\begin{Bmatrix}\lambda_1{}^4\lambda_2{}^4\ldots\lambda_n{}^4+\left(\lambda_1{}^2\lambda_2{}^2\ldots\lambda_n{}^2\right)\\ \begin{pmatrix}\lambda_1{}^2\lambda_3{}^2\ldots\lambda_n{}^2+\lambda_2{}^2\lambda_3{}^2\ldots\lambda_n{}^2+\ldots\\ \lambda_1{}^2\ldots\lambda_{n-1}{}^2\end{pmatrix}s+\\ \left(\lambda_1{}^2\lambda_2{}^2\ldots\lambda_n{}^2\right)\begin{pmatrix}\lambda_1{}^2\lambda_4{}^2\ldots\lambda_n{}^2+\lambda_2{}^2\lambda_4{}^2\\ \ldots\lambda_n{}^2+\ldots\lambda_3{}^2\ldots\lambda_{n-1}{}^2\end{pmatrix}s^2\\ +\ldots+\left(\lambda_1{}^2\lambda_2{}^2\ldots\lambda_n{}^2\right)s^n\end{Bmatrix} \quad \text{(B.91)}$$

$$\left(1+\frac{s\xi^2}{2^2}+\frac{s^2\xi^4}{2^2.4^2}+\ldots\right)\begin{bmatrix}\lambda_2{}^4\ldots\lambda_n{}^4+\left(\lambda_2{}^2\ldots\lambda_n{}^2\right)\left(\lambda_3{}^2\ldots\lambda_n{}^2+\ldots+\lambda_2{}^2\ldots\lambda_{n-1}{}^2\right)s+\\ \left(\lambda_2{}^2\ldots\lambda_n{}^2\right)\left(\lambda_2{}^2\lambda_3{}^2\ldots\lambda_n{}^2+\ldots+\lambda_2{}^2\ldots\lambda_{n-2}{}^2\right)s^2+\\ \ldots+\left(\lambda_2{}^2\ldots\lambda_n{}^2\right)s^{n-1}+\lambda_1{}^4\lambda_3{}^4\ldots\lambda_n{}^4+\left(\lambda_1{}^2\lambda_3{}^2\ldots\lambda_n{}^2\right)*\\ \begin{pmatrix}\lambda_3{}^2\ldots\lambda_n{}^2+\ldots+\\ \lambda_1{}^2\lambda_3{}^2\ldots\lambda_{n-1}{}^2\end{pmatrix}s+\left(\lambda_1{}^2\lambda_3{}^2\ldots\lambda_n{}^2\right)*\\ \left(\lambda_4{}^2\ldots\lambda_n{}^2+\ldots+\lambda_1{}^2\lambda_3{}^2\ldots\lambda_{n-2}{}^2\right)s^2+\ldots+\\ \left(\lambda_1{}^2\lambda_3{}^2\ldots\lambda_n{}^2\right)s^{n-1}+\ldots+\lambda_1{}^4\ldots\lambda_{n-1}{}^4+\\ \left(\lambda_1{}^2\ldots\lambda_{n-1}{}^2\right)\left(\lambda_2{}^2\ldots\lambda_{n-1}{}^2+\ldots+\lambda_1{}^2\ldots\lambda_{n-2}{}^2\right)s+\\ \left(\lambda_1{}^2\ldots\lambda_{n-1}{}^2\right)\left(\lambda_2{}^2\ldots\lambda_{n-1}{}^2+\ldots+\lambda_1{}^2\ldots\lambda_{n-2}{}^2\right)s^2+\\ \ldots+\left(\lambda_1{}^2\ldots\lambda_{n-1}{}^2\right)s^{n-1}\end{bmatrix}=$$

$$= \left[-\frac{A_0}{2} - \left(\frac{A_1}{2} + \frac{A_0}{2^2.4} \right) s - \left(\frac{A_0}{2^2.4^2.6} + \frac{A_1}{2^2.4} + \frac{A_2}{2} \right) s^2 - \ldots \right] * \begin{Bmatrix} \lambda_1^4 \lambda_2^4 \ldots \lambda_n^4 + \left(\lambda_1^2 \lambda_2^2 \ldots \lambda_n^2 \right) \\ \left(\begin{matrix} \lambda_1^2 \lambda_3^2 \ldots \lambda_n^2 + \lambda_2^2 \lambda_3^2 \ldots \lambda_n^2 + \ldots \\ \lambda_1^2 \ldots \lambda_{n-1}^2 \end{matrix} \right) s + \\ \left(\lambda_1^2 \lambda_2^2 \ldots \lambda_n^2 \right) \left(\begin{matrix} \lambda_1^2 \lambda_4^2 \ldots \lambda_n^2 + \lambda_2^2 \lambda_4^2 \\ \ldots \lambda_n^2 + \ldots \lambda_3^2 \ldots \lambda_{n-1}^2 \end{matrix} \right) s^2 \\ + \ldots + \left(\lambda_1^2 \lambda_2^2 \ldots \lambda_n^2 \right) s^n \end{Bmatrix} \tag{B.92}$$

