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ABSTRACT

REMEDIATION AND REUSE OF CHROMIUM CONTAMINATED SOILS THROUGH COLD TOP EX-SITU VITRIFICATION

by Wiwat Kamolpornwijit

More than 150 sites in Hudson County, New Jersey are identified as chromium contaminated sites. Hexavalent chromium, highly soluble in water, is considered as an environmental and health hazard, classified as a group A human carcinogen. In this research, the feasibility was performed to study the possibility of remediation of chromium contaminated soil by ex-situ vitrification and to evaluate reuse potential of vitrified products as highway construction aggregate. A series of physical and chemical analysis was conducted on nine soil samples collected from different chromium contaminated sites. Results were analyzed for their compatibility for vitrification. Sand and carbon were added to enhance vitrification process. Vitrification was performed and the vitrified products were subjected to further chemical and physical tests. TCLP chromium concentration results verified a successful remediation. The vitrified product properties complied with the New Jersey Department of Transportation standards, designating high reuse potential.

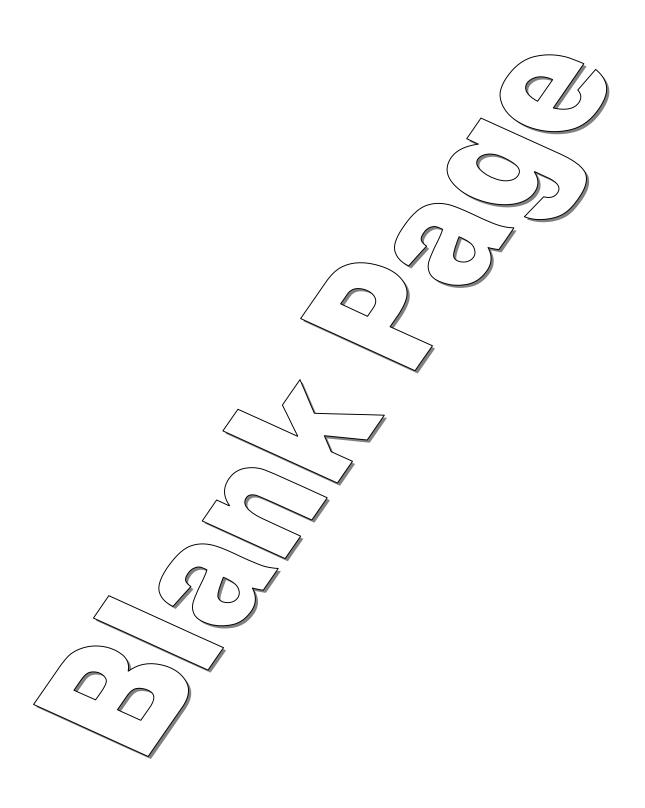
REMEDIATION AND REUSE OF CHROMIUM CONTAMINATED SOILS THROUGH COLD TOP EX-SITU VITRIFICATION

by Wiwat Kamolpornwijit

A Thesis
Submitted to the Faculty of
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Department of Civil and Environmental Engineering

January 1996



APPROVAL PAGE

REMEDIATION AND REUSE OF CHROMIUM CONTAMINATED SOILS THROUGH COLD TOP EX-SITU VITRIFICATION

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The author dedicates this thesis to his beloved parents.

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TABLE OF CONTENTS

Chapter	Page
1 INTRODUCTION	1
2 LITERATURE SURVEY	4
2.1 Chromium.	4
2.1.1 Natural Chromium.	4
2.1.2 Anthropogenic Chromium	4
2.1.3 Production and Health Hazards of Chromate	3 5
2.1.4 Oxidation and Reduction Reaction of Chrom	ium7
2.1.4.1 pH	9
2.1.4.2 Organic Matter	10
2.1.4.3 Redox Potential	11
2.1.4.4 Reducing Agent	12
2.1.4.5 Oxidizing Agent	13
2.2 Vitrification	14
2.2.1 Cost of Operation	17
2.2.2 Chemical Composition of Soils	17
2.2.3 Vitrified Products	18
2.3 Vitrification of Chromium Contaminated Soils	18

