A screening assessment of solidification/stabilization for storm water residuals

Erin Ezell Krielow
Louisiana State University and Agricultural and Mechanical College, ekriell@lsu.edu

Follow this and additional works at: https://digitalcommons.lsu.edu/gradschool_theses

Part of the Civil and Environmental Engineering Commons

Recommended Citation

This Thesis is brought to you for free and open access by the Graduate School at LSU Digital Commons. It has been accepted for inclusion in LSU Master’s Theses by an authorized graduate school editor of LSU Digital Commons. For more information, please contact gradetd@lsu.edu.
A SCREENING ASSESSMENT OF SOLIDIFICATION/STABILIZATION FOR STORM WATER RESIDUALS

A Thesis

Submitted to the Graduate Faculty of the Louisiana State University and Agriculture and Mechanical College
in partial fulfillment of the Requirements for the degree of Master of Science in Civil Engineering

in

The Department of Civil and Environmental Engineering

by

Erin Krielow
B.S. in Environmental Engineering
Louisiana State University, 2001
August, 2003
ACKNOWLEDGMENTS

I would like to first thank my advisor, Dr. John Sansalone, without whom this would have never been possible. Thank you for always encouraging me to do my best and inspiring me to achieve things that I thought were impossible. I admire your curiosity and sincerely thank you for your guidance throughout this experience. A genuine thanks to the funding agencies, USEPA and UWMRC, involved in making this research happen. I would like to extend a special thanks to my committee, Dr. Frank Cartledge, Dr. Jo Dweck, and Dr. Marty Tittlebaum, for your guidance, assistance, and support throughout my research. To everyone at the Annex, Chad Cristina, Christopher Dean, Hong Lin, Teng Zheng, Zhou Ping, Eng Chong Voon, Sheng Yuhong, Carolina Pinto, Tianpeng Guo, and Gaoxiang Ying, thanks for all of the laughs, I could not have asked for a better group of people to work with. Thank you to Aimee B, roomie, colleague, aerobic dance buddy, and great friend, for always being there for me. Sincere appreciation to “the help”, Austin Richardson, Michael Markey, Natalie Magill, Will Barlett, and Chase Nettles for all of your hard work and dedication. I would like to thank my mom and dad for showing me the meaning of hard work throughout my life and always providing me with everything I have needed to be successful in my many endeavors. Thanks to my big brother for the advice and encouragement you have provided all of these years. To all of my family and friends, thank you for all of your endless support. And a special thanks to Tyler, for the love and happiness you have brought into my life and the palship and support you have provided me.
# TABLE OF CONTENTS

ACKNOWLEDGMENTS ................................................................................................ ii

LIST OF TABLES ........................................................................................................... iv

LIST OF FIGURES .......................................................................................................viii

ABSTRACT ..................................................................................................................... xii

CHAPTER 1. INTRODUCTION .................................................................................... 1
  1.1 REFERENCES............................................................................................................ 9

CHAPTER 2. GRANULOMETRIC AND CHEMICAL CHARACTERISTICS OF URBAN RAINFALL-RUNOFF RESIDUALS CAPTURED BY BMPS ........... 11
  2.1 SUMMARY .............................................................................................................. 11
  2.2 INTRODUCTION .................................................................................................. 12
    2.2.1 Regulatory Hazardous Waste Characterization .............................................. 17
    2.2.2 Solidification/Stabilization ............................................................................. 18
  2.3 OBJECTIVES ........................................................................................................ 18
  2.4 BACKGROUND ..................................................................................................... 19
  2.5 METHODOLOGY ................................................................................................ 22
    2.5.1 Experimental Sites ........................................................................................ 22
      2.5.1.1 Baton Rouge, Louisiana Site ................................................................. 22
      2.5.1.2 Little Rock, Arkansas Sites ................................................................. 23
      2.5.1.3 Cincinnati, Ohio Sites ......................................................................... 24
    2.5.2 Experimental Methods ................................................................................. 25
      2.5.2.1 QA/QC ................................................................................................. 25
      2.5.2.2 Sample Preparation .............................................................................. 26
      2.5.2.3 Particle Size Distribution (PSD) Analyses ........................................... 26
      2.5.2.4 Particle Density .................................................................................... 27
      2.5.2.5 Specific Surface Area (SSA) and Total Surface Area (SA) ................. 29
      2.5.2.6 Inorganic Constituent Determination ................................................... 31
      2.5.2.7 Power Law ........................................................................................... 34
      2.5.2.8 Surface Charge ................................................................................... 35
      2.5.2.9 Toxicity Characteristic Leaching Procedure (TCLP) ......................... 38
  2.6 RESULTS .............................................................................................................. 41
    2.6.1 Particle Size Distribution (PSD) ................................................................ 41
    2.6.2 Particle Density ($\rho_s$) ............................................................................... 43
    2.6.3 Specific Surface (SSA) and Total Surface Area (SA) .............................. 51
    2.6.4 Inorganic Constituent Determination ....................................................... 52
    2.6.5 Surface Charge ........................................................................................... 53
    2.6.6 Power Law Application to Inorganic Constituent Data ......................... 53
    2.6.7 Toxicity Characteristic Leaching Procedure .......................................... 61
  2.7 CONCLUSIONS .................................................................................................. 63
  2.8 REFERENCES ..................................................................................................... 64
CHAPTER 3. HYDRATION AND UNCONFINED STRENGTH BEHAVIOR OF
CEMENT-BASED SOLIDIFIED STORM WATER RESIDUALS

3.1 SUMMARY

3.2 INTRODUCTION

3.3 OBJECTIVES

3.4 BACKGROUND

3.5 METHODOLOGY

3.6 RESULTS

3.7 CONCLUSIONS

3.8 IMPLICATIONS

3.9 REFERENCES

3.10 NOMENCLATURE

CHAPTER 4. METAL SPECIES LEACHING FROM CEMENTITIOUS-
SOLIDIFIED RAINFALL-RUNOFF RESIDUALS
LIST OF TABLES

Table 2.1 EPA’s fresh and marine water toxicity limits for metal concentrations in fresh and marine water bodies and EPA’s 40 CFR Part 503 limits for heavy metal concentrations present in sludge and solid wastes................................................................. 32

Table 2.2 Summary of selected granulometric and inorganic constituent characteristics for residuals captured by BMPs at each experimental site.............................................. 42

Table 2.3 Comparison of textural classification fractions for BMP residuals from each of the 5 experimental sites as compared to results from particle gradations of inlet sediments of a storm water management pond studied by Marsalek et al. (1997)......................... 45

Table 2.4 Resulting $\alpha$ and $\beta$ values from the power law application to the normalized granulometric mass and the normalized metal mass data acquired from the five experimental sites..............................................................................................................60

Table 3.1 Chemical composition of cements obtained from a cement company in New Orleans, La. and utilized in the application of S/S to urban-rainfall runoff residuals captured from an experimental facility located in Baton Rouge, La. ......................... 87

Table 3.2 Material proportions utilized in preparation of S/S specimens; for both coarse and total residuals. ............................................................................................................ 98

Table 3.3 Summary of the cement density measurements and their respective standard deviations for PC = type I portland cement, SC = slag cement, and PS = 1:1 mass ratio mixture of type I portland and slag cements.............................................................................. 101

Table 3.4 Summary of elastic modulus values for UCS specimens prepared with type I Portland (PC) and 1:1 type I Portland/slag (PS) cements and the total (TR), coarse (CR), and fine (FR) gradations of residuals.............................................................................. 122

Table 4.1 Chemical composition of the base cement powders utilized in the S/S treatment of the storm residuals. The Lone Star Cement Kiln located in New Orleans, Louisiana provided the composition data.................................................. 155

Table 4.2 Designated material proportions utilized in preparation of bulk S/S material. .......................................................................................................................... 157

Table 4.3 EPA regulatory limits assessed to the treated and untreated rainfall-runoff residual waste............................................................................................... 164

Table 4.4 TCLP extract metal concentrations leached from untreated total, coarse and fine gradations of residuals. .............................................................................. 172
Table 4.5 Cd, Cu, Pb, and Zn metals concentrations in µg/L leached by the pure cement control samples during TCLP. ................................................................. 176

Table 4.6 Concentrations of Cd, Cu, Pb, and Zn in µg/L leached from the type I portland cement (PC) treated total and coarse fractions of the rainfall-runoff residuals. .......... 177

Table 4.7 Concentrations of Cd, Cu, Pb, and Zn in µg/L leached from the slag cement (SC) treated total and coarse fractions of the storm residuals. ................................. 178

Table 4.8 Concentrations of Cd, Cu, Pb, and Zn in ppb leached from the 1:1 type I portland slag cement (PS) treated total and coarse fractions of the storm residuals. ..... 179

Table 4.9 Metal mass leached from untreated residuals through TCLP and total metal mass associated with each gradation determined in the characterization study of the residuals with the fp values that represent the percent of the total metal mass leached during TCLP. .................................................................................................................. 180

Table 4.10 fR calculations in (%) for PC S/S application to the TR, CR, and FR rainfall-runoff solids and the final extract pH measurements. ........................................ 181

Table 4.11 fL calculations in (%) for the slag cement (SC) S/S application to the total and coarse gradations of rainfall-runoff solids and the final extract pH measurements following the rotation period of the TCLP. ................................................. 182

Table 4.12 fL calculations in (%) for the 1:1 mass ratio of type I portland cement to slag cement (PS) S/S application to the total and coarse gradations of rainfall-runoff solids and the final extract pH measurements following the rotation period of the TCLP. .... 183
LIST OF FIGURES

Figure 2.1 Flow chart for the determination of the proper extraction fluid to use for TCLP ........................................................................................................................................... 40

Figure 2.2 Particle size distributions (PSD) on a mass basis for BMP sites. $M_s =$ total gradation dry mass. ........................................................................................................................................... 44

Figure 2.3 Granulometric and metal distributions for residuals captured by I-10 site BMPs (settling basin and filter). Total gradation, $SA (m^2)$ and mass (mg) of Pb, Cu, Cd, and Zn are each on 1000.0 g basis. Cumulative axes are 0 to 100% of total gradation SA or metal mass (based on 1000.0 g). Total gradation metal mass shown in plots............. 46

Figure 2.4 Granulometric and metal distributions for residuals captured by I-30-I-40 site BMPs (settling basin and filter). Total gradation, $SA (m^2)$ and mass (mg) of Pb, Cu, Cd, and Zn are each on 1000.0 g basis. Cumulative axes are 0 to 100% of total gradation SA or metal mass (based on 1000.0 g). Total gradation metal mass shown in plots............. 47

Figure 2.5 Granulometric and metal distributions for residuals captured by HD-NLR site BMPs (settling basin and filter). Total gradation, $SA (m^2)$ and mass (mg) of Pb, Cu, Cd, and Zn are each on 1000.0 g basis. Cumulative axes are 0 to 100% of total gradation SA or metal mass (based on 1000.0 g). Total gradation metal mass shown in plots............. 48

Figure 2.6 Granulometric and metal distributions for residuals captured by BH-12 site BMPs (settling basin and filter). Total gradation, $SA (m^2)$ and mass (mg) of Pb, Cu, Cd, and Zn are each on 1000.0 g basis. Cumulative axes are 0 to 100% of total gradation SA or metal mass (based on 1000.0 g). Total gradation metal mass shown in plots............. 49

Figure 2.7 Granulometric and metal distributions for residuals captured by 1-SE site BMPs (settling basin and filter). Total gradation, $SA (m^2)$ and mass (mg) of Pb, Cu, Cd, and Zn are each on 1000.0 g basis. Cumulative axes are 0 to 100% of total gradation SA or metal mass (based on 1000.0 g). Total gradation metal mass shown in plots............. 50

Figure 2.8 Surface charge trends as a function of pH (left and bottom axes of each plot) and point of zero charge (pzc-pH) trends as a function of gradation (right and upper axes of each plot) for rainfall-runoff residuals captured by the I-10 site BMPs (settling basin and filter). Data symbols represent mean of replicate analyses and range bars represent standard deviations of replicates....................................................................................... 54

Figure 2.9 Surface charge trends as a function of pH (left and bottom axes of each plot) and point of zero charge (pzc-pH) trends as a function of gradation (right and upper axes of each plot) for rainfall-runoff residuals captured by the I-30-I-40 site BMPs (settling basin and filter). Data symbols represent mean of replicate analyses and range bars represent standard deviations of replicates. ....................................................................................... 55
Figure 2.10 Surface charge trends as a function of pH (left and bottom axes of each plot) and point of zero charge (pz-c-pH) trends as a function of gradation (right and upper axes of each plot) for rainfall-runoff residuals captured by the HD-NLR site BMPs (settling basin and filter). Data symbols represent mean of replicate analyses and range bars represent standard deviations of replicates. .......................................................... 56

Figure 2.11 Surface charge trends as a function of pH (left and bottom axes of each plot) and point of zero charge (pz-c-pH) trends as a function of gradation (right and upper axes of each plot) for rainfall-runoff residuals captured by the BH-12 site BMPs (settling basin and filter). Data symbols represent mean of replicate analyses and range bars represent standard deviations of replicates.......................................................... 57

Figure 2.12 Surface charge trends as a function of pH (left and bottom axes of each plot) and point of zero charge (pz-c-pH) trends as a function of gradation (right and upper axes of each plot) for rainfall-runoff residuals captured by the 1-SE site BMPs (settling basin and filter). Data symbols represent mean of replicate analyses and range bars represent standard deviations of replicates.......................................................... 58

Figure 2.13 Inorganic constituent data for the five experimental sites to fit to power law distributions using normalized metal and particle masses................................................ 59

Figure 2.14 Plots of metal concentration [µg/L] from acid-digested residuals (sampled from I-10E BMP) as a function of residual particle size. Inset figures illustrate TCLP extract metals concentrations [µg/L] for the I-10E BMP residuals to EPA fresh water chronic toxicity limits for Cd, Cu, Pb, and Zn, and TCLP limits for Cd and Pb.............. 62

Figure 3.1 Schematic of the experimental set-up for the non-conventional DTA analyses. ......................................................................................................................... 95

Figure 3.2 Schematic of a sample and the polystyrene insulation cradle associated with the sample. ............................................................................................................. 96

Figure 3.3 PSDs of cements and cement/slag mixtures in ethyl alcohol as a function of time and particle diameter analyzed using laser diffraction. .............................................. 100

Figure 3.4 TG and DTG plots of the Type I Portland cement paste (PC) without waste addition after 1, 5, and 24 hours of hydration................................................................. 103

Figure 3.5 TG and DTG plots for the slag cement paste (SC) without waste addition after 1, 5, and 24 hours of hydration. ................................................................. 104

Figure 3.6 TG and DTG plots for the 1:1 mass ratio mixture of type I Portland cement and slag cement (PS) without waste addition after 1, 5, and 24 hours of hydration...... 105
Figure 3.7 TG and DTG of the type I Portland cement (PC), slag cement (SC), and 1:1 mass ratio mixture of type I Portland and slag cement (PS) pastes without waste addition after 4 weeks of hydration.......................................................... 108

Figure 3.8 Results of the non-conventional DTA (NCDTA) analyses and total evolved heat for the experimental cements without waste addition prepared with a water to cement ratio of 0.5. ........................................................................................................ 110

Figure 3.9 Temperature difference between the reference temperature and the actual temperature within the reacting samples over 24 hours for hydration of PC stabilized specimens. Control specimens contained only PC and no residuals; compared to stabilized residual specimens that contained 10, 20, or 30% PC. Residual specimens contained either fine residuals <75 \( \mu m \) (FR), coarse residuals >75 \( \mu m \) (CR) or total residuals (TR) representing the entire gradation.......................................................... 111

Figure 3.10 Temperature difference between the reference temperature and the actual temperature within the reacting samples over 24 hours for hydration of SC stabilized specimens. Control specimens contained only PS and no residuals; compared to stabilized residual specimens that contained 10, 20, or 30% SC. Residual specimens contained either coarse residuals >75 \( \mu m \) (CR) or total residuals (TR) representing the entire gradation. .................................................................................................................. 112

Figure 3.11 Temperature difference between the reference temperature and the actual temperature within the reacting samples over 24 hours for hydration of PS stabilized specimens. Control specimens contained only PS and no residuals; compared to stabilized residual specimens that contained 10, 20, or 30% PS. Residual specimens contained either fine residuals <75 \( \mu m \) (FR), coarse residuals >75 \( \mu m \) (CR) or total residuals (TR) representing the entire gradation..................................................................................... 113

Figure 3.12 Heat evolved over 24 hours for hydration of PC stabilized specimens. Control specimens contained only PC and no residuals; compared to stabilized residual specimens that contained 10, 20, or 30% PC. Residual specimens contained either coarse residuals >75 \( \mu m \) (CR) or total residuals (TR) representing the entire gradation. .......................................................... 114

Figure 3.13 Heat evolved over 24 hours for hydration of SC stabilized specimens. Control specimens contained only SC and no residuals; compared to stabilized residual specimens that contained 10, 20, or 30% PC. Residual specimens contained either coarse residuals >75 \( \mu m \) (CR) or total residuals (TR) representing the entire gradation. ........... 115

Figure 3.14 Heat evolved over 24 hours for hydration of PS stabilized specimens. Control specimens contained only PS and no residuals; compared to stabilized residual specimens that contained 10, 20, or 30% PC. Residual specimens contained either coarse residuals >75 \( \mu m \) (CR) or total residuals (TR) representing the entire gradation. ......... 116

Figure 3.15 UCS test and elastic modulus (E) results for 7 day cures of type I portland cement (PC) additions to the total and coarse gradations of residuals. ......................... 123
Figure 3.16 UCS test and elastic modulus (E) results for 28 day cures of type I portland cement (PC) additions to the total and coarse gradations of residuals. ........................................ 124

Figure 3.17 USC test and elastic modulus (E) results for the 7-day cures of 1:1 type I portland/slag cement (PS) additions to the total and coarse gradations of residuals. ..... 125

Figure 3.18 UCS test and elastic modulus (E) results for 28-day cures of 1:1 type I portland/slag cement (PS) additions to the total and coarse gradations of residuals. ..... 126

Figure 3.19 UCS test results for 7-day and 28-day cures of type I portland cement (PC) control samples followed by merged plots of all 7-day and 28-day cures of PC based samples............................................................................................................................ 128

Figure 3.20 UCS test results for 7-day and 28-day cures of 1:1 type I portland/slag cement (PS) control samples followed by merged plots of all 7-day and 28-day cures of PS based samples. ......................................................................................................................... 129

Figure 4.1 Granulometric and selected metal distributions for the I-10E site storm water residuals. Total SA and total mass of Pb, Cu, Cd, and Zn are each on a 1000.0 g basis. Cumulative axes are 0 to 100%. ......................................................................................................................... 165

Figure 4.2 Cd [µg/L] in TCLP extracts for specimens prepared with total (TR) and coarse gradations (CR) of residuals with 10, 20, and 30% by mass additions of type I portland cement (PC), slag cement (SC) and a 1:1 mass ratio mix of type I portland to slag cement (PS) additions, and 28d cured specimens prepared with the fine gradation of residuals (FR) with 10, 20, and 30% by mass additions of PC (SC and PS were not tested with the FR, due to a lack of residuals). .............................................................................. 167

Figure 4.3 Cu [µg/L] in TCLP extracts for 7d and 28d cured specimens prepared with TR and CR with 10, 20, and 30% by mass additions of PC, SC and PS additions, and 28d cured specimens prepared with the FR with 10, 20, and 30% by mass additions of PC (SC and PS were not tested with the FR, due to a lack of residuals). .............................................. 168

Figure 4.4 Pb [µg/L] in TCLP extracts for 7d and 28d cured specimens prepared with TR and CR with 10, 20, and 30% by mass additions of PC, SC and PS additions, and 28d cured specimens prepared with the FR with 10, 20, and 30% by mass additions of PC (SC and PS were not tested with the FR, due to a lack of residuals). ................. 169

Figure 4.5 Zn [µg/L] in TCLP extracts for specimens prepared with TR and CR with 10, 20, and 30% by mass additions of PC, SC, and PS (cure = 7d and 28d), and specimens prepared with FR with 10, 20, and 30% by mass additions of PC (cure = 28d)(SC and PS were not tested with the FR, due to a lack of residuals). ........................................ 170
ABSTRACT

Metal species infused particulate matter associated with urban rainfall-runoff is a unique and profuse source of pollution. Generated from urban activities, such as traffic activity and vehicular/infrastructure abrasion, contaminated residual material is deposited to roadways during dry weather and transported to surrounding environments and/or best management practice (BMP) treatment facilities during wet-weather events. These particulates range in size from 1 µm to 10000 µm and are contaminated with metal species that originate from such sources as vehicular body wear (Cu), tire wear (Zn), and brake dust (Pb). Depending on the efficiencies of the BMP treatment facilities, these containment systems have the potential to be an abundant source of solid and potentially hazardous waste.

Rainfall-runoff residual matter was collected from five urban BMP sites and characterized for granulometric indices. The sites were located in Baton Rouge, LA, Little Rock, AR, North Little Rock, AR, and Cincinnati, OH. The residual matter collected from the five BMP sites was characterized as a function of particle size for particle mass, particle size distribution (PSD), particle density ($\rho_s$), total surface area (SA), specific surface area (SSA), and metal species contamination. This characterization study showed that the majority of the metal species mass contamination is associated with the coarse to mid-sized range of particles with large amounts of SA, while the predominance of metal species concentration contamination is found in the fine particulates with high SSA.
Cement-based solidification/stabilization (S/S) was applied to residual matter recovered from the BMP facility located in Baton Rouge, LA, using three cement types. Cement-based S/S has been used in the treatment of a wide range of metal contaminated wastes, but there is no record of the technology being applied to rainfall-runoff residuals. Three gradations (total (entire gradation), coarse (> 75 μm), and fine (< 75 μm)) of rainfall-runoff residuals were treated using a type I portland cement (PC), a slag cement (SC), and a 1:1 mass ratio of type I portland cement and slag cement (PS). An assessment of the solidification of the treated residuals was made using techniques to analyze the hydration behavior and physical strength and the leaching potential of the untreated and treated residuals was assessed in order to determine the stabilization effectiveness of the S/S application to the rainfall-runoff residuals.
CHAPTER 1. INTRODUCTION

Changing demographics favoring the increase in urban and suburban populations have resulted in the significant increase in vehicular transportation and commensurate increases in vehicular/infrastructure pollutant generation. Expansion of transportation and urban land uses that result from urbanization introduce more impervious surfaces these constructed environs. These impervious surfaces act as efficient conveyors of pollutant mass when subject to rainfall-runoff. These pollutants such as metal species partition between the aqueous and particulate-bound phase in the urban environs as a function of time. Rainfall-runoff transports these particulate-bound pollutants (entrained with aqueous phase) pollutants to terrestrial and aquatic environments.

From these urban and suburban land uses, rainfall-runoff from pavements and major arterial roadways has the most impact on surrounding urban terrestrial and water environments. Due to the vehicular pollutant generation and the interaction between vehicles and infrastructure, rainfall-runoff from pavements and arterial roadways transports significant loads of particulate matter, contaminated in particular with metals. A significant fraction of this contaminated particulate matter originates from the abrasive interaction between vehicular components and infrastructure. Many vehicular components are coated with Zn-galvanizing. The Zn galvanizing process also utilizes Cd, therefore both Zn and Cd are common in transportation land use runoff. Other metals generated by such activities and transported in rainfall-runoff include lead (Pb) originating from tetraethyl lead in gasoline and abrasion of brake pads, cadmium (Cd) derived from diesel oil and tire abrasion, and copper (Cu) generated by wear of bearings, bushings, brake linings and corrosion of wires (Amrhein et al. 1990; Amrhein et al. 1992;
Glenn et al. 2002). These metals are leached from abraded material deposited in the right-of-way, leached from infrastructure or partitions to and from particulate matter in rainfall-runoff.

In receiving waters and in surficial soils and sediments, both aqueous and particulate-bound metals detrimentally influence the aesthetic and functional values of the environment. Metal pollutants impose toxic conditions on urban terrestrial and aquatic environments. Metals, such as Cd, Cu, Pb and Zn that arise from transportation activities, industrial operation, deteriorating infrastructure, leaching, and other sources, can be toxic to organisms in these environments (Mason 1991). The metal-containing transportation land use rainfall-runoff discharges impact the biological integrity of the receiving water bodies, particularly the abundance and diversity of flora and fauna (Chocat et al. 2001). Rainfall-runoff impacts to these water bodies also impairs beneficial uses, such as potable water supply, fishing, aesthetic qualities, as well as the quality of the urban landscape with respect to recreation (Chocat et al. 2001). Other adverse impacts of urban rainfall-runoff on urbanized areas include flooding, erosion, dissolved oxygen depletion and nutrient enrichment of urban waterways (Marsalek et al. 2002a).

Urban rainfall-runoff discharges have attracted the focus of regulatory agencies for over the last two decades in the USA. In 1987, the 1972 Clean Water Act was amended to include the National Pollutant Discharge Elimination System (NPDES), a national program to address storm water discharges. Under the NPDES Phase II regulations, rainfall-runoff discharge permits are required for all municipalities in urbanized areas with populations greater than 100,000 unless the NPDES permitting authorities specify otherwise (EPA 1999). The implementation of the NPDES by the EPA
has served as a means of designating and controlling pollutant sources from rainfall-runoff as well as providing an initial line of defense for our nation’s water quality.

Due to regulatory implementation of NPDES Phase II, innovative treatment technologies will be developed and various control and treatment strategies will be implemented. Based on addressing NPDES Phase I requirements, rainfall-runoff management systems have been applied sometimes as “treatment trains”, which represent a sequence of control and treatment measures, and are referred to as best management practices (BMPs) (Marsalek et al. 2002b). A BMP is a structural or non-structural measure employed in storm water management, for storm water quantity and/or quality control (Marsalek et al. 2002b). Many BMPs that have been developed incorporate detention or retention basins that serve to contain the runoff. In these basins, the runoff is clarified and particles entrained in the runoff are settled out through sedimentation. Other BMPs integrate some form of filtration to remove particulate matter. In order to ensure the continued BMP viability, these sedimentation and filtration systems must be maintained and particulate matter left from the treatment of the rainfall-runoff (residual material) removed periodically and managed.

The residual material associated with urban rainfall-runoff exists in significant quantities. Annual volumes of rainfall-runoff particulate matter exceed sludge volumes generated from either municipal wastewater or combined sewer overflow (CSO) treatment (Field et al. 1994). The amount of potential residuals (particulate matter captured by full implementation of BMPs for a given urban area) generated by rainfall-runoff for an urban area can be estimated based on land use determination (i.e. area of major arterial roadway pavement), annual rainfall, runoff volumes and constituent loads
for a given metropolitan area. For example, for a metropolitan area with a population of 2 million, a major arterial roadway area of 40 km$^2$, a mean annual rainfall of 1000 millimeters, a volumetric runoff coefficient of 0.7, the total volume of runoff is $2.8 \times 10^6$ for the 40 km$^2$ only. With an average rainfall-runoff total suspended solids loading from this land use of 400 mg/L (Sansalone et al. 1998), the total solid content entrained in the storm water is calculated to be $1.1 \times 10^6$ kg of dry solids. Due to the quantities of these solids and metals associated with these solids, these solids also present a concern as a potential solid hazardous material when trapped as residuals (Sansalone and Buchberger 1997).

The characterization process involved in defining a material or waste as hazardous includes three steps. Initially, one should determine if the waste is excluded from hazardous waste regulation by reviewing the code of federal regulations (40 CFR Part 261). If the waste is not excluded by regulation, then the next step is to determine whether or not the waste is specifically listed by regulation as hazardous. Those hazardous wastes listed include wastes from specific and non-specific sources, discarded commercial chemical products, and mixtures of wastes that are known to contain a listed hazardous waste (regardless of relative quantities). The final step for a waste or a material to be considered hazardous requires that a waste must exhibit certain characteristics of a hazardous waste outlined by EPA’s code of federal regulations (40 CFR Part 261). The four specified characteristics that are used to characterize wastes as hazardous are ignitability, corrosivity, reactivity, and toxicity. A waste is considered to have ignitability if its flashpoint is less than 140 °F (60 °C). The waste is considered corrosive if its pH is less than 2 or greater than 12. If the waste is unstable under normal conditions, it is
considered reactive and if the waste leaches toxic chemicals in excess of regulatory levels, then it is considered toxic.

The primary characteristic that defines a hazardous waste is determination of the waste’s toxicity. The toxicity associated with a waste is evaluated by performing the Toxicity Characteristic Leaching Procedure (TCLP). Designed to determine the availability of both organic and inorganic constituents present in a waste, the TCLP is an extraction test that results in the creation of a leachate comparable to what would be produced by the waste in the environment (EPA SW-846 Method 1311, 1992). The resulting TCLP extract is analyzed for metals, including Cd, As, Cr, and Pb. The concentrations of these chemicals found in the sample are then evaluated against regulatory levels to determine whether the waste exhibits the Toxicity Characteristic (TC). If a waste exhibits the TC, then it is designated by the waste code associated with the chemical that exceeded the regulatory levels (EPA 2001). In the case that a waste is considered hazardous, precautions must be taken in handling the waste and treatment must be applied before disposal.

Solidification/Stabilization (S/S) is a widely applied treatment for the management and disposal for many wastes and is one of the most popular technologies for treating and disposing of hazardous wastes (Park 2000). S/S processes were first applied to radioactive waste and have since been utilized in the United States for over fifty years (Wilk 1999). Combinations of solidification and stabilization (S/S) have been and still are applied to: 1) the remediation of hazardous waste sites; 2) the treatment of residue from other treatment processes; and 3) the treatment of contaminated land where large quantities of soil containing contaminants are encountered (LaGrega et al. 1994).
Evaluations of S/S applications have demonstrated that S/S may be suited for the treatment of contaminated rainfall-runoff residuals captured by treatment BMPs and polluted land embankment soils alongside heavily trafficked transportation networks. Also, another reason for choosing S/S as an applicable treatment strategy for the metal enriched rainfall-runoff residuals is because S/S is frequently the technology of choice for immobilizing soils and sludges containing one or more metal contaminants (Means et al. 1995).

Solidification and stabilization have different treatment goals and can be defined individually. The solidification and stabilization of a waste occurs by means of physical and chemical processes, respectively. Solidification refers to those techniques that focus on the containment of hazardous components by enhancing the physical characteristics of the waste. In solidification processes, the hazardous constituents do not necessarily chemically react with reagents, but are instead mechanically locked, or encapsulated, within the solidified matrix (EPA 1986). The processes of stabilizing the chemicals present in the waste involve a chemical reaction between the chemical and constituents of the binder added to treat the waste. By adding materials that ensure that the contaminants are kept in their least mobile and non-toxic forms, such as addition of lime or sulfide to a metal contaminated waste, the stabilization mechanisms encourage the precipitation and immobilization of the metal ions (EPA 1986; Roy et al. 1992). The solidification and stabilization processes are designed together in order to accomplish one or more of the following objectives: 1) reduce the contaminant mobility or solubility; 2) improve the handling and physical characteristics of the waste by producing a solid with no free
liquid; 3) decrease the exposed surface area across which transfer or loss of contaminants may occur (Means et al. 1995).

The most widely applied S/S technology incorporates the use of a cement-based binder. Cement is most often chosen as the binder to be applied in S/S because of its ability to reduce the permeability of the waste form, encapsulate waste particles by surrounding them with an impermeable coating, and chemically bind free liquids and fix hazardous constituents by reducing their solubility (Wilk, 1990). Cement-based S/S has been applied successfully to many metallic wastes containing such metals as Cd, Cu, Pb, Ni, and Zn, as well as complex wastes containing oils, vinyl chloride, asbestos and other materials (Barth et al. 1990).

In a cement-based application of S/S, a cement or pozzolanic binder is added to the waste and is allowed to stiffen through hydration over time. During the stiffening of the matrix, the wastes are incorporated into the cement matrix and undergo physical and chemical changes that serve to immobilize the pollutants and successfully encapsulate the waste. The highly alkaline nature of the cement binder allows the metals to precipitate as their respective insoluble hydroxides given that the pH at which most metals reach their lowest solubility is 10 (Patterson 1985). In this precipitation mechanism of cement-based S/S, the metal hydroxides are immobilized in the dense cementitous matrix where the ionic transport is decreased as a result of the reduction in the porosity and permeability of the matrix (EPA 1989). Also occurring in cementitous applications of S/S is the encapsulation of chemicals within the crystalline structure of the binder, where the chemicals are trapped within the S/S material and cannot be released to the environment. Depending on the chemical constituents of the waste stream and the binder, the S/S
treatment may permanently reduce toxicity and/or water solubility of hazardous chemicals and create a monolithic waste form that limits chemical mobility due to its low permeability and small surface area (Akhter et al. 2000).