Equating coefficients of similar powers of s, for s^0 terms:

$$\lambda_2^4 \ldots \lambda_n^4 + \lambda_1^4 \lambda_3^4 \ldots \lambda_n^4 + \ldots + \lambda_1^4 \ldots \lambda_{n-1}^4 = -\frac{A_0}{2} \lambda_1^4 \lambda_2^4 \ldots \lambda_n^4 \tag{B.93}$$

Solving for A_0:

$$\boxed{A_0 = -2 \frac{\lambda_2^4 \ldots \lambda_n^4 + \lambda_1^4 \lambda_3^4 \ldots \lambda_n^4 + \ldots + \lambda_1^4 \ldots \lambda_{n-1}^4}{\lambda_1^4 \lambda_2^4 \ldots \lambda_n^4}} \tag{B.94}$$

From s^1 terms:

$$\begin{bmatrix} \left(\lambda_2^2 \ldots \lambda_n^2 \right) \left(\lambda_3^2 \ldots \lambda_n^2 + \ldots + \lambda_2^2 \ldots \lambda_{n-1}^2 \right) + \\ \left(\lambda_1^2 \lambda_3^2 \ldots \lambda_n^2 \right) \left(\lambda_3^2 \ldots \lambda_n^2 + \ldots + \lambda_1^2 \lambda_3^2 \ldots \lambda_{n-1}^2 \right) + \ldots \\ + \left(\lambda_1^2 \ldots \lambda_{n-1}^2 \right) \left(\lambda_2^2 \ldots \lambda_{n-1}^2 + \ldots + \lambda_1^2 \ldots \lambda_{n-2}^2 \right) + \\ \frac{\xi^2}{2^2} \left(\lambda_2^4 \ldots \lambda_n^4 + \lambda_1^4 \lambda_3^4 \ldots \lambda_n^4 + \ldots + \lambda_1^4 \ldots \lambda_{n-1}^4 \right) \end{bmatrix} =$$

$$\begin{bmatrix} -\frac{A_0}{2} \left(\lambda_1^2 \lambda_2^2 \ldots \lambda_n^2 \right) \left(\lambda_1^2 \lambda_3^2 \ldots \lambda_n^2 + \lambda_2^2 \lambda_3^2 \ldots \lambda_n^2 + \ldots + \lambda_1^2 \ldots \lambda_{n-1}^2 \right) \\ -\left(\frac{A_1}{2} + \frac{A_0}{2^2.4} \right) \left(\lambda_1^4 \lambda_2^4 \ldots \lambda_n^4 \right) \end{bmatrix} =$$

$$= -\frac{A_0}{2}\left[\begin{array}{l}\left(\lambda_1^{\,2}\lambda_2^{\,2}\ldots\lambda_n^{\,2}\right)\left(\lambda_1^{\,2}\lambda_3^{\,2}\ldots\lambda_n^{\,2}+\lambda_2^{\,2}\lambda_3^{\,2}\ldots\lambda_n^{\,2}+\ldots+\lambda_1^{\,2}\ldots\lambda_{n-1}^{\,2}\right)+\\ \frac{1}{2.4}\left(\lambda_1^{\,4}\lambda_2^{\,4}\ldots\lambda_n^{\,4}\right)\end{array}\right] \qquad \text{(B.95)}$$

$$-\left(\frac{A_1}{2}\right)\left(\lambda_1^{\,4}\lambda_2^{\,4}\ldots\lambda_n^{\,4}\right)$$

$$\left[\begin{array}{l}\left(\lambda_2^{\,2}\ldots\lambda_n^{\,2}\right)\left(\lambda_3^{\,2}\ldots\lambda_n^{\,2}+\ldots+\lambda_2^{\,2}\ldots\lambda_{n-1}^{\,2}\right)+\\ \left(\lambda_1^{\,2}\lambda_3^{\,2}\ldots\lambda_n^{\,2}\right)\left(\lambda_3^{\,2}\ldots\lambda_n^{\,2}+\ldots+\lambda_1^{\,2}\lambda_3^{\,2}\ldots\lambda_{n-1}^{\,2}\right)+\ldots\\ +\left(\lambda_1^{\,2}\ldots\lambda_{n-1}^{\,2}\right)\left(\lambda_2^{\,2}\ldots\lambda_{n-1}^{\,2}+\ldots+\lambda_1^{\,2}\ldots\lambda_{n-2}^{\,2}\right)+\\ \frac{\xi^2}{2^2}\left(\lambda_2^{\,4}\ldots\lambda_n^{\,4}+\lambda_1^{\,4}\lambda_3^{\,4}\ldots\lambda_n^{\,4}+\ldots+\lambda_1^{\,4}\ldots\lambda_{n-1}^{\,4}\right)\end{array}\right]= \qquad \text{(B.96)}$$