TABLE OF CONTENTS (Continued)

Chapter	Page
3 EXPERIMENTAL PROGRAM	22
3.1 Experimental Program.	22
3.2 Soil Samples Collection	22
3.3 Chemical Characteristic Tests for Soil Samples	23
3.4 Physical Characteristic Tests for Soil Samples	24
3.5 Soil Sample preparation for Vitrification	24
3.6 Vitrification Process	25
3.7 Chemical Characteristic Tests for Vitrified Samples	25
3.8 Physical Characteristic Tests for Vitrified Samples	26
3.9 Quality Control.	27
4 RESULTS AND DISCUSSIONS	29
4.1 Test Results and Dicussions of Soil Samples	29
4.2 Physical Identification of Vitrified Samples	33
4.3 Test Results and Discussions of Vitrified Samples	35
4.3.1 Chemical Test Results and Discussions	35
4.3.2 Physical Test Results and Discussions	38
4.3.2.1 Specific Gravity and Adsorption	38
4.3.2.2 Unit Weight	39
4.3.2.3 Moisture Content and Colorimetric Test	39

TABLE OF CONTENTS (Continued)

Chapter	Page
4.3.2.4 Friable Material	39
4.3.2.5 Sodium Sulfate Soundness	40
4.3.2.6 LA Abrasion Test	40
4.4 Volume Reduction	42
5 SUMMARY AND CONCLUSIONS	44
APPENDIX A GRAIN SIZE DISTRIBUTION CURVES OF SOIL SAMPLE	ES46
APPENDIX B GRAIN SIZE DISTRIBUTION CURVES OF VITRIFIED SAMPLES	51
APPENDIX C QUALITY CONTROL CHECKS FOR VITRIFIED SAMPLE TESTS	E 56
APPENDIX D EXPERIMENTAL PROCEDURE	60
REFERENCES	65

LIST OF TABLES

Table	Page
3.1 Site Name, NJDEP Site Number	, and Responsible Party23
3.2 Control Limits for Physical Prope	erty Tests28
4.1 Chromium Concentration in Soil	Samples30
4.2 Chemical Composition of Soil Sa	amples31
4.3 Physical Characteristics of Soil S	amples31
4.4 Chromium Concentration of Vitri	fied Samples36
4.5 Physical Characteristics of Vitrifi	ed Samples37
4.6 Physical Property Requirements	38
4.7 Adjusted Percent Weight Loss in	LA Abrasion Tests40
4.8 Potential Volume Reduction from	1 Vitrification43
C 1 Control Limits for Quality Control	ol Checks56
C 2 QC Checks for Specific Gravity (Dry), Fine Aggregates56
C 3 QC Checks for Specific Gravity (Dry), Coarse Aggregates57
C 4 QC Checks for Specific Gravity (SSD), Fine Aggregates57
C 5 QC Checks for Specific Gravity	(SSD), Coarse Aggregates57
C 6 QC Checks for Adsorption, Fine	Aggregates58
C 7 QC Checks for Adsorption, Coar	se Aggregates58
C 8 QC Checks for Sodium Sulfate S	Soundness, Fine Aggregates58
·C 9 QC Checks for Unit Weight	59

LIST OF FIGURES

Figure Page
2.1 The Eh-pH Diagram for the Various Chromium Species
2.2 Critical Soil Redox Potential for Chromate, Iron, and Nitratefacing 11
2.3 Critical Soil Redox Potential for Manganese
2.4 The pE-pH Diagram for HCrO ₄ /Cr(OH) ₃ and Reducing Agents
4.1 Multiplying Factors for LA Abrasion Test
A 1 Grain Size Distribution Curve of RDI
A 2 Grain Size Distribution Curve of CD
A 3 Grain Size Distribution Curve of GAR
A 4 Grain Size Distribution Curve of LSP
A 5 Grain Size Distribution Curve of RR
A 6 Grain Size Distribution Curve of DS
A 7 Grain Size Distribution Curve of TPR
A 8 Grain Size Distribution Curve of CPR
A 9 Grain Size Distribution Curve of RM
B 1 Grain Size Distribution Curve of RDI 1
B.2 Grain Size Distribution Curve of RDI 2
B 3 Grain Size Distribution Curve of CD.
B 4 Grain Size Distribution Curve of GAR
B 5 Grain Size Distribution Curve of LSP.