Urban rainfall-runoff impacted residues and soils were treated in this research using cementitious S/S and the effectiveness of the treatment application was physically and chemically tested. Many physical and chemical methods have been developed for the efficiency testing of S/S applications. The physical tests are utilized to evaluate the solidification success of the S/S and have been used to differentiate strength attributes of different binders, to determine compliance with performance objectives, to establish material handling characteristics, and to select large-scale equipment (Means et al. 1995). The chemical testing of the S/S material involves leaching and extraction tests that are used to assess the stabilization efficiency of the treatment application. In the case of the rainfall-runoff residuals, the physical strength and toxic leaching of the resulting material was of most interest. The physical strength of the material was tested using an unconfined compressive strength testing method commonly used in the strength assessment of S/S material and the TCLP leaching test was utilized to evaluate the leaching potential of the material.

With the knowledge of the strength characteristics and leaching potential of the S/S treated storm water solid waste, the industrial utilization of the material can be assessed. The characterization of the physical and leaching properties of the treated waste can also provide a benchmark for further optimization for the S/S material to possibly be used for other large-scale functions. The removal of this rainfall-runoff waste
from the environment and the potential applicability of its cost-effective cementitious
treated form would be beneficial to both the environment and the economy.

1.1 REFERENCES

Contaminated Soils I: Soil Characterization.” J. Environ. Eng., 126(11), 999-
1003.


organic matter mobilization in roadside soils.” Environ. Sci. Technol., 26, 703-
709.


redefined from storm water removal to integrated management.” Water Science
and Technology 43(5): 61-68.

Stabilization/Solidification of Hazardous Wastes.” pp. 1-1 – 8-3

Environmental Protection Agency. (1989). “Stabilization/Solidification of CERCLA and
RCRA Wastes, Physical Test, Chemical Testing Procedures, Technology
Screening, and Field Activities.” EPA/625/6-89/022.

treatment of urban storm water runoff from separate storm drainage systems.”

associated with snow exposed to urban traffic and winter storm maintenance


storm water impacts on an urban stream with a detention pond.” Water Science
and Technology 45(3)


CHAPTER 2. GRANULOMETRIC AND CHEMICAL CHARACTERISTICS OF URBAN RAINFALL-RUNOFF RESIDUALS CAPTURED BY BMPS

2.1 SUMMARY

Most urban rainfall-runoff best management practices (BMPs) provide varying degrees of quantity and quality control either by design or unintentionally. Anthropogenic solids captured by such BMPs represent a mass of residuals that must be managed on a scale equivalent to that of wastewater solids. However, the physical and chemical characteristics of these residuals are fundamentally different than biosolids and therefore residuals control strategies will be different. This study examines such characteristics as they influence the fate and management of residuals and associated metal elements. Five urban sites with common BMPs (detention, filters, vegetated swales, porous pavement) were investigated. The \( d_{50m} \) for residuals from all sites ranged from 149 - 1153 \( \mu m \) and the entire gradation range was from \(-1 \mu m\) to \(+10,000 \mu m\). While residual mass distributions were dominated by the coarse fraction (\( > 75 \mu m \)), specific surface area (SSA) generally increased with decreasing particle size. Over 80% of the total surface area (SA) was associated with the fraction of the gradation \( > 75 \mu m \) for all BMPs. Specific gravity of residuals ranged from 1.8 to 2.8 with no consistent trend across the gradation or between coarse and fine fractions separated at 75 \( \mu m \). For all BMP sites over 80% of the metal mass was associated with residuals larger than 75 \( \mu m \), with the exception of one BMP whose trend was similar to other BMPs but at a 60% level of metal mass. Point of zero charge (pzc-pH) values ranged from 6 to 9 with either a slightly increasing pzc-pH with increasing particle size or with a relatively constant pzc-pH. A power law model relating cumulative granulometric mass to residual metal mass was developed and successfully applied for residuals from each site BMP. While metal concentrations on these
residuals exceeded freshwater discharge limits, occasionally exceeded 503 limits the TCLP limits were not exceeded at any site for any metal. Results suggest that residuals must be controlled with a long-term management plan, otherwise unmanaged disposal of these residuals can result in chronic metal loadings to the receiving environment.

2.2 INTRODUCTION

The growth of urban populations and the commensurate increase in infrastructure and motor vehicle transportation over the last 100 years have caused an increase in the generation and delivery of anthropogenic constituents such as metals and particulates. Surface transportation infrastructure such as pavement systems alters the natural infiltration capability of the soil and also generates anthropogenic constituents from interaction with urban activities. Consequences include changes to rainfall-runoff hydrology, local climate changes, and increased delivery of anthropogenic constituent mass to the urban atmosphere and receiving waters (U.S. EPA 1992). Urban roadways and transportation land use corridors are a significant fraction of the impervious surfaces associated with the urban watersheds that result from urbanization. According to previous research, urban rainfall runoff degrades the water quality of urban water bodies at such low levels of imperviousness as 10 to 20 percent (May et al. 1997). Urban and motor vehicle transportation activities generate significant loads of metals particulates, organics and pathogens that accumulate along roadways and are transported through the rainfall-runoff process to surface soils, receiving waters or to storm water control strategies. The rainfall intensity, runoff rate, and storm duration can affect the amount and type of contaminants removed from pavement surfaces and transported to surrounding environs (Wanielista and Yousef 1993).
Aqueous and particulate-bound metals in rainfall-runoff have their origin from a number of transportation and urban sources. These sources commonly generate Zn, Cd, Cu and Pb, which are commonly identified in rainfall-runoff studies from these land uses (Sansalone and Buchberger 1997). Specific sources of these metals include abrasion of automotive parts; specifically, Cu is associated with thrust bearings, bushings, and brake linings, and Zn and Pb are linked to motor oil (Novotny and Chester 1981). Cu depositions result from the abrasion and wear of the automotive bearings, bushings and brakes. The Zn and Pb pollutants originating from motor oil is deposited directly from vehicles onto roadway surfaces. Other metals identified in rainfall-runoff include Cr, which originates in brake linings and metal plating of guardrails and automobile parts, and Ni, which also originates from brake linings (Novotny and Chester 1981; EPA 1995a). The Cr constituents deposited to urban surfaces are a result of the wear of automotive brake linings and the leaching of the metal plating from the guardrails and vehicular components. Sources of Pb and Zn from fuel exhaust particulates have also been well established in studies (Purohit et al. 2001).

Previous research characterized influent classes of anthropogenic particles as suspended ($d_{50m} < \approx 10$ to 25 µm, $\rho_s = 2.40$ to 2.50), settleable ($d_{50m} = \approx 25$ to 75 µm, $\rho_s = 2.40$ to 2.50) and sediment ($d_{50m} > 75$ µm, $\rho_s = 2.50 – 2.70$) particles captured by rainfall-runoff best management practices, BMPs (Lin and Sansalone 2003). These solids, usually managed as a high solid content sludge (> 10%) represent a significant volume of “residual” solid-phase material that must be managed as a solid waste or as a hazardous waste. The sources of the runoff residual solids include abraded particulate material, abraded vehicular-pavement material as well as particles from atmospheric deposition that include combustion and other by-products from vehicles (Thomson et al. 1997; Bent et al. 2001). Land
embankment soils along side highways; especially those located in urbanized and industrial areas represent a significant source of residual solid material loaded by rainfall-runoff (USEPA 1999a, Sansalone et al. 1998). Urban land-use soils are directly loaded by runoff from urban surfaces and are thus contaminated with the metals that are generated by traffic activity. Metals, such as Pb and Cu, have very low solubilities at natural pH levels and these metals are readily removed by sedimentation, surface complexation processes, or chemical precipitation in the surface layers of soils, such as those existing in the urban land embankments (Hampson 1986). The metals associated with the residual solid material that is trapped in BMPs are treated and removed from the environment, but the metals that are sorbed to the surface layers of the soils that exist in urban environments and are proximate to pavement surfaces remain in the environment and require treatment.

In all cases, the residual solids in rainfall-runoff are either deposited to surrounding soil or aqueous environments, diverted to drainage facilities for quantity control or treatment BMPs that are utilized for water quality control. The untreated metal-contaminated solid material deposited to soil and aqueous environments impacts the biota present in the surrounding eco-system. Different contaminants have varying biological effects depending on the physical and chemical properties of each constituent, the concentrations present in the environment, the sensitivities of biota to adverse physical and chemical characteristics of the rainfall-runoff, and the ability of the system and the individual organism to assimilate a given constituent or a given mixture of constituents (Buckler and Granato 1999). One mechanism by which metal contaminants cause toxicological problems in biota is known as isomorphic substitution, where an element substitutes for another but may not be able to serve the same function for the biota (Buckler and Granato 1999).
In the event that the rainfall-runoff is diverted to BMP facilities, the residual material is captured and managed. Variations of most rainfall-runoff BMPs in common use (detention, filtration, settling) collect and temporarily store rainfall-runoff, promoting particle separation, or these BMPs utilize unit operation/process mechanisms to improve water quality. In order to maintain the effectiveness of the BMPs, periodic maintenance is required, including handling and disposal of the accumulated residual matter.

The annual volume of rainfall-runoff runoff residuals resulting from BMP treatment techniques can equal or exceed sludge volumes generated from municipal wastewater or combined sewer overflow (CSO) treatment (Field and O’Shea 1993). The annual sludge volume associated with combined sewer overflow (CSO), based on a combined sewer area of 2.25x10^6 acres, average storm runoff of 16.5 in/yr (419 mm/yr) (Heany et al. 1977; Field and O’Shea 1993) and treatment process efficiency ratios of 0.3-6 % volume sludge/influent flow (Huibregste et al. 1982; Field and O’Shea 1993), is 11 - 228 x10^6 m^3 with average percent solids of 0.7-3.2 (Gupta et al. 1977; Field and O’Shea 1993). In the case of urban rainfall-runoff, annual sludge volumes are 27 – 547 x10^6 m^3 with 0.5-12 average percent solids (Gupta et al. 1977; Field and O’Shea 1993) based on a combined sewer area of 5.99x10^6 acres, average storm runoff of 14.8 in/yr (376 mm/yr) (Heany et al. 1977; Field and O’Shea 1993) and treatment process efficiency ratios of 0.3-6 % volume sludge/influent flow (Huibregste et al. 1982; Field and O’Shea 1993). In addition to these entrained residuals captured by BMPs, the soils adjacent to pavements also represent a significant sink for residual solids associated with rainfall-runoff. Both the residual solids and adjacent soils represent significant sinks for transportation land use constituents such as metal elements (Teng et al. 2002). Residuals in these soil-residual complexes represent a wide gradation of
metal enriched particulate matter ranging in size from smaller than 1 µm to greater than 10,000 µm (Sansalone et al. 1998).

With respect to the capture of rainfall-runoff solids by BMPs, a simple calculation can be carried out for a single land use; in this example transportation land use. Assume a urban population of $10^5$ in an urban area with total interstate pavement area of 40 km$^2$. Assume annual rainfall of 1000 mm and a volumetric runoff coefficient, C, equal to 0.7. Runoff volume based on these assumptions is $28 \times 10^9$ L. Suspended solids concentrations (exclusive of settleable and sediment fractions) in rainfall-runoff from this land use is approximately 200 mg/L (Sansalone and Buchberger 1997, Sansalone et al. 1998) This 40 km$^2$ generates $5.6 \times 10^6$ kg of suspended solids (dry basis) or $14 \times 10^6$ m$^3$ annually assuming a porosity ($\eta$) of 0.50 and full capture of all runoff residuals. For this magnitude of volume landfills do not have the capacity to accommodate the disposal of this solid or hazardous waste (Mulligan et al. 2001).

Periodic maintenance of rainfall-runoff BMPs and removal of accumulated residual materials from these treatment systems is necessary to keep the treatment systems operating effectively. Residual material that is removed from these BMPs must be handled and disposed of properly. The residuals must first be assessed to determine if they show characteristics of a hazardous waste. In the event that the residuals do not show characteristics of a hazardous waste, then the solids can be disposed of as a solid waste. Many industries and municipalities have disposed of non-hazardous rainfall-runoff residuals in the same way they would have any other contaminated soil (Jones et al. 1994). In some cases, rainfall-runoff solids have been mixed with other soil and reused as backfill on construction projects (Jones et al. 1994) and cover for landfills (EPA 1999). However, if the rainfall-runoff residual material is determined to be hazardous, then they must be managed accordingly.
2.2.1 Regulatory Hazardous Waste Characterization

A hazardous waste characteristic is a property indicating that a waste poses sufficient threat to deserve a regulation noting the waste as hazardous (EPA 2001). According to the USEPA, there are four such criteria: 1) if a waste contains harmful chemicals, and has other factors that indicate that it could pose a threat to human health and the environment in the absence of special regulation, then it is a toxic listed waste; 2) if a waste contains dangerous chemicals that could pose a threat to human health and the environment even when properly managed, then it is known as an acutely hazardous waste; 3) if the waste typically exhibits one of the four characteristics of hazardous waste described in the hazardous waste identification regulations (ignitability, corrosivity, reactivity, toxicity), then it is considered a hazardous waste; and 4) if the EPA has cause to believe that, for some other reason, the waste typically fits within the statutory definition of hazardous waste developed by Congress, then it is considered hazardous.

Toxicity is the foremost hazardous waste characteristic of concern in the case of urban and transportation land use rainfall-runoff particles and BMP residuals. In order to determine toxicity, the USEPA has established the Toxicity Characteristic Leaching Procedure (TCLP) designated as SW-846 Method 1311, a procedure intended to produce a leachate comparable to what would be produced by the material in the environment. The leachate is analyzed for 39 chemicals, including such as Cd, As, Cr, and Pb. The concentrations of these chemicals found in the sample are then evaluated against regulatory levels to determine whether the waste exhibits the Toxicity Characteristic (TC). If a waste exhibits the TC, the waste is designated by the waste code associated with the compound or element that exceeded the regulatory level.
2.2.2 Solidification/Stabilization

Solidification/stabilization (S/S) processes are effective in treating hazardous wastes for reuse or disposal and have been identified as the best demonstrated available technology (BDAT) for many of the Resource Conservation and Recovery Act (RCRA) non-wastewater hazardous waste subcategories (Means et al. 1995). S/S processes are designed and used to accomplish one or more of the following goals: 1) reduce contaminant/ pollutant mobility or solubility; 2) improve the handling and physical characteristics of the waste by producing a solid with no free liquid; and/or 3) decrease the exposed surface area across which exchange or loss of contaminants may occur (Means et al. 1995).

S/S treatment techniques possess the flexibility needed to accommodate wastes with mixtures of contaminants and can economically handle large volumes of wastes. S/S is frequently the technology of choice for immobilizing soils and sludges containing one or more metal contaminants (Means et al. 1995), which make S/S processes applicable to the treatment of rainfall-runoff solid waste.

2.3 OBJECTIVES

There were three objectives of this study for the Baton Rouge; Little Rock, North Little Rock, and Cincinnati BMPs. The first objective was to quantify the physical granulometric characteristics of BMP residuals captured by these BMPs from similar urban transportation land use sites in these urban localities. The specific physical granulometric characteristics examined included particle size gradation indices, particle density, specific surface area, and total surface area. Such characteristics influence the transport, fate and management of these residuals. The second objective was to examine surface charge and metal mass associated with these residuals as a function of gradation. Such characteristics
influence the function of BMPs and suggest management strategies for the capture, disposal and reuse of these residuals. These objectives will provide a better understanding of rainfall-runoff residuals allow for the development of more effective alternatives regarding practical residuals handling and management. Also, the knowledge of the physical and chemical characteristics of the waste is pertinent in the selection of an adequate binder to be applied in the S/S technology for residuals. The final objective was to determine through TCLP the characteristics of the leachate from rainfall-runoff residuals in relationship to freshwater limits (USEPA 1999b), 503 land disposal limits (USEPA 1994) and hazardous waste designations. In this final objective three gradations of residuals were tested. First the total gradation of particle sizes was analyzed, followed by the coarse (>75 µm) and fine (<75 µm) fractions. Granulometric results were also examined with respect to these fractions.

2.4 BACKGROUND

Past studies of anthropogenic rainfall-runoff solids have demonstrated that metal concentrations associated with these solids are introduced to the benthic layer of receiving waters. These metals pose a chronic threat to small organisms including worms, crustaceans and insect larvae that are consumed by fish and can become a threat up through the food chain (Mulligan et al. 2001). Previous research of storm water solids has generally focused on the potential for the transfer of inorganic metal pollutants from the solids to the surrounding receiving water or to biota (Liebens 2001), but very few studies have physically and chemically examined BMP residuals for the purpose of more effective treatment and management.

Studies carried out in Florida evaluated the contamination of sediments in nine storm water retention/detention ponds from Ocala (central Florida) to Miami (southeastern Florida)
to help prepare management guidelines for rainfall-runoff treatment ponds. Studies concluded that metal concentrations in accumulated bottom sediments of the ponds were below that of the regulatory levels set by the Florida Department of Environmental Protection and that the optimal average clean out time for such a pond is approximately 25 years (Yousef et al. 1991).

In another study of rainfall-runoff residuals, characteristics of storm water basin sediments were evaluated for a pond located in Kingston, Ontario, Canada (Marsalek et al. 1997). The basin was constructed in 1982 to treat runoff from the buildings and parking lots associated with a newly built shopping plaza (Marsalek et al. 1997). In 1997, based on Canadian regulations, the metals concentrations associated with the sediments in this pond were above the limits to allow reuse in urban areas or disposed of in municipal landfills. Further analyses indicated that 70-90% of the total metals found on these sediments were in potentially mobile forms (Marsalek et al. 1997). This increase in mobility of metals is most likely due to anaerobic conditions in the basin and decreased pH leading to speciation changes, increased dissolution of immobilized or partitioned metals, and therefore increased mobility of metals.

In 1996, a project conducted in Florida studied sediment and debris samples from storm water BMPs such as wet detention ponds, dry retention ponds, swales, road shoulders, sand filters, and street sweepers. Fifty-three pollutants, including metals commonly associated with traffic pollutants, such as Pb, Zn, Cr, Cu, Cd and Ni, were found in detectable concentrations at all of the sites, but none the exceeded the minimum detection limits set by the Florida Department of Environmental Protection (Cox 1996).
In order to properly control urban rainfall-runoff and trap transported contaminated sediments, detention/retention, equalization and sedimentation basins are commonly included as an integral part of rainfall-runoff treatment. Due to the highly intermittent nature of rainfall-runoff flows and the need for water quantity control, storage systems are a common pretreatment or primary treatment alternative (Field et al. 1994). In many cases such combined water quantity-quality basins applied for rainfall-runoff quality are designed based on residence time, particle size gradation, particle density and surface loading rate.

Many studies of contaminated aquatic sediments as a result of anthropogenic activities have been conducted. Rainfall-runoff studies evaluating metal concentrations have shown that higher concentrations of metals (on a solid-phase basis) are associated with smaller particles (Viklander 1997). While this is expected based on the definition of solid-phase concentration, studies based on mass have demonstrated that most of the mass is associated with the predominance of the granulometric mass (Cristina et al. 2002). Studies of sediments dredged from the bottom of a New York/New Jersey harbor have been conducted. The sediments contained 33, 37, 377, and 617 mg/kg of As, Cd, Cr and Pb, respectively (Stern et al. 2000). Another study done by Marsalek et al., metals concentrations observed in sediments gathered at the outlet of a storm water management pond were 80, 149, and 406 ppm for Cu, Pb and Zn (Marsalek et al. 1997). The EPA 40 Code of Federal Regulation (CFR) Part 503 rule set limits as part of a comprehensive risk assessment of metals in sludge for the use and disposal of sewage sludge (EPA 1993). The regulatory limits for Cd, Cu, Pb and Zn are 20, 750, 150, and 1400 ppm, respectively.
2.5 METHODOLOGY

2.5.1 Experimental Sites

BMP residuals from 5 sites loaded by rainfall-runoff in 4 urban areas were examined in this study. Two of the BMP sites were located in Cincinnati, OH, along southbound interstate 75 approaching downtown Cincinnati. These BMPs were a grassed swale and a porous pavement infiltration system both located in the same watershed. One BMP site was a linearly extended detention channel located in Little Rock, AR at the junction of interstate 30 and 40 and the other at the inlet of a detention basin originally designed for water quantity control of parking lot runoff from a 10 acre retail asphalt parking area. The final site studied was located in Baton Rouge, LA, on eastbound interstate 10 over City Park Lake and the BMP at this site was a treatment train consisting of a grit chamber, settling basin and series of filters. While the BMPs were different at each site, loadings, land use and cover conditions were similar at each site.

2.5.1.1 Baton Rouge, Louisiana Site

Baton Rouge, Louisiana, is located in south central Louisiana on the east bank of the Mississippi River in East Baton Rouge Parish. With the 74th largest population of the 318 metropolitan statistical areas (MSA) in the United States, municipal Baton Rouge has a population of 413,000 with approximately half of that population located within the corporation limits of the city (http://quickfacts.census.gov/qfd/states/22/22033.html). Baton Rouge receives annual mean rainfall of 63.08 inches (1602.23 mm) and annual mean snowfall of 0.2 inches (5.08 mm) (Jay Grymes, Louisiana Office of State Climatology 2003, http://www.losc.lsu.edu/stations.php?Id=btr).
Located at the eastbound end of the interstate 10 eastbound lanes over City Park Lake, the experimental site in Baton Rouge is designated as I-10E and the average daily traffic (ADT) count is 70,433 in the eastbound direction only. The roadway surface of the bridge is constructed of Portland cement concrete (PCC). Runoff from the 544-m² pavement catchment is transported to the experimental treatment facility, located directly below the catchment and comprised of an 80-L grit separator, a 2130-L settling basin and a series of buoyant upflow filters. Residuals were collected from each unit operations after a season of rainfall-runoff event loadings. These residuals were combined and taken back to the laboratory for drying. Once back in the laboratory the residuals were dried for approximately one week at 40 °C before experimental analyses.

2.5.1.2 Little Rock, Arkansas Sites

Located in central Arkansas, Little Rock serves as the capital city of Arkansas. Little Rock is situated on the south bank of the Arkansas River in Pulaski County. The population of the Little Rock -North Little Rock MSA is ranked 72nd among the 318 MSAs in the U.S with 590,000 people (http://quickfacts.census.gov/qfd/states/05/05119.html). Annually, Little Rock experiences average high and low temperatures of 81.4 °F (27.4 °C) and 39.5 °F (4.2 °C) and average rainfall and snowfall of 48 inches (1219.2 mm) and 5.2 inches (132.1 mm), respectively (http://www.littlerock.com/general_info/fast_facts.asp).

The Little Rock BMP site is located in the median of Interstate 30 (I-30) near the junction of Interstates 30 and 40 on the north side of the Arkansas River. The section of interstate has an ADT of approximately 103,000. The site was designated as I-30-I-40. Urban drainage to the detention channel is contributed from the interstate pavement as well as from
the urban area of Goshen Heights in North Little Rock. Residuals were retrieved from the linear concrete detention channel located in the median between I-30 and I-40.

The second of the two sites sampled in Little Rock is located in North Little Rock. An unlined detention basin BMP designed for water quantity control for rainfall-runoff from an asphalt-paved parking lot loaded by retail traffic. The detention basin is located in the northwest corner of a 10-acre parking area loaded by retail and truck traffic. The parking area drains to the detention basin that was designed to reduce the peak of the 25-year rainfall-runoff event from the parking lot to pre-development conditions. The sampling location title was abbreviated to HD-NLR.

2.5.1.3 Cincinnati, Ohio Sites

The City of Cincinnati, Ohio has a population of 331,000 and is located in Hamilton County in the southwest corner of Ohio (http://quickfacts.census.gov/qfd/states/39/39061.html). With the 23rd highest population of the 318 MSAs in the U.S, the greater Cincinnati consolidated metropolitan statistical area (CMSA) has a population of approximately 2 million and includes 13 counties from northern portions of Kentucky and southeastern sections of Indiana (http://www.gcce.com/about_cincinnati/). Greater Cincinnati receives, annually, average rain and snowfall of 41.33 inches (1050.7 mm) and 23.4 inches (595.3 mm) with annual average high and low temperatures of 86°F (30 °C) and 21 °F (-6.1 °C), respectively (http://www.wunderground.com/NORMS/DisplayNORMS.asp?AirportCode=KLUK&SafeCityName=Cincinnati&StateCode=OH&Units=none&IATA=CVG).

Two BMP sites were sampled in Cincinnati. The first BMP, a grassed swale is located between the median of the northbound and southbound lanes of inter state 75, a major north-south interstate connecting Michigan to Florida. From a storm water grassed swale, a
common BMP concept used to recover residuals (Yu et al. 2001), residuals were recovered
towards the upper end of this swale. The drainage swale is directly loaded by asphalt
pavement runoff. As runoff enters the vegetated swale velocity is reduced and the particles are
removed by filtration by the vegetation, settling of particulates, and infiltration into the
subsurface zone (Yu et al. 2001). Residuals for this study were collected at the northernmost
sampling location near the upper end of the grassed swale. The sampling site is designated as
the twelfth residual location, thus making the site designation BH-12. The average daily
traffic (ADT) for this site (south and northbound) was 165,000.

The second site that was sampled in Cincinnati was located directly on the paved
shoulder of southbound inter state 75. A porous pavement surface of a partial exfiltration
reactor (PER) located at the paved shoulder directly by lateral sheet flow (q_{sf}) from the asphalt
pavement was sampled for strained residuals. The sampling site was referred to as 1-SE. The
influent particulates transported in q_{sf} were strained on the surface of the PER, forming a
schmutzdecke. The average daily traffic (ADT) for this site (south and northbound) was
165,000.

2.5.2 Experimental Methods

2.5.2.1 QA/QC

Quality control and assurance (QA/QC) conditions were included in this study to
ensure accurate, precise, and statistically significant data. For mass-based particle size
distributions, mass balances were greater than 95%. Triplicate specimens were analyzed for
particle density (\(\rho_s\)), specific surface area (SSA), and surface charge. Acid digestion
procedures and metals analyses were carried out in duplicate. Standard deviations and
arithmetic means were calculated for all analyses. For those replicate analyses with a standard deviation more than 20% of the arithmetic mean, the respective analyses were repeated.

Method blank samples were prepared and analyzed for every acid digestion, for every pH level examined in the surface charge experiments, and for every 20 TCLP tests. Granular activated carbon samples (1100 m²/g, Sansalone et al. 1998) were analyzed in triplicate as control specimens for SSA measurements. One soil standard sample of known metal content was acid-digested to evaluate metal recovery through the digestion process along with every 10 residual samples that were acid digested and analyzed for metals.

2.5.2.2 Sample Preparation

In preparation for analyses, BMP residuals were dried in a constant temperature room and constant humidity for approximately one week. A continuous temperature of 40°C with a constant humidity of 20% was maintained throughout the drying process of the BMP residuals. Once the samples were dried, a mortar and pestle was used to carefully disaggregate any particulate clusters. After disaggregating the dry material, the samples were stored in a dessicator until analysis.

2.5.2.3 Particle Size Distribution (PSD) Analyses

Granulometric indices for particulate materials can vary over orders of magnitude and while there is not distinct change in indices over a small increment of size; the differences in behavior between the coarse and fine fractions of a gradation are generally recognized (Santamarina et al. 2002). The forces governing the behavior of coarse-grained granular materials, such as soils, are different from those affecting fine-grained granular material (Santamarina et al. 2002). The size at which the designation is made between coarse and fine fractions for engineering classification is generally 75 µm. This is also the nominal size
designation between sand and silt-size particles. The American Society for Testing of Materials (ASTM) defines particle sizes as: sand, 2000-75 μm; silt, 75-5 μm; clay, less than 5 μm (ASTM).

The ASTM D 422 test method for mechanical sieve analysis was used to determine the particle size distributions of the samples (ASTM 1990) with modification to include a larger number of sieves than prescribed by the method. The protocol given in ASTM D 421 was utilized in preparation of the samples prior to mechanical sieve analysis (ASTM 1990). These analyses provided a mass balance as well as a particle size gradation (PSD) for each sample from all of the experimental sites. The mass gradation of the residuals was also determined in these analyses. Using a total of seventeen standard stainless steel sieves (3/8 in., No. 4, No. 10, No. 20, No. 30, No. 40, No. 50, No. 60, No. 80, No. 100, No. 140, No. 200, No. 230, No. 270, No. 325, No. 400, No. 500 and the pan), eighteen particle size classes ranging in size from 9500 to 25 μm were separated. Generally, a hydrometer analysis is performed for particles with diameter less than 75 μm (Lu et al. 2000); however, for further physical and chemical characterization analyses, such as specific surface area, surface charge, and metals analyses, mechanical sieve analysis proved to be the best protocol instead of suspending particles in aqueous solution (ASTM 1993; Sansalone et al. 1998). Measurements of the total dry residual mass were taken before and after sieve analyses to ensure a recovery of > 95%.

2.5.2.4 Particle Density

The particle density, \( \rho_s \), of the dry particulates (for discrete residual size classes) was determined using helium gas pycnometry using ASTM D 5550-94 (ASTM 1994). Gas
Pycnometry is a non-destructive process that provides a means of determining the true volume of a sample of solids through a series of pressure readings. Helium gas was utilized due to inertness and small size of the helium molecule (0.098 nm in diameter) enabling the gas to penetrate into meso and micropores of the particles (Lowell and Shields 1991). The pycnometer was a Multi-Pycnometer by Quantachrome Corporation (Serial Number 11498010901, Model Number MVP-3DC). Triplicate representative samples of known mass of each gradation ($M_s$) were analyzed in order to calculate an arithmetic mean $\rho_s$ for each size gradation. Prior to specific gravity measurements, the samples were dried at a temperature of 40°C and placed in a desiccator overnight. The dry samples were then placed into a stainless steel cylinder of known volume and positioned into the instrument for analysis. Two pressure measurements, $P_1$ and $P_2$, were recorded and equation (1) was used to calculate the volume of the particulate mass present in the cylinder.

\[
V_s = V_c - V_r \left( \frac{P_1}{P_2} - 1 \right)
\]

$V_s$: Calculated sample volume (cm$^3$)

$V_c$: Cylinder volume (cm$^3$)

“Large” = 147.499 cm$^3$

“Small” = 25.644 cm$^3$

“Micro” = 12.561 cm$^3$

$V_r$: Reference volume (cm$^3$)

“Large” = 91.281 cm$^3$

“Small” = 13.964 cm$^3$

“Micro” = 7.156 cm$^3$

$P_1$: Initial pressure measurement (psi)

$P_2$: Final pressure measurement (psi)

Once the volume of the particle mass is determined from (1), $\rho_s$ is calculated by (2):

\[
\rho_s = \frac{M_s}{V_s}
\]
M\(_S\) : measured mass of dry particulate (g)
V\(_S\) : measured volume of sample (cm\(^3\))

Arithmetic mean \(\rho_s\), and standard deviations were calculated and evaluated to ensure they were within 20% of the mean value. Additional analyses were carried out for those samples whose standard deviations were more than 20% of the mean \(\rho_s\).

2.5.2.5 Specific Surface Area (SSA) and Total Surface Area (SA)

SSA captures the combined effects of particle gradation, size, porosity and shape in a measurement that is independent and complementary to grain size distribution (Sansalone et al 1998, Santamarina 2002). The SSA of a particle is the ratio of particle SA to particle mass or volume (depending on the definition), thus the trend is expected to exhibit increasing SSA as particle size decreases (Santamarina et al. 2002; Sansalone et al. 1998). While this trend should theoretically be monotonically increasing for solid, spherical particles of the same density, this is rarely the case (Sansalone et al 1998). The derived measurement of total SA (using a mass definition, the product of mass and SSA for a given particle size) provides an index of the potential and capacity of a negatively-charged rainfall-runoff particulate to sorb metal cation mass from the aqueous phase (Sansalone et al. 1998).