$$=\left[\begin{array}{l}\left(\lambda_2^{\,4}\ldots\lambda_n^{\,4}+\lambda_1^{\,4}\lambda_3^{\,4}\ldots\lambda_n^{\,4}+\ldots+\lambda_1^{\,4}\ldots\lambda_{n-1}^{\,4}\right)*\\ \left[\frac{\left(\lambda_1^{\,2}\lambda_3^{\,2}\ldots\lambda_n^{\,2}+\lambda_2^{\,2}\lambda_3^{\,2}\ldots\lambda_n^{\,2}+\ldots+\lambda_1^{\,2}\ldots\lambda_{n-1}^{\,2}\right)}{\left(\lambda_1^{\,2}\lambda_2^{\,2}\ldots\lambda_n^{\,2}\right)}+\frac{1}{2.4}\right]\\ -\left(\frac{A_1}{2}\right)\left(\lambda_1^{\,4}\lambda_2^{\,4}\ldots\lambda_n^{\,4}\right)\end{array}\right]$$

Solving for A_1:

$$A_1=\left\{\begin{array}{l}\left(\lambda_2^{\,4}\ldots\lambda_n^{\,4}+\lambda_1^{\,4}\lambda_3^{\,4}\ldots\lambda_n^{\,4}+\ldots+\lambda_1^{\,4}\ldots\lambda_{n-1}^{\,4}\right)\\ \left[\frac{\left(\lambda_1^{\,2}\lambda_3^{\,2}\ldots\lambda_n^{\,2}+\lambda_2^{\,2}\lambda_3^{\,2}\ldots\lambda_n^{\,2}+\ldots+\lambda_1^{\,2}\ldots\lambda_{n-1}^{\,2}\right)}{\left(\lambda_1^{\,2}\lambda_2^{\,2}\ldots\lambda_n^{\,2}\right)}+\frac{1}{2.4}\right]\\ -\left(\lambda_2^{\,2}\ldots\lambda_n^{\,2}\right)\left(\lambda_3^{\,2}\ldots\lambda_n^{\,2}+\ldots+\lambda_2^{\,2}\ldots\lambda_{n-1}^{\,2}\right)-\\ \left(\lambda_1^{\,2}\lambda_3^{\,2}\ldots\lambda_n^{\,2}\right)\left(\lambda_3^{\,2}\ldots\lambda_n^{\,2}+\ldots+\lambda_1^{\,2}\lambda_3^{\,2}\ldots\lambda_{n-1}^{\,2}\right)-\ldots\\ -\left(\lambda_1^{\,2}\ldots\lambda_{n-1}^{\,2}\right)\left(\lambda_2^{\,2}\ldots\lambda_{n-1}^{\,2}+\ldots+\lambda_1^{\,2}\ldots\lambda_{n-2}^{\,2}\right)\\ -\frac{\xi^2}{2^2}\left(\lambda_2^{\,4}\ldots\lambda_n^{\,4}+\lambda_1^{\,4}\lambda_3^{\,4}\ldots\lambda_n^{\,4}+\ldots+\lambda_1^{\,4}\ldots\lambda_{n-1}^{\,4}\right)\end{array}\right\}/\frac{2}{\left(\lambda_1^{\,4}\lambda_2^{\,4}\ldots\lambda_n^{\,4}\right)} \qquad \text{(B.97)}$$

Using the values for A_0 and A_1 Equation (B.88) can be written as follow:

$$\frac{2w^2J_0(i\sqrt{s}\xi)}{i\sqrt{s}J_1(i\sqrt{s})}\left(\sum_{n=1}^{\infty}\frac{1}{\lambda_n^{\,2}(s+\lambda_n^{\,2})}\right)=\frac{w^2(A_0+A_1s+\ldots)}{-s} \qquad \text{(B.98)}$$