LIST OF FIGURES (Continued)

Figure	Page
B 6 Grain Size Distribution Curve of RR	54
B 7 Grain Size Distribution Curve of DS	54
B 8 Grain Size Distribution Curve of TPR	55
B 9 Grain Size Distribution Curve of CPR	55

CHAPTER 1

INTRODUCTION

Chromium is a metallic element and naturally occurs as mineral chromite. Chromium in a trace amount is essential for nutrition of humans and other forms of life. There are many forms of chromium existing naturally and anthropologically, but the stable and most prevalent forms are trivalent and hexavalent chromium. Chromium is utilized in multiple industries, mostly in metallurgical, refractory, and chemical manufacturing. Hexavalent chromium is well known as group A human carcinogen with sufficient human evidence, classified by US Environmental Protection Agency. Both hexavalent and trivalent chromium are associated with allergic contact dermatitis. Hexavalent chromium is water soluble in the full pH range, while trivalent chromium tends to be adsorbed on soil surface or precipitates as chromium hydroxide in slightly acidic and alkaline media. The high mobility of hexavalent chromium causes the potential hazard contamination to surrounding media, i.e., groundwater and surface water.

Chromium ore was imported and chromium was extracted in New Jersey during the early part of the century. From 1905 to 1971, chromate production from chromite ore was operated by three facilities in Hudson County, New Jersey. It was estimated that over two million tons of chromite ore processing residue was leftover and used as a fill material in construction sites and wetland, grading materials in roadway and other construction in residential, commercial, industrial, and recreational areas. New Jersey Department of

Environmental Protection (NJDEP) has identified more than 150 sites in Hudson County, New Jersey as the chromium contaminated areas. The chromium concentration at these contaminated sites ranges from a few ppm to 5 percent by weight. In some sites almost 100 percent of hexavalent chromium salt precipitation was detected.

Several treatment technologies for chromium contaminated soil were purposed, and assessed for effectiveness, volume reduction, end-product durability, and economics. Vitrification was selected as a potential innovative treatment technology for the feasibility study. In the vitrification process, hexavalent chromium will be reduced to trivalent chromium and incorporated into the glass matrix of the vitrified products, which are physically and chemically similar to obsidian. If the vitrified products are no longer hazard, then it should be delisted into non-hazard material. The durability and strength properties of vitrified products are compatible to granite and pyrex. Hence vitrified product can be reused as an aggregate in concrete and asphalt cement. Other contaminant imparted in soil will be also remediated by means of thermal treatment such as the pyrolysis or decomposition of toxic organic materials and encapsulation of other toxic heavy metals.

In this research the feasibility of remediation and reuse of chromium contaminated soils by cold top ex-situ vitrification were studied. The effectiveness of the remediation was verified by the chemical analysis of TCLP leachate chromium concentration from the vitrified products. The potential reuse value was evaluated based on the compatible properties of vitrified products to the standard properties of aggregates established by New Jersey Department of Transportation (NJDOT). This research is a part of the

remediation program, funded by NJDEP, and performed by New Jersey Institute of Technology and Stevens Institute of Technology. New Jersey Institute of technology was responsible for the physical characteristic tests and verification of reusable value of the samples, while Steven Institute of Technology was responsible for the chemical analysis. In the remediation program, the feasibility study was conducted on two phases, the engineering-scale and pilot-scale. The research described in this thesis belonged to the engineering-scale part. In the engineering-scale test, chemical and physical characteristics of both original soils and vitrified products were performed. The results were analyzed, and the feasibility of remediation and potential reusing was determined. Vitrification was performed by Corning, Inc. In the pilot-scale test, the economical concern and end-products reuse will be evaluated which will not be included in this thesis.