Particle surface area (SA) can be an index for sorbed solute mass. Measurement of total surface area (SA) and specific surface area (SSA) was carried out using a modified EGME Method (Sansalone et al. 1998). The EGME method utilizes ethylene glycol monoethyl ether, EGME (HOCH\(_2\)CH\(_2\)OCH\(_2\)CH\(_3\)), a highly polar liquid with a high vapor pressure. All SSA measurements were run in triplicate for each particle size. Granular activated carbon (GAC) was run in triplicate as a control. GAC has a specific surface area of known value and was used as a control in the analyses of the total and specific surface areas.
of the residuals. The GAC used in these experiments was a Filtersorb F400 with a reported SSA of 1100 m$^2$/g by the N$_2$-BET method (Calgon 1995).

Dried residual specimens had been previous separated into size classes and further dried in an evacuated dessicator for 24 hours to ensure a dry original weight. The EGME was carefully applied, drop-by-drop, to each residual sample having a precisely known mass of approximately 1 g of residuals, using a 5 mL glass pipette. Larger residual sizes greater than 1000 µm required a precisely known mass of approximately 5 to 10 g of residuals. The quantities of EGME applied to the residual samples were sufficient to visually coat the entirety of the residual specimens without leaving excess EGME on the glass Petri dishes. The EGME coated residual particulate samples were placed in a desiccator with an EGME and calcium chloride (CaCl$_2$) solvate mixture. The ratio of EGME to calcium chloride (CaCl$_2$) in this solvate mixture was 1:2.3 (EGME = 240 g, CaCl$_2$ = 560 g). The dessicator was evacuated for a 30 to 45 minute period, after which the dessicator was sealed allowing the EGME/CaCl$_2$ solvate to create a constant EGME vapor pressure within the desiccator without any partial pressure from water vapor. Under a constant vapor pressure, the excess EGME coating the residual surfaces evaporated until equilibrium where a monolayer of EGME existed on the surface of the particles.

Following an initial 24-hour period in the evacuated dessicator, gravimetric readings were taken every 4 hours until three consecutive 4 hour readings were recorded within 0.1 mg of each other, for each sample. The mass of EGME retained on the surface was determined and the SSA was calculated using the following formula (Sansalone et al. 1998):

$$\text{SSA} = \frac{W_s}{0.000286W_i}$$ (3)
SSA: Specific surface area (m²/g)

\( W_a \): Measured weight of EGME retained by sample (g)

\( W_s \): Measured weight of dry sample (g)

Calculation of total surface area was accomplished by multiplying the SSA by the total mass retained for each individual size gradation.

\[
SA_i = (m_i)(SSA_i)
\]  

\( SA_i \): Surface area of sample size class having particle diameter \( i \) (m²)

\( m_i \): Mass of sample size class having particle diameter \( i \) (g)

\( SSA_i \): Specific surface area of sample size class having particle diameter \( i \) (m²/g)

SA values for all sites were then normalized to 1000 dry grams of mass before plotting.

### 2.5.2.6 Inorganic Constituent Determination

The inorganic constituent analysis of the urban rainfall-runoff residuals focused on Cd, Cu, Pb and Zn, four metals most commonly associated with urban rainfall-runoff. The USEPA has set regulatory limits regarding the levels of these metals that introduce acute and chronic toxicity to aquatic biota in fresh and marine waters (USEPA 1999b). These regulatory limits are presented in Table 2.1. Levels of Cd, Cu, Pb and Zn present in urban rainfall-runoff and on the residuals associated with the runoff often exceed USEPA and State EPA surface water discharge criteria on an event basis (Sansalone et al. 1997). Also presented in Table 2.1 are the Part 503 Rule limits for metals present in solids and sludge that have the potential to be land applied. These limits are applicable when considering disposal and/or reuse of the urban rainfall-runoff residuals.

In order to extract the metals from the urban rainfall-runoff residuals, a nitric acid-hydrochloric acid digestion for metals outlined in SW-846 Method 3015 (USEPA 1990). The
Table 2.1 EPA’s fresh and marine water toxicity limits for metal concentrations in fresh and marine water bodies and EPA’s 40 CFR Part 503 limits for heavy metal concentrations present in sludge and solid wastes.

<table>
<thead>
<tr>
<th>Metal</th>
<th>EPA Fresh Water Toxicity Limits</th>
<th>EPA Marine Water Toxicity Limits</th>
<th>Part 503 Rule Regulatory Limit (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acute (µg/L)</td>
<td>Chronic (µg/L)</td>
<td>Acute (µg/L)</td>
</tr>
<tr>
<td>Pb</td>
<td>65</td>
<td>2.5</td>
<td>210</td>
</tr>
<tr>
<td>Cu</td>
<td>13</td>
<td>9</td>
<td>4.8</td>
</tr>
<tr>
<td>Cd</td>
<td>4.3</td>
<td>2.2</td>
<td>42</td>
</tr>
<tr>
<td>Zn</td>
<td>120</td>
<td>120</td>
<td>90</td>
</tr>
</tbody>
</table>

Reference: (USEPA 1999b and USEPA 1994)
digestion process involved digesting a precisely known dry mass of a residual size class (approximately 0.5-1.0 grams). The residual samples were digested in duplicate and each digestion run included a pure acid (method blank) sample. The particulate samples were weighed and then placed in 100 mL-beakers to which 12.0 mL of acid (9.0 mL-nitric acid + 3.0 mL-hydrochloric acid) was added. The beakers were covered with watch glasses and placed on a hot plate at 175 °C (347 °F) for 2 hours. Following the 2-hour digestion period, the samples were diluted with 10.0 mL of DI water and poured through pre-washed paper filters. DI water was added to the filtrate until the final filtrate volume was 100.0 mL. After digestion, filtration and dilution, the filtrate was analyzed for Fe, Ni, Cu, Cr, Zn, As, Pb, Mn, Al, Ca, Mg, and Cd using a Perkin-Elmer Elan 9000 Inductively Coupled Plasma - Mass Spectrophotometer (ICP-MS). The protocol outlined by the EPA in SW-846 Method 6020 for ICP-MS analysis was utilized (EPA 1996).

The inorganic constituent results obtained through ICP-MS analysis were aqueous concentration units expressed as [µg/L] or [ppb]. These concentrations were multiplied by the final volume of filtrate from the digestion process (100 mL) and divided by the measured particulate mass of the dry residual sample digested to achieve mass-based concentration units of [µg/g]. In order to evaluate the total metal mass present on each gradation of the urban rainfall-runoff residuals, a calculation was carried out according to (5), where the mass fraction of each size gradation of the PSD was multiplied by the mass-based concentrations of the metals in order to achieve the total metal mass in (mg).

\[ \text{Me}_i = (m_i)(c_i) \]  \hspace{1cm} (5)

\[ \text{Me}_i: \text{ Mass of inorganic constituent present on the particles with diameter } i \text{ (mg)} \]
mᵢ: Mass fraction normalized to 1000 dry grams of particles with diameter i

cᵢ: Mass concentration of inorganic constituent bound to particles with diameter i [µg/g]

Results of these calculations yielded the total inorganic constituent data for each size gradation and were cummatively summed and presented as the total mass of inorganic constituents over the entire PSD.

2.5.2.7 Power Law

The power law can describe many natural classes of particles such as fine sediments, airborne dust, and suspended particles in seawater, in particular when the data described occurs across a range of scales (Bader 1970). In many particulate systems, including particles transported in rainfall-runoff, properties of the particle size distribution, may be accurately represented by a two parameter, hyperbolic power-law function, as expressed in the following equation (Patterson et al. 1999).

\[ y = \alpha x^{-\beta} \]  \hspace{1cm} (6)

In this expression, y and x represent measured data depending on the system of interest, while \( \alpha \) and \( \beta \) are empirical constants resulting from the model fitting of the data. For example y can represent the particle number density (PND) with x representing the diameter of the particle. For this study, a power law was applied to examine the relationship between paired cumulative metal mass (Cd, Pb, Zn and Cu) and cumulative particle mass for residuals from each site BMP as summarized in equation 7. Both metal mass and cumulative mass were summed from the largest particle diameter (9500 µm) down to the smallest diameter (25 µm).

\[ M_{\text{cum}}^{\text{metal}} = \alpha M_{\text{cum}}^{-\beta} \]  \hspace{1cm} (7)

Ecum: Normalized cumulative metal mass
\[ M_{\text{cum}}: \text{Normalized cumulative particle mass} \]

Since a power law model plots as a straight line in log-log space, cumulative normalized data were plotted in a log-log format. The two empirical constants, \( \alpha \) and \( \beta \), were calculated in each power law application to site BMP residuals. The metal mass was normalized to the total metal mass across the gradation and the particle mass was normalized data were calculated as follows:

The \( \alpha \) coefficient is an index for the amount of total amount of metal mass associated with the entire gradation of particles, while the \( \beta \) value represents the slope of the power law distribution indicating the amount of metal mass associated with a given particle size. Using the determined \( \alpha \) and \( \beta \) values for residuals from a particular site BMP one could predict the cumulative metal mass that is associated with a given cumulative particle mass based solely on granulometric mass for the same operating and loading conditions of that BMP.

### 2.5.2.8 Surface Charge

The surface charge on residuals was determined using a modified potentiometric titration, in which the residuals were suspended in different solutions of specific pH levels (Van Reij and Peech 1972). Surface charge analysis is important in determining the potential for species adsorption or complexation to the surface of the residuals. Titration methods used to determine pzc-pH are only accurate in a pH range of 3-9 (McBride 1994). When determining pzc-pH, the OH\(^-\) and H\(^+\) ions that are measured are those that occupy the exchange sites, known as index ions (McBride 1994). The limitation of this measurement is that cations and anions that are not classified as index ions are chemically adsorbed to the surface of particles and thus alter the surface charge of the particle (McBride 1994). These
chemisorbed anions and cations cannot be distinguished from index ions when determining the PZC. Thus, when chemisorbed cations are present the surface positive charge is increased and the PZC measured is higher than the actual PZC and when chemisorbed anions are present the surface negative charge is increased and the measure PZC is lower than the actual value (McBride 1994).

Triplicate samples for 14 gradations (850 µm – 25 µm) of particles were analyzed separately for surface charge at pHs 6, 7, 8, and 9. The largest gradations (9500-2000 µm) were not analyzed for surface charge, due to the fact that these larger particles do not reach a point of zero charge. Approximately 0.5 dry milligrams of particulates for each particle size were kept separate and were placed into separate 50-mL centrifuge tubes. A room temperature (25°C) batch solution of 0.01 M-KCl titrate was adjusted to a pH of 6, 7, 8, or 9 using dilute solutions of hydrochloric acid and/or potassium hydroxide as titrants. To each centrifuge tube with the 0.5 mg particulate samples, 50 mL of the titrated 0.01 M-KCL solution was added. Control samples were prepared using the titrated 0.01 M-KCl solution and empty centrifuge tubes (no particulate addition). For the control samples, 50 mL of the titrated 0.01 M-KCl solution was added to blank centrifuge tubes, kept at room temperature (25°C) and analyzed along with the particulate samples. All centrifuge tubes were tightly sealed and kept at room temperature (25°C). The tubes were then placed on a reciprocating table and agitated for 24 hours. After agitation, the samples were allowed to settle overnight. Once the samples were settled, 25.0 mL of the supernatant was titrated back to the original specific pH of 6, 7, 8, or 9 using hydrochloric acid (HCl) and potassium hydroxide (KOH) solutions of 0.01 or 0.005 molarity. The use of 0.01 M or 0.005 M was determined by evaluating the amount of titrant needed to adjust the solution to the original pH. If the solution required adjustment of more
than one pH unit, then the 0.01 M titrant was used; otherwise the 0.005 M titrant was applied.

The volume of the titrant (HCl or KOH) used to titrate each sample was recorded and the hydrogen ion (H\(^+\)) or hydroxide ion (OH\(^-\)) concentrations were used to calculate the charge in µmol/g of each sample through the following equation:

\[
C_i = \left( \frac{M(V_H \pm V_{MH})}{V_s \cdot V_T} \right) \frac{W(1000)}{V(1000)}
\]

(8)

\(C_i\): Charge for sample of size i (µmol/g)

\(M\): Molarity of the HCl or KOH solution used to titrate the sample (mol)

\(V_H\): Volume of titrant used to titrate sample (mL)

\(V_{MH}\): Mean volume of H\(^+\) or OH\(^-\) added to triplicate control samples (mL). This value is subtracted when the solution used for \(V_H\) is the same as the solution used for \(V_{MH}\), otherwise, this volume is added.

\(V_s\): Volume of the supernatant (25.0 mL)

\(V_T\): Volume of the total sample (50.0 mL)

\(W\): Exact weight of the material added to the centrifuge tube (~ 0.5 mg)

The surface charge of the particulates was found by dividing the charge \(C_i\) by the mean specific surface area \(SSA_{mi}\) of each particle gradation using the following equation (9).

\[
SC_i = \frac{C_i}{SSA_{mi}}
\]

(9)

\(SC_i\): Surface charge for sample of particle size range \(i\) (µmol/m\(^2\))

\(C_i\): Charge for sample of particle size range \(i\) (µmol/g)

\(SSA_{mi}\): mean specific surface area of particles of gradation \(i\) (m\(^2\)/g)

37
The charge crossover from positive to negative surfaces is known as the point of zero charge (PZC). The point of zero charge (pzc-pH) was determined using a linear interpolation of the surface charge data results within the pH range where the charge changes from positive to negative.

2.5.2.9 Toxicity Characteristic Leaching Procedure (TCLP)

Leaching tests were carried out on the total (entire gradation), coarse (> 75 µm) and fine (≤ 75 µm) fractions of residuals captured at the I-10E site to determine the leaching potential of the heavy metals from the gradations of residuals. The Toxicity Characteristic Leaching Procedure (TCLP, SW-846 Method 1311) is a regulatory instrument for determining toxicity of wastes and also for classifying wastes as hazardous (EPA 1998). TCLP tests were run only on the I-10E residuals because these residuals were the most readily available and also because further research regarding the handling and disposal of these solids was to be conducted. TCLP tests were performed on the I-10E residuals and the resulting leachates were analyzed for metals using ICP-MS analysis. Blank extraction fluids without waste addition were prepared and tested as method blanks in accordance with the QA/QC in the TCLP procedure. The leachates were analyzed for Cd, Cu, Pb, and Zn concentrations. The concentrations of the constituents found in the leachates were then evaluated against regulatory levels to determine whether the residuals exhibit Toxicity Characteristics (TC).

Before TCLP could be executed, three initial procedures were completed on the residuals, a percent solids determination, a particle size reduction, and the extraction fluid determination. A percent solids determination was first carried out to establish the moisture content of the residuals and determine whether they should be handled as slurry. Since the residuals were dried extensively, 100% of the sample was considered solid. Particle size
reduction was carried out using a mortar and pestle. For the most part, all of the residuals had particle diameters less than 10 mm. For those residuals in the total and coarse fractions that had particle diameters equal to and greater than 10 mm, these residuals were further ground until the particle diameter was less than 10 mm. Using approximately 5 grams of each of the gradations of the residuals, determination of the extraction fluid was performed. Extraction fluid #1 was utilized throughout testing. The flow chart presented in Figure 2.1 dictates the extraction fluid determination as was performed.

Extraction fluid #1 was prepared using 2-L of DI water, 12.5 grams of sodium hydroxide (solid) and 22.8 mL of glacial acetic acid (17.4 N). The DI water, sodium hydroxide and glacial acetic acid were placed in 2-L bottles and mixed using a magnetic stir bar and magnetic stir plate at a speed of approximately 600 revolutions per minute (rpm). The final pH of the fluid was adjusted to within the range of 4.88 to 4.93.

All TCLP analyses were run in triplicate. A blank (using the same extraction fluid as used in the samples) was run in the extraction vessels for every 20 sample extracts analyzed in the vessels. A total of eighteen extraction bottles were used for TCLP requiring one run of blank extraction fluids to be analyzed. A minimum sample size of 100.0 dry grams was used for the TCLP analyses. The amount of extraction fluid was determined, through equation (10) shown below, to be 2000 g, which was approximately 2 L.

\[
W_e = \frac{20 \cdot P_s \cdot W_w}{100}
\]

\(W_e\): Weight of extraction fluid needed (g)

\(P_s\): Percent solids in the waste (%)

\(W_w\): Weight of the waste (g)
Figure 2.1 Flow chart for the determination of the proper extraction fluid to use for TCLP
The 100 g of residual sample and the 2000 g of extraction fluid were added to the extraction bottle, sealed tightly, and placed on a rotary agitation device. The extraction bottles were rotated at a speed of $30 \pm 2$ revolutions per minute (rpm) for $18 \pm 2$ hours with the ambient air temperature maintained at $23 \pm 2 \, ^{\circ}C \ (73.4 \pm 2 \, ^{\circ}F)$. Following the 18-hour agitation period, the material was separated to liquid and solid phases using pressure filtration with Whatman 0.7 \mu m pore size, 9.0 cm diameter glass fiber filters. The filters were acid-washed prior to filtration with a 2% trace-metal nitric acid solution and DI water. The filtrate was analyzed as the TCLP extract. The pH of the TCLP extract was measured and recorded. Following the pH measurement, the extract was acidified using trace-metal nitric acid until the pH measurement was below 2.

The TCLP extracts were further digested using 100.0 mL of the fluid. The 100.0 mL of fluid was placed in a beaker with 12.0 mL of acid (9.0 mL of nitric acid + 3.0 mL of hydrochloric acid) and digested according to the protocol outlined for nitric acid-hydrochloric acid digestion for metals in Standard Methods 3030 F (ASTM 1994). Duplicate samples were analyzed along with one pure acid (blanks) sample with each experiment run. The digested extracts were filtered and diluted with a 2% trace-metal nitric acid solution. The filtrate was analyzed, using ICP-MS, for Fe, Ni, Cu, Cr, Zn, As, Pb, Mn, Al, Ca, Mg. A Perkin-Elmer Elan 6000 Inductively Coupled Plasma - Mass Spectrophotometer (ICP-MS) following SW-846 Method 6020 for ICP-MS analysis (EPA 1996).

2.6 RESULTS

2.6.1 Particle Size Distribution (PSD)

A summary of the rainfall-runoff residuals granulometry captured in each BMP at each site is presented in Table 2.2. Land use and BMP types are also identified in Table 2.2.
Table 2.2 Summary of selected granulometric and inorganic constituent characteristics for residuals captured by BMPs at each experimental site.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Land Use:</td>
<td>Transportation (Detention Basin)</td>
<td>Transportation (Detention Channel)</td>
<td>Retail Parking (Detention Basin)</td>
<td>Transportation (Vegetated Swale)</td>
<td>Transportation (PER Porous Pavement)</td>
</tr>
<tr>
<td>ADT:</td>
<td>70,433</td>
<td>103,000</td>
<td>N/A</td>
<td>165,000</td>
<td>165,000</td>
</tr>
<tr>
<td>(d_{10}(\mu m)):</td>
<td>176 (\mu m)</td>
<td>175 (\mu m)</td>
<td>44 (\mu m)</td>
<td>155 (\mu m)</td>
<td>96 (\mu m)</td>
</tr>
<tr>
<td>(d_{30}(\mu m)):</td>
<td>359 (\mu m)</td>
<td>336 (\mu m)</td>
<td>76 (\mu m)</td>
<td>436 (\mu m)</td>
<td>287 (\mu m)</td>
</tr>
<tr>
<td>(d_{50}(\mu m)):</td>
<td>761 (\mu m)</td>
<td>438 (\mu m)</td>
<td>149 (\mu m)</td>
<td>1153 (\mu m)</td>
<td>542 (\mu m)</td>
</tr>
<tr>
<td>(d_{60}(\mu m)):</td>
<td>1528 (\mu m)</td>
<td>485 (\mu m)</td>
<td>164 (\mu m)</td>
<td>1999 (\mu m)</td>
<td>764 (\mu m)</td>
</tr>
<tr>
<td>(d_{90}(\mu m)):</td>
<td>7845 (\mu m)</td>
<td>1296 (\mu m)</td>
<td>1249 (\mu m)</td>
<td>9500 (\mu m)</td>
<td>8369 (\mu m)</td>
</tr>
<tr>
<td>Particle Density, (\rho_s (g/cm^3)), ASTM D5550-94</td>
<td>2.4-2.7</td>
<td>1.9-3.4</td>
<td>1.8-2.5</td>
<td>2.1-2.8</td>
<td>2.0-2.6</td>
</tr>
<tr>
<td>Specific Surface Area, SSA (m²/g), Sansalone et al 1998</td>
<td>3.5 – 30</td>
<td>3.5 – 410</td>
<td>32.9-133.6</td>
<td>3.8 – 39.7</td>
<td>16.9-54.1</td>
</tr>
<tr>
<td>Surface Area, SA, (m²) 1000-g basis, Sansalone et al 1998</td>
<td>0.04-28.80</td>
<td>1.88-35.91</td>
<td>7.26-98.09</td>
<td>0.93-20.33</td>
<td>3.84-28.76</td>
</tr>
<tr>
<td>Metals [µg/g], (\text{Pb}):</td>
<td>36 – 172</td>
<td>28 – 1159</td>
<td>4 – 105</td>
<td>5 – 1332</td>
<td>5 – 260</td>
</tr>
<tr>
<td>(\text{Cd}):</td>
<td>0.29 -3.36</td>
<td>0.42 - 2.4</td>
<td>0.14 -1.87</td>
<td>0.16 -6.17</td>
<td>0.49 -8.79</td>
</tr>
<tr>
<td>(\text{Cu}):</td>
<td>2 – 339</td>
<td>9 – 768</td>
<td>0.27 -5.93</td>
<td>5 – 686</td>
<td>0.19 -9.60</td>
</tr>
<tr>
<td>(\text{Zn}):</td>
<td>31 - 906</td>
<td>325 -2736</td>
<td>212 -2920</td>
<td>114 -6639</td>
<td>402-10099</td>
</tr>
</tbody>
</table>
PSDs for residuals from each site BMP are presented in Figure 2.2. Percent mass recoveries for the five sites are also presented in Table 2.2. Results demonstrate that the mass fraction of the “fine” residuals (<75 µm) is less than 10% for all BMP sites except the North Little Rock detention basin where the “fine” residuals represented less than 30% of the mass fraction.

By comparison, a study of a rainfall-runoff management pond by Marsalek et al., indicated that the particle size distribution of sediments at the inlet of the pond was described as being dominated by gravel and sand with 72% sand and 28% gravel (Marsalek et al. 1997). Given the definitions of clay, silt and sand; and assuming that gravel is everything with particle diameter greater than 2000 µm, the PSD data acquired from the five sites associated with this study was compared, in Table 2.3, to the bottom sediments found at the inlet of the rainfall-runoff pond studied by Marsalek et al. From this comparison, it can be seen that the inlet of the management pond was dominated by the rapid sedimentation of sand and gravel particles. For the most part, the captured residuals at the inlet of the rainfall-runoff treatment pond studied by Marsalek et al. were coarser than the residuals collected from the 5 BMP sites in this research.

2.6.2 Particle Density (\(\rho_s\))

The particle densities of each particle size increment for each site were analyzed in triplicate. The ranges of \(\rho_s\) for each site BMP are presented in Table 2.2. The range of particle densities ranged from 1.8 g/cm\(^3\) for the BMP at HD-NLR to 3.4 g/cm\(^3\) for the BMP at I-30-40. Particle density plots are included in Figures 2.3-2.7 for each site. These plots illustrate the variability of the \(\rho_s\) data, the mean values and standard deviations of particle density, all as
Figure 2.2 Particle size distributions (PSD) on a mass basis for BMP sites. $M_S =$ total gradation dry mass.
Table 2.3 Comparison of textural classification fractions for BMP residuals from each of the 5 experimental sites as compared to results from particle gradations of inlet sediments of a storm water management pond studied by Marsalek et al. (1997)

<table>
<thead>
<tr>
<th>Site Designation</th>
<th>Gravel (&gt; 2000 µm)* (%)</th>
<th>Sand (2000 µm – 75 µm)* (%)</th>
<th>Silt (74 µm – 2 µm)* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marsalek et al. (1997)</td>
<td>72</td>
<td>28</td>
<td>0</td>
</tr>
<tr>
<td>I-10E</td>
<td>34</td>
<td>61</td>
<td>5</td>
</tr>
<tr>
<td>I30-I40</td>
<td>5</td>
<td>91</td>
<td>4</td>
</tr>
<tr>
<td>HD-NLR</td>
<td>5</td>
<td>65</td>
<td>30</td>
</tr>
<tr>
<td>BH-12</td>
<td>40</td>
<td>56</td>
<td>4</td>
</tr>
<tr>
<td>1-SE</td>
<td>25</td>
<td>67</td>
<td>8</td>
</tr>
</tbody>
</table>

Figure 2.3 Granulometric and metal distributions for residuals captured by I-10 site BMPs (settling basin and filter). Total gradation, SA (m$^2$) and mass (mg) of Pb, Cu, Cd, and Zn are each on 1000.0 g basis. Cumulative axes are 0 to 100% of total gradation SA or metal mass (based on 1000.0 g). Total gradation metal mass shown in plots.
Figure 2.4 Granulometric and metal distributions for residuals captured by I-30-I-40 site BMPs (settling basin and filter). Total gradation, SA (m²) and mass (mg) of Pb, Cu, Cd, and Zn are each on 1000.0 g basis. Cumulative axes are 0 to 100% of total gradation SA or metal mass (based on 1000.0 g). Total gradation metal mass shown in plots.
Figure 2.5 Granulometric and metal distributions for residuals captured by HD-NLR site BMPs (settling basin and filter). Total gradation, SA (m$^2$) and mass (mg) of Pb, Cu, Cd, and Zn are each on 1000.0 g basis. Cumulative axes are 0 to 100% of total gradation SA or metal mass (based on 1000.0 g). Total gradation metal mass shown in plots.
Figure 2.6 Granulometric and metal distributions for residuals captured by BH-12 site BMPs (settling basin and filter). Total gradation, SA (m²) and mass (mg) of Pb, Cu, Cd, and Zn are each on 1000.0 g basis. Cumulative axes are 0 to 100% of total gradation SA or metal mass (based on 1000.0 g). Total gradation metal mass shown in plots.
Figure 2.7 Granulometric and metal distributions for residuals captured by 1-SE site BMPs (settling basin and filter). Total gradation, SA (m$^2$) and mass (mg) of Pb, Cu, Cd, and Zn are each on 1000.0 g basis. Cumulative axes are 0 to 100% of total gradation SA or metal mass (based on 1000.0 g). Total gradation metal mass shown in plots.
a function of particle diameter. Previous results found in the literature have indicated that \( \rho_s \) of particulates in storm water sewers range from 2.19-2.56 g/cm\(^3\) (Jacopin et al. 1999). Previous research on snowmelt solids indicates that the coarse fraction (>75 \( \mu \)m) had a mean particle density of 2.86 g/cm\(^3\) and a fine particle (<75 \( \mu \)m) mean density of 2.75 g/cm\(^3\) (Cristina et al. 2002). With the exception of the I-10E site, the consistency in the results presented and the literature referenced is that the coarse fraction of the particles (> 75 \( \mu \)m) has a mean \( \rho_s \) that is statistically significantly lower (\( P = 0.7357 \)) than the fine particles (< 75 \( \mu \)m) at the 95 % confidence level.

### 2.6.3 Specific Surface (SSA) and Total Surface Area (SA)

Incremental specific (SSA) on a mass basis and resulting total surface area (SA) results are plotted as a function of size gradation and illustrated using vertical bar graphs in Figures 2.3-2.7 for each of the 5 BMP sites. Cumulative SA (as a percent) are also included in the plots. On a mass basis, while the definition of SSA indicates that SSA should increase with decreasing particle size, as was the case for the Cincinnati and Baton Rouge BMP sites, the Little Rock and North Little Rock sites results indicated higher SSA with coarser particles as compared to finer residuals.

In order to compare the results of the 5 BMP sites, the total SA results were normalized to a 1000-g dry mass basis. These normalized SA results are plotted in Figure 2.3-2.7 and illustrate that the majority of the SA is associated with the sand and gravel fractions of the residual gradation. For all sites over 80% of the total SA was associated with residuals larger than 75 \( \mu \)m. Since the fine fraction of the gradation did not account for a large portion of the residual mass a trend opposite that of SSA is seen in the SA results.
2.6.4 Inorganic Constituent Determination

Metal mass associated with residual specimens from the 5 BMP sites are graphically illustrated in Figures 2.3-2.7 as a function of size gradation. Expressed as milligrams (mg), of metal mass associated with the residuals these results were also normalized to a 1000-dry gram basis for each particle size increment over the entire gradation. The 1000-dry gram basis allows direct inspection of the plots with respect to mg of metal mass per kg of dry residual with respect to incremental size or across the gradation on a cumulative basis. The normalization allows a solid-based concentration to be evaluated implicitly from each mass distribution. The cumulative metal mass trends on a percentage basis in Figure 2.3 through 2.7 are summed from largest particle size to smallest size across the gradation. The total mass of metal across the entire gradation per 1000-g of dry residuals is identified in each metal plot. Results demonstrate that for all sites except the detention basin at the HD-NLR site that > 80% of the mass of Zn, Cd, Cu and Pb is associated with residuals > 75 µm. While the detention basin at the HD-NLR site is an exception to the above result, the trends are the same but at > than 60%. The lower mass percentage can be explained using Figure 2.2 that demonstrates the residual size gradation for the HD-NLR detention basin is much finer on a granulometric mass basis than all other site BMPs.

The limits set by the EPA 40 CFR Part 503 Rule, presented and discussed in the introductory sections, are listed in Table 2.1. On a total gradation basis solid-phase concentrations of Pb were exceeded for the HD-NLR detention basin, the Cincinnati BH-12 vegetated swale and the Cincinnati 1-SE porous pavement BMPs.
2.6.5 Surface Charge

The surface charge data obtained for the five sites is presented graphically in Figures 2.8 through 2.12 for residuals from each site BMP. Surface charge trends as a function of pH are plotted on the left and bottom axes of each plot. Point of zero charge (pzc-pH) trends as a function of gradation are plotted on the right and upper axes of each plot for rainfall-runoff residuals captured by the site BMPs. Data symbols represent mean of replicate analyses and range bars represent standard deviations of replicates.

Surface charge results generally exhibit relatively constant or slightly increasing pzc-pH values with increasing particle size. The surface charge results of the residual sizes illustrate a steady decline in charge as the pH becomes more basic. The point of zero charge (PZC) for each gradation is illustrated in the graphs as the point at which the surface charge curve crosses from a positive to negative charge for each residual size.

2.6.6 Power Law Application to Inorganic Constituent Data

The relationship between cumulative granulometric and cumulative metal mass of BMP residuals was examined using a power law model. Figure 2.13 presents plots of cumulative granulometric mass and cumulative metal mass on a log-log scale for each site BMP. Cumulative data were summed from 9500 µm to 25 µm. In each of these plots a power law model is fit to the cumulative data. Results of the power law model fit of the data (SSE and r²) are summarized in Table 2.4 along with calculated α and β values for each site BMP. Results for all site BMPs indicate that a power law can describe the relationship between cumulative granulometric mass and cumulative metal mass. The α value provides an
Figure 2.8 Surface charge trends as a function of pH (left and bottom axes of each plot) and point of zero charge (pzc-pH) trends as a function of gradation (right and upper axes of each plot) for rainfall-runoff residuals captured by the I-10 site BMPs (settling basin and filter). Data symbols represent mean of replicate analyses and range bars represent standard deviations of replicates.
Figure 2.9 Surface charge trends as a function of pH (left and bottom axes of each plot) and point of zero charge (pzc-pH) trends as a function of gradation (right and upper axes of each plot) for rainfall-runoff residuals captured by the I-30-I-40 site BMPs (settling basin and filter). Data symbols represent mean of replicate analyses and range bars represent standard deviations of replicates.
Figure 2.10 Surface charge trends as a function of pH (left and bottom axes of each plot) and point of zero charge (pzc-pH) trends as a function of gradation (right and upper axes of each plot) for rainfall-runoff residuals captured by the HD-NLR site BMPs (settling basin and filter). Data symbols represent mean of replicate analyses and range bars represent standard deviations of replicates.
Figure 2.11 Surface charge trends as a function of pH (left and bottom axes of each plot) and point of zero charge (pzc-pH) trends as a function of gradation (right and upper axes of each plot) for rainfall-runoff residuals captured by the BH-12 site BMPs (settling basin and filter). Data symbols represent mean of replicate analyses and range bars represent standard deviations of replicates.
Figure 2.12 Surface charge trends as a function of pH (left and bottom axes of each plot) and point of zero charge (pzc-pH) trends as a function of gradation (right and upper axes of each plot) for rainfall-runoff residuals captured by the 1-SE site BMPs (settling basin and filter). Data symbols represent mean of replicate analyses and range bars represent standard deviations of replicates.
Figure 2.13 Inorganic constituent data for the five experimental sites to fit to power law distributions using normalized metal and particle masses
Table 2.4 Resulting $\alpha$ and $\beta$ values from the power law application to the normalized granulometric mass and the normalized metal mass data acquired from the five experimental sites.