Now by using the Residue theorem, the transform function F(s) is analytic, except for singularities. In this discussion, when F(s) is analytic, the inverse transform of F(s) is given by:

$$f(\tau) = L^{-1}\{F(s)\} = \sum_{1}^{\infty} \rho(\tau) \tag{B.99}$$

Our function:

$$F(s) = \frac{P(s)}{Q(s)} = \frac{w^2(A_0 + A_1 s + \ldots)}{-s} \tag{B.100}$$

If s is a simple pole of F(s):

$$\rho(\tau) = \frac{P(s)}{Q'(s)} e^{-s\tau} \tag{B.101}$$

When s = 0:

$$\boxed{P(s) = w^2 A_0} \tag{B.102}$$

$$\boxed{Q'(s) = -1} \tag{B.103}$$

$$\rho(\tau) = -w^2 A_0 \tag{B.104}$$

Where:

$$A_0 = -2\frac{\lambda_2^{\,4}\ldots\lambda_n^{\,4} + \lambda_1^{\,4}\lambda_3^{\,4}\ldots\lambda_n^{\,4} + \ldots + \lambda_1^{\,4}\ldots\lambda_{n-1}^{\,4}}{\lambda_1^{\,4}\lambda_2^{\,4}\ldots\lambda_n^{\,4}} \tag{B.94}$$

Then:

$$\boxed{\rho(\tau) = 2w^2\frac{\lambda_2^{\,4}\ldots\lambda_n^{\,4} + \lambda_1^{\,4}\lambda_3^{\,4}\ldots\lambda_n^{\,4} + \ldots + \lambda_1^{\,4}\ldots\lambda_{n-1}^{\,4}}{\lambda_1^{\,4}\lambda_2^{\,4}\ldots\lambda_n^{\,4}}} \tag{B.105}$$

When $s \neq 0$:

$$\frac{2w^2 J_0(i\sqrt{s}\xi)}{i\sqrt{s}J_1(i\sqrt{s})}\left(\sum_{n=1}^{\infty}\frac{1}{\lambda_n{}^2(s+\lambda_n{}^2)}\right)=$$

$$\frac{2w^2 J_0(i\sqrt{s}\xi)}{i\sqrt{s}J_1(i\sqrt{s})}*$$

$$\frac{\left(\lambda_2{}^2(s+\lambda_2{}^2)\lambda_3{}^2(s+\lambda_3{}^2)...+\lambda_1{}^2(s+\lambda_1{}^2)\lambda_3{}^2(s+\lambda_3{}^2)...+...\right)}{\left(\lambda_1{}^2(s+\lambda_1{}^2)\lambda_2{}^2(s+\lambda_2{}^2)...\lambda_n{}^2(s+\lambda_n{}^2)\right)}=\frac{P(\xi,s)}{Q(s)}$$

(B.106)

$$Q(s)=i\sqrt{s}J_1(i\sqrt{s})\left(\lambda_1{}^2(s+\lambda_1{}^2)\lambda_2{}^2(s+\lambda_2{}^2)...\lambda_n{}^2(s+\lambda_n{}^2)\right)=0 \tag{B.107}$$

$$\lambda_i\neq 0\Rightarrow\left\{\begin{array}{l} J_1(i\sqrt{s})=0;\ i\sqrt{s}=\lambda\Rightarrow s=-\lambda^2; \\ J_1(\lambda_n)=0,\ n=1,2,3,.. \\ Or \\ (s+\lambda_i{}^2)=0\Rightarrow s=-\lambda_i{}^2\Rightarrow \end{array}\right\}$$
$$\Rightarrow\left\{\lambda_i \text{ multiple pole of order 2}\right\} \tag{B.108}$$

Using the Residue theorem for multiple poles:

$$\rho_{\lambda_i}(\tau)=e^{-\lambda_i{}^2\tau}\left[\beta_1+\tau\beta_2\right] \tag{B.109}$$

$$\beta_1=\lim_{s\to-\lambda_i{}^2}\frac{d}{ds}\left(\begin{array}{l}(s+\lambda_i{}^2)^2\dfrac{2w^2 J_0(i\sqrt{s}\xi)}{i\sqrt{s}J_1(i\sqrt{s})(s+\lambda_1{}^2)(s+\lambda_2{}^2)...(s+\lambda_i{}^2)...(s+\lambda_n{}^2)} \\ \dfrac{\left(\lambda_2{}^2(s+\lambda_2{}^2)\lambda_3{}^2(s+\lambda_3{}^2)...+\lambda_1{}^2(s+\lambda_1{}^2)\lambda_3{}^2(s+\lambda_3{}^2)...+...\right)}{\left(\lambda_1{}^2(s+\lambda_1{}^2)\lambda_2{}^2(s+\lambda_2{}^2)...\lambda_i{}^2(s+\lambda_i{}^2)...\lambda_n{}^2(s+\lambda_n{}^2)\right)}\end{array}\right) \tag{B.110}$$