CHAPTER 2

LITERATURE SURVEY

2.1 Chromium

2.1.1 Natural Chromium

Natural chromium in soil originated from the chromite mineral in magma which upon exposure to the atmosphere, solidifies to form the igneous rock. Many kinds of chromium minerals are formed, e.g., chromite (FeO.Cr₂O₃ or MgO.Cr₂O₃), and incorporated in the rock. After the weathering process the chromium minerals are transformed and transported to other parts and form sediment rock or after the long weathering process become soil.

Chromium is the seventh most abundant element in the earth crust with the average concentration of 100 mg/kg [1]. There are many kinds of chromium-containing minerals but chromite is the most economical one. Chromite ore contains mostly chromium oxides (Cr₂O₃), iron oxides (FeO) and lesser amounts of magnesium oxide (MgO), aluminum oxide (Al₂O₃), and silicondioxide (SiO₂) [23].

2.1.2 Anthropogenic Chromium

Anthropogenic sources of chromium are generated from many kinds of industries. The major industries processing chromium are the metallurgical, refractory, and chemical manufacturing, which account for roughly 60%, 20%, and 20% of chromite ore

consumption, respectively [2]. It is estimated that half of the airborne contaminated chromium is generated from the coal and oil combustion [1]. Chromium contamination in water typically originates from the chemical manufacturing, while chromite ore processing residue is the major source of chromium contaminated soils. The chromite ore residue was used as fill material in construction site, grading for roads or filling of wetland.

The speciation of chromium in the wastes depends upon the manufacturing processes. Hexavalent chromium is found in the waste stream of chemical manufacturing, primary metal production, chrome plating industry, and textile manufacturing. Trivalent chromium is found in steel production, ferrochromium production, refractory production, cement production, MSW incineration, and chrome ore refining.

2.1.3 Production and Health Hazards of Chromate

Mineral chromite, FeO.Cr₂O₃, is inert and insoluble in water and acid. In the chromate manufacturing process, chromite ore is pulverized and mixed with soda ash, Na₂CO₃, and lime, CaO, and heated to 1100°C to 1500°C to produce sodium chromate, Na₂CrO₄, which is highly water soluble. Solubility of Na₂CrO₄ at 20°C to 30°C is 5.2 mole/kg of water [1]. Most soluble chromate compounds are leached with the remaining slowly dissolving [25], such as calcium chromate (CaCrO₄), with a solubility of 0.00071 mole/kg of water at 20°C to 30°C[1]. The concentrations of slowly dissolving chromate found in chromite ore processing residue range from 0.7 to 5 percent by weight [25]. The leaching of chromate from slowly dissolving compounds can last for decades which is potentially environment and human health hazards.

The concentration of chromium is critically high at the soil surface because of the capillary rise of chromate from the slowly soluble compounds. The rising rate depends upon the meteorological condition. The surface concentration is important since it is used to determined the exposure hazard. Chromium has been found under buildings constructed over the waste sites, as distinguished by its bright yellow color with concentrations as high as 37,000 mg/kg [25].

Chromium ingestion causes acute toxicity with gastrointestinal symptoms and bleeding, and may result in kidney or liver failure. Hexavalent chromium is considered a group A human carcinogen with sufficient evidence, essentially to respiratory systems. The Threshold Limit Value (TLV) for chromium established in EPA 40 CFR is 0.05 mg/m³. Hexavalent chromium is found to be adsorbed by the human body faster than trivalent chromium [26]. The mutagenic potentials of hexavalent chromium are positive while inactive in trivalent chromium, except the direct contact with DNA. Hexavalent chromium can be reduced to trivalent chromium when exposed to human organs, primarily by bodily fluids, i.e., gastric juices, lining fluid in respiratory track, and secondarily inside the individual cell by mitochondria, cytosol, and so on. The reduction of hexavalent chromium by lactic acid in human sweat was also reported [3]. Excess hexavalent chromium then gets into nucleus and is subjected to reduction reaction. The reduction occurs can effect DNA molecules and causes the cancer induction [26].