<table>
<thead>
<tr>
<th>Site</th>
<th>Inorganic Constituent</th>
<th>Alpha Value ($\alpha$)</th>
<th>Beta Value ($\beta$)</th>
<th>Coefficient of Determination ($R^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-10 E</td>
<td>Cd</td>
<td>0.9412</td>
<td>1.4327</td>
<td>0.9849</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>0.9592</td>
<td>2.2570</td>
<td>0.9858</td>
</tr>
<tr>
<td></td>
<td>Pb</td>
<td>0.9699</td>
<td>0.9696</td>
<td>0.9912</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>0.9521</td>
<td>2.0016</td>
<td>0.9910</td>
</tr>
<tr>
<td>I-30-I40</td>
<td>Cd</td>
<td>0.9643</td>
<td>0.6452</td>
<td>0.9922</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>0.8142</td>
<td>1.0431</td>
<td>0.9168</td>
</tr>
<tr>
<td></td>
<td>Pb</td>
<td>0.9628</td>
<td>0.6136</td>
<td>0.9811</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>0.9528</td>
<td>0.6042</td>
<td>0.9881</td>
</tr>
<tr>
<td>HD-NLR</td>
<td>Cd</td>
<td>1.0172</td>
<td>1.1024</td>
<td>0.9976</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>0.9956</td>
<td>1.0984</td>
<td>0.9992</td>
</tr>
<tr>
<td></td>
<td>Pb</td>
<td>1.0045</td>
<td>1.3994</td>
<td>0.9995</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>0.9982</td>
<td>1.1694</td>
<td>0.9991</td>
</tr>
<tr>
<td>1-SE</td>
<td>Cd</td>
<td>1.0104</td>
<td>2.1364</td>
<td>0.9963</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>1.0003</td>
<td>2.0781</td>
<td>0.9974</td>
</tr>
<tr>
<td></td>
<td>Pb</td>
<td>1.0142</td>
<td>2.0867</td>
<td>0.9991</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>0.9786</td>
<td>2.5835</td>
<td>0.9975</td>
</tr>
<tr>
<td>BH-12</td>
<td>Cd</td>
<td>0.9869</td>
<td>2.8806</td>
<td>0.9974</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>0.9656</td>
<td>3.5369</td>
<td>0.9906</td>
</tr>
<tr>
<td></td>
<td>Pb</td>
<td>1.0315</td>
<td>3.4258</td>
<td>0.9936</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>0.9662</td>
<td>2.1996</td>
<td>0.9946</td>
</tr>
</tbody>
</table>
index for the quantity of metal mass associated with the gradation while the $\beta$ value provides an index for the distribution of metal mass across the gradation.

### 2.6.7 Toxicity Characteristic Leaching Procedure

TCLP extracts for each residual size increment for the I-10E BMP site were analyzed for metals and compared to the EPA regulatory metal concentration limits for fresh water bodies (USEPA 1999b). TCLP, a procedure designed to simulate aggressive leaching in the environment, was applied to BMP residuals captured at the I-10E site. This experimental site captured and treated urban rainfall-runoff that would otherwise flow directly into City Park Lake. City Park Lake is a fresh water body, thus fresh water regulations presented in Table 2.1 are applicable to these results. The total, coarse (> 75 μm) and fine residuals (< 75 μm) were separated and the extraction procedure was performed on each of these gradation fractions.

Results of TCLP analysis depict the metal concentrations leached from by the residuals. The inset plots in Figure 2.14 illustrate the resulting TCLP concentrations for the gradations, as well as the fresh water regulation for the metals Cd, Cu, Pb and Zn. The extract metal concentrations of the fine residuals exceeded Cu and Zn fresh water limits by a factor of 10. In comparison the larger plots illustrate the trends in metal concentration as a function of particle size subject to acid digestion. For acid-digested residuals Cu and Zn concentrations increased with decreasing particle size. With the exception of several of the larger particle sizes, a similar, but more erratic trend to Cu and Zn occurred for Cd and Pb was dominated by a few of the largest residual fractions.
Figure 2.14 Plots of metal concentration [µg/L] from acid-digested residuals (sampled from I-10E BMP) as a function of residual particle size. Inset figures illustrate TCLP extract metals concentrations [µg/L] for the I-10E BMP residuals to EPA fresh water chronic toxicity limits for Cd, Cu, Pb, and Zn, and TCLP limits for Cd and Pb.
2.7 CONCLUSIONS

Five urban BMP sites of similar land use, located in three states, were sampled for rainfall-runoff residuals. The BMPs included a detention basin, settling basin, vegetated swale, porous pavement and a porous media filter. Four of the BMPs were loaded by urban transportation land use runoff and the final BMP was loaded by retail/commercial parking lot runoff. The granulometric and chemical characteristics of residuals captured by BMPs at each site were examined and quantified.

The median size of the captured residuals based on mass ($d_{50m}$) for all BMPs ranged from 149 - 1153 $\mu$m, a range that included the spectrum from fine to coarse sand-size material. The entire size gradation of captured residuals at all site BMPs ranged was from $< 1 \mu$m to $>10,000 \mu$m. The efficiency of capture of each of these sizes by the particular BMP was not an objective of this study. However, the captured residual mass distributions for all BMPs were dominated by the coarse fraction ($> 75 \mu$m). For all residual gradations, specific surface area (SSA) generally increased with decreasing particle size although the increase was not monotonic as would be expected for solid spherical particles. With respect to total surface area, a measure that accounts for the granulometric mass distribution, over 80% of the total surface area (SA) was associated with the fraction of the gradation $> 75 \mu$m for all BMPs. Consistent with total SA, for all BMPs over 80% of the metal mass was associated with residuals larger than 75 $\mu$m, with the exception of one BMP whose trend was similar to other BMPs but at a 60% level of metal mass. Specific gravity of captured residuals for all BMPs ranged from 1.8 to 2.8. Across BMPs there was no consistent trend across the gradation or between coarse and fine fractions separated at 75 $\mu$m. Point of zero charge (pzc-pH) values
ranged from 6 to 9 with either a slightly increasing pzc-pH with increasing particle size or with a relatively constant pzc-pH. A power law model relating cumulative granulometric mass to residual metal mass was developed and successfully applied for residuals from each site BMP. While metal concentrations on these residuals exceeded freshwater discharge limits, occasionally exceeded 503 limits the TCLP limits were not exceeded at any site for any metal. Results indicate that while the BMP residuals at all sites were not considered hazardous waste based on TCLP, freshwater discharge limits and Part 503 land application limits were exceeded on either a site or metal basis. Both granulometric and chemical analysis results of the BMP residuals suggest that alternative management techniques such as solidification/stabilization may be viable. While the characteristics of urban rainfall-runoff residuals are significantly different from municipal wastewater sludge, the annual generated volume of this residual sludge is similar to that of municipal wastewater sludge. The characteristics and volume of this residual sludge will require management techniques based on an understanding of this residual material.

2.8 REFERENCES


Greater Cincinnati Chamber of Commerce, (http://www.gecc.com/about_cincinnati/).


2.9 NOMENCLATURE

The following symbols are used in this chapter:

1 N: normality of one  
1-SE: site designation for the sampling site located along the shoulder of I-75 in Cincinnati, OH  
12-BH: site designation for the sampling site located in the median of I-75 in Cincinnati, OH  
\( \alpha \): alpha constant resulting from the application of the power law  
Al: aluminum  
As: arsenic  
ASTM: American Society for Testing of Materials  
\( \beta \): beta constant resulting from the application of the power law  
BMP: best management practice  
c\(_i\): mass concentration of inorganic constituent bound to the surface of particles with diameter \( i \) \([\mu g/g]\)  
C\(_i\): charge of sample of size \( i \) \([\mu mol/g]\)  
Ca: calcium  
CaCl\(_2\): calcium chloride  
Cd: cadmium  
CH\(_3\)COOH: glacial acetic acid  
CFR: code of federal regulations  
CMSA: consolidated metropolitan statistical area  
Cr: chromium
cm: centimeters
cm³: cubic centimeters
Cu: copper
°C: degrees Celsius
°F: degrees Fahrenheit
d₁₀: particle diameter at which 10% of the particle gradation mass is finer
d₃₀: particle diameter at which 30% of the particle gradation mass is finer
d₅₀: particle diameter at which 50% of the particle gradation mass is finer
d₅₀ₐₘ: particle diameter at which 50% of the particle gradation mass is finer
d₆₀: particle diameter at which 60% of the particle gradation mass is finer
d₉₀: particle diameter at which 90% of the particle gradation mass is finer
DTA: differential thermal analysis
EGME: ethylene glycol monoethyl ether
Fe: iron
GAC: granular activated carbon
H⁺: hydrogen ion
HCl: hydrochloric acid
HD-NLR: site designation for the sampling site located in Cincinnati, OH
HOCH₂CH₂OCH₂CH₃: ethylene glycol monoethyl ether
I-10 E: site designation for the sampling site in Baton Rouge, LA
I-30: interstate 30
I-30 – I-40: site designation for the sampling in Little Rock, AR
I-40: interstate 40
I-75: interstate 75
ICP-MS: inductively coupled plasma - mass spectrophotometer
ISSS: International Soil Science Society
KCl: potassium chloride
KOH: potassium hydroxide
L: liter
M: molarity (mol)
mᵢ: mass of solids having particle diameter i (g)
µm: micrometers (microns)
mm: millimeters
Mg: magnesium
Mn: manganese
MSA: metropolitan statistical area
m²: square meters
m²/g: square meters per gram
Mᵢ: known mass of each gradation used to calculate particle density
Mᵢₑ: mass of inorganic constituent present on particles with diameter i (mg)
NaOH: sodium hydroxide
Ni: nickel
OH⁻: hydroxide ion
P: probability
P₁: initial pressure reading in the helium pycnometry process (psi)
P2:  final pressure reading in the helium pycnometry process (psi)
Pb:  lead
ρ_s:  particle density (g/cm³)
PCC: portland cement concrete
PER: partial exfiltration reactor
PSD: particle size distribution
PVC: poly-vinyl chloride
PZC: point of zero charge
q_{sf}: lateral pavement sheet flow
QA/QC: quality assurance/quality control
rpm: revolutions per minute
SA_i: surface area of solids having particle diameter i (m²)
SC_i: surface charge of sample of size i (µmol/m²)
S/S: solidification and stabilization
SSA: specific surface area (m²/g)
SSA_i: specific surface area of solids having particle diameter i (m²/g)
SSA_m_i: mean specific surface area of particles of gradation i (m²/g)
TC: toxicity characteristic
TCLP: toxicity characteristic leaching procedure
TSS: total suspended solids
USDA: United States Department of Agriculture
USEPA: United States environmental protection agency
V_C: cylinder volume used to calculate particle density (cm³)
V_{H}: volume of H⁺ or OH⁻ used to titrate sample in surface charge procedure (cm³)
V_{MH}: mean volume of H⁺ or OH⁻ added to triplicate blank samples (cm³)
V_R: reference volume used to calculate particle density (cm³)
V_S: sample volume used to calculate particle density (cm³)
V_S: supernatant volume used to calculate surface charge (cm³)
V_T: total sample volume used to calculate surface charge (cm³)
W: exact weight of solid sample used in surface charge procedure (g)
W_a: measured weight of EGME retained by sample (g)
W_d: measured weight of dry sample (g)
x: Cumulative normalized particle mass (g)
y: Cumulative normalized metal mass (g)
Zn: zinc
CHAPTER 3. HYDRATION AND UNCONFINED STRENGTH BEHAVIOR OF CEMENT-BASED SOLIDIFIED STORM WATER RESIDUALS

3.1 SUMMARY

Particulate-laden sludge generated from rainfall-runoff controls represents an annual residual mass that is similar in magnitude to biosolids mass from wastewater treatment. Due to the elevated levels of metal elements, management of these rainfall-runoff residuals requires technologies that will immobilize these metal elements along with the poorly-cohesive granular matrix. One such technology is cementitious solidification/stabilization (S/S). In this study, cement-based S/S was applied to urban rainfall-runoff residuals recovered from an experimental treatment facility loaded by urban rainfall-runoff in Baton Rouge, Louisiana. Recovered residuals were separated into total (entire gradation), coarse (> 75 µm), and fine (< 75 µm) gradations. Each gradation was treated using three types of cement; type I Portland cement (PC), slag cement (SC), and 1:1 type I Portland/slag cement (PS). Cement/residual specimens were prepared using 10, 20 and 30% cement additions. Specimen unconfined compressive strength (UCS) was examined at 7 and 28 days. Results indicate PC provided the greatest strength gain to residual specimens of all gradations. Total and coarse gradations of residuals displayed the greatest strength, while fine residuals were only weakly solidified. Specimen hydration was examined through non-conventional differential thermal analysis (NCDTA), thermal gravimetry (TG) and differential thermal gravimetry (DTG) analyses. With and without residuals the PC achieved the greatest rate of hydration, followed by PS specimens. The SC specimens did not exhibit significant rate of hydration except in the presence of residuals.
3.2 INTRODUCTION

Anthropogenic activities such as vehicular surface transportation generate particulate and metal element constituents that are mobilized and transported by rainfall-runoff. The conveyance, mobilization and transport capacity of these surfaces, such as pavement, are increased because these surfaces are impervious and with a low relative roughness as compared to pre-development conditions. For example, 49 of the 50 states in the USA (excluding Alaska) contain 42,700 miles (68,719 km) of interstate highways (1718 km² of pavement area assuming two interstate directions per mile of 0.025 km wide pavement) upon which 23% of all vehicular surface transportation traffic occurs (Cox et al., 1996).

Rainfall-runoff transports a wide gradation of particulate matter, either containing metal elements or become substrates onto which metal elements are adsorbed. Specific sources of metal elements in rainfall-runoff or snowmelt include, vehicle emissions (Pb), abrasion of brake linings (Cu and Ni), wear and abrasion of vehicular components (Cr and Cu), tire abrasion (Zn), pavement abrasion and leaching from metallic infrastructure and from vehicles (Novotny and Chesters 1981, Sansalone and Buehberger 1997).

Due to the diffuse and stochastic nature of rainfall, runoff and constituents associated with runoff is a challenging to control and treat. Currently, in-situ and catchment-scale best management practices (BMPs) are being implemented, for both quantity and quality control. A BMP is defined as a device, practice, or method for removing, reducing, retarding, or preventing targeted storm water runoff quantity, constituents, pollutants, and contaminants from reaching receiving waters (Strecker et al., 2001). BMPs as unit operations and processes generate residual material captured
through treatment. Proper performance of BMPs requires the removal and disposal of these residuals; typically as a solid waste with elevated metal levels or as a hazardous waste. Whether designated a solid or hazardous waste these residuals can exhibit either acute or chronic toxicity unless properly managed.

Accompanying the potential for toxicity impacts by these residuals is the magnitude of rainfall-runoff residuals generated that requires management with respect their interaction with the environment. The annual volume of storm-generated flow is approximately 80% of sanitary sewage flow and in most cases, the observed annual volumes of residuals associated with the storm water flow can equal or exceed sludge volumes generated from municipal wastewater treatment (Field et al. 1994). The total suspended solids (TSS) concentrations associated with storm water runoff are much greater than that of wastewater or CSO, which results in the increased volumes of residuals and sludge associated with storm water runoff (Field et al. 1994). In addition, if settleable and sediment solids transported by rainfall-runoff are considered, in addition to the suspended fraction the mass of residuals that require management can be up to an order of magnitude greater (on an event-basis) than sewage dry weather flows (Sansalone et al. 1998). Estimated annual residual sludge volumes based on the suspended solids fraction delivered by rainfall-runoff in the U.S.A. range from 27 to 547 x 10^6 m³ with a sludge solids content ranging from 0.5 to 12 percent (Field et al. 1994). In addition to considerations of toxicity and the magnitude of residuals generated, is the largely inorganic (~ 70%) and granular nature of these solids (Sansalone et al. 1998), suggesting the potential applicability of solidification/stabilization.
3.2.1 Solidification/Stabilization

Solidification and stabilization (S/S) are treatment mechanisms applied in combination to manage solid and liquid residual materials. S/S processes are designed to accomplish one or more of the following objectives: reduction of contaminant mobility or solubility, improvement of physical and handling properties of the residual material by producing a solid with no free liquid, and minimization of exposed surface areas across which contaminant loss or transfer may occur (Means et al. 1995).

The terms “solidification” and “stabilization” are utilized in referring to mechanisms of the treatment technology. Numerous other terms such as “immobilization” and “fixation” have been used to denote the treatment, but “solidification” and “stabilization” are the preferred terms because they encompass the variety of mechanisms that may contribute to contaminant immobilization by this technology (Means et al. 1995). The processes associated with solidification and those concerning stabilization have disparate goals in treatment and can be defined individually. Though when combined, these treatment technologies combine to produce a very effective means of physically and chemically handling a residual material.

Solidification is a process in which materials are added with a main focus of transforming the residual material into a stable solid. Solidification refers to those techniques that concentrate on the containment of hazardous components by enhancing the physical characteristics of the residual material. The physical solidification improves engineering properties, such as bearing capacity, stress-strain behavior, trafficability, encapsulation, and reduced permeability of stabilized residual material forms (Park 2000). The processes involved with solidification do not infer that any form of chemical
reaction has occurred (Cohen et al. 1997). In processes of solidification, chemical reaction may or may not result between the additive and the residual material (Means et al., 1995). The hazardous constituents do not necessarily chemically react with reagents, but are instead mechanically locked, or encapsulated, within the solidified matrix (EPA 1986). A decrease in exposed contaminant surface area is observed as a result of solidification processes. With the decrease in this exposed surface area, the risk of the contaminants spreading to surrounding environments is decreased.

The primary focus of stabilization processes is to decrease the mobility and solubility of the contaminants by chemical fixation. Stabilization converts a residual material to a more chemically stable form with or without the improvement of the physical properties of the waste (Means et al. 1995). Stabilization incorporates the use of additives that result in physicochemical reactions that transform the contaminant to a less mobile form. Chemical additives, such as lime and sulfide, promote reactions that immobilize the contaminants by transforming them to non-toxic species such as hydroxides and sulfides (EPA 1986; Roy et al 1992).

Applications of S/S have been carried out for remediation of residue material at hazardous waste sites, the treatment of residue from other treatment processes, and the treatment of contaminated land where large quantities of soil containing contaminants are encountered (LaGrega et al. 1994). Design of an efficient S/S process for rainfall-runoff BMP residuals focuses on the physical solidification and chemical stabilization.

The efficiency and treatment duration of S/S is dependant on the manner in which the contaminants exist in the final product and the binder and additives used to treat the waste (Roy et al. 1992). Following the application of S/S, the waste may be physically
and/or chemically encapsulated within the final matrix. Physical entrapment of a waste residual (whether chemical altered or not) encapsulates the residual material within the binder and the residual material is protected by this encapsulating coating from surrounding environmental conditions that could result in the leaching of the hazardous components (Roy et al. 1992). The chemical entrapment of the waste refers to the occurrence of a reaction between the waste and the binder resulting in the formation of new, stable and non-toxic phases of the waste (Roy et al. 1992). Cement-based and pozzolanic binders, or a combination of the two, are the binders of choice in the S/S industry today (Means et al. 1995).

S/S technologies that utilize cement or pozzolanic binders treat the residual material through conversion of the material into a stable aggregated material. Some advantages of using cement-based processes are the availability and low costs of binder materials, mixing equipment for these binder materials, expertise locally and worldwide, the ability to make a strong physical barrier under adverse conditions, and the flexibility of tailoring the properties for different applications (McDaniel et al. 1990; Conner 1990). Cement-based S/S also has disadvantages, including the porous nature of the S/S treated residual materials, increase in residual materials volumes due to binder addition, and the potential of solidified/stabilized product quality due to the presence of impurities (such as metal elements) at high enough concentrations to impact the product in ways that effect product use and life cycle (Means et al. 1995).

The S/S of hazardous wastes by cement-based binders is a technology that has been applied to many types of wastes and industrial effluents, mainly those containing heavy metals (Conner 1990; Means et al. 1995; Cartledge et al. 1989). Cement-based S/S
has been applied to plating wastes containing various metals such as cadmium, chromium, copper, lead, nickel, and zinc, all of which are found in storm water residuals (Barth et al. 1990). The basic nature of cement provides a highly alkaline system that promotes the precipitation of these metals as insoluble hydroxides. The lowest solubility of most metals is reached at a pH of 10, thus the alkaline nature of cement is suitable for the precipitation and immobilization of the metal contaminants (Patterson 1985).

Through the precipitation mechanism of cement-based S/S, the metal hydroxides are trapped in the dense matrix of the cement where the transport of ions is decreased due to the reduction in the porosity and permeability of the matrix (EPA 1989). Depending on the physical and chemical residual material characteristics and those of the binder, the S/S treatment may permanently reduce toxicity and/or water solubility of hazardous materials and create a monolithic waste form that limits contaminant mobility due to low permeability and small surface area (Akhter et al. 2000).

Solidification of hazardous wastes through mixing with hydraulic binders, such as portland cement, has great potential for reducing contaminant leachability by physical means (Stegemann et al., 1996). The setting characteristics and hydration behavior of the cement binder in the presence of the waste is a key factor in the resulting physical solidification effectiveness. The hydration degree achieved by the cement binder is indicative of the physical strength of S/S treated waste. Testing of the hydration behavior and strength parameters of solidified wastes involves thermal analysis (TA) techniques and unconfined compressive strength (UCS) testing, respectively. With the testing of these parameters, a better knowledge of the mechanical characteristics and physical
efficiency of the S/S treatment application is attained and proper handling and/or industrial utilization of the material can be considered.

3.3 OBJECTIVES

The goal of this study was to examine the hydration and strength behavior of cement-based solidified rainfall-runoff residuals that were collected from rainfall-runoff BMPs at an experimental site in urban Baton Rouge, Louisiana. Study specimens were generated from an experimental matrix that varied parameters including residual size fractions, cement materials, and cement/residual ratios. There were three objectives of this study. The objectives were each examined for the total residual gradation, the coarse fraction (> 75 µm) and the fine fraction (< 75 µm) of residuals. Each objective was evaluated for cementitious binders of type I Portland cement (PC), slag cement (SC), and 1:1 type I Portland slag cement (PS) added to residual specimens using 10, 20 and 30% cement additions. The first objective was to examine the stress-strain behavior of matrix specimens through unconfined compressive strength (UCS) testing at 7 and 28 days of curing. Specimens strength testing was evaluated based on peak unconfined strength and the initial stress-strain modulus. The second objective examined the hydration behavior of cement types with and without residual additions. Hydration behavior was examined by thermogravimetric analyses (TG) and derivative thermogravimetry (DTG) of the cement pastes was performed followed by a non-conventional differential thermal analysis (NCDTA). The TG, DTG, and NCDTA procedures served to determine which cement and cement/residual combination displayed the most desirable characteristics in terms of setting and hydration behavior. The NCDTA was performed as a test to examine the setting characteristics of the cement pastes and to evaluate the effects of the
presence of residuals on the early stages of cement hydration. A sub-task of this hydration objective was to characterize particle size distributions (PSD) and particle densities of cements in order to fully evaluate all potential factors that may influence the solidification properties of the S/S product.

3.4 BACKGROUND

Rainfall-runoff residual material ranges in size from coarse gravel-size to fine colloidal-size particulates (-1 to 10,000+ µm). Previous examination of particulate matter in rainfall-runoff has demonstrated consistent trends in relationships between total surface area (SA) and metal mass, and specific surface area (SSA) and metal concentration (Sansalone et al. 1998). Results have demonstrated that anthropogenic metal element mass is associated with the coarse fraction of the PSD due to the higher values of total SA, whereas higher SSA and higher metal concentrations (both by definition) are associated with the finer particle sizes.

Cementitious S/S is a process that uses a cement or pozzolanic binder to convert the waste to an aggregate and is most commonly applied to cases where the contaminants of concern are heavy metals in cationic forms such as Cd\(^{+2}\) and Pb\(^{+2}\) (Buchler et al., 1996). Many studies have examined the solidification and strength characteristics of wastes treated using cement-based S/S.

Shively et al (1986) conducted a study where S/S was applied to sludge with metal hydroxide additions. Using type II Portland cement, the hydroxides of As, Cd, Cr, and Pb were treated. Cylindrical specimens 3 inches (76 mm) in height and 1.57 inches (40 mm) in diameter were prepared using a water to cement ratio of 1.0 by weight and a waste to cement ratio of 0.5 by weight. The samples were cured for 14 days in 100%...
humidity and tested for unconfined compressive strength using ASTM method C39-836. Results indicated that the presence of metal hydroxides hindered the formation of the cement matrix and as a result the compressive strengths of the specimens was lowered (Shively et al., 1986).

Diez et al (1997) tested the strength characteristics of cement stabilized Cd contaminated wastes. Using a water to cement ratio of 0.5, type I ordinary Portland cement (OPC) was spiked with various levels of Cd to simulate stabilization of a Cd waste. Cylindrical specimens 0.4 inches (10 mm) in diameter and 2.4 inches (60 mm) in height were prepared and cured for 2, 7 and 28 days and unconfined compressive strength examined. Results indicated that compressive strength was only slightly decreased by Cd addition (Diez et al., 1997).

Research on the application of S/S for spent abrasive media from bridge repainting operations containing Cr, Cd and Pb was conducted at the University of Texas at Austin. Type I-II Portland cement was applied with a water to cement ratio of 0.35 for the treatment of the media. Unconfined compressive strength was tested on 28 day cured cylindrical specimens 3 inches (76 mm) in diameter and 6 inches (152 mm) in height. The results of the strength tests indicated that all of the cement/waste mixtures achieved at least 1000-psi (6.89 MPa) compressive strength, which is above the EPA regulatory limit of 50 psi (0.34 MPa) (Webster and Loehr 1996). EPA considers a stabilized/solidified material with strength of 50 psi to have a satisfactory UCS (USEPA OSWER Directive No. 9431.00-2A). A minimum strength of 50 psi (0.34 MPa) is set as the provision for a stable foundation for materials to be placed up it, including construction equipment and impermeable caps and cover material (Barth et al., 1990).
Wang and Vipulanandan studied the S/S application to chromium-contaminated wastes. A potassium chromate waste was applied to Portland cement in 0.5, 2, and 5 percent by weight of cement additions and a water to cement ratio of 0.5 was used. Samples 1.5 inches (38 mm) in diameter and 3.15 inches (80 mm) in height were tested for UCS and it was found that the specimens with higher waste additions resulted in lower UCS, but all specimens met and/or exceeded the EPA compressive strength requirement (50 psi or 0.34 MPa) for S/S treated waste (Wang and Vipulanandan 2000).

In order to achieve the desired S/S effectiveness in the strength characteristics and hydration behavior, it is important to have an understanding of the chemical characteristics of the selected binder to be applied in S/S (Means et al. 1995). The original size, spatial distribution, and composition of cement particles have a large influence on hydration kinetics, microstructure development, and ultimate properties of cement-based materials (Bentz et al. 1999). The PSD of cement is an important characteristic in regards to overall strength, setting behavior and the initial heat release. A study done by Bentz, Garboczi, Haeker, and Jensen showed that the setting time of coarser cements was longer and that due to the longer setting time, the strength of coarse cements was lowered (Bentz et al. 1999). Further binding characterization can be achieved through thermal analysis methods. TG and DTG are thermal analysis techniques used to characterize cements and their hydration products (Dweck et al. 2000a). NCDTA is a technique used to monitor the initial exothermic reactions and analyze cement hydration and the effects of waste addition on cement hydration (Dweck et al. 2003).

TG measures weight changes in a material as a function of temperature and/or time under a controlled atmosphere and is principally used as a measurement of a
material's thermal stability. TG is also used to indirectly determine the composition of a material. TG measures weight changes in a material as a function of temperature and/or time under a controlled atmosphere and is principally used as a measurement of a material's thermal stability. TG analyses have been used to study the effects of chemicals present in cement-solidified radioactive wastes, as well as of tannery wastes (Hafez et al. 1994; Dweck et al. 2000). DTG is the derivative of TG and is used to analyze the mass change that occurs over the change in temperature with respect to time.

Knowledge of the mechanisms involved with the water movement in a drying/hydrating cement paste is critical for designing concrete matrices incorporating special materials, such as wastes (Bentz et al. 2001). In previous S/S research, the effect of a waste's presence on cement hydration has been evaluated through observation. In the research done by Shively et al, the effects of metal species on the hydration behavior of the cement were a function of the type of metals. The setting of the cements with Cd waste addition was not noticeably different, whereas the presence of Pb waste retarded the cement setting and the presence of As resulted in rapid (within 15 minutes) setting (Shively et al. 1986). The cadmium nitrate (Cd(NO₃)₂) added to the OPC in the S/S research conducted by Diez et al caused a precipitation reaction to occur and thus retarded cement hydration reactions (Diez et al. 1997). In a waste solidification study done by Dweck, Ferreia da Silva, Aderne, Buchler and Cartledge, the NCDTA technique was used and the presence of solid tannery wastes were found to accelerate initial hydration stages of slag cements (Dweck et al. 2003).
3.5 METHODOLOGY

3.5.1 Residual Collection Site

Baton Rouge, Louisiana, is located in south central Louisiana on the east bank of the Mississippi River in East Baton Rouge Parish. With the 71st largest population of the 318 metropolitan statistical areas (MSA) in the United States, municipal Baton Rouge has a population of 413,000 with approximately half of that population located within the corporation limits of the city (http://quickfacts.census.gov/qfd/states/22/22033.html). East Baton Rouge Parish has a land area of 472.1 square miles. Baton Rouge has a subtropical climate and receives annual mean rainfall of 63.08 inches (1602.23 mm) and only a trace level of snow (Jay Grymes, Louisiana Office of State Climatology 2003, http://www.losc.lsu.edu/stations.php?Id=btr). Located at the eastbound end of the interstate 10 eastbound lanes over City Park Lake, the experimental site in Baton Rouge is designated as I-10E and the average daily traffic (ADT) count is 70,433 in the eastbound direction only. The roadway surface of the bridge is constructed of Portland cement concrete (PCC). Runoff from the 544-m² pavement catchment is transported to the experimental treatment facility, located directly below the catchment and comprised of an 80-L grit separator, a 2130-L settling basin and a series of buoyant upflow filters. Once flow ended residuals were collected from each unit operations after each rainfall-runoff event (volumes were fully-captured) in approximately 48 hours.

3.5.2 Waste Residual Preparation

Residuals from all unit operations were combined and dried in a constant temperature room at 40°C and constant humidity of 20% for approximately one week prior to experimentation. Once the samples were dried, a mortar and pestle was used to
carefully disaggregate the particulate clusters from recovered residuals. The dry weight of the total residual sample was then measured and recorded. Following the weight measurement and disaggregation of the residuals, half of the gradation was set aside for use as total residual and the other portion was sieved using the ASTM D 422 mechanical sieve procedure (ASTM 1990). Using a 200 mesh United States Standard Sieve, the residuals were separated into coarse and fine fractions. The opening size of a 200 mesh stainless is 75 µm, thus the coarse fraction represents those residuals having a particle diameter of 75 µm and higher, and the fine fraction is comprised of those residuals with particle diameter smaller than 75 µm.

3.5.3 QA/QC

All experiments and measurements were performed in duplicate or triplicate with the exception of TG and DTG analysis. The TG and DTG analysis required approximately one hour, thus due to time constraints the measurement of the hydration degree of the specimens at specific curing times were unable to be duplicated. Particle analyses for the cement density evaluation were run in triplicate and the S/S specimens for UCS testing were prepared and tested in triplicate. The NCDTA procedure was performed on duplicate specimens. Arithmetic means and standard deviations among replicates were calculated and observed for consistency. Measurements with standard deviations above 20% of the arithmetic means were re-analyzed.

Method blank samples were analyzed in the NCDTA procedure and experimental control samples were run in the NCDTA procedure and for the testing of UCS. In the NCDTA procedure, a reference temperature was obtained from an empty blank vessel and an experimental control sample of pure cement was analyzed in order to compare the
results of a pure cement sample to those with residual addition. In the UCS testing, pure
cement specimens were cast and tested, comparing resulting strength to those of
specimens with residual addition.