$$\beta_1=\lim_{s\to-\lambda_i{}^2}\frac{d}{ds}\left(\begin{array}{l}\dfrac{2w^2 J_0(i\sqrt{s}\xi)}{i\sqrt{s}(s+\lambda_1{}^2)(s+\lambda_2{}^2)...(s+\lambda_n{}^2)}* \\ \dfrac{\left(\lambda_2{}^2(s+\lambda_2{}^2)\lambda_3{}^2(s+\lambda_3{}^2)...+\lambda_1{}^2(s+\lambda_1{}^2)\lambda_3{}^2(s+\lambda_3{}^2)...+...\right)}{\left(\lambda_1{}^2(s+\lambda_1{}^2)\lambda_2{}^2(s+\lambda_2{}^2)...\lambda_i{}^2...\lambda_n{}^2(s+\lambda_n{}^2)\right)}\end{array}\right) \tag{B.111}$$

$$\beta_1 = \lim_{s\to-\lambda_i^2} \frac{2w^2}{\lambda_1^2\lambda_2^2\ldots\lambda_i^2\ldots\lambda_n^2} \frac{d}{ds} \left(\frac{J_0(i\sqrt{s}\xi)}{i\sqrt{s}(s+\lambda_1^2)(s+\lambda_2^2)\ldots(s+\lambda_n^2)} \right) \left(\frac{\left(\lambda_2^2(s+\lambda_2^2)\lambda_3^2(s+\lambda_3^2)\ldots + \right)}{\left(\lambda_1^2(s+\lambda_1^2)\lambda_3^2(s+\lambda_3^2)\ldots + \ldots \right)} \right) \Big/ \left((s+\lambda_1^2)(s+\lambda_2^2)\ldots(s+\lambda_n^2) \right) \quad \text{(B.112)}$$

$$\lim_{s\to-\lambda_i^2} \frac{\left\{ \begin{array}{l} \left(\frac{-i\xi}{2\sqrt{s}} J_1(i\sqrt{s}\xi) \left(\lambda_2^2(s+\lambda_2^2)\lambda_3^2(s+\lambda_3^2)\ldots + \lambda_1^2(s+\lambda_1^2)\lambda_3^2(s+\lambda_3^2)\ldots + \ldots \right) + J_0(i\sqrt{s}\xi) \right) \\ \left(\lambda_2^2(s+\lambda_2^2)\lambda_3^2(s+\lambda_3^2)\ldots + \lambda_1^2(s+\lambda_1^2)\lambda_3^2(s+\lambda_3^2)\ldots + \ldots \right)' \end{array} \right\}^2}{\left[\begin{array}{l} \left(i\sqrt{s}(s+\lambda_1^2)(s+\lambda_2^2) \right) \\ \ldots(s+\lambda_n^2) \end{array} \right] \left[\begin{array}{l} \left((s+\lambda_1^2)(s+\lambda_2^2)\ldots \right) \\ (s+\lambda_n^2) \end{array} \right]} \cdot \left\{ \begin{array}{l} \left(\left(i\sqrt{s}(s+\lambda_1^2)(s+\lambda_2^2)\ldots(s+\lambda_n^2) \right) \left((s+\lambda_1^2)(s+\lambda_2^2)\ldots(s+\lambda_n^2) \right) \right) - \\ \left(\left(i\sqrt{s}(s+\lambda_1^2)(s+\lambda_2^2)\ldots(s+\lambda_n^2) \right) \left((s+\lambda_1^2)(s+\lambda_2^2)\ldots(s+\lambda_n^2) \right) \right)' \\ \left(\lambda_2^2(s+\lambda_2^2)\lambda_3^2(s+\lambda_3^2)\ldots + \lambda_1^2(s+\lambda_1^2)\lambda_3^2(s+\lambda_3^2)\ldots + \ldots \right) J_0(i\sqrt{s}\xi) \end{array} \right\} =$$