From literature [5], air borne hexavalent chromium concentration was determined from 21 sites representative of contaminated unpaved and partially paved commercial/industrial sites. Results revealed levels threefold lower than current threshold

limit value. Therefore, it can be concluded that no significant health hazard for on-site or nearby workers [5].

Hexavalent chromium has inhalation risk per unit dose of 1.2*10⁻²(g/m³)⁻¹, with an inhalation slope factor of 42 (mg/kg-day)⁻¹ [27]. Unit risk values should be taken into account instead of TLV when considering the health hazard of residents living near a contaminated site.

.

2.1.4 Oxidation and Reduction Reaction of Chromium

It has been estimated that about two or three millions tons of chromite ore residue were leftover in Hudson County, New Jersey. The chromite ore residue, after passing chromate production process contains 2-7 % of chromium by weight. The concentration of total chromium in contaminated soil from 42 sites in New Jersey was found in the range of 5-19,000 mg/kg. Hexavalent chromium accounted for 1-5 % of total chromium or 0.5-780 mg/kg [24]. There are many existing forms of both trivalent and hexavalent chromium in soil. The fractionation of chromium depends upon the oxidation-reduction reaction, which mostly occurs in the aqueous media in the environment. The common trivalent chromium ions are hexaaquochromium $[Cr(H_2O)_6]^{3+}$, cation, and dichromate $[Cr_2O_7]^{2-}$, chromate $[CrO_4]^{2-}$, anion, for hexavalent chromium.

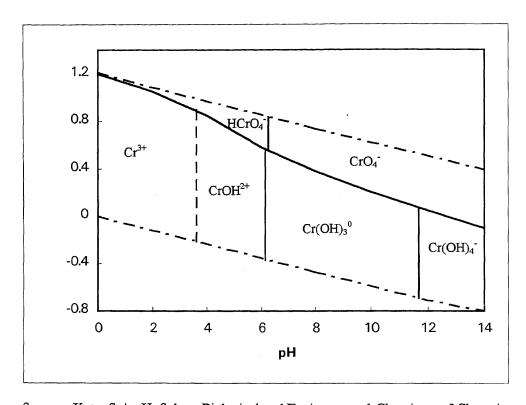
In contaminated soil, consisting of clay, the cationic trivalent chromium is potentially attracted and adsorbed by the negatively charged potential on clay surface, while hexavalent chromium is present as an anion chromate, and is soluble in water and may precipitate as salt when the soil becomes dried. The precipitation of CrO_4^{2-} salt

causes the occurring and reoccurring of the blush, colorful salt precipitating on the soil surface, essentially when the CrO_4^{2-} concentration is high enough. James [3] found that the occurring of blush might be possible at the minimum concentration of hexavalent chromium between 200-650 mg/l.

The hazards of chromium residue come from its hexavalent form, considered a carcinogen [7]. Hexavalent chromium is soluble in the full pH range, while trivalent chromium tends to precipitate as Cr(OH)₃ when pH is raised above 5.5, or be adsorbed on the soil surface. The pH of Chromite ore residue usually ranges from 10 to 11 [6], this condition promotes the precipitation of trivalent chromium as Cr(OH)₃. However, trivalent chromium could complex with organic ligands and form organic complexes increasing Cr(III) solubility [15]. From a literature [15], it was found that when dissolved organic carbon concentration in floodwater of wetland increased, the amount of dissolved Cr(III) also increased. The adsorption of Cr(III) by suspended solid was also detected to be lower at higher DOC concentration.

Trivalent chromium is considered to be more stable than hexavalent chromium. It dissociates in the hot acidic condition, while hexavalent chromium dissolves well in water and better in alkaline or hot water [6].

The dominant species of chromium, which also indicates the potential hazard in soil, is controlled by the oxidation-reduction reaction of chromium in soils. The reduction or oxidation potential of chromium in soil depends on many factors such as pH, redox potential, organic matters, reducing agents, and oxidizing agents. Reduction is found to



Source : Katz, S.A., H. Salem. Biological and Environmental Chemistry of Chromium. VCH Pub. New York. 1994

Figure 2.1 The Eh-pH Diagram for the Various Chromium Species

be mainly caused by ferrous iron (Fe(II)), organic matter, and reduced sulfide. Oxidation is caused by manganese ion (Mn(III) and Mn(IV)).