3.5.4 Cement Characterization

Three cements, PC, SC, and PS, were used in the S/S application to rainfall-runoff
residuals. A cement company in New Orleans, Louisiana, provided 700 pounds (317.5
kg) of PC and 700 pounds (317.5 kg) of SC. Table 3.1 presents the chemical analyses of
the PC and SC. PSDs of the cements were analyzed using a laser diffraction particle size
analyzer. The dry cement powders were then analyzed for particle density through helium
pycnometry. The hydration products and setting behaviors of the cements were studied
using thermal analysis procedures including TG, DTG, and NCDTA.

3.5.4.1 Cement Particle Size Distributions (PSDs)

Particle size distributions of the PC, SC, and PS were analyzed using a LISST-
Portable Laser Diffraction Particle Size Analyzer (Sequoia Scientific Incorporated). In
this study laser-diffraction was used to measure particle volume concentrations as a
function of size, from which number and mass distributions can be determined. For the
laser-diffraction equipment utilized a laser beam formed from collimating the output of a
diode laser is projected through the sample of cement particles suspended in ethyl
alcohol, illuminating particles. The scattering of the laser across multiple angles is
detected in the focal plane of a receiving lens. The focal plane is an engineered detector
consisting of 32 logarithmically spaced rings corresponding to 32 discrete particle size
increments ranging from 1.00 to 250.00-µm. Assuming particles in suspension are
homogenous spheres, the instrument predicts the scattering energy of the laser across the
Table 3.1 Chemical composition of cements obtained from a cement company in New Orleans, La. and utilized in the application of S/S to urban-rainfall runoff residuals captured from an experimental facility located in Baton Rouge, La.

<table>
<thead>
<tr>
<th>Composition % (as oxides)</th>
<th>Cement Type</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PC&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ca</td>
<td>64</td>
</tr>
<tr>
<td>Si</td>
<td>21.2</td>
</tr>
<tr>
<td>Al</td>
<td>4.5</td>
</tr>
<tr>
<td>Fe</td>
<td>3.1</td>
</tr>
<tr>
<td>Mg</td>
<td>4</td>
</tr>
<tr>
<td>SO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2.7</td>
</tr>
<tr>
<td>Sulfide</td>
<td>0</td>
</tr>
<tr>
<td>Total Alkalis&lt;sup&gt;1&lt;/sup&gt;</td>
<td>0.54</td>
</tr>
</tbody>
</table>

<sup>1</sup>: Total Alkalis = Na Equivalent  
<sup>2</sup>: PC = Type I Portland Cement  
<sup>3</sup>: SC = Slag Cement
detection rings using the solution to the Maxwell equations for light scattering by particles (Mie theory). An energy distribution curve is generated for each discrete particle size. For the entire gradation, the measured energy distribution will be the weighted sum of all the discrete energy distribution curves (Riley and Agrawal 1991).

For the PC, SC, and PS, a solution consisting of cement and ethyl alcohol was created for the laser diffraction particle size analysis. The dilute solution was comprised of 0.02 grams of the respective cement particles and 200 grams of ethyl alcohol. Ethyl alcohol was utilized in this experiment to avoid hydration and dissolution reactions that occur when cement is added to water. The solution was placed into the analyzer, particles remained suspended through automated mixing in the laser chamber and the analyzer programmed to record a distribution every 5 seconds for 5 minutes. The distribution from the analyzer was converted to a mass-based $d_{50m}$ distribution through the following equations. The analyzer assumes spherical particles, thus the volumes of the particles at the $i^{th}$ size increment are calculated using (1).

$$V_{pi} = \frac{4}{3} \pi r_i^3 \quad (1)$$

$V_{pi} =$ volume of particles at the $i^{th}$ particle size increment (cm$^3$)

$r_i =$ particle radius at the $i^{th}$ particle size increment (µm)

The number of particles per unit volume for the $i^{th}$ particle size increment is calculated with a conversion to cm$^3$ from µm$^3$.

$$N_i = \frac{x \cdot D}{V_{pi} \cdot 10^6} \quad (2)$$

$N_i =$ number of particles at the $i^{th}$ particle size increment (# of particles/cm$^3$)

$x =$ measured volume concentration value from particle size analyzer [µL/L]
Based on (2), the $d_{50n}$ (number-based $d_{50}$) was calculated for each distribution over the 5-minute period and analyzed. This $d_{50n}$ was calculated for each PSD using a percent finer calculation and a linear interpolation to find the particle size that represents 50% of the distribution. Of the 60 PSDs measured over the 5-minute period, it was found that after an initial period of 40 seconds the PSDs stabilized. Following this initial 40-second interval, the distributions over the remaining 260 seconds of sampling were stabilized and the PSD at 40 seconds utilized as the cement PSD.

### 3.5.4.2 Cement Particle Density

The ASTM D5550-94 test method for gas pycnometry was used to determine the densities ($\rho_s$) of the cements (ASTM 1994). Using two pressure readings and a dry cement granulometric mass, the pycnometry procedure produced a measurement of the true volume of a heterogeneous dry solid mixture. The gas pycnometry procedure was carried out using helium gas on a Multi-Pycnometer manufactured by Quantachrome Corporation (Serial Number 11498010901, Model Number MVP-3DC). Helium gas was used in this procedure due to the inertness and small size of the helium atom enabling it to penetrate even the smallest pores and crevices associated with the fine cement particles (Lowell and Shields 1991).

The cement density analyses were run in triplicate. Cement samples were first gravimetrically measured and the sample masses ($M_S$) were recorded. There are three measurement settings associated with the pycnometer that correlate to three sizes (large, small, and micro) of stainless steel vessels for specimen accommodation. The volume of
the cement particles in the cylinder was calculated using the pressure measurements and formula (3).

\[ V_S = V_c - \frac{V_R}{\frac{P_1}{P_2} - 1} \]  

(3)

\( V_S \): Sample volume (cm\(^3\))

\( V_c \): Cylinder volume (cm\(^3\))

- “Large” = 147.499 cm\(^3\)
- “Small” = 25.644 cm\(^3\)
- “Micro” = 12.561 cm\(^3\)

\( V_R \): Reference volume (cm\(^3\))

- “Large” = 91.281 cm\(^3\)
- “Small” = 13.964 cm\(^3\)
- “Micro” = 7.156 cm\(^3\)

\( P_1 \): Initial Pressure Reading (psi) (1 psi = 6.89 kPa)

\( P_2 \): Final Pressure Reading (psi) (1 psi = 6.89 kPa)

Once the volume of the solid sample was known, \( \rho_s \) was calculated by (4):

\[ \rho_s = \frac{M_S}{V_S} \]  

(4)

\( M_S \): mass of each gradation (g)

\( V_S \): volume of sample (cm\(^3\))

3.5.4.3 Thermal Analysis: Thermogravimetry (TG) and Derivative Thermogravimetry (DTG) and Non-Conventional Differential Thermal Analysis (DTA)

In this study, TG served as a means of cement hydration product determination through the evaluation of the change in mass of a specimen over a specified change in temperature. Mass readings are taken real time during TG and mass changes are analyzed in order to determine which main hydration components of the specimen were
decomposed during the temperature change, thus leading to a determination of the hydration degree of the cement specimen. 

Thermogravimetric analyses were performed on the three cement pastes to examine their hydration behavior. The cement pastes were prepared with a water to cement ratio of 0.5 and no residual addition. The specimens were mixed in small sealed 50-mL plastic bags to prevent atmospheric air interference effects on the hydration of the pastes. An additional protective seal was added to the bags. Specimens were analyzed after 1, 5, and 24 hours and 4 weeks of hydration. With such a broad span of sampling times, the cement hydration products of the early and late stages of hydration were analyzed. The initial TG experiments were performed to analyze the early period of hydration and determine the actual percent of initial gypsum present in the cements. Knowing the gypsum content of cement is beneficial to the analyses of the hydration behavior of the cement. Gypsum is added to Portland cement clinker to regulate the otherwise extreme setting reaction which occurs in the presence of water (QCL Group 1999). Cement strength is greatly reduced by rapid setting times, thus the addition of gypsum and its effect on the setting speed increases the strength obtained by the cement (QCL Group 1999). The 4-week analyses were examined in order to evaluate the setting behavior of the paste at this time interval in anticipation of the 28-day curing application in the S/S treatment. 

TG and DTG analyses were carried out using a TG2950 High Resolution Analyzer manufactured by TA Instruments. To begin the TG procedure, a platinum pan with a diameter of approximately 6 mm was first thoroughly cleaned with ethyl alcohol and tared. Approximately 10-15 mg of cement specimen was added to the pan for
analyses. At a rate of 1 °C/min the instrument heated the specimen from room temperature (25 °C) to 35 °C and maintained this temperature for 60 minutes in order to dry the specimen. The dried specimen was then heated to 1000 °C at a rate of 10 °C/minute. A controlled inert nitrogen atmosphere, regulated by a 100-mL/min-nitrogen gas flow through the test chamber, was maintained throughout all steps of the procedure. The analyzer was accompanied with Thermal Advantage Software that graphed the specimen mass losses over the course of the heating process and aided in the assembly of the TG and DTG plots.

Differential thermal analysis (DTA) is a dynamic analysis of endothermic and exothermic reactions where an inert (consistent) reference condition is measured real time in parallel with the temperature measurement of the specimen. Throughout the DTA analysis, both the specimen and reference are subjected to the same heating or cooling procedure. The difference between the specimen and inert reference temperature is plotted versus time and the area under the curve that results is related to the energy involved in the sample transformation.

In the NCDTA procedure used throughout this research, the specimens were not subjected to a heating or cooling procedure as in conventional DTA analyses. Instead, the specimens analyzed through NCDTA were heated by an exothermic reaction that occurred within the specimens and the reference temperature was taken as the ambient air temperature. The principal difference between the NCDTA procedure and conventional DTA procedures was the method of heating or cooling. The heating or cooling processes are always imposed upon specimens analyzed through DTA, but in NCDTA the heating
The initial stages of cement hydration were analyzed in real time using the NCDTA experiment. Based on temperature variations among the specimens and the reference (room) temperature, the exothermic reactions of the hydration process were monitored through the NCDTA procedure. The evaluation of the setting behaviors of the cements with and without the addition of residuals revealed the setting time extension as a result of the residual material.

The NCDTA procedure was also applied to the S/S specimens. A water to cement mass ratio of 0.5 was used throughout the procedure and water to residual mass ratios of 0.2 for total and coarse wastes and 0.5 for fine waste were used. For the S/S treated residuals, all three experimental cements were tested in 10, 20, and 30 % additions to the total, coarse, and fine residuals. The experiment required 24 hours for the testing of the PC specimens and 48 hours for the examination of the SC and PS specimens. A constant room temperature of approximately 25 °C was maintained throughout the NCDTA procedures.

Using thermocouples and a computer aided data interface, four specimens were analyzed in each NCDTA procedure. The experimental set-up consisted of four simultaneous temperature measurements: one method blank volume without cement, one experimental control specimen with cement only, and replicates of a cement/residual combination. A Vernier Lab Pro processor interface is capable of storing 12,000 data points internally or transferring the data to a computer. In the NCDTA procedure, the interface was connected to a computer and programmed to acquire a temperature reading
every minute for 24 or 48 hours. A schematic is presented in Figure 3.1 for the NCDTA experimental set up. The diagram in Figure 3.2 illustrates the arrangement of each specimen. In order to provide adequate insulation from the surrounding environment, the samples were placed in 120 mL sterilized plastic reactors and covered with an insulated lid. These reactors were then placed into a series of polystyrene vessels. The inner polystyrene vessel was 6 oz. (177 mL) in size and surrounded the plastic reactor. The outer vessel was 12 oz. (355 mL) in size and served as additional insulation to the inner vessel with the reactor placed inside. A Vernier stainless steel temperature probe penetrated the outer cap at the top of each vessel through the reactor lid into sample as shown in Figure 3.2. Each of the temperature probes were secured in a polypropylene membrane in order to avoid being fixed within and adhered to the hydrated paste after solidification.

3.5.5 Preparation of S/S Unconfined Compressive Strength Test Specimens

Cylindrical specimens were prepared in triplicate for UCS testing of rainfall-runoff residuals. Specimen material was prepared using a water to cement of 0.5. In addition a water to dry residuals ratios of 0.2 for the total and coarse gradations and 0.5 for the fine gradation to satisfy the residuals moisture demand was required. The necessary portions of cement, residuals and water required for triplicate core preparation were thoroughly mixed in a one-liter bottle and distributed into three pre-labeled test cylinder molds. The cylindrical specimens were prepared in test molds that were 4 inches (101 mm) in height and 2 inches (51 mm) in diameter. It was determined that each test cylinder could hold 300 grams of dry residuals, thus preparation of the triplicate bulk material required a total of 900 grams of residuals. The moisture demand of the total
Figure 3.1 Schematic of the experimental set-up for the non-conventional DTA analyses.
Figure 3.2 Schematic of a sample and the polystyrene insulation cradle associated with the sample.
(TR) and coarse (CR) residuals was met by adding 10 mL of water to every 50 grams of residuals. In order to meet the moisture demand of the fine (FR) residuals, 25 mL of water was added to every 50 g of residuals. Upon meeting the moisture demand of the respective residuals, dry cement and water were added to produce a water to cement ratio of 0.5. Table 3.2 illustrates the amounts of materials used in the preparation of the bulk material used to compose the triplicate specimens.

The S/S cylindrical specimens were allowed to cure for 7 and 28 days in constant temperature-humidity chambers of 25°C and 100 percent humidity. Following the designated curing time, specimens were removed from the plastic cylinders and tested for UCS.

3.5.6 Unconfined Compressive Strength (UCS)

The Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens outlined by ASTM C39-96 was utilized in the analysis of the unconfined compressive strength (UCS) of the solidified storm water residuals (ASTM 1996). The UCS testing apparatus consisted of a 10,000 force-pound (44,4482 N) compression ring 7.5 inches (0.19 m) in diameter (Serial No. 11 manufactured by Rainhart Company) secured to a 50 kilo-Newton load frame (Model Designation EL25-284 manufactured by Engineering Laboratory Equipment Limited). The compression ring was calibrated according to the United States National Institute of Standards and Technology by the Morehouse Instrument Company Force Calibration Laboratory located in York, Pennsylvania (Calibration number 11J1802). Specimens were capped with 0.5 inch (1.27 cm) thick neoprene pads and loaded at a strain rate of 0.05 in/min (1.7 mm/min). Specimen strain and load ring deflection readings were taken every 30 seconds.
Table 3.2 Material proportions utilized in preparation of S/S specimens; for both coarse and total residuals.

<table>
<thead>
<tr>
<th>Cement Addition (%)</th>
<th>Water Demand of Residuals (mL)</th>
<th>Residuals (g)</th>
<th>Water (g)</th>
<th>Dry Cement (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>180</td>
<td>900</td>
<td>45</td>
<td>90</td>
</tr>
<tr>
<td>20</td>
<td>180</td>
<td>900</td>
<td>90</td>
<td>180</td>
</tr>
<tr>
<td>30</td>
<td>180</td>
<td>900</td>
<td>135</td>
<td>270</td>
</tr>
</tbody>
</table>
The compression ring gauge measured the force applied to the specimens by measuring the deflection of the ring in thousandths of an inch. These measurements were converted to pound-force units (lbf) using the calibration curve of the compression ring. In order to calculate the stress measurements, the resulting lbf measurements were divided by the average cross sectional area (in\(^2\)) of the cylinder specimen. The stress measurements were converted to MPa and are presented in this research in both SI (MPa) and English (psi) units. Measurements of strain were converted to cm and are presented in this research in both SI (cm) and English (in) units. Stress-strain relationships were developed based on the data acquired from the UCS tests. The slope of the linear portion of the stress versus strain graph was then used to calculate a strength modulus.

3.6 RESULTS

3.6.1 Cement PSDs and Particle Density

Each mass-based cement d\(_{50m}\) calculated based on measurements from laser diffraction, are presented in Figure 3.3. The d\(_{50m}\) of the PC analyzed through laser diffraction analyses was 10.82 µm, 10.39 µm and the PS was 14.14 µm. Actual size gradations are presented in the right plots of Figure 3.3. In a study published by Bentz, Garboczi, Hacker and Jensen, cement particle size distributions were analyzed with respect to cement hydration. Cement with average size particles of 5 and 30 µm were assessed and it was found that the degree of hydration greater for the average cement size of 5 µm PSD for every analysis (Bentz et al. 1999).

Particle density measurements were taken of the cements in triplicate using helium pycnometry. Results from these analyses are summarized in Table 3.3. The
Figure 3.3 PSDs of cements and cement/slag mixtures in ethyl alcohol as a function of time and particle diameter analyzed using laser diffraction.
Table 3.3 Summary of the cement density measurements and their respective standard deviations for PC = type I portland cement, SC = slag cement, and PS = 1:1 mass ratio mixture of type I portland and slag cements.

<table>
<thead>
<tr>
<th>Cement</th>
<th>( \rho_s ) (g/cm(^3))</th>
<th>Standard Deviation (n=3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
<td>3.178</td>
<td>0.001</td>
</tr>
<tr>
<td>SC</td>
<td>2.899</td>
<td>0.005</td>
</tr>
<tr>
<td>PS</td>
<td>2.989</td>
<td>0.002</td>
</tr>
</tbody>
</table>
highest density cement was PC at 3.178 g/cm³ (σ = .001), with the PS and SC slightly denser at 2.899 (σ = .002) and 2.989 g/cm³ (σ = .005), respectively. Published values of Portland cement particle density is reported as approximately 3.15 g/cm³ (Hannak et al. 1988). Depending on the slag source, the particle density of slag cement ranges from 2.85-2.94 g/cm³ (SCA 2003, http://www.slagcement.org/proportioning.htm). The particle density values exhibited by the experimental cements were found to be consistent with the literature.

3.6.2 Thermal Analysis: Thermogravimetry (TG) and Differential Thermogravimetry (DTG) and Non-Conventional Differential Thermal Analysis (DTA)

The TG and DTG plots for the 1, 5, and 24-hour hydration times are summarized for the type I Portland (PC) paste in Figure 3.4, for the slag cement (SC) paste in Figure 3.5, and for the 1:1 type I portland/slag mixed (PS) cement in Figure 3.6.

Figures 3.4 through 3.6 demonstrate that the initial 1 and 5-hour TG analyses for the PC and PS pastes resulted in DTG curves with peaks occurring between 50 °C and 100 °C, 100 °C and 150 °C, 400 °C and 650 °C. The DTG plots for the SC illustrated a significantly muted peak patterns to the PC and PS plots, but all SC peaks were at least a factor of 10 lower than those of the PC and PS. In all the plots the initial peaks in the DTG curves represent the water released from the tobermorite gel (calcium silicate hydrated gel 3CaO·2SiO₂·xH₂O) formed during cement hydration and the second peaks represent water released from hydrated calcium sulfate. The latter 400 °C and 650 °C peaks present in the DTG plots of the PC and PS pastes, result respectively, from reactions associated with the decomposition of calcium hydroxide (Ca(OH)₂) and the carbon dioxide being released from carbonate decomposition, when present in the
Figure 3.4 TG and DTG plots of the Type I Portland cement paste (PC) without waste addition after 1, 5, and 24 hours of hydration.
Figure 3.5 TG and DTG plots for the slag cement paste (SC) without waste addition after 1, 5, and 24 hours of hydration.
Figure 3.6 TG and DTG plots for the 1:1 mass ratio mixture of type I Portland cement and slag cement (PS) without waste addition after 1, 5, and 24 hours of hydration.
specimen. These latter peaks are significantly lower in the DTG plots of the SC paste indicating that the calcium hydroxide is not being formed to the same extent as in the PC and PS pastes after the same time of hydration. In the third early stage of cement hydration, the accelerating period, when setting begins due to crystallization of CaOH₂ and tobermorite formed from the hydration of the tricalcium silicate (C₃S) (Dweck 2001; Dweck et al. 2003). The setting rate increases significantly until a maximum value of heat evolution and paste temperature are reached (Dweck et al. 2003). One method of measuring the hydration degree of a cement paste is to quantify the amount of Ca(OH)₂ present in the sample, which can be calculated using the water loss from Ca(OH)₂ in the TG heating process (Dweck et al. 2001). Upon evaluating the lack of DTG curves indicating Ca(OH)₂ dehydration, it can be noted that the SC pastes did not reach or pass the third stage of cement hydration in the first 5 hours of hydration.

After 24 hours of hydration, the PC cement was solidified, the PS cements showed some solidification, and the SC cement exhibited no degree of hydration. The TG analysis of the 24-hour hydrated PC and PS cement pastes resulted in DTG curves exhibiting peaks between 35 °C and 200 °C, as well as between 400 °C to 450 °C. The DTG analysis of the 24-hour hydrated SC specimen showed similar initial peaks to the PC and PS samples, but beyond 200 °C any peaks exhibited by the SC sample were small and insignificant. The overall DTG trend exhibited by the SC specimen indicates that hydration products, such as ettringite (Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O) and calcium hydroxide, were not extensively formed during the 24-hour hydration period. The initial DTG peaks that were prominent with the PC and PS specimens and much less prominent for the SC specimen are associated to the release of water from tobermorite gel and
ettringite phases. The formation of ettringite is caused by the hydration of cement clinker minerals with gypsum that is added to dry cement to control the setting characteristics of the cement (Dweck et al. 2000a). The peaks occurring at 400 °C to 450 °C in the 24-hour hydrated PC and PS samples resulted from the dehydroxilation of the calcium hydroxide present in the pastes. Compared to the 1 and 5 hour hydrated specimens, these latter peaks were higher for the 24-hour hydrated samples due to the higher degree of hydration and the formation and presence of higher amounts of calcium hydroxide. The highest 400 °C to 450 °C peaks for the 24-hour hydrated specimens were exhibited by the PC cement with a maximum derivative weight loss of approximately 0.8% per minute over the temperature increase.

The TG and DTG results after 4 weeks of hydration were analyzed for the three cement pastes and the results are presented in Figure 3.7. The TG and DTG curves all displayed the same general behavior as that representative of 24-hour hydration; only there were higher DTG peaks for the PC and PS pastes at the 4-week hydration time period indicating higher degrees of hydration. The TG curve of the 4-week hydrated PC and PS samples illustrated an overall weight loss of approximately 15%, whereas those hydrated for only 24 hours show overall weight loss of less than 5%. The increased weight loss in the 4-week specimens is due to the higher combined moisture losses associated with the specimens that have had a longer hydration time. This weight loss indicated by the TG analysis occurs only up to about 400 °C and includes moisture from CSH (tobermorite gel) as well as other minor hydrated compounds after 200 °C (Dweck et al. 2000). The 4-week TG and DTG plots were of the same form for the PC and PS pastes, but varied in peak amplitude with cement type, as PC paste had the highest degree
Figure 3.7 TG and DTG of the type I Portland cement (PC), slag cement (SC), and 1:1 mass ratio mixture of type I Portland and slag cement (PS) pastes without waste addition after 4 weeks of hydration.
of hydration, followed by the PS cement. The DTG curve for the 4-week hydrated SC paste displayed a similar initial peak to the PC and PS pastes, but beyond 200 °C there were no peaks. The lack of DTG peaks associated with the SC pastes indicates that even after 4 weeks of hydration there were no significant hydration products formed and thus there was no significant degree of hydration achieved by the paste.

Cement hydration and cement/residual specimen hydration was also examined with NCDTA. Cement pastes were prepared with 100 g of cement and 50 g of water, a 0.5 water to cement ratio, and monitored for a 24-hour period. Results are summarized in Figure 3.8. The area under the curve was calculated at 10-minute intervals and the resulting areas were summed in order to determine the amount of heat evolved (energy) during the experiment as a function of hydration time. The evolved heat calculations for the pastes are represented graphically in kilo-Joules (kJ). Progress of the cement reaction is indicated by these heat measurements (Dweck et al. 2003).

Cements were mixed with the residuals and NCDTA was performed to monitor the effects of the residuals on the hydration of the cements. Cement to residual mass ratios of 0.1, 0.2, and 0.3 were utilized for the cement addition to total (TR), coarse (CR) and fine (FR) residuals. In preparation of each specimen, the respective cement and water amounts were added to 50 g of dry residuals. In all experiments, a specimen containing only cement was analyzed as a control. This control specimen was prepared using 50 g of cement and 25 g of water. The resulting plots of the NCDTA experiments are presented in Figures 3.9 through 3.11. The evolved heat integrals are presented in Figures 3.12-3.14.
Figure 3.8 Results of the non-conventional DTA (NCDTA) analyses and total evolved heat for the experimental cements without waste addition prepared with a water to cement ratio of 0.5.
Figure 3.9 Temperature difference between the reference temperature and the actual temperature within the reacting samples over 24 hours for hydration of PC stabilized specimens. Control specimens contained only PC and no residuals; compared to stabilized residual specimens that contained 10, 20, or 30% PC. Residual specimens contained either fine residuals <75 μm (FR), coarse residuals >75 μm (CR) or total residuals (TR) representing the entire gradation.
Figure 3.10 Temperature difference between the reference temperature and the actual temperature within the reacting samples over 24 hours for hydration of SC stabilized specimens. Control specimens contained only PS and no residuals; compared to stabilized residual specimens that contained 10, 20, or 30% SC. Residual specimens contained either coarse residuals >75 µm (CR) or total residuals (TR) representing the entire gradation.
Figure 3.11 Temperature difference between the reference temperature and the actual temperature within the reacting samples over 24 hours for hydration of PS stabilized specimens. Control specimens contained only PS and no residuals; compared to stabilized residual specimens that contained 10, 20, or 30% PS. Residual specimens contained either fine residuals <75 µm (FR), coarse residuals >75 µm (CR) or total residuals (TR) representing the entire gradation.
Figure 3.12 Heat evolved over 24 hours for hydration of PC stabilized specimens. Control specimens contained only PC and no residuals; compared to stabilized residual specimens that contained 10, 20, or 30% PC. Residual specimens contained either coarse residuals >75 μm (CR) or total residuals (TR) representing the entire gradation.
Figure 3.13 Heat evolved over 24 hours for hydration of SC stabilized specimens. Control specimens contained only SC and no residuals; compared to stabilized residual specimens that contained 10, 20, or 30% PC. Residual specimens contained either coarse residuals >75 µm (CR) or total residuals (TR) representing the entire gradation.
Figure 3.14 Heat evolved over 24 hours for hydration of PS stabilized specimens. Control specimens contained only PS and no residuals; compared to stabilized residual specimens that contained 10, 20, or 30% PC. Residual specimens contained either coarse residuals >75 µm (CR) or total residuals (TR) representing the entire gradation.
As seen from the NCDTA curves and the resulting evolved heat (area under each curves), the PC and PS cement pastes exhibited a high initial exothermic reaction, indicating that hydration did occur in the first 24 hours of setting. The evolved heat illustrated in Figure 3.12 demonstrated that the PC paste emitted the greatest heat and obtained the highest degree of hydration over the 24-hour period. The PS specimen demonstrated a considerable degree of hydration, as can be seen in the evolved heat graph in Figure 3.14. In comparison to the PC results, the 50% mix of slag in the PS yielded a higher heat evolution than that of 50% of the PC, indicating that there is (are) additional reaction(s) in the PS paste. Independently, the SC did not react significantly as indicated by NCDTA, as shown in Figure 3.10 and the evolved heat plot, in Figure 3.13, of hydration in the initial 24-hour period of setting.

In Figure 3.9, the NCDTA plots for PC addition to the TR and CR gradations of the residuals indicate that the increased addition of PC resulted in higher peak temperature values, but a close look at the plots reveals that the maximum values for the cement/residual specimens do not occur in the same time frame as the PC control. This observation indicates that the residuals impose a retarding effect on the hydration of the cement. Figure 3.9 presents the comparison of increasing PC addition to the TR and CR gradations of the residuals, which illustrates that the residual gradation influenced the behavior of the cement hydration in the same manner. The evolved heat plots summarized in Figure 3.12 indicate that the higher the PC addition to residuals (from a cement/residual ratio of 0.1 to 0.3), the higher is the amount of heat evolved from the specimen. This increase in heat evolved is indicative of the PC cement hydration specimen reaching a higher amount of hydrated cement. Of the three experimental
cements, the PC cement with residuals addition achieved the highest degree of hydration in the first 24 hours.

The NCDTA plots presented in Figure 3.10 for the SC specimens illustrate no significant peaks, indicating that these specimens exhibited little to no hydration throughout the experimental period. The experimental time frame allotted to these specimens was extended to 48 hours due to the lack of observed hydration in the initial 24-hour period. Even at 48 hours resulted in very little additional hydration of the specimens; however, the heat evolved as shown in Figure 3.13 for the SC specimens do indicate that the presence of the residual had a small exothermic effect on the SC paste. In the case of the 10% SC addition to the TR and CR gradations of the residual, the results displayed a higher amount of heat evolved from the cement/residual specimens than from the SC control paste. This exothermic behavior could possibly be a result of some of the residual components reacting and aiding in the hydration of the SC paste, as was seen in a study conducted by Dweck et al. that observed some slag cement hydration reactions that were significantly accelerated by the presence of the waste (Dweck et al. 2003).

The hydration behavior demonstrated by the PS paste with residual addition was similar to the behavior of the PC paste. PS specimens hydrated within the first 24 hours. Figure 3.11 presents the NCDTA curves for the PS paste. These curves differ in magnitude, but are very similar in shape to those presented for the PC paste in Figure 3.9. Another similarity seen between the PC and PS pastes was with the trend of higher maximum NCDTA peaks with increasing addition of cement to the residuals. These higher peaks were seen in the 30% PS addition to the TR and CR gradations and indicate
that compared to the 10% and 20% PS additions, a higher degree of hydration was achieved. The plots in Figure 3.11 indicate that the NCDTA peaks of the PS control occurred before the peaks of the PS/residual specimens. This trend indicates that the residual is causing hydration retardation to the PS paste just as was the case in the PC specimens. The results of the NCDTA for PS shown in Figure 3.14 indicate that the heat evolved within the specimens increased with increasing cement addition. The effects of cement hydration by the waste gradation were negligible for the 10 and 30% PS additions to the waste. For the 20% PS addition, the PS paste added to the total gradation produced more heat than the PS added to the coarse fraction. As this was the only instance of this phenomenon, there was no significant trend that would lead to any conclusions of increased hydration retardation by either the TR or CR gradations of residuals.

The NCDTA plots for the PC and PS additions to the FR gradation of residuals are represented with their respective pastes in Figures 3.9 and 3.11. The evolved heat plots of the PC and PS additions to the FR gradation are presented with their respective pastes in Figures 3.12 and 3.14. In the analyses of the PC and PS cement additions to only the FR gradation of residuals, the SC was not included in the investigation. The SC was excluded due to its lack of hydration performance in previous experimentation. The PC and PS cements were both added in 0.1, 0.2 and 0.3 cement/residual rations to the FR gradation. Results of these analyses indicate that for that hydration did not occur for all of the PS additions to the FR gradation. For the 10 and 20 % PC paste additions to the FR gradation, cement hydration was not achieved. The only FR/cement specimen indicating a slight NCDTA peak and indicating some degree of cement hydration was the 30 % PC addition. Compared to the PC control sample, the peak demonstrated by the 30 % PC
addition to the FR gradation of residuals was delayed by almost 6 hours. This delay indicates that the FR gradation retarded the cement hydration process.

3.6.3 Unconfined Compressive Strength (UCS)

The strength of solidified/stabilized residuals was examined through unconfined compressive strength testing. Cement to residuals ratios of 0.1, 0.2, and 0.3 were used to create specimens 0.05 m (2 in) in diameter and 0.10 m (4 in) in height. Total and coarse residuals were tested at 7 and 28 days. Due to the limited amount of fine residuals, FR specimens were only prepared using the PC for 28-day cures.

Following the appropriate cure times, the specimens were removed from the molds and prepared for UCS testing. The specimens that were prepared using the SC did not solidify, thus only those specimens prepared with PC and the PS were tested for UCS.

The EPA regulatory limit for satisfactory compressive strength is 50 psi (0.34 MPa) (USEPA OSWER Directive No. 9431.00-2A). All of the PC and PS specimens, with the exception of the FR specimens, exceeded this regulation.