$$= \frac{\left\{ \begin{array}{l} \left(\frac{-\xi}{2\lambda_i^2} J_1(\lambda_i\xi) \left(\lambda_1^2(-\lambda_i^2+\lambda_1^2)\ldots\lambda_{i-1}^2(-\lambda_i^2+\lambda_{i-1}^2)\lambda_{i+1}^2(-\lambda_i^2+\lambda_{i+1}^2)\ldots \right) J_0(\lambda_i\xi) \right) \\ \left(\lambda_2^2(s+\lambda_2^2)\lambda_3^2(s+\lambda_3^2)\ldots + \lambda_1^2(s+\lambda_1^2)\lambda_3^2(s+\lambda_3^2)\ldots + \ldots \right)' \end{array} \right\}}{\left[\begin{array}{l} \left(\lambda_i(-\lambda_i^2+\lambda_1^2)(-\lambda_i^2+\lambda_2^2) \right) \\ \ldots(-\lambda_i^2+\lambda_n^2) \end{array} \right] \left[\begin{array}{l} \left((-\lambda_i^2+\lambda_1^2)(-\lambda_i^2+\lambda_2^2) \right) \\ \ldots(-\lambda_i^2+\lambda_n^2) \end{array} \right]} \cdot \left\{ \begin{array}{l} \left(\left(\lambda_i(-\lambda_i^2+\lambda_1^2)(-\lambda_i^2+\lambda_2^2)\ldots(-\lambda_i^2+\lambda_n^2) \right) \left((-\lambda_i^2+\lambda_1^2)(-\lambda_i^2+\lambda_2^2)\ldots(-\lambda_i^2 s+\lambda_n^2) \right) \right) \\ -\left(\left(i\sqrt{s}(s+\lambda_1^2)(s+\lambda_2^2)\ldots(s+\lambda_n^2) \right) \left((s+\lambda_1^2)(s+\lambda_2^2)\ldots(s+\lambda_n^2) \right) \right)' \\ \left(\lambda_1^2(s+\lambda_1^2)\ldots\lambda_{i-1}^2(s+\lambda_{i-1}^2)\lambda_{i+1}^2(s+\lambda_{i+1}^2)\ldots \right) J_0(\lambda_i\xi) \end{array} \right\}$$

(B.113)

If we set:

$$H_{1i} = \left(\lambda_1^2(-\lambda_i^2+\lambda_1^2)\ldots\lambda_{i-1}^2(-\lambda_i^2+\lambda_{i-1}^2)\lambda_{i+1}^2(-\lambda_i^2+\lambda_{i+1}^2)\ldots \right) \quad \text{(B.114)}$$

$$\boldsymbol{H_{2i}} = \lim_{s \to -\lambda^2_i} \left(\lambda_2^{\,2}(s+\lambda_2^{\,2})\lambda_3^{\,2}(s+\lambda_3^{\,2})... + \lambda_1^{\,2}(s+\lambda_1^{\,2})\lambda_3^{\,2}(s+\lambda_3^{\,2})... + ... \right)' \quad \text{(B.115)}$$

$$\boldsymbol{H_{3i}} = \begin{pmatrix} \left(\lambda_i(-\lambda_i^{\,2}+\lambda_1^{\,2})(-\lambda_i^{\,2}+\lambda_2^{\,2})...(-\lambda_i^{\,2}+\lambda_n^{\,2}) \right) * \\ \left((-\lambda_i^{\,2}+\lambda_1^{\,2})(-\lambda_i^{\,2}+\lambda_2^{\,2})...(-\lambda_i^{\,2}s+\lambda_n^{\,2}) \right) \end{pmatrix} \quad \text{(B.116)}$$

$$\boldsymbol{H_{4i}} = \lim_{s \to -\lambda^2_i} \left(\left(i\sqrt{s}(s+\lambda_1^{\,2})(s+\lambda_2^{\,2})...(s+\lambda_n^{\,2}) \right) \left((s+\lambda_1^{\,2})(s+\lambda_2^{\,2})...(s+\lambda_n^{\,2}) \right) \right) \quad \text{(B.117)}$$

Then:

$$\beta_1 = \frac{2w^2}{\lambda_1^{\,2}\lambda_2^{\,2}...\lambda_i^{\,2}...\lambda_n^{\,2}} * \left(\frac{\left(\frac{-\xi}{2\lambda_i^{\,2}} J_1(\lambda_i\xi)H_{1i} + J_0(\lambda_i\xi)H_{2i} \right) H_{3i} - H_{4i}H_{1i}J_0(\lambda_i\xi)}{\left[H_{3i} \right]^2} \right) = \frac{2w^2}{\lambda_1^{\,2}\lambda_2^{\,2}...\lambda_i^{\,2}...\lambda_n^{\,2}} \left(K_{1i} \frac{-\xi}{2\lambda_i^{\,2}} J_1(\lambda_i\xi) + (K_{2i} - K_{3i}) J_0(\lambda_i\xi) \right) \quad \text{(B.118)}$$

Note that:

$$\frac{H_{1i}}{H_{3i}} = K_{1i} \quad \text{(B.119)}$$

$$\frac{H_{2i}}{H_{3i}} = K_{2i} \quad \text{(B.120)}$$

$$\frac{H_{1i}H_{4i}}{\left(H_{3i}\right)^2} = K_{3i} \quad \text{(B.121)}$$

From Equations (B.114) – (B.117) we can argue that K_{1i}, $K_{2i,}$ and K_{3i} are constants dependent only on λ_i.