2.1.4.1 pH. The reduction rate of Cr(VI) to Cr(III) was found to be rapid in the acidic condition [8, 11]. The reduction equilibrium in equation 2.1 to 2.3 [1] also indicate the preference of reduction in the acidic media; hydrogen ions and hydroxyl ions are incorporated with the reaction in the manner that lowering pH will increase the reduction rate. However, Cr(III) will precipitate as chromium hydroxide Cr(OH)₃ in the alkaline or slightly acidic environment or when pH is higher than 5.5. The Eh-pH diagram for the various chromium species is shown in Figure 2.1.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$
 (2.1)

$$CrO_4^{2-} + 4H_2O + 3e^- \rightarrow \left[Cr(OH)_4\right]^{2-} + 7OH^-$$
 (2.2)

$$CrO_4^{2-} + 4H_2O + 3e^- \rightarrow [Cr(OH)_3] + 5OH^-$$
 (2.3)

The pH also indirectly influences the reaction by changing the negative charges on clay surface by dissolving the hydroxyl group in clay surface structure [4], as shown in equation 2.4. When pH increases, the reaction is prone to shift to the right, increasing the negative charges on the surface. Despite of increasing the Cr(OH)₃ precipitation, Cr(III) which is present in the cation forms, will be increasingly adsorbed at higher pH. The lesser available Cr(III), after adsorption and precipitation, leads to the lower oxidation rate. James [3] found that after spiking soluble Cr(III) and Cr(VI) into the soils, within pH range of 8-10, about 100 % of Cr(VI) added was recovered without reduction or sorption, while the concentration of Cr(VI) in soils was slightly decreased instead of

lesser available Cr(III), after adsorption and precipitation, leads to the lower oxidation rate. James [3] found that after spiking soluble Cr(III) and Cr(VI) into the soils, within pH range of 8-10, about 100 % of Cr(VI) added was recovered without reduction or sorption, while the concentration of Cr(VI) in soils was slightly decreased instead of increased when soluble Cr(III) was added, which indicated that no oxidation occurred. He concluded that very slight oxidation occurred in the alkaline condition.

$$\exists SiOH \to \exists SiO^- + H^+ \tag{2.4}$$

Soil is also known as a good buffer. Soil pH will remain quite constant, even through natural acid addition such as acid precipitation [3]. Therefore the alkaline condition of contaminated soil, caused by the chromite ore residue, may remain potentially unchanged suggesting that there is no oxidation-reduction reaction in alkaline soil.

2.1.4.2 Organic Matter. Organic matter serves as the electron donor in the reduction reaction; it may complex with Cr(III) increasing its solubility. The organically complexed ligands are less adsorbed by soils and less prone to oxidation [15]. The reduction of Cr(VI) by organic matter is catalyzed by biological activity. Losi, et al., [11] found that the mixture of soil and organic matter after passing through sterilization and then reinnoculation possessed reduction rate of one third higher than the sterilized mixture. Though we can not use this number to justify the biological activity, but it indicates the potential effect of microorganism activities.

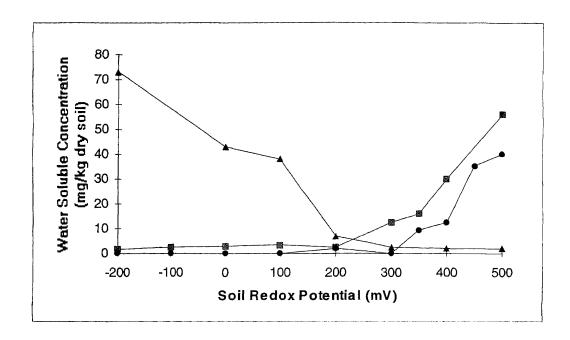