Relative to hydration time, those samples that were allowed to hydrate for 28 days exhibited smooth textures and good handling characteristics, whereas those that were cured for only 7 days were slightly damp and had rough surface characteristics. The specimens with higher cement addition were more physically stable and easier to handle than those with the lesser amounts of cement. There were no apparent differences in the samples prepared with TR gradation and the samples prepared with the CR gradation of residuals. The specimens made with the FR gradation displayed poor setting characteristics compared to those specimens that were made with the TR and CR residual
gradations with the same cement amounts and cured for the same amount of time. The FR specimens with 0.10 PC additions did not solidify.

A summary of the elastic modulus values is presented in Table 3.4. The specimens were tested in triplicate and mean values of stress and strain were plotted and the elastic modulus was calculated from this plot. The increasing amount of cement added to the residuals had the most pronounced effect on the strength of the specimens. With only one exception, the 7-day 0.2 PC application to the TR gradation, the higher cement to residuals ratios resulted in an increase in the strength of the specimens.

The performances of the cements in UCS testing were consistent with the data collected from the NCDTA analyses. As mentioned previously in the analyses of the NCDTA results, the specimens prepared with SC did not hydrate. The strongest specimens were those prepared with PC. The specimens prepared with the PS exhibited intermediate strength, but were surpassed in performance by the specimens prepared with PC.

The graphical stress versus strain relationships and moduli calculations for the 7-day cure for specimens prepared with PC and TR and CR gradations are represented in Figure 3.15. The 28-day cure for the TR, CR, and FR specimens prepared with PC are represented in Figure 3.16. As the amount of cement added to the residuals increased, the elastic modulus became larger. Generally, higher elastic modulus values were observed for specimens with greater cement addition that were cured for longer times, with the exception of the 7-day cure of the 0.2 addition of PC to the TR gradation.

The graphs presented in Figure 3.17 are for results from the UCS testing of the 7-day cures of the PS application to the TR and CR residual gradations. Figure 3.18
Table 3.4 Summary of elastic modulus values for UCS specimens prepared with type I Portland (PC) and 1:1 type I Portland/slag (PS) cements and the total (TR), coarse (CR), and fine (FR) gradations of residuals.

<table>
<thead>
<tr>
<th>Cement Addition</th>
<th>Total Residuals</th>
<th>Coarse Residuals</th>
<th>Fine Residuals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E 7-day (MPa)</td>
<td>E 28-day (MPa)</td>
<td>E 7-day (MPa)</td>
</tr>
<tr>
<td>10 % PC</td>
<td>1.47 (541.6 psi)</td>
<td>1.28 (613.5 psi)</td>
<td>1.81 (667.0 psi)</td>
</tr>
<tr>
<td>10 % PS</td>
<td>0.40 (148.0 psi)</td>
<td>0.81 (293.1 psi)</td>
<td>0.25 (86.1 psi)</td>
</tr>
<tr>
<td>20 % PC</td>
<td>3.12 (1380.9 psi)</td>
<td>1.87 (601.2 psi)</td>
<td>1.87 (680.3 psi)</td>
</tr>
<tr>
<td>20 % PS</td>
<td>1.79 (653.1 psi)</td>
<td>0.99 (675.1 psi)</td>
<td>1.03 (382.1 psi)</td>
</tr>
<tr>
<td>30 % PC</td>
<td>2.14 (725.6 psi)</td>
<td>2.58 (937.3 psi)</td>
<td>3.07 (1111.3 psi)</td>
</tr>
<tr>
<td>30 % PS</td>
<td>2.01 (681.8 psi)</td>
<td>2.47 (811.6 psi)</td>
<td>1.45 (527.3 psi)</td>
</tr>
</tbody>
</table>

¹: Due to the limited amount of fine material, only PC was added to the fine residuals in 0.10, 0.20, and 0.30 additions. The specimens with 0.10 addition of PC to the fine residuals did not harden, thus the UCS of the specimens could not be determined.
Figure 3.15 UCS test and elastic modulus (E) results for 7 day cures of type I portland cement (PC) additions to the total and coarse gradations of residuals.
Figure 3.16 UCS test and elastic modulus (E) results for 28 day cures of type I portland cement (PC) additions to the total and coarse gradations of residuals.
Figure 3.17 USC test and elastic modulus (E) results for the 7-day cures of 1:1 type I portland/slag cement (PS) additions to the total and coarse gradations of residuals.
Figure 3.18 UCS test and elastic modulus (E) results for 28-day cures of 1:1 type I portland/slag cement (PS) additions to the total and coarse gradations of residuals.
represents the stress strain and modulus data for the UCS of 28 day hydrated specimens prepared with PS and the TR and CR residual gradations. These specimens included in these data sets exhibited the expected strength characteristics relative to cure time and cement addition. The strongest samples resulted from the 28-day cure of the 30 % cement application to the residuals, where as the weakest specimens were cured for only 7 days with 10 % cement addition.

Figures 3.19 and 3.20 summarize the stress-strain and elastic modulus data collected throughout the tests for UCS. Overall, the PC was the best binder applied to the rainfall-runoff residuals. The specimens prepared with PC had the highest degrees of hydration and displayed the best strength characteristics. With respect to the control specimens, the presence of the residuals did limit the strength of all specimens, but as the amount of cement addition to the residuals increased, the strength of the treated residuals was comparable to the strength of the cement control specimens.

3.7 CONCLUSIONS

This research examined the unconfined strength and hydration behavior of rainfall-runoff residuals solidified and stabilized with cementitious admixtures that included Portland cement, Slag cement and a mixture of Portland-Slag. Characterization of the cements and the cement/residual specimens provided this research with an insight as to the strength and hydration behavior of these binders.

The TG and DTG analyses demonstrated that the PC and PS pastes hydrated while the SC paste did not present significant hydration over the duration of the examinations.
Figure 3.19 UCS test results for 7-day and 28-day cures of type I portland cement (PC) control samples followed by merged plots of all 7-day and 28-day cures of PC based samples.
Figure 3.20 UCS test results for 7-day and 28-day cures of 1:1 type I portland/slag cement (PS) control samples followed by merged plots of all 7-day and 28-day cures of PS based samples.
NCDTA analyses conducted on PC, SC, and PS pastes, as well as the PC, SC, and PS additions to the rainfall-runoff residual wastes indicated that the presence of the TR and CR gradations had similar significant effects on the retardation of the hydration of the material and minimization of the heat evolved in these specimens, whereas the presence of FR gradation greatly hindered the hydration and reduced the heat evolved in the hydration reactions of the S/S specimens. The NCDTA procedure indicated that the hydration degree of the specimens increased by approximately 10% with each incremental cement increase to the TR and CR gradations, however a goal of S/S technology is to apply the least amount of cement necessary to maintain the production of material that is physically and chemically stable. However, increasing cement addition did not improve the hydration of the FR specimens. Through the NCDTA method, it was found that the total heat evolved was indicative of hydration degree achieved by the specimens, in that the higher amount of heat evolved resulted in the formation of a stronger specimen.

The lack of hydration seen with the FR specimens can be attributed to the many factors. Recalling the results of TCLP extract analyses of the residuals, the highest heavy metals concentrations were associated with the FR gradation. Previous studies (Tashiro et al. 1977) reported that in the presence of heavy metals such as Zn, Pb, and Cu the hydration of cement was retarded. Cement hydration is repressed due to the formation of double salts formed between the heavy metals and the calcium ions dissolved from the cement (Park 2000). These interference reactions associated with the heavy metals presence are possibly the reason for the lack of cement hydration in the metal contaminated FR specimens. Another possible reason for the lack of hydration with the
FR specimens is the high water demand associated with the fine material. Fine materials, such as clays, have exhibit strong water adsorbing characteristics, and thus affect the water available for cement hydration reactions (Akhter et al. 2000).

Physical solidification characteristics of the S/S treated TR, CR, and FR residual gradations were analyzed through unconfined compressive strength (UCS) testing. Evaluations were made on the variable physical effects on the S/S material by the three gradations of residuals through the development of stress-strain relationships and unconfined peak strength determination. According to the EPA, a stabilized/solidified material with an ultimate strength of 50 psi (0.34 MPa) is a satisfactory UCS (USEPA OSWER Directive No. 9431.00-2A). The S/S material that included only the SC paste failed to meet this criterion. The highest UCS values resulted from the residuals treated with the PC. The size gradation of the residuals was a significant factor in the resulting strength of the S/S material. Of the total, coarse, and fine residual additions, the TR and CR exhibited similar satisfactory strengths, but the FR specimens exhibited very poor strength characteristics.

The highest strength values observed in this study were from residuals made with 0.2 and 0.3 cement to residuals ratios. In some instances, the specimens with 0.2 mass ratio cement addition exhibited the highest UCS values making this amount of cement suitable for the treatment needs of the residuals. With regard to cure time, longer cure times are always favorable to the physical durability of the cement. The results obtained in this study proved that extensive cure times favorably increase the durability of the treated waste, thus a 28-day cure was determined to be the most effective in the S/S application.
3.8 IMPLICATIONS

The physical attributes of solidified residuals are important in determining the potential industrial applications of the material. A regulatory minimum strength of 50 psi (0.34 MPa) has been set by the EPA as an indicator of the strength a material must possess in order to provide a stable foundation for materials to be placed upon. According to the EPA, material that demonstrates strength of at least 50 psi is able to withstand the weight of construction equipment, impermeable caps and cover material. Landfills and other various situations that seek to prevent water infiltration use impermeable caps and cover material. The guidelines recommended by this research for the preparation of solidified storm water waste result in the production of material that exceeds strength of 50 psi, thus the material is trusted to withstand the weight of heavy equipment and impermeable cover materials. Such applications that could potentially incorporate the use of the solidified storm water waste include the construction of roadway materials and impermeable cap foundations. Further research will establish the contaminant stability and the leaching potential of the solidified residuals in order to determine additional underground applications of the material. Until the leachability of the material is assessed, the potential for harm to groundwater resources is unknown.

3.9 REFERENCES


SCA (2003), Slag Cement Association (http://www.slagcement.org/proportioning.htm).


### 3.10 NOMENCLATURE

*The following symbols were used in this chapter:*

- $\Delta l$: change in sample length (in)
- $\varepsilon$: strain (inches)
- $\sigma$: stress (psi)
- $A$: Cross sectional area of the cylindrical specimen (in$^2$)
- ADT: average daily traffic
- ASTM: American Society for Testing and Materials
- BMP: best management practice
- $C$: runoff coefficient
- $Cd$: cadmium
- $Cd^{2+}$: cationic form of cadmium
- $Cr$: chromium
- $CR$: coarse residuals (< 75 $\mu$m)
- $cm$: centimeters
- $cm^3$: cubic centimeters
- $Cu$: copper
- $^\circ$C: degrees Celsius
- $^\circ$F: degrees Fahrenheit
- $D$: dilution factor
- $d_{50}$: particle diameter at which 50% of the particle gradation mass is finer
- $d_{50nm}$: mass-based particle diameter where 50% of the particle gradation mass is finer
- $d_{50n}$: number-based particle diameter where 50% of the particle gradation mass is finer
- $d_i$: particle diameter at the $i^{th}$ particle size increment
- DTA: differential thermal analysis
- DTG: differential thermal gravimetry
- $E$: Young’s elastic modulus
- $E_{7\text{-day}}$: Young’s elastic modulus for 7-day cured specimens
- $E_{28\text{-day}}$: Young’s elastic modulus for 28-day cured specimens
- $F$: force applied to the cylindrical specimen (lb)
- $FR$: fine residuals ($> 75 \mu m$)
- $g/cm^3$: gram per centimeter cubed
- I-10 E: site designation for the sampling site in Baton Rouge, LA
- ICP-MS: inductively coupled plasma - mass spectrophotometer
- $L$: liter
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>M:</td>
<td>molarity (mol)</td>
</tr>
<tr>
<td>m²:</td>
<td>square meters</td>
</tr>
<tr>
<td>mᵢ:</td>
<td>mass of solids having particle diameter i (g)</td>
</tr>
<tr>
<td>mL:</td>
<td>milliliters</td>
</tr>
<tr>
<td>µm:</td>
<td>micrometers</td>
</tr>
<tr>
<td>mm:</td>
<td>millimeters</td>
</tr>
<tr>
<td>m²/g:</td>
<td>square meters per gram</td>
</tr>
<tr>
<td>Mₛ:</td>
<td>known mass of each gradation used to calculate particle density</td>
</tr>
<tr>
<td>Nᵢ:</td>
<td>number of particles at the iᵗʰ particle size increment (# of particles/cm³)</td>
</tr>
<tr>
<td>Ni:</td>
<td>nickel</td>
</tr>
<tr>
<td>OPC:</td>
<td>ordinary portland cement</td>
</tr>
<tr>
<td>P₁:</td>
<td>initial pressure reading in the helium pycnometry process (psi)</td>
</tr>
<tr>
<td>P₂:</td>
<td>final pressure reading in the helium pycnometry process (psi)</td>
</tr>
<tr>
<td>Pb:</td>
<td>lead</td>
</tr>
<tr>
<td>Pb⁺²:</td>
<td>cationic form of lead</td>
</tr>
<tr>
<td>ρᵢ:</td>
<td>particle density (g/cm³)</td>
</tr>
<tr>
<td>PC:</td>
<td>type I portland cement</td>
</tr>
<tr>
<td>PS:</td>
<td>1:1 type I portland/slag cement mixture</td>
</tr>
<tr>
<td>PSD:</td>
<td>particle size distribution</td>
</tr>
<tr>
<td>psi:</td>
<td>per square inch</td>
</tr>
<tr>
<td>PVC:</td>
<td>poly-vinyl chloride</td>
</tr>
<tr>
<td>SA:</td>
<td>surface area (m²)</td>
</tr>
<tr>
<td>SC:</td>
<td>slag cement</td>
</tr>
<tr>
<td>S/S:</td>
<td>solidification and stabilization</td>
</tr>
<tr>
<td>SSA:</td>
<td>specific surface area (m²/g)</td>
</tr>
<tr>
<td>TA:</td>
<td>thermal analysis</td>
</tr>
<tr>
<td>TC:</td>
<td>toxicity characteristic</td>
</tr>
<tr>
<td>TCLP:</td>
<td>toxicity characteristic leaching procedure</td>
</tr>
<tr>
<td>TG:</td>
<td>thermal gravimetry</td>
</tr>
<tr>
<td>TR:</td>
<td>total residuals</td>
</tr>
<tr>
<td>UCS:</td>
<td>unconfined compressive strength</td>
</tr>
<tr>
<td>USB:</td>
<td>universal serial bus</td>
</tr>
<tr>
<td>USEPA:</td>
<td>United States environmental protection agency</td>
</tr>
<tr>
<td>Vᵣ:</td>
<td>cylinder volume used to calculate particle density (cm³)</td>
</tr>
<tr>
<td>Vᵣₛ:</td>
<td>reference volume used to calculate particle density (cm³)</td>
</tr>
<tr>
<td>Vₛ:</td>
<td>sample volume used to calculate particle density (cm³)</td>
</tr>
<tr>
<td>Vᵢ:</td>
<td>volume of particles at the iᵗʰ particle size increment (cm³)</td>
</tr>
<tr>
<td>x:</td>
<td>raw value from particle analyzer (µL/L)</td>
</tr>
<tr>
<td>Zn:</td>
<td>zinc</td>
</tr>
</tbody>
</table>
CHAPTER 4. METAL SPECIES LEACHING FROM CEMENTITIOUS-SOLIDIFIED RAINFALL-RUNOFF RESIDUALS

4.1 SUMMARY

Rainfall-runoff solids and residuals from the treatment of rainfall-runoff, by Best Management Practices (BMPs) are contaminated with metals including Cd, Cu, Pb, and Zn. For a given urban area the granulometric mass is significant that it cannot be accommodated by common landfill disposal practices. While cement-based solidification/stabilization (S/S) has been applied to many types of solid and hazardous wastes, there is no history of application for rainfall-runoff residual waste. Total and coarse (>75 µm) gradations of rainfall-runoff residual material collected from a rainfall-runoff BMP were treated using a type I portland cement (PC), a slag cement (SC), and a 1:1 mass ratio of type I Portland to slag cement (PS). Cement mass percentages of 10, 20, and 30 were added to the residuals and cured for 7 and 28-day periods. The toxicity characteristic leaching procedure (TCLP) was applied to the solidified specimens, as well as for three gradations of unsolidified residuals and also for pure cement control samples. The leaching potential of the pure cement specimens and the unsolidified total, coarse (>75 µm) and fine (<75 µm) fractions of residuals were analyzed and compared to the unsolidified specimens to determine the effectiveness of cementitious solidification. Based on the reduction of metal leaching and strength characteristics, the most effective binder applied to the residuals was the PS. Results showed that for the three metals Cd, Cu, and Zn, the 28-day curing period was most effective in reducing the leaching potential of these metals, while the 7-day curing most effectively reduced the leaching of Pb. The two separate residual gradations did not exhibit significant effects on the S/S
treatment effectiveness, thus for full-scale implementation of separation of the residual
gradation between fine and coarse fractions is not necessary.

4.2 INTRODUCTION

As the human population continues to increase in the USA and worldwide and
land use patterns become more urbanized, rainfall-runoff is becoming the leading source
of pollution. Impervious surfaces linked with such developed areas, such as roadways,
pavements, and infrastructure, generate and accumulate anthropogenic particulate matter.
Traffic activity and anthropogenic activities associated with urbanized areas generate
constituents such as metal species that accumulate on and with such anthropogenic
particulate matter. These anthropogenic particulates become entrained in rainfall-runoff
and are transported to adjacent aquatic and terrestrial surroundings. Both the aqueous
phase and solid phase fractions transport contaminants that are acute and chronic threats
to the aesthetic and ecological function of the environment.

Particulate matter entrained in rainfall-runoff is enriched by numerous sources of
metal species contamination prior to deposition of particulate matter in the environment.
Particulate matter accumulated on pavement is mainly traffic-generated. Primary inputs
include tire-pavement abrasion, vehicular part abrasion, leakage and litter (Novotny et al.
1994; Sansalone and Buchberger 1997; Sansalone et al. 1998). Sources of metal species
such as Cu, Zn, and Cr, include vehicular and infrastructure corrosion, leaching from
metallic infrastructure and leaching from abraded vehicular components (Novotny et al.
1994). Other toxic materials responsible for metal species contamination of urban and
transportation land use particulates include gasoline and tires, which deposit Pb and Zn,
respectively (Novotny et al. 1994).
Cd, Cu, Pb and Zn are the common targeted metal species in the treatment of rainfall-runoff. In urban and transportation land use, Cd, Cu, Pb and Zn exist in the dissolved (ionic complexed) and particulate phases (colloidal, suspended, and settleable). Although potentially less bioavailable, immediately the particulate bound forms of Cd, Cu, Pb, and Zn represent a chronic threat to the environment; in part due to the substantial quantities that particulate-bound metals are present (Buckler and Granato 1999; Breault and Granato 2000).

Metal species associated with the anthropogenic particulates entrained in rainfall-runoff are transported in significant quantities. Along with the transported particulates, proximate surficial soils in and around urban areas are subjected to and are contaminated by rainfall-runoff (Teng et al. 2002). A more concentrated and point source of rainfall-runoff metal species containing solid waste are Best Management Practices (BMPs). Given the mass and concentration of contamination in rainfall-runoff, the treatment of this runoff would generate residual solid waste equal to or greater amounts of solids presently being generated by municipal wastewater treatment (Field et al. 1994). The annual sludge volume associated with combined sewer overflow (CSO), based on a combined sewer area of 2.25x10^6 acres, average storm runoff of 16.5 in/yr (Heany et al. 1977; Field et al. 1994) and treatment process efficiency ratios of 0.3-6 % volume sludge/influent flow (Huibregste et al. 1982; Field and O’Shea 1993), is 11 - 228 x10^6 m^3 with average percent solids of 0.7-3.2 (Gupta et al. 1977; Field et al. 1994). At the most, with 3.2 % solids of a 228x10^6 m^3 sludge volume, 7.3x10^3 m^3 of solids are generated for these CSO conditions.
A calculation can be made in order to illustrate the magnitude of the amount of residuals generated by rainfall-runoff. Assume that an urban area with a population of $10^6$ and total interstate area of 40 km$^2$ receives annual precipitation of 1000 mm. With an average total suspended solids (TSS) value of 200 mg/L for urban rainfall runoff and a runoff volume coefficient of 0.7, this 40-km$^2$ area generates $5.6 \times 10^9$ grams of suspended solids (dry basis) or $14 \times 10^6$ m$^3$ assuming a porosity ($\eta$) of 0.50 (Sansalone et al. 1998; Sansalone and Buchburger 1997). This volume of solids generated by rainfall-runoff is nearly double the value calculated for annual solids generated by the CSO conditions assumed.

Depending on the treatment effectiveness, these large quantities of contaminated residuals can be accumulated in rainfall-runoff treatment facilities. While landfilling or land disposal is widely used in managing such large amounts of municipal solid waste (biosolids), the potentially toxic nature of the metal species contaminants in rainfall-runoff sludge is a major concern with respect to the potential release of contaminants to surface and ground water (Hannak et al. 1988).

4.2.1 Solidification/Stabilization (S/S)

Solidification/Stabilization (S/S) has proven to be a cost-effective treatment technique for managing many complex waste materials. Utilized to treat wastes since the 1950s, S/S treatment has been used to manage many wastes, particularly those classified as hazardous (Wilk 1999). Identified as the best demonstrated available technology (BDAT) for treating a wide range of Resource Conservation and Recovery Act (RCRA) non-wastewater listed and characteristic wastes, S/S processes are flexible enough to accommodate mixtures of contaminants and economical enough to be used for large
volumes of waste (Means et al. 1995). In terms of economics, S/S, which costs approximately $100 per ton of material treated, can be compared to soil washing, which costs $170 per ton of material treated (Van Duren et al. 2002). The processes of S/S incorporates binder reagents, such as cement, and are designed to treat these wastes by improving physical aspects of the waste and/or chemically altering hazardous constituents within the waste. The physical mechanisms of treatment involve the capture (microencapsulation) of hazardous constituents within the resulting physical structure of the solidified waste matrix (Chan et al. 2000). Chemical treatments of the waste are intended to convert the toxic constituents into insoluble and less toxic forms, such as hydroxide and sulfide compounds (Conner 1990; Jang et al. 2000).

S/S has been applied to hazardous and nonhazardous wastes including, nuclear and non-nuclear, inorganic and organic, liquid and solid (Means et al. 1995). The application of S/S to these wastes varies with binder addition. Selection of the proper S/S binder to be utilized for a given waste requires an understanding of the chemistry of the bulk material, the contaminants, and the binder, as well as of the complex interactions among these components, in order to achieve targeted results (Means et al. 1995). S/S technologies are grouped as organic or inorganic depending on the binder utilized in the treatment. Organic S/S procedures involve thermoplastic binders and organic polymerization as a means of treating such hazardous wastes as painting and refinery waste sludges containing toxic metals and organics (Barth et al. 1990; Tittlebaum et al. 1985). Organic S/S has not been as widely utilized in practice as inorganic S/S, which includes cement and pozzolanic-based S/S (Barth et al. 1990). The most common form of
the S/S technology uses an inorganically characterized cement or pozzolanic binder to convert wastes to a solid form (Akhter et al. 2000).

4.2.2 Stabilization Mechanisms

A variety of contaminated soils, as well as sludges, have been treated using processes of cement-based solidification and stabilization. Using a cement or pozzolanic binder, the waste is converted to a solid (if required) and, depending on the constituents of the waste stream and the binder, the treatment may reduce toxicity and/or water solubility of hazardous materials (Akhter et al. 2000). For wastes with metal species contamination existing in concentrations that are too low for economical recovery, but high enough to present a toxicity hazard, cement-based S/S appears both cost-effective and safe due to the conversion of harmful metals to highly insoluble salts which do not leach out into surrounding environments (Cartledge et al. 1990). Cement-based S/S is most commonly applied in cases where the contaminants of concern are metal species in cationic forms e.g. Cd\(^{2+}\), Cr\(^{3+}\), Pb\(^{2+}\) (Buchler et al. 1996), such as those metals bound to the surfaces of rainfall-runoff residuals.

Stabilization of metal species occurs through chemical reactions that occur between the metal species and binder constituents. The highly alkaline nature of cement-based materials reduces the solubility of many toxic and hazardous inorganics, including metal species, and inhibits microbiological processes that may be detrimental to the final setting of the material (Glasser 1997). The chemical processes involved in the chemical fixation of contaminants using cement binders allow the waste to become part of the solidified matrix material through chemical bonds (Akhter et al. 2001; Naik et al. 2001). The basic nature of the cement encourages the formation of the hydroxide and sulfide
forms of the metal species. As hydroxides and sulfides, these metals are less toxic to surrounding environments due to their lower slower leaching rates than the original cationic species (Jang et al. 2000).

4.2.3 TCLP: Stabilization Optimization

In order to examine the effectiveness of an S/S application, the toxicity characteristic leaching procedure (TCLP), designated as EPA SW-846 Method 1311, is performed. The TCLP test is most commonly used by the USEPA and state agencies to evaluate the leaching potential of stabilized wastes (Means et al. 1995). The evaluation of the leaching behavior is an important aspect for the long-term protection of the environment, whether the materials are to be landfilled or reused (Baur et al. 2001). The TCLP is a leaching test designed to simulate potentially harsh environmental conditions and evaluate the leaching characteristics exhibited by the treated waste under these conditions. In the leaching test, the waste is exposed to a leachant and the contaminant concentrations resulting from the leachate produced are measured and compared to a previously established standard and/or regulatory limits (Means et al. 1995). The TCLP is used to evaluate maximum “worst-case” leachate concentrations achievable in the field; however, several studies have shown that TCLP leaching of cement-based waste forms may not necessarily yield maximum concentrations (Barth et al. 1990). Through TCLP testing, factors such as waste form, binder system, curing time and cement-to-waste ratio have been identified to influence the leachability of a waste after S/S treatment (Wang et al. 2000).
4.3 OBJECTIVES

This study had two objectives. The first objective of this study was to perform TCLP on rainfall-runoff particulates and assess the Cd, Cu, Pb, and Zn concentrations leached by three separate gradations of residuals. A representative portion of the total gradation, including the entire gradation of rainfall-runoff particles (<1 to > 10,000 µm), was first analyzed by the TCLP for metal species contamination. The total particle distribution was separated between the fine fraction (< 75 µm) and the coarse fraction (> 75 µm) using a number 200 U.S. standard size sieve. The resulting TCLP analyses allow for the evaluation of metal species contamination for both the fine and coarse gradations. The potential for leaching from the fine or coarse gradations without S/S is examined through this objective. The known leaching potential of the residual gradations is also required as a control against which TCLP results of solidified residuals is compared.

The second objective was to apply S/S to the total, coarse, and fine gradations of residuals and evaluate the behavior of the solidified residuals for three cement mixes. Type I portland (PC), slag (SC), and a 1:1 mixture of these two cements (PS) were tested for 7 and 28 day periods of curing to solid ratios of cement of 0.10, 0.20, and 0.30 applied to the three gradations of residuals. The leaching potential of the resulting specimens were analyzed using TCLP. Complete assessments regarding the metal species leaching behaviors as a function of cure time, amount of cement, residual gradation, and cement type were analyzed.

4.4 BACKGROUND

Contaminated particulates associated with rainfall-runoff range in size from 1 µm to greater than 10,000 µm (Sansalone et al. 1998). While the finer particles tend to have
higher concentrations of metal species, the mid-range to coarse gradation contains most of the metal species mass (Viklander 1997; Sansalone et al. 1998). The predominance of specific surface area (SSA) is associated with fine particles, while the predominance of total surface area is associated with mid-range to coarse particles.

Research of interest to this study of rainfall-runoff residuals was conducted on contaminated spent abrasive media used to sand blast a highway bridge. This study conducted by Webster et al., in 1996, observed the contamination of two gradations of the media and evaluated the effectiveness of S/S on the waste. The media reportedly showed traffic generated metal species contamination similar to the rainfall-runoff residuals. The TCLP testing of the untreated media reported that the metal species contamination associated with the media was in sufficient quantities to have the waste listed as a hazardous waste (Webster et al. 1996). The two media gradations, sand and dust (fines), were separated and metals concentrations were assessed. The dust was a fine powdery material that passed through a U.S. Standard # 200 sieve (75 µm) (Webster et al. 1996). The separated media sand had TCLP leachate metal species concentrations of 1.04 mg/L for Cr; 0.8 mg/l for Cd, and 7.22 mg/L for Pb and the separated media dust had concentrations of 3.76 mg/L for Cr; 1.01 mg/L for Cd; and 4.91 mg/L for Pb (Webster et al. 1996). The metal species concentration trends of the sand and dust gradations of the media parallel those observed in coarse and fine gradations of the storm residuals, in that the dust-size media had higher concentrations than the sand media for two, Cr and Cd, of the three metals. For the metal species concentrations of the TCLP leachates of the total, coarse and fine gradations of rainfall-runoff residuals in this study, the Cd, Cu, and Zn concentrations were highest for the fine residuals.
S/S has been used as a treatment technique for many hazardous wastes, including those contaminated with metal species. Identified as the best demonstrated available treatment (BDAT) for wastes containing Cd and Pb, S/S processes are used to manage and immobilize numerous types of contaminants (Means et al. 1995). Stabilization, also known as fixation, refers to processes of chemical bonding or specific interactions between the waste and the binding agent to immobilize the toxic substances within the waste (Tittlebaum et al. 1985; Cocke 1990). In cement-based stabilization, metal laden wastes are chemically stabilized through the conversion of the metal species from their cationic forms to insoluble hydroxides, oxides and sulfides. This conversion is made with the aid of the highly alkaline nature of cement. Potential leaching of the metals trapped within the S/S matrix is assessed though extraction and/or leaching tests. Although many forms of extraction/leaching analyses exist, the TCLP is the most widely used throughout the United States, due to the fact that the test is required by RCRA implementing regulations for determining toxicity (Means et al. 1995).

The previously mentioned research conducted by Webster et al., in 1996, applied S/S to the contaminated san blasting media and evaluated the leaching potential of the material through TCLP testing. The regulatory TCLP limits for the metal species associated with the media are 0.6 mg/L for Cr; 0.11 mg/L for Cd and 0.75 mg/L for Pb (EPA 1998). S/S was applied to the unseparated sand/dust media using types I-II portland cement and TCLP tests were conducted to assess the stabilization of the metal species. The leachates of the treated media were found to have metal species concentrations below regulatory limits indicating that the Cr, Cd, and Pb associated with the waste were successfully immobilized.
Through TCLP and other methods of analyses, correlations have been drawn regarding sampling preparation, protocol techniques and the resulting leaching characteristics. Three major factors that affecting leaching potential are the acid/base reactions that determine the pH within the waste, the pH dependant reactions that determine whether the contaminants are in mobile or immobile forms, and the diffusion that transports mobile contaminants from the waste (Kim et al. 2001).

Many studies have established pH relationships with stabilization effectiveness and the resulting leaching characteristics of treated metallic wastes. Research reported by Chan et al. (2000) evaluated the application of cementitious S/S to an asbestos waste containing metal species from an automobile brake manufacturing facility. Several cement to waste ratios were applied and it was observed that the material with higher cement content caused an increase in pH (Chan et al. 2000). Naturally high pH values are usually desirable for metal species immobilization because most metal hydroxides have a minimum solubility pH range of 7.5-11. Although a high pH is sought for the containment of most metals (As, Cr, Ni, Cu) excess alkalinity causing the pH to rise above 12 results in solubilization of some metals (Pb), making them mobile and toxic to surrounding environments (Chan et al. 2000). Cartledge et al. (1990) observed a similar pH related metal precipitation phenomenon in an S/S investigation of the behavior of Cd and Pb salts. In this study, fluctuations in pH due to cement hydration processes caused immobilized Pb salts to undergo solubilization and reprecipitation (Cartledge et al. 1990). These Pb precipitates were found to bind to the surface of the cement which then made them easily accessible to leach water and more soluble under the basic conditions than the pure lead hydroxide forms (Cartledge et al. 1990).
In a study reported to optimize S/S mixtures, Parapar et al. (1998) evaluated the alkaline effects of various binder additions to a metallic waste contaminated with Pb, Cd, Cr, and Zn. The study utilized portland cement combined with six separate additive variations of fly ash, blast furnace slag, and hydrated lime. Observations were made regarding the acid neutralizing effects of the additives with respect to stabilization of the metals. The buffering effects of the additives should not produce excessively high pHs because some amphoteric metals such as, for example, lead (Pb), can be leached (Parapar et al. 1998). Results of this study found that hydrated lime consumes acid equivalents up to a pH of 7, and portland cement and slag contribute similar basic equivalents within pH range of 8-10. The conditions provided by these materials are suitable for adequate stabilization of metal species.