$$\beta_2 = \lim_{s\to-\lambda_i^2} \frac{2w^2}{\lambda_1^2\lambda_2^2\ldots\lambda_i^2\ldots\lambda_n^2} * \left(\begin{array}{l} (s+\lambda_i^2)^2 \dfrac{J_0(i\sqrt{s}\xi)}{i\sqrt{s}(s+\lambda_1^2)(s+\lambda_2^2)\ldots(s+\lambda_n^2)} \\ \dfrac{\left(\lambda_2^2(s+\lambda_2^2)\lambda_3^2(s+\lambda_3^2)\ldots+\lambda_1^2(s+\lambda_1^2)\lambda_3^2(s+\lambda_3^2)\ldots+\ldots\right)}{\left((s+\lambda_1^2)(s+\lambda_2^2)\ldots(s+\lambda_n^2)\right)} \end{array} \right) \quad \text{(B.122)}$$

$$\beta_2 = \frac{2w^2}{\lambda_1^2\lambda_2^2\ldots\lambda_i^2\ldots\lambda_n^2} \left(\begin{array}{l} \dfrac{J_0(\lambda_i\xi)\left(\begin{array}{l}\lambda_1^2(-\lambda_i^2+\lambda_1^2)\lambda_2^2(-\lambda_i^2+\lambda_2^2)\ldots\lambda_{i-1}^2 \\ (-\lambda_i^2+\lambda_{i-1}^2)\lambda_{i+1}^2(-\lambda_i^2+\lambda_{i+1}^2)\ldots\end{array}\right)}{\lambda_i(-\lambda_i^2+\lambda_1^2)\ldots(-\lambda_i^2+\lambda_{i-1}^2)(-\lambda_i^2+\lambda_{i+1}^2)\ldots(-\lambda_i^2+\lambda_n^2)} \\ \left((-\lambda_i^2+\lambda_1^2)(-\lambda_i^2+\lambda_2^2)\ldots(-\lambda_i^2+\lambda_n^2)\right) \end{array} \right) \quad \text{(B.123)}$$

$$\boxed{\beta_2 = \frac{2w^2}{\lambda_1^2\lambda_2^2\ldots\lambda_i^2\ldots\lambda_n^2} \frac{H_{1i}}{H_{3i}} J_0(\lambda_i\xi) = \frac{2w^2 K_{1i}}{\lambda_1^2\lambda_2^2\ldots\lambda_i^2\ldots\lambda_n^2} J_0(\lambda_i\xi)} \quad \text{(B.124)}$$

$$\boxed{\rho_{\lambda_i}(\tau) = e^{-\lambda_i^2\tau} \left[\begin{array}{l} \dfrac{2w^2}{\lambda_1^2\lambda_2^2\ldots\lambda_i^2\ldots\lambda_n^2}\left(K_{1i} \dfrac{-\xi}{2\lambda_i^2} J_1(\lambda_i\xi) + (K_{2i}-K_{3i})J_0(\lambda_i\xi)\right) + \\ \tau \dfrac{2w^2 K_{1i}}{\lambda_1^2\lambda_2^2\ldots\lambda_i^2\ldots\lambda_n^2} J_0(\lambda_i\xi)) \end{array} \right]} \quad \text{(B.125)}$$

$$\boxed{\begin{array}{l} \rho(\tau) = L^{-1}\left\{ \dfrac{2w^2 J_0(i\sqrt{s}\xi)}{i\sqrt{s}J_1(i\sqrt{s})}\left(\sum_{n=1}^{\infty}\dfrac{1}{\lambda_n^2(s+\lambda_n^2)}\right)\right\} = \\ \left\{ \begin{array}{l} 2w^2 \dfrac{\lambda_2^4\ldots\lambda_n^4+\lambda_1^4\lambda_3^4\ldots\lambda_n^4+\ldots+\lambda_1^4\ldots\lambda_{n-1}^4}{\lambda_1^4\lambda_2^4\ldots\lambda_n^4} + \\ \quad \sum_{i=1}^{n}\left\{ \dfrac{2w^2}{\lambda_1^2\lambda_2^2\ldots\lambda_i^2\ldots\lambda_n^2} \left[\begin{array}{l} \left(K_{1i}\dfrac{-\xi}{2\lambda_i^2}J_1(\lambda_i\xi)+(K_{2i}-K_{3i})J_0(\lambda_i\xi)\right)+ \\ \tau K_{1i}J_0(\lambda_i\xi) \end{array} \right] e^{-\lambda_i^2\tau} \right\} \end{array} \right\} \end{array}} \quad \text{(B.126)}$$