Several studies conducted on the stabilization of metal species have found that the leaching of metals is a function of the cure time allowed for S/S specimens. Jang et al. (2000) assessed the S/S effectiveness of a cement/fly ash mixture on metal species contamination in tailing wastes generated from the mining of metals. Samples were cured for 3, 7 and 28 days and through TCLP testing it was observed that a decreased quantity of leached metal species was obtained when a longer cure time was used for solidification/stabilization (Jang et al. 2000). In a study reported by Park, S/S was applied to hazardous wastes containing metal species using cementitious materials. Using the TCLP method on specimens cured for 1 day, 3, 7 and 28 days it was observed that for the S/S of Cr, Cd, and Pb, the leached metals ions decreased with curing time (Park 2000). A cooperative study by Ahkter et al. and Miller et al. on the treatment of As contaminated soils evaluated TCLP results on untreated and treated soils. TCLP performed on the soils
showed As levels to exceed EPA toxicity characteristic (TC) limits, thus characterizing this soil as a hazardous waste (Ahkter et al. 2000). A bench scale S/S study using types I and V portland cements was applied to As-contaminated soils and the specimens were cured for 7, 28, 60 and 120 days (Miller et al. 2000). The TCLP results of this study established that S/S practice in general shows decreasing leachability with increasing cure time. This study further discussed that in a typical cement paste after 28 days the hydration reactions are only 65-75% complete and that the increasing degree of hydration of the specimens is generally associated with increasing strength and density, and decreasing permeability (Miller et al. 2000).

Incorporation of pozzolanic additions to cement for improved S/S effectiveness has been studied. Fly ash, slag and metakaolin, three pozzolanic additives, were integrated with ordinary portland cement (OPC) in six binder mixtures and studied for S/S efficiency by Pera et al. (1997). The six binder mixtures were combined with a synthetic Cr waste to evaluate the effects of the binder additions on the leaching and structural characteristics of the material. The leaching characteristics were tested using procedure set by French standards and it was determined that the OPC alone and the OPC with slag addition both successfully immobilized the Cr (Pera et al. 1997). The addition of fly ash and metakaolin proved not to be favorable to Cr fixation. In conclusion, the OPC alone was found to produce the best results with the slag integration providing the best performance of all of the additives (Pera et al. 1997).
4.5 METHODOLOGY

4.5.1 Experimental Site: Baton Rouge, Louisiana

The experimental site sampled throughout this study is located in Baton Rouge, Louisiana. Located on the east bank of the Mississippi River, Baton Rouge has a population over 200,000 within its city limits (http://quickfacts.census.gov/qfd/states/22/22033.html). The surrounding areas that make up the metropolitan statistical area (MSA) of Baton Rouge, Louisiana, combine for a total metropolitan population of over 400,000 (http://quickfacts.census.gov/qfd/states/22/22033.html). Baton Rouge experiences a semi-tropical climate with mild winters and consistently warm weather from May until September. The months of July and January have the highest, 81.7°F (27.6°C), and lowest, 50.1°F (10.1°C), average temperatures, respectively (National Weather Service, http://www.srh.noaa.gov/lix/html/BTR_F6.shtml). Precipitation is frequent in Baton Rouge with an annual average rainfall of 60.9 inches (1546.9 mm), the highest rainfall occurring in the month of July. Snow is insignificant in Baton Rouge, as the annual mean snowfall measured is 0.2 inches (5.08 mm) (Jay Grymes, Louisiana Office of State Climatology 2003, http://www.losc.lsu.edu/stations.php?Id=btr).

The sampling facility located in Baton Rouge is situated at the base of the I-10 eastbound bridge abutment. The I-10 bridge deck is constructed of reinforced portland cement concrete and is located over a fresh water body known as City Park Lake. All rainfall-runoff generated on the surface of the bridge, with the exception of the diverted eastbound flows, flows directly into the lake. The experimental site receives rainfall-runoff from the three eastbound lanes of the I-10 Bridge that see an average daily traffic
count of approximately 70,000 eastbound. Runoff generated from a 544-m² pavement drainage area is transported to the site through a semi circular PVC pipe that is located below the expansion joint of the east bridge abutment. Diverted runoff is channeled to the experimental site where the runoff is treated. The initial unit operation included in the treatment train of the experimental site is an 80 L grit chamber. This stage of management allows the coarse gravel-type particles entrained in the stream to be separated from the flow. The second unit operation is a 2130-L settling basin. In this final stage of treatment the runoff is further clarified by means of sedimentation.

4.5.2 Residuals Capture

The storm residuals treated throughout this study were retrieved from the grit chamber and settling basin located at the I-10 experimental facility. Following a storm event, the runoff contained in these basins was typically given a settling time of two days before sediment removal. After settling, the clarified supernatant of the basins were siphoned and the solids and sludge were removed from each basin. The solids and sludge were then taken back to the lab, combined in order to attain the entire rainfall-runoff particle size distribution, and dried.

4.5.3 Waste Residual Preparation

In order to dry the sludge and solids, this material was placed in a chamber with a constant temperature of 40°C and a constant humidity of 20%. Following approximately three days of drying, the moisture content of the samples was negligible (< 1%). The dry residuals were removed from the drying chamber and weighed. The total weight was recorded and the residual agglomerations were separated using a mortar and pestle. Following the separation of the solids, the residuals were divided into two equal parts by
mass. Half of the residuals were left intact and used for testing the total gradation of the particles. The remaining residuals were separated into coarse (particle diameter > 75 µm) and fine (particle diameter < 75 µm) gradations. The separation process was accomplished through mechanical sieve analysis using the U.S. Standard # 200 sieve. The fractionated residuals were then used for the analyses of the coarse and fine gradation behavior in S/S and TCLP.

4.5.4 S/S Specimen Preparation

Using three types of cement, solidified/stabilized rainfall-runoff residual samples were prepared. A type I portland cement and a slag cement were utilized. Table 4.1 represents the chemical composition of each cement. A third cement mix that combined equal ratios of the type I portland and slag cements was used to prepare S/S specimens. The 1:1 type I portland and slag cement mix was prepared by manually mixing equal amounts of the cement powders.

S/S was applied to three gradations of rainfall-runoff residuals using the type I portland cement, the slag cement, and the 1:1 type I Portland/slag mix cement. These samples were cured for 7 and 28 days. The recovered amount of fine residuals was limited, thus the fine gradation was treated using only type I portland cement and a 28 day cure time.

The S/S samples were prepared in bulk quantities using 10, 20, and 30 percent by dry residual weight of cement. In order to allow adequate water content for cement hydration, in addition to the water/cement ratio a water/residuals ratio was incorporated in preparation of the specimens. Water/residuals ratios were determined by adding water in sufficient quantities as to wet the surfaces of the residuals while avoiding any free
Table 4.1 Chemical composition of the base cement powders utilized in the S/S treatment of the storm residuals. The Lone Star Cement Kiln located in New Orleans, Louisiana provided the composition data.

<table>
<thead>
<tr>
<th>Chemical Composition % (as oxides)</th>
<th>Cement Type</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Type I Portland Cement</td>
</tr>
<tr>
<td>Ca</td>
<td>64</td>
</tr>
<tr>
<td>Si</td>
<td>21.2</td>
</tr>
<tr>
<td>Al</td>
<td>4.5</td>
</tr>
<tr>
<td>Fe</td>
<td>3.1</td>
</tr>
<tr>
<td>Mg</td>
<td>4</td>
</tr>
<tr>
<td>SO₃</td>
<td>2.7</td>
</tr>
<tr>
<td>Sulfide</td>
<td>0</td>
</tr>
<tr>
<td>Total Alkalis¹</td>
<td>0.54</td>
</tr>
</tbody>
</table>

¹ Total Alkalis = Na Equivalent
water. The water/residuals ratio was determined to be 0.2 for the total and coarse gradations and 0.5 for the fine gradation. It was noted that these residual gradations exhibited hydrophobic behavior upon the addition of water. The water to cement ratio of 0.5 was used due to its major influence on the pore structure and permeability of the cured specimens (Akhter et al. 2000).

The initial step in the bulk preparation of the S/S material was to gravimetrically measure 900 g of residuals (300 g for each specimen) and place them into the mixing chamber. The water demand of the residuals was then satisfied using the water/residual ratios previously calculated. Due to the hydrophobic nature of the residuals, a rapidly rotating mechanical rod mixer was used to thoroughly mix the water and residuals ensuring wetness of the surface areas of the particles. The cement was then added to the water and residuals followed by the water necessary to achieve the 0.5-water/cement ratio. The mechanical mixer was again used to thoroughly integrate the cement into the surface wet residuals. Table 4.2 presents the volume and mass of water, cement and residuals that were required to prepare specimens to meet the three-cement/residual ratios.

The mixed sample was transferred from the mixing chamber to three separate plastic molds. The specimens were placed into the molds in three equal lifts. After addition of each lift, the specimen was tapped down to allow settling and to avoid the occurrence of air voids in the final set specimen. Prior to the addition of the next lift, the surface of the specimen was roughened using a metal to ensure bonding between lifts. After completing the specimen transfer to the plastic molds, the molds were capped and
Table 4.2 Designated material proportions utilized in preparation of bulk S/S material.

<table>
<thead>
<tr>
<th>Percent by Residuals Weight of Cement (%)</th>
<th>Water Required for Water/Residuals Ratio(^1) (mL)</th>
<th>Water Required for Water/Residuals Ratio(^2) (mL)</th>
<th>Mass of Residuals (g)</th>
<th>Water Requirement for Cement (g)</th>
<th>Mass of Dry Cement (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>180</td>
<td>450</td>
<td>900</td>
<td>45</td>
<td>90</td>
</tr>
<tr>
<td>20</td>
<td>180</td>
<td>450</td>
<td>900</td>
<td>90</td>
<td>180</td>
</tr>
<tr>
<td>30</td>
<td>180</td>
<td>450</td>
<td>900</td>
<td>135</td>
<td>270</td>
</tr>
</tbody>
</table>

\(^1\): Volume of water required for total and coarse residual gradations
\(^2\): Volume of water required for fine residual gradations
the samples were allowed to cure in chambers with a constant room temperature of 25 °C (77 °F) and a constant humidity of 100%. Following the 7 and 28-day respective cure times, the samples were removed from the plastic molds by cutting the mold using a fine rotary cutting tool.

4.5.5 Toxicity Characteristic Leaching Procedure (TCLP)

The TCLP tests were carried out using Method 1311 outlined SW-846, the EPA publication for test methods evaluating solid wastes. The SW-846 document published by the EPA outlines physical/chemical methods for the regulated and regulatory communities to use in responding to RCRA-related sampling and analysis requirements (EPA 1992). The scope and application of the TCLP, as summarized in SW-846, is to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphase wastes (EPA 1992).

The TCLP was applied to all of the untreated and S/S treated rainfall-runoff residual waste specimens. The resulting leachates of the untreated total, coarse and fine rainfall-runoff residuals were analyzed for metal species concentrations in order to determine the level of toxicity associated with these wastes. The TCLP results for the treated wastes were used to analyze the treatment effectiveness of the S/S application to rainfall-runoff residual wastes. Using the TCLP, the cement types and cement/residual ratios were examined for leaching potential.

Prior to the TCLP test of the treated and/or untreated waste, a number of preliminary steps occurred. The initial step required a percent solids determination of the specimen. This step required no experimentation as all of the samples tested throughout this research were either dry solidified materials or dehydrated waste residuals. Following
the percent solids determination, a particle size reduction of the specimens was required. The material tested through TCLP must be smaller than 1 cm in its narrowest dimension and must be capable of passing through a 9.5 mm (0.375 in.) standard sieve. Since the S/S specimens were cured in cylindrical form, it was necessary to crush the samples to meet the size requirements of the TCLP test. The final step was to determine the appropriate extraction fluid to be used in the TCLP testing of the specimens. There are two extraction fluids. Extraction fluid #1 is prepared by adding 12.5 grams of sodium hydroxide (NaOH) and 22.8 mL of glacial acetic acid (CH₃COOH) to one gallon of DI water and extraction fluid #2 is prepared by adding 22.8 mL of glacial acetic acid (CH₃COOH) to one gallon of DI water. In order to choose a fluid, a solid sample of the unsolidified residuals was stirred vigorously in de-ionized water and the pH was recorded. Based on the alkalinity of the waste, extraction fluid #1 was determined to be appropriate for testing the leaching potential of the untreated residuals. The solution was prepared and thoroughly mixed using a magnetic stir bar and plate and the final pH of the fluid was adjusted to be within ± 0.05 of 4.93. In order for a direct comparison to be made between treated and untreated samples, extraction fluid #1 was also used to test the stabilization of the cement-based S/S applied to the waste material.

S/S specimens as well as untreated residual samples were tested in triplicate for leaching potential in triplicate. Throughout TCLP testing, 100 g of material was utilized and the following equation (1) was used to determine the adequate amount of extraction fluid needed to perform the TCLP on this amount of material:

\[ W_E = \frac{20 \cdot P_S \cdot W_w}{100} \]  \hspace{1cm} (1)

\( W_E \): Weight of the extraction fluid (g)
A sample weight of 100 g was used consistently throughout testing and all specimens were 100% solids, thus 2000 g of extraction fluid was added to the vessels for TCLP testing. The specimens were combined with the extraction fluid and were set on a rotary tumbler and allowed to rotate at a rate of approximately 30 revolutions per minute (rpm) for a period of 20 hours.

The TCLP vessels were removed from the rotation devices after 20 hours and the extraction solutions were filtered. Using pressure filtration, 250 mL of the TCLP extracts were filtered on acid-washed 0.7 μm diameter glass fiber filters. Measurements of pH were recorded prior to and following pressure filtration. Before storing the filtered extracts, the filtrate was acidified using trace metal grade nitric acid to obtain a final pH measurement below 2. The acidified samples were stored under refrigeration with a constant temperature of approximately 4 °C (39.2 °F).

4.5.6 Acid Digestion

The TCLP extracts were digested for metals using the nitric acid-hydrochloric acid digestion procedure outlined by Standard Method 3030 F (Eaton et al. 1995). The digestion procedure was carried out on 100 mL of the extracts. Method blank samples of 9 mL of nitric acid and 3 mL of hydrochloric acid were digested along with the extract samples for QA/QC purposes. The 100 mL volume of extract was transferred to a glass flask and 9 mL and 3 mL of nitric and hydrochloric acids were added respectively. The glass flasks were covered with watch glasses, placed on a hot plate and heated at 150-175
°C (302-347 °F) for 2 hours. The samples were then filtered using pre-washed filters and the filtrate was then diluted by a factor of 10 with a 10% nitric acid solution.

4.5.7 ICP-MS Analysis

The digested method blanks and extract samples were analyzed for metals using a Perkin Elmer Inductively Coupled Plasma - Mass Spectrophotometer (ICP-MS) Elan 9000. ICP-MS analyses were conducted according to the procedure summarized in Method 6020 of the SW-846 EPA publication. All of the specimens were analyzed for Na, Mg, Al, Ca, Cr, Mn, Fe, Ni, Cu, Zn, As, Ag, Cd, and Pb. The resulting concentrations (in µg/L) were adjusted for dilution by multiplying by a factor of 10. Triplicate samples were analyzed and the arithmetic mean values were reported. Standard deviations were calculated and evaluated. All samples with standard deviations more than 20% of the mean value were re-analyzed.

The metals data obtained through the TCLP and subsequent ICP-MS analyses were analyzed to evaluate the leaching potential of the treated and untreated residuals. The metal concentrations leached by the untreated residuals were evaluated based on the total metal mass associated with the residual gradations. The total metal mass present in the residual gradation was determined in the characterization study of the residuals. The concentrations of the metals leached from the residuals through the TCLP tests were compared to the total metal mass determined in the characterization study. Based on the total metal mass, the percent of this total metal mass leached from the residuals during the TCLP test was calculated as follows:

\[
f_{p_1} = \left( \frac{C_{L_1} \cdot V_E}{M_{T_1}} \right) \cdot 100\%
\]
The metal concentrations associated with the untreated residuals and the pure cement control samples were used in order to quantify the concentrations of metals leached from the stabilized wastes. The percent of metals leached from the treated specimens was calculated as:

\[
f_{Li} = \left( \frac{C_{Si}}{C_{Ri} + C_{Ci}} \right) \cdot 100\% \tag{3}
\]

\(f_{Li}\): fraction of metal \(i\) leached during TCLP (%)

\(C_{Si}\): concentration of metal \(i\) leached by the treated residuals (\(\mu g/L\))

\(C_{Ri}\): concentration of metal \(i\) leached by the untreated residuals (\(\mu g/L\))

\(C_{Ci}\): concentration of metal \(i\) leached by the pure cement control specimen (\(\mu g/L\))

Using this calculation, the percent of metals retained within the cement/residual matrix was calculated as:

\[
f_{R} = 100 - f_{L} \tag{4}
\]

\(f_{R}\): percentage of metals retained by the cement/residual matrix (%)

\(f_{Li}\): fraction of metal \(i\) leached during TCLP (%)

Using the calculated fractions of metals retained within the matrix and metals leached by the treated specimens, the effectiveness of this application of S/S was evaluated for Cd, Cu, Pb, and Zn.
4.5.8 Comparisons to Regulatory Limits

The TCLP extracts of the treated and untreated total, coarse and fine gradations of waste were analyzed for concentrations of Cd, Cu, Pb and Zn and compared to three distinct classifications of EPA regulatory limits. The leached concentrations of all four metals evaluated for the untreated residuals and the stabilized waste were first compared to the EPA fresh water chronic toxicity limits. The fresh water limits are applicable to rainfall-runoff solids because in many cases, rainfall-runoff residuals are transported from bridge decks directly to receiving waters, as is the case in the I-10 E site. Given that metals concentrations are above the fresh water toxicity limits, the rainfall-runoff residuals in the receiving water represent a potential toxic effect, such as oxygen depletion, to the aquatic environment. Of the metals Cd, Cu, Pb and Zn, only Cd and Pb are listed as toxicity characteristic constituents and have regulatory levels set for the leaching of these metals during TCLP testing. The Cd and Pb concentrations associated with the untreated residuals were compared to the regulatory levels set for the toxic constituent concentrations identified by the TCLP test. The regulatory limits of Cd and Pb for the TCLP limits, and of Cd, Cu, Pb, and Zn for the fresh water toxicity are presented in Table 4.3.

4.6 RESULTS AND DISCUSSION

Figure 4.1 represents the results of the granulometric characterization of the rainfall-runoff residuals recovered from the I-10 experimental site in Baton Rouge, LA. Based on the metal species data in Figure 4.1, calculations of an index designated as \( f_P \) were performed to analyze the amount metal species leached through TCLP from the untreated residuals with respect to the total metal species mass associated with the
Table 4.3 EPA regulatory limits assessed to the treated and untreated rainfall-runoff residual waste

<table>
<thead>
<tr>
<th>Metal</th>
<th>Fresh Water Chronic Toxicity Limits* ($\mu$g/L)</th>
<th>TCLP Limits ($\mu$g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>2.2</td>
<td>1000</td>
</tr>
<tr>
<td>Cu</td>
<td>9.0</td>
<td>N/A</td>
</tr>
<tr>
<td>Pb</td>
<td>2.5</td>
<td>5000</td>
</tr>
<tr>
<td>Zn</td>
<td>120.0</td>
<td>N/A</td>
</tr>
</tbody>
</table>

*: Reference, USEPA 1999
Figure 4.1 Granulometric and selected metal distributions for the I-10E site storm water residuals. Total SA and total mass of Pb, Cu, Cd, and Zn are each on a 1000.0 g basis. Cumulative axes are 0 to 100%.
gradation. With the exception of the Zn leached from the fine residual gradation, the metal species leached from the residuals represented no more than 40% of the total metal mass associated with the solids. The mass of Zn leached from the fine residual gradation represented more than 100% of the total mass of Zn present in fine gradation. It is unclear as to what caused this to occur. One possibility could be that due to the focus on the fine residual gradation in the TCLP test, the concentration of the metal was increased. Whereas, in the analysis with the total gradation, the presence of the fine material is not as pronounced.

Figures 4.2-4.5 represent the Cd, Cu, Pb and Zn leached by the untreated residuals and the treated specimens. The resulting metal species concentrations are plotted per residual gradation (total, coarse, and fine) as a function of binder (type I portland cement (PC), slag cement (SC), and 1:1 mass ratio mixture of type I portland cement and slag cement(PS)) and mass percent of binder addition (10, 20 and 30%). Plotted as vertical lines in Figures 4.2-4.5 are the metal species concentrations of the untreated residuals and regulatory limits for each metal. The EPA fresh water chronic toxicity limits are represented for Cd, Cu, Pb and Zn, and the toxicity characteristic (TC) limits are represented for Cd and Pb.

The concentration levels of Cd, Cu, Pb, and Zn in the TCLP extracts of the untreated total and coarse gradations exceeded the EPA fresh water toxicity limits. The TCLP extract of the untreated fine gradation of rainfall-runoff residuals exhibited Pb concentrations that fell below the fresh water limits, while the fresh water chronic toxicity limits for Cd, Cu, and Zn were exceeded. The TC limits of Cd and Pb were not exceeded for any gradation of the rainfall-runoff residuals.
Figure 4.2 Cd [µg/L] in TCLP extracts for specimens prepared with total (TR) and coarse gradations (CR) of residuals with 10, 20, and 30% by mass additions of type I portland cement (PC), slag cement (SC) and a 1:1 mass ratio mix of type I portland to slag cement (PS) additions, and 28d cured specimens prepared with the fine gradation of residuals (FR) with 10, 20, and 30% by mass additions of PC (SC and PS were not tested with the FR, due to a lack of residuals).
Figure 4.3 Cu [µg/L] in TCLP extracts for 7d and 28d cured specimens prepared with TR and CR with 10, 20, and 30% by mass additions of PC, SC and PS additions, and 28d cured specimens prepared with the FR with 10, 20, and 30% by mass additions of PC (SC and PS were not tested with the FR, due to a lack of residuals).
Figure 4.4 Pb [µg/L] in TCLP extracts for 7d and 28d cured specimens prepared with TR and CR with 10, 20, and 30% by mass additions of PC, SC and PS additions, and 28d cured specimens prepared with the FR with 10, 20, and 30% by mass additions of PC (SC and PS were not tested with the FR, due to a lack of residuals).
Figure 4.5 Zn [µg/L] in TCLP extracts for specimens prepared with TR and CR with 10, 20, and 30% by mass additions of PC, SC, and PS (cure = 7d and 28d), and specimens prepared with FR with 10, 20, and 30% by mass additions of PC (cure = 28d)(SC and PS were not tested with the FR, due to a lack of residuals).
Presented in Table 4.4 are the final pH measurements and the Cd, Cu, Pb and Zn concentrations leached by the untreated total, coarse, and fine gradations of residuals during TCLP. The leaching of Cd, Pb and Zn by the untreated rainfall-runoff solids proved to be a function of particle size gradation. The highest Cd and Zn concentrations were leached from the fine gradation of residuals and the maximum Pb concentrations were leached from the coarse gradation of the residuals. The Cu concentrations for the total, coarse, and fine gradations were all within 5 mg/L of each other, thus Cu was not leached from a specific gradation of residuals.

Presented in Figure 4.2 are the Cd concentrations leached by 7-day and 28-day cured specimens with PC, SC, and PS additions to the total and coarse fractions of residuals in mass ratios 0.10, 0.20, and 0.30 of binder to cement and the 28-day cured specimens with PC additions to the fine gradation of residuals in mass ratios of 0.10, 0.20, and 0.30. The 7-day cured specimen prepared with the total residual gradation and the 0.30 mass ratio addition of PC was the only specimen that resulted in a higher leached concentration of Cd than the respective untreated residual gradation. The Cd concentrations leached from the treated specimens prepared with the coarse and fine gradations were all below the Cd concentrations leached by the untreated residual gradations.

With the addition of cement, the leached Cd concentrations were lowered compared to the concentrations leached from the untreated residual gradations. The 28-day cured specimens generally exhibited lower Cd concentrations than the 7-day cured samples, and the leached Cd concentrations decreased with increasing cement addition. As seen in S/S practice in general, increasing cure time results in decreased leachability.
Table 4.4 TCLP extract metal concentrations leached from untreated total, coarse and fine gradations of residuals.

<table>
<thead>
<tr>
<th>Waste Gradation</th>
<th>TCLP Leachate pH$^1$</th>
<th>TCLP Leachate Metal Concentrations$^2$ (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cd</td>
</tr>
<tr>
<td>Total Residuals</td>
<td>6.3</td>
<td>3.7</td>
</tr>
<tr>
<td></td>
<td>$\sigma = 0.02$</td>
<td>$\sigma = 0.8$</td>
</tr>
<tr>
<td>Coarse Residuals</td>
<td>6.5</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td>$\sigma = 0.29$</td>
<td>$\sigma = 1.9$</td>
</tr>
<tr>
<td>Fine Residuals</td>
<td>6.2</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td>$\sigma = 0.05$</td>
<td>$\sigma = 0.3$</td>
</tr>
</tbody>
</table>

$^1$: pH measurement taken after 18-hour rotation period, n=3
$^2$: for all metal concentrations n = 3
(Miller et al. 2000). With respect to the regulatory limits associated with Cd, the TC limit of 1000 µg/l of Cd was not exceeded by the untreated residuals or the treated residuals. The EPA fresh water chronic toxicity limit for Cd was exceeded by the untreated residuals and was met by 70% of the treated residuals.

Figure 4.3 represents the Cu concentrations leached by the untreated residuals and the treated specimens. The three plots in Figure 4.3 represent the Cu concentrations associated with the treated and untreated total, coarse and fine residual gradations. Plotted as vertical lines are the concentrations of the untreated residuals and the EPA fresh water toxicity limit for Cu.

The Cu concentrations leached by the treated residuals were consistently higher than the Cu concentrations leached by the untreated residuals. This trend is a result of the increased alkalinity imposed by the addition of the cement binders. The mechanism of stabilization involves the precipitation of the metals to their respective hydroxides and sulfides (Roy et al. 1992), thus Cu is converted to either Cu(OH)₂ and/or Cu(II)S. According to the CRC Handbook of Chemistry and Physics, Cu(OH)₂ and Cu(II)S are both soluble in alkaline solutions (Lide and Frederikse 1996). The highest concentrations of Cu were leached from specimens treated with the PC. The final pH measurements of these extracts are presented in Table 4.10 and were found to be in the range of 11.0-11.9, which is very basic. In Table 4.4, the final pH measurements of the TCLP extracts of the untreated residuals are presented and were found to be in the range of 6.2-6.5. After examining the leachate pH measurements with respect to the leached Cu concentrations, it was found that the increase in alkalinity with the addition of the binders caused the Cu present in the treated specimens to solubilize and leach out into the extract solutions.
With respect to the EPA fresh water chronic toxicity limits, all of the untreated and treated specimens exceeded the limit set for Cu.

Figure 4.4 represents the concentrations of Pb leached from the untreated and treated residuals. The vertical lines present in the plots represent the Pb concentrations leached by the untreated residuals and the TC and EPA fresh water chronic toxicity regulatory limits set for Pb.

Due to the fact that Pb is soluble in very alkaline solutions (pH>11) (Chan et al. 2000), greater additions of binder result in the solubilization of Pb and increased leaching of the metal. Concentrations of Pb leached from the specimens cured for 28 days were higher than the Pb concentrations leached from specimens cured for 7 days. The pH measurements associated with the TCLP extracts of the 28-day cured samples were in the same range (11.0 - 11.9) as the specimens cured for 7 days. The higher degree of hydration that exists in specimens that have longer cure times may have caused the increase in Pb leached from the 28-day samples.

Of the treated specimens, 54% exhibited lower leached concentrations of Pb compared to Pb concentrations leached from the untreated residuals. With respect to the regulatory limits, neither the untreated or treated samples exceeded the TC limit set for Pb. The Pb leached from the untreated residuals exceeded the EPA fresh water toxicity limit, and only 15% of the treated samples met the limit.

Figure 4.5 represents the concentrations of Zn leached for the treated and untreated residuals, along with the EPA fresh water chronic toxicity limit for Zn. The addition of the binders to all three gradations of residuals resulted in lowered concentrations of leached Zn. All of the extracts of the treated specimens exhibited lower
Zn concentrations than the extracts of the untreated residuals. Overall, a decrease in the amount of Zn leached from the treated specimens was exhibited with increasing addition of cement. The EPA fresh water regulatory limit for Zn was exceeded by all three gradations of residuals and met by only 15% of the treated specimens.

Table 4.5 presents the concentration values of Cd, Cu, Pb and Zn leached by the pure cement control samples. The values presented in Table 4.5 were those used in the calculations of $f_L$ and $f_R$. The metal concentration values for Cd, Cu, Pb and Zn of the stabilized samples are organized by cement type and presented in Tables 4.6-4.8. Table 4.9 presents the percentage of metal mass leached from the untreated residuals through TCLP from the total metal mass associated with each gradation from the characterization study. The data presented in Tables 4.6-4.8 are the $C_S$ values used in the calculation of the $f_L$ and $f_R$ indices. The $f_L$ and $f_R$ values and the final pH measurements of the TCLP leachates are arranged for all of the stabilized samples in Tables 4.10-4.12 according to cement type.

A review of Tables 4.10-4.12 shows that for Cd, Cu, and Pb, the most effective binder was the SC. The lowest leached concentrations for Cd, Cu, and Pb were exhibited by the residuals treated with the SC binder, while the highest leached concentrations of these metals were exhibited by the residuals treated with PC. For Zn, the lowest leached concentrations were exhibited by the residuals treated with the SC and PS binders. These two binders exhibited similar effectiveness in reducing the leaching of Zn, while the addition of PC to the residuals resulted in the highest leached concentrations of Zn.
Table 4.5 Cd, Cu, Pb, and Zn metals concentrations in µg/L leached by the pure cement control samples during TCLP.

<table>
<thead>
<tr>
<th>Cement Type</th>
<th>Cure Time</th>
<th>TCLP Leachate pH$^1$</th>
<th>TCLP Leachate Metal Concentration$^2$ (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cd</td>
<td>Cu</td>
</tr>
<tr>
<td>PC</td>
<td>28 d</td>
<td>11.8 σ = 0.04</td>
<td>1.1 σ = 0.9</td>
</tr>
<tr>
<td></td>
<td>7 d</td>
<td>12.0 σ = 0.07</td>
<td>3.9 σ = 1.6</td>
</tr>
<tr>
<td>SC</td>
<td>28 d</td>
<td>11.1 σ = 0.03</td>
<td>0.2 σ = 0.1</td>
</tr>
<tr>
<td></td>
<td>7 d</td>
<td>11.3 σ = 0.12</td>
<td>0.5 σ = 0.2</td>
</tr>
<tr>
<td>PS</td>
<td>28 d</td>
<td>11.6 σ = 0.19</td>
<td>0.2 σ = 0.0</td>
</tr>
<tr>
<td></td>
<td>7 d</td>
<td>11.8 σ = 0.07</td>
<td>0.8 σ = 1.3</td>
</tr>
</tbody>
</table>

$^1$: pH measurement taken after 18-hour rotation period, n = 3

$^2$: For all metal concentrations n = 3
Table 4.6 Concentrations of Cd, Cu, Pb, and Zn in µg/L leached from the type I portland cement (PC) treated total and coarse fractions of the rainfall-runoff residuals.

<table>
<thead>
<tr>
<th>C:R¹</th>
<th>Residual Gradation²</th>
<th>7d TCLP Leachate Metal Concentration³ (µg/L)</th>
<th>28d TCLP Leachate Metal Concentration³ (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cd</td>
<td>Cu</td>
</tr>
<tr>
<td>0.10</td>
<td>TR</td>
<td>2.7</td>
<td>212.0</td>
</tr>
<tr>
<td></td>
<td>σ = 0.8</td>
<td>σ = 6.2</td>
<td>σ = 5.9</td>
</tr>
<tr>
<td>0.10</td>
<td>CR</td>
<td>1.4</td>
<td>175.3</td>
</tr>
<tr>
<td></td>
<td>σ = 0.2</td>
<td>σ = 6.8</td>
<td>σ = 2.2</td>
</tr>
<tr>
<td>0.20</td>
<td>TR</td>
<td>1.8</td>
<td>194.7</td>
</tr>
<tr>
<td></td>
<td>σ = 0.5</td>
<td>σ = 21.5</td>
<td>σ = 9.7</td>
</tr>
<tr>
<td>0.20</td>
<td>CR</td>
<td>2.2</td>
<td>172.0</td>
</tr>
<tr>
<td></td>
<td>σ = 0.2</td>
<td>σ = 12.5</td>
<td>σ = 1.4</td>
</tr>
<tr>
<td>0.30</td>
<td>TR</td>
<td>3.7</td>
<td>163.0</td>
</tr>
<tr>
<td></td>
<td>σ = 1.4</td>
<td>σ = 11.1</td>
<td>σ = 0.6</td>
</tr>
<tr>
<td>0.30</td>
<td>CR</td>
<td>0.10 TR</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>σ = 0.0</td>
<td>σ = 68.0</td>
<td>σ = 0.1</td>
</tr>
<tr>
<td>0.20</td>
<td>TR</td>
<td>0.3</td>
<td>178.3</td>
</tr>
<tr>
<td></td>
<td>σ = 0.2</td>
<td>σ = 13.0</td>
<td>σ = 2.0</td>
</tr>
<tr>
<td>0.20</td>
<td>CR</td>
<td>2.5</td>
<td>141.0</td>
</tr>
<tr>
<td></td>
<td>σ = 0.5</td>
<td>σ = 19.9</td>
<td>σ = 3.9</td>
</tr>
<tr>
<td>0.20</td>
<td>FR</td>
<td>0.3</td>
<td>434.0</td>
</tr>
<tr>
<td></td>
<td>σ = 0.2</td>
<td>σ = 96.2</td>
<td>σ = 0.4</td>
</tr>
<tr>
<td>0.30</td>
<td>TR</td>
<td>1.9</td>
<td>172.7</td>
</tr>
<tr>
<td></td>
<td>σ = 1.0</td>
<td>σ = 25.4</td>
<td>σ = 6.1</td>
</tr>
<tr>
<td>0.30</td>
<td>CR</td>
<td>1.9</td>
<td>141.7</td>
</tr>
<tr>
<td></td>
<td>σ = 0.6</td>
<td>σ = 10.0</td>
<td>σ = 1.1</td>
</tr>
<tr>
<td>0.30</td>
<td>FR</td>
<td>0.2</td>
<td>261.7</td>
</tr>
</tbody>
</table>

*: For these specimens, n = 2
¹: Mass ratio of cement to residual waste
²: Waste gradation treated (TR: total waste gradation; CR: coarse (> 75µm) waste gradation, FR: (<75 µm)
³: For metal concentrations, n = 3, unless otherwise noted
Table 4.7 Concentrations of Cd, Cu, Pb, and Zn in ppb leached from the slag cement (SC) treated total and coarse fractions of the storm residuals.

<table>
<thead>
<tr>
<th>C:R</th>
<th>Residual Gradation</th>
<th>7d TCLP Leachate Metal Concentration (µg/L)</th>
<th>28d TCLP Leachate Metal Concentration (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cd</td>
<td>Cu</td>
</tr>
<tr>
<td>0.10</td>
<td>TR</td>
<td>2.0</td>
<td>77.6</td>
</tr>
<tr>
<td></td>
<td>CR</td>
<td>1.5</td>
<td>63.0</td>
</tr>
<tr>
<td>0.20</td>
<td>TR</td>
<td>3.2</td>
<td>59.4</td>
</tr>
<tr>
<td></td>
<td>CR</td>
<td>1.3</td>
<td>53.8</td>
</tr>
<tr>
<td>0.30</td>
<td>TR</td>
<td>1.3</td>
<td>50.4</td>
</tr>
<tr>
<td></td>
<td>CR</td>
<td>0.7</td>
<td>75.7</td>
</tr>
</tbody>
</table>

1: Mass ratio of cement to residual waste
2: Gradation of waste treated (TR: total waste gradation; CR: coarse (> 75µm) waste gradation)
3: For metal concentrations, n = 3, unless otherwise noted
Table 4.8 Concentrations of Cd, Cu, Pb, and Zn in ppb leached from the 1:1 type I portland/slag cement (PS) treated total and coarse fractions of the storm residuals.

<table>
<thead>
<tr>
<th>C:R</th>
<th>Residual Gradation</th>
<th>7d TCLP Leachate Metal Concentration (µg/L)</th>
<th>28d TCLP Leachate Metal Concentration (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cd</td>
<td>Cu</td>
</tr>
<tr>
<td>0.10</td>
<td>TR</td>
<td>1.8</td>
<td>111.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>σ = 0.1</td>
<td>σ = 11.0</td>
</tr>
<tr>
<td>0.10</td>
<td>CR</td>
<td>2.2</td>
<td>87.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>σ = 0.4</td>
<td>σ = 22.7</td>
</tr>
<tr>
<td>0.20</td>
<td>TR</td>
<td>2.5</td>
<td>109.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>σ = 0.2</td>
<td>σ = 19.7</td>
</tr>
<tr>
<td>0.20</td>
<td>CR</td>
<td>1.6</td>
<td>100.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>σ = 0.7</td>
<td>σ = 12.1</td>
</tr>
<tr>
<td>0.30</td>
<td>TR</td>
<td>1.5</td>
<td>112.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>σ = 0.6</td>
<td>σ = 8.1</td>
</tr>
<tr>
<td>0.30</td>
<td>CR</td>
<td>1.3</td>
<td>108.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>σ = 0.8</td>
<td>σ = 16.2</td>
</tr>
</tbody>
</table>

1: Mass ratio of cement to residual waste
2: Gradation of waste treated (TR: total waste gradation; CR: coarse (> 75µm) waste gradation)
3: For metal concentrations, n = 3, unless otherwise noted
Table 4.9 Metal mass leached from untreated residuals through TCLP and total metal mass associated with each gradation determined in the characterization study of the residuals with the $f_p$ values that represent the percent of the total metal mass leached during TCLP.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Gradation</th>
<th>Metal Mass Leached during TCLP (mg)</th>
<th>Total Metal Mass Present in Gradation (mg)</th>
<th>$f_p^1$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>Total$^2$</td>
<td>0.01</td>
<td>3.80</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>Coarse$^2$</td>
<td>0.01</td>
<td>0.35</td>
<td>2.03</td>
</tr>
<tr>
<td></td>
<td>Fine$^2$</td>
<td>0.01</td>
<td>0.03</td>
<td>35.79</td>
</tr>
<tr>
<td>Cu</td>
<td>Total$^2$</td>
<td>0.09</td>
<td>6.14</td>
<td>1.53</td>
</tr>
<tr>
<td></td>
<td>Coarse$^2$</td>
<td>0.10</td>
<td>5.38</td>
<td>35.79</td>
</tr>
<tr>
<td></td>
<td>Fine$^2$</td>
<td>0.10</td>
<td>0.76</td>
<td>13.07</td>
</tr>
<tr>
<td>Pb</td>
<td>Total$^2$</td>
<td>0.01</td>
<td>8.13</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>Coarse$^2$</td>
<td>0.04</td>
<td>7.63</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td>Fine$^2$</td>
<td>0.02</td>
<td>0.50</td>
<td>3.53</td>
</tr>
<tr>
<td>Zn</td>
<td>Total$^2$</td>
<td>6.46</td>
<td>20.25</td>
<td>31.90</td>
</tr>
<tr>
<td></td>
<td>Coarse$^2$</td>
<td>3.33</td>
<td>17.53</td>
<td>18.98</td>
</tr>
<tr>
<td></td>
<td>Fine$^2$</td>
<td>9.51</td>
<td>2.73</td>
<td>&gt; 100</td>
</tr>
</tbody>
</table>

1: fraction of the total mass of metal leached from the untreated residual gradation during TCLP
2: Total = entire gradation; coarse = > 75 µm; fine = < 75 µm
Table 4.10 $f_R$ calculations in (%) for PC S/S application to the TR, CR, and FR rainfall-runoff solids and the final extract pH measurements.

<table>
<thead>
<tr>
<th>Cement: Type I Portland Cement (PC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C:W 1</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>0.10</td>
</tr>
<tr>
<td>0.10</td>
</tr>
<tr>
<td>0.20</td>
</tr>
<tr>
<td>0.20</td>
</tr>
<tr>
<td>0.30</td>
</tr>
<tr>
<td>0.30</td>
</tr>
<tr>
<td>0.10</td>
</tr>
<tr>
<td>0.10</td>
</tr>
<tr>
<td>0.10</td>
</tr>
<tr>
<td>0.20</td>
</tr>
<tr>
<td>0.20</td>
</tr>
<tr>
<td>0.20</td>
</tr>
<tr>
<td>0.30</td>
</tr>
<tr>
<td>0.30</td>
</tr>
<tr>
<td>0.30</td>
</tr>
</tbody>
</table>

1: Mass ratio of cement to residual waste
2: Gradation of waste treated (TR: total waste gradation; CR: coarse (> 75µm) waste gradation)
Table 4.11 \( f_L \) calculations in (%) for the slag cement (SC) S/S application to the total and coarse gradations of rainfall-runoff solids and the final extract pH measurements following the rotation period of the TCLP.

<table>
<thead>
<tr>
<th>Cement: Slag Cement (SC)</th>
<th>7d TCLP</th>
<th>28d TCLP</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cement:</strong> Slag Cement (SC)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>**C:**W</td>
<td><strong>Residual Gradation</strong></td>
<td><strong>Extract pH</strong></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \mu )</td>
</tr>
<tr>
<td>0.10</td>
<td>TR</td>
<td>7.2</td>
</tr>
<tr>
<td>0.10</td>
<td>CR</td>
<td>7.3</td>
</tr>
<tr>
<td>0.20</td>
<td>TR</td>
<td>8.4</td>
</tr>
<tr>
<td>0.20</td>
<td>CR</td>
<td>8.4</td>
</tr>
<tr>
<td>0.30</td>
<td>TR</td>
<td>8.8</td>
</tr>
<tr>
<td>0.30</td>
<td>CR</td>
<td>8.4</td>
</tr>
<tr>
<td>0.10</td>
<td>TR</td>
<td>7.6</td>
</tr>
<tr>
<td>0.10</td>
<td>CR</td>
<td>7.6</td>
</tr>
<tr>
<td>0.20</td>
<td>TR</td>
<td>8.7</td>
</tr>
<tr>
<td>0.20</td>
<td>CR</td>
<td>9.0</td>
</tr>
<tr>
<td>0.30</td>
<td>TR</td>
<td>8.9</td>
</tr>
<tr>
<td>0.30</td>
<td>CR</td>
<td>8.9</td>
</tr>
</tbody>
</table>

1: Mass ratio of cement to residual waste
2: Gradation of waste treated (TR: total waste gradation; CR: coarse (> 75\( \mu \)m) waste gradation)
Table 4.12 \( f_L \) calculations in (%) for the 1:1 mass ratio of type I portland cement to slag cement (PS) S/S application to the total and coarse gradations of rainfall-runoff solids and the final extract pH measurements following the rotation period of the TCLP.

**Cement:** 1:1 Mass Ratio of Type I Portland and Slag Cements (PS)

<table>
<thead>
<tr>
<th>C:W (^1)</th>
<th>Residual Gradation (^2)</th>
<th>Extract pH</th>
<th>7d TCLP</th>
<th>28d TCLP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cd ( f_L ) (%)</td>
<td>Cu ( f_L ) (%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \mu )</td>
<td>( \sigma )</td>
</tr>
<tr>
<td>0.10</td>
<td>TR</td>
<td>10.0 ( \sigma = 0.6 )</td>
<td>39.9</td>
<td>2.3</td>
</tr>
<tr>
<td>0.10</td>
<td>CR</td>
<td>9.6 ( \sigma = 0.9 )</td>
<td>51.9</td>
<td>9.0</td>
</tr>
<tr>
<td>0.20</td>
<td>TR</td>
<td>11.1 ( \sigma = 0.3 )</td>
<td>56.8</td>
<td>4.5</td>
</tr>
<tr>
<td>0.20</td>
<td>CR</td>
<td>11.0 ( \sigma = 0.3 )</td>
<td>36.2</td>
<td>17.0</td>
</tr>
<tr>
<td>0.30</td>
<td>TR</td>
<td>11.3 ( \sigma = 0.1 )</td>
<td>34.0</td>
<td>14.0</td>
</tr>
<tr>
<td>0.30</td>
<td>CR</td>
<td>11.4 ( \sigma = 0.2 )</td>
<td>30.0</td>
<td>17.7</td>
</tr>
</tbody>
</table>

\(^1\): Mass ratio of cement to residual waste

\(^2\): Gradation of waste treated (TR: total waste gradation; CR: coarse (> 75μm) waste gradation)
4.7 CONCLUSIONS

The TCLP leachate analysis of Cd, Cu, Pb and Zn for the total, coarse and fine gradations of the rainfall-runoff residuals indicated that Cd and Zn are highly associated with the fine particles, while the coarse gradation of residuals contains the highest levels of Pb. From a treatment perspective, one could utilize this finding to effectively treat for one of these two sets of metals. For example, if the metal species characteristics of a certain site exhibit higher concentrations of Cd and Zn, then treatment goals for this particular site could concentrate on removing the fine fraction of residuals to remove the majority of these metals. Treatment implications could further be optimized using this knowledge of the metal species concentrations as a function of particle gradation.

The application of S/S to the total and coarse gradations resulted in similar stabilization of the Cd, Cu, Pb and Zn present in the residuals. Therefore, unless one is intentionally targeting the treatment of metals that are associated with the coarse gradation, such as Pb, the separation of the rainfall-runoff residual gradation is not necessary. The separation of the gradation in an industrial application of the treatment technique would be impractical and would not result in a significant increase in effectiveness in the overall treatment of the rainfall-runoff solids.

Overall, of the cements applied for the stabilization of residual based Cd, Cu, Pb and Zn, the SC addition resulted in the greatest reduction of leaching of the metals. For the specific metals, the SC applications resulted in the most effective chemical stabilization of Cd, Cu and Pb and the PS applications resulted in the most effective chemical stabilization of Zn. The PC application to the residuals resulted in the highest leachate concentrations of Cd, Cu, Pb and Zn. The possible reason for the higher Cu and
Pb levels in the leachates of the PC samples compared to those of the SC and PS could be that the PC addition introduced a higher alkalinity to the solutions than the SC and PS. The increase in pH caused by the PC caused higher solubilization of Cu and Pb hydroxides than the other two binders. Due to the fact that the SC specimens did not harden in the 7-day or 28-day applications, industrial applications of this material might be difficult. Based on the reduced leaching of the metals and the ability of the material to harden in the 7 and 28 day curing periods, the PS was the most successful stabilizing binder tested for the rainfall-runoff residuals.

There were minor differences exhibited by the metals leached by the 7-day and the 28-day curing of the specimens. Generally, for Cd, Cu and Zn, the 28-day curing of the specimens resulted in lower leached concentrations than the 7-day curing. The Pb concentrations leached by the 28-day cured specimens were consistently higher than those leached by the 7-day specimens. This trend is believed to be a result of the higher alkaline conditions introduced by the higher degree of hydration of the binders associated with the 28-day curing of the specimens. In general, the literature reports that long-term effects of S/S demonstrate reduced leachability with increasing cure times (Akhter et al. 1997).

The TC limits were assessed to the untreated residuals, but only for Cd and Pb, as these were the only two metals observed that had limits set under these regulations. These limits were not exceeded by the total, coarse, or fine gradations of rainfall-runoff residuals, indicating that these residuals are not considered hazardous. The fresh water chronic toxicity limits set by the EPA were also assessed to the untreated residuals leachate concentrations for Cd, Cu, Pb, and Zn. These limits were exceeded by the
untreated residuals for Cd, Cu, Pb and Zn, indicating that the presence of these residuals in a fresh water body would impose chronic toxicity to the aquatic biota.

The leached metal concentrations of the S/S treated total and coarse gradations of residuals were compared to the fresh water chronic toxicity limits, since these were exceeded by the untreated residuals. Of the treated specimens, 70% met the EPA fresh water limit set for Cd and only 15% of the treated specimens met the fresh water limits set for Pb and Zn. The fresh water chronic toxicity limit for Cu was not met by any of the treated specimens. Due to the inconsistency in the treatment of the metals, industrial application of the S/S material in direct contact with fresh water bodies is not permitted.

Utilization possibilities of the stabilized cement/storm residuals material are extensive, due to the fact that the material did not exceed the limits set by the TCLP toxicity characterization. Being within the limits of these regulations means that this S/S material can be utilized in industrial applications that involve land application. With this material deemed suitable for land application, depending on strength requirements, the S/S material could be applied as part of the foundation of highways, parking lots and/or buildings. The S/S material could also possibly be used to construct concrete detention basins and/or channels for the treatment of rainfall-runoff.

4.8 REFERENCES


4.9 NOMENCLATURE

The following symbols were used in this chapter:

ASTM: American Society for Testing and Materials
BDAT: best demonstrated available technology
BMP: best management practice
C_{\text{Cl}}: concentration of metal \( i \) leached by the pure cement control specimen (\( \mu \text{g/L} \))
C_{\text{CL}}: concentration of metal \( i \) leached by the untreated residuals (\( \mu \text{g/L} \))
C_{\text{CR}}: concentration of metal \( i \) leached by the untreated residuals (\( \mu \text{g/L} \))
C_{\text{CS}}: concentration of metal \( i \) leached by the treated residuals (\( \mu \text{g/L} \))
Cd: cadmium
Cd^{2+}: cationic form of cadmium
CH_{3}COOH: acetic acid
cm: centimeters
cm^{3}: cubic centimeters
Cr: chromium
CR: coarse residuals (< 75 \( \mu \text{m} \))
Cu: copper
Cu(OH)_{2}: copper hydroxide
Cu(II)S: copper sulfide
{o}C: degrees Celsius
DI: de-ionized
{o}F: degrees Fahrenheit
f_{\text{Li}}: fraction of metal \( i \) leached during TCLP (%)
f_{\text{Pi}}: fraction of the total mass of metal \( i \) leached from the untreated residual gradation during TCLP (%)
f_{\text{R}}: percentage of metals retained by the cement/residual matrix (%)
FR: fine residuals (\( \geq 75 \mu \text{m} \))
ICP-MS: inductively coupled plasma-mass spectrophotometer
L: liter
m^{2}: square meters
mL: milliliters
\mu m: micrometers
mm: millimeters
MSA: metropolitan statistical area
M_{\text{T}}: total mass of metal \( i \) associated with the untreated residuals (mg)
NaOH: sodium hydroxide
Ni: nickel
OPC: ordinary portland cement
Pb: lead
Pb\(^{2+}\): cationic form of lead
Pb(OH)\(_2\): lead hydroxide
P\(_S\): Percent solids of the specimen (%)
PC: type I portland cement
ppb: parts per billion
PS: 1:1 type I portland/slag cement mixture
QA/QC: quality assurance/quality control
RCRA: resource conservation and recovery act
SC: slag cement
S/S: solidification and stabilization
SSA: specific surface area (m\(^2\)/g)
TCLP: toxicity characteristic leaching procedure
TR: total residuals
V\(_E\): volume of extraction fluid (L)
W\(_E\): Weight of the extraction fluid (g)
W\(_W\): Weight of the specimen (g)
Zn: zinc
 CHAPTER 5. SUMMARY AND CONCLUSIONS

Anthropogenically contaminated rainfall-runoff particulate matter captured and enriched in Best Management Practices (BMPs) are a significant source of solid and potentially hazardous waste. Solids within transportation land use right-of-ways, especially those located in urbanized and industrial areas, are loaded by rainfall-runoff directly from urban surfaces and are directly contaminated with the metal species (Cd, Cu, Pb and Zn) that are generated by traffic activity. Along with contaminated soils and sediments, the particulate matter that is generated from vehicular and infrastructure interactions including abrasion of vehicular material (engine, brake, and tire wear) and wear of transportation infrastructure, such as pavement (Bris et al. 1999), that contribute significant quantities of residual waste. A major source of rainfall-runoff solid waste and potentially hazardous waste that will increase significantly in the future are those residuals recovered from BMPs. These residuals exist with a combination of metal species in a wide size gradation ranging in size from smaller than 1 µm to greater than 10,000 µm (Sansalone et al. 1998).

The volume of residual matter associated with rainfall-runoff exists in amounts equal to or in excess of the volume of sludge presently generated by municipal wastewater treatment (Field et al. 1994). It is estimated that annual residual/sludge volumes for urban rainfall-runoff in the United States range from 27 to 547 million m$^3$ at an average solids content ranging from 0.5 to 12 percent, whereas annual sludge volumes for combined sewer overflow (CSO) in the United States range from 11 to 228 million m$^3$ with 0.7 to 3.2 percent solids (Field et al. 1994). From this estimation, the volume of residual material associated with rainfall runoff more than doubles the amount of sludge
that must be managed. With these volumes of rainfall-runoff residuals, handling and disposal of this material requires consideration, but due to the metal species associated with the rainfall-runoff residuals, conventional handling of solid waste, such as land application or landfilling, may be restricted due to toxicity and regulatory issues.

In this study, residual particulate samples from five urban BMP sites were recovered and characterized for physicochemical granulometric indices. The experimental facilities were located in Baton Rouge, LA, Little Rock, AR, North Little Rock, AR, and Cincinnati, OH. The BMPs associated with the sampling sites varied from site to site. Examples of the BMPs sampled in this research included a detention channel, an urban vegetated swale, porous pavement, and detention basins. The residuals captured from these facilities were analyzed as a function of gradation for particle mass, particle size distribution (PSD), particle density ($\rho_s$), total surface area (SA), specific surface area (SSA), surface charge, and metal species (Cd, Cu, Pb, and Zn).

These characterization parameters were analyzed for the five sites and relationships among the parameters were established. Through the characterization of the residuals, a correlation between PSD, SA, SSA, and metal species contamination was drawn. The higher values of SA were associated with the coarse-based (>75 $\mu$m) gradation of the residuals, and this portion of the gradation exhibited high mass of metals, where as the fine gradation (<75 $\mu$m) of the residuals exhibited high values of SSA and high concentrations of metals. These trends have been demonstrated by rainfall-runoff residual matter in previous studies (Viklander 1997; Sansalone et al. 1998).

The total (entire gradation), coarse (>75 $\mu$m), and fine (< 75 $\mu$m) gradations of the residual matter collected from the BMP facility in Baton Rouge, LA, were analyzed for
leaching potential using the toxicity characteristic leaching procedure (TCLP). The resulting leached metal species were compared to the EPA toxicity characteristic (TC) limits for Cd and Pb and EPA fresh water chronic toxicity limits for Cd, Cu, Pb and Zn. All three gradations of residuals exceeded the fresh water chronic toxicity limits, but did not exceed the TC limits, thus the residual are not characterized as a hazardous waste.

Although the residuals are not characterized as hazardous, if the residuals are deposited to a fresh water body, they have the potential to create acute and chronic toxic conditions, and result in oxygen depletion.

With the results of the characterization study of the BMP residuals, appropriate residuals management techniques were evaluated, in particular solidification and stabilization (S/S). S/S processes are frequently used to immobilize soils and sludges containing metal species contaminants and can be designed to accommodate large volumes of waste (Means et al. 1995). With the metal species contamination associated with rainfall-runoff residuals and the large volumes of residuals, S/S treatment was determined to be applicable to rainfall-runoff residuals.

In general, S/S treatment processes are designed to accomplish one or more of the following: reduced metal species mobility and/or solubility, improved handling and physical characteristics of the waste by producing a solid with no free liquid, and decreased surface area across which transfer or loss of contaminants may occur (Means et al. 1995). The most common form of the S/S technology uses a cement or pozzolanic binder to convert the waste to an aggregate. The S/S of hazardous wastes by cement-based binders is a technology that has been applied to many types of wastes and
industrial effluents, mainly those containing heavy metals (Means et al. 1995; Cartledge et al. 1990).

In this study, the BMP residuals recovered from the experimental facility located in Baton Rouge, LA, were treated using cement-based S/S. A cement kiln located in New Orleans, LA provided mass quantities of a type I portland cement (PC) and a slag cement (SC). At the suggestion of the manufacturer, a 1:1 mass ratio of the type I portland cement and the slag cement (PS) was mixed and used in the application of S/S.

Prior to the application of the S/S technology to the residuals, the cements were analyzed for PSD, particle density, and hydration behavior. Laser diffraction was used to determine the PSD of the cements. From previous research, it was found that cements with PSD with d_{50} values of 5 µm had a higher hydration degree than those with a d_{50} of 30 µm (Bentz et al. 1999). The PSDs analyzed for the PC, SC, and PS all had d_{50} values of approximately 10 µm. Particle densities were determined using helium pycnometry and it was determined that the PC has the highest density of 3.18 g/cm³, followed by the PS (ρs = 2.99 g/cm³) and SC (ρs = 2.90 g/cm³), respectively. The densities of the PC and SC were compared to density ranges found in the literature for type I portland cement and slag cement and the density values evaluated for the experimental PC and SC fell within these ranges. The hydration behavior of the cements was determined using thermal analysis techniques. Thermogravimetry (TG) and derivative thermogravimetry (DTG) were used to examine the hydrated cement at the initial and later stages of hydration. The results of the TG and DTG analyses showed that the PC achieved the highest degree of hydration of the three cements based on the amount of CaOH formed during hydration. The TG and DTG analyses indicated that the SC did not hydrate in the initial 24 hours of
curing and even after 4 weeks of cure time did not reach a significant amount of hydration.

Following the cement characterization, S/S was applied to the rainfall-runoff residuals using the PS, SC, and PS. Three gradations, total (entire gradation), coarse (>75 µm), and fine (<75 µm), of the rainfall-runoff residuals were treated using S/S. The total and coarse residuals were treated using 10, 20, and 30% by mass of PC, SC, and PS cement additions and cured for 7 and 28 days. Due to the limited amount of fine residuals, the S/S application to the fine residuals was examined using only the PC and cured for only a 28-day period. The S/S specimens were tested for hydration behavior, mechanical strength, and leaching potential.

A non-conventional differential thermal analysis technique (NCDTA) was performed on the control cement specimens and the cement with residuals addition in order to test the hydration behavior of the specimens. Through NCDTA analyses, it was found that the residuals introduced a retardation effect on the hydration of the pastes. The total and coarse residuals caused the same degree of retardation, whereas the fine residuals imposed the most significant retardation of cement hydration. The PC specimens released the highest amounts of heat, indicating that these specimens reached the highest degrees of hydration. In the evaluation of the heat evolved within the samples, it was found that the SC specimens with residuals addition reached a higher degree of hydration than the pure SC control specimens. The exothermic reaction associated with the SC and residual specimens could possibly be a result of some components of the residuals reacting and aiding in the hydration of the SC paste, as was seen in a study
conducted by Dweck *et al.* that observed slag cement hydration reactions that were significantly accelerated by the presence of the waste (Dweck *et al.* 2003).

The physical solidification of the S/S specimens was tested for unconfined compressive strength (UCS). EPA considers a stabilized/solidified material with strength of 50 psi (0.34 MPa) to have a satisfactory UCS (USEPA OSWER Directive No. 9431.00-2A). A minimum strength of 50 psi (0.34 MPa) is set as the provision for a stable foundation for materials to be placed up it, including construction equipment and impermeable caps and cover material (Barth *et al.* 1990). The cylindrical specimens were 2 in (51 mm) in diameter and 4 in (102 mm) in height and were tested with a strain rate of 0.05 in/min (1.7 mm/min). The SC specimens were not tested for UCS, due to the fact that the specimens were not significantly solidified after 7 and 28 days. The PC and PS specimens were failed and the stress and strain measurements were plotted. All of the PC and PS specimens, except the PC with fine residual addition, had ultimate strength values that exceeded the EPA regulatory limit of 50 psi (0.34 MPa). The elastic modulus (E) of each of the specimens was analyzed using the slope of the curves resulting from the graphs of the incremental stress values plotted as a function of the incremental strain values. The modulus values were compared and it was found that the 28 day cured total residual specimens with PC addition exhibited the highest strength. The 20 and 30% cement additions and 28 day curing yielded the highest mechanical strength in terms of modulus for these specimens. These specimens also exhibited the highest hydration degrees throughout the NCDTA experiments. The hydration degree indicates a level of binding, thus the observation of the same specimens exhibiting the highest degree of hydration and the highest UCS is appropriate.
The specimens that were failed through UCS testing were crushed and tested for leaching potential using the toxicity characteristic leaching procedure (TCLP). The results of the Cd, Cu, Pb, and Zn metal concentrations of the TCLP extracts were analyzed and compared to the EPA toxicity characteristic (TC) listings for Cd and Pb and the EPA fresh water chronic toxicity regulation limits for Cd, Cu, Pb, and Zn. The TCLP extracts of the treated residuals were also compared to TCLP extracts of the untreated residuals. Calculations were made to determine the fraction of the metals leached (fL) and the fraction of the metals stabilized and retained by the cement matrix (fR), based on the untreated residual metal concentrations and the metal concentrations leached by the pure cement control samples. Through these analyses it was determined that Cd and Zn were the most stabilized metals, with fR values as high as 90% for Cd and 98% for Zn in the SC addition to the total and coarse gradations. Cu and Pb were stabilized in some cases, but not consistently. The most effective stabilization came from the SC binder. The concentrations of the metals leached from the specimens stabilized with SC were the lowest, followed by the PS and then the PC. Overall, the higher binder additions resulted in more effective stabilization, but in some cases the higher binder addition resulted in higher concentrations of leached metals, especially Cu.

The main objectives of this research were to gain more knowledge regarding the characteristics of rainfall-runoff residuals and to test the application of S/S to the residuals as a possible management, disposal, or reuse technique to be used for the residuals. The characterization of the rainfall-runoff residuals from the five BMP sites established the granulometric characteristics of the residuals in order for rainfall-runoff treatment techniques to be more appropriately designed to handle the residual matter. The
physical and chemical characteristics of the residuals also aided in the selection of the
appropriate binder for the application of S/S. In order to achieve successful treatment of a
waste through S/S, the selection of the binder to be utilized requires an understanding of
the chemistry of the waste, the contaminants, and the binder (Means et al. 1995). With
the knowledge of the metal species associated with the residuals, cement-based binders
were applied to the residuals.

Cement-based S/S proved to be an effective handling and treatment technique for
rainfall-runoff residuals. The separation of the residuals into coarse and fine gradations of
residuals did not improve the strength or leaching characteristics of the S/S material. In
fact, the S/S specimens with the fine fraction of residuals showed very poor setting and
strength characteristics. The treatment of these residuals by S/S must further be studied in
order to determine the appropriate binder to be utilized for treatment of these residuals.
Of the binders applied in this research, the PC proved to have the highest mechanical
strength and the SC proved to provide the most effective stabilization of the metals
species associated with the residuals. In further research of S/S treatment for rainfall
runoff residuals, the application of additives to portland cement, such as slag and/or fly
ash, in quantities that do not reduce the strength of the specimens should be studied.
Since the desired result of S/S applications is for the waste/binder specimens to have a
high mechanical strength and also to exhibit minimal leaching, a combination of the
strength of the portland cement and the stabilization of the slag cement may be
appropriate.

Through further research, the strength and leaching potential of solidified rainfall
runoff residuals can be further investigated and optimized. Once the S/S technique is
aptly designed to produce a material that exhibits high strength and minimal leaching and the long-term effectiveness of the treatment is assessed, the application possibilities for the material can be significant. The S/S material produced in this research with the PC and PS applications to the total and coarse gradations exceeded the strength limits required by the EPA to provide a stable foundation for materials to be placed upon it, including construction equipment. Having met this strength regulation, this material could be applied as impermeable caps and cover material for landfills. To bring the S/S treatment “full circle” in this case, the solidified residuals could be used to construct concrete detention facilities for the treatment and containment of rainfall-runoff.

5.1 REFERENCES


VITA

Erin Ezell Krielow was born on November, 10, 1979, in Jennings, Louisiana. She attended high school in Lafayette, Louisiana, graduating in 1997. Erin attended Louisiana State University in the Fall of 1997. As an undergraduate student, Erin was a member of the LSU Marching Band. Erin received her Bachelor of Science degree in environmental engineering in May of 2001 and began her graduate studies the following month. Erin will receive a Master of Science in Civil Engineering degree in August of 2003.