Final solution

$$\Psi_1(\xi,\tau) = L^{-1}\left\{First\,Term - Second\,Term + Third\,Term\right\} =$$

$$\left\{\begin{array}{l}
\dfrac{w(4-w)}{2}\left[\left(\dfrac{1}{4.2}-\dfrac{\xi^2}{2^2}\right)-\tau\right]+ \\
\displaystyle\sum_{n=1}^{\infty}\dfrac{w(4-w)}{2}\dfrac{J_0(\lambda_n\xi)}{\lambda_n{}^2 J_0(\lambda_n)}e^{-\lambda_n{}^2\tau}- \\
w^2\left[\dfrac{1}{4^2.3}-\dfrac{1}{4}\left(\dfrac{1}{4}-\dfrac{\xi^2}{2}\right)-\dfrac{\xi^4}{4^2}+\left(\dfrac{1}{2}-\xi^2\right)\tau-2\tau^2\right]+ \\
4w^2\displaystyle\sum_{n=1}^{\infty}\dfrac{J_0(\lambda_n\xi)}{\lambda_n{}^4 J_0(\lambda_n)}e^{-\lambda_n{}^2\tau}+ \\
2w^2\dfrac{\lambda_2{}^4\ldots\lambda_n{}^4+\lambda_1{}^4\lambda_3{}^4\ldots\lambda_n{}^4+\ldots+\lambda_1{}^4\ldots\lambda_{n-1}{}^4}{\lambda_1{}^4\lambda_2{}^4\ldots\lambda_n{}^4}+ \\
\displaystyle\sum_{i=1}^{n}\left\{\begin{array}{l}\dfrac{2w^2}{\lambda_1{}^2\lambda_2{}^2\ldots\lambda_i{}^2\ldots\lambda_n{}^2} \\ \left[\left(K_{1i}\dfrac{-\xi}{2\lambda_i{}^2}J_1(\lambda_i\xi)+(K_{2i}-K_{3i})J_0(\lambda_i\xi)\right)+\tau K_{1i}J_0(\lambda_i\xi)\right]e^{-\lambda_i{}^2\tau}\end{array}\right\}
\end{array}\right\} \qquad \text{(B.127)}$$

Final solution based on Ψ_0 and Ψ_1

$$\Psi = \Psi_0 + \varepsilon\Psi_1 + \varepsilon^2\Psi_2 + \ldots$$

$$\Psi = 1 + \frac{w}{2}\left(\frac{1}{2} - \xi^2\right) - 2w\tau + \sum_{n=1}^{\infty} \frac{wJ_0(\lambda_n \xi)}{\frac{\lambda_n^{\,2}}{2} J_0(\lambda_n)} e^{-\lambda_n^{\,2}\tau} +$$

$$\varepsilon \left(\begin{array}{l} \dfrac{w(4-w)}{2}\left[\left(\dfrac{1}{4.2} - \dfrac{\xi^2}{2^2}\right) - \tau\right] + \sum_{n=1}^{\infty} \dfrac{w(4-w)}{2} \dfrac{J_0(\lambda_n \xi)}{\lambda_n^{\,2} J_0(\lambda_n)} e^{-\lambda_n^{\,2}\tau} - \\ w^2\left[\dfrac{1}{4^2.3} - \dfrac{1}{4}\left(\dfrac{1}{4} - \dfrac{\xi^2}{2}\right) - \dfrac{\xi^4}{4^2} + \left(\dfrac{1}{2} - \xi^2\right)\tau - 2\tau^2\right] + \\ 4w^2 \sum_{n=1}^{\infty} \dfrac{J_0(\lambda_n \xi)}{\lambda_n^{\,4} J_0(\lambda_n)} e^{-\lambda_n^{\,2}\tau} + \\ 2w^2 \dfrac{\lambda_2^{\,4} \ldots \lambda_n^{\,4} + \lambda_1^{\,4} \lambda_3^{\,4} \ldots \lambda_n^{\,4} + \ldots + \lambda_1^{\,4} \ldots \lambda_{n-1}^{\,4}}{\lambda_1^{\,4} \lambda_2^{\,4} \ldots \lambda_n^{\,4}} + \\ \sum_{i=1}^{n} \left\{ \dfrac{2w^2}{\lambda_1^{\,2} \lambda_2^{\,2} \ldots \lambda_i^{\,2} \ldots \lambda_n^{\,2}} \left[\begin{array}{l} \left(K_{1i} \dfrac{-\xi}{2\lambda_i^{\,2}} J_1(\lambda_i \xi) + (K_{2i} - K_{3i}) J_0(\lambda_i \xi) \right) \\ + \tau K_{1i} J_0(\lambda_i \xi) \end{array} \right] e^{-\lambda_i^{\,2}\tau} \right\} \end{array} \right) \quad \text{(B.128)}$$

Subject to:

$$J_1(i\sqrt{s}) = 0 \Rightarrow \text{ if } i\sqrt{s} = \lambda \Rightarrow \left\{\lambda_1 = 3.8317, \lambda_2 = 7.0156, \lambda_3 = 10.1735 \ldots \lambda_n\right\}$$

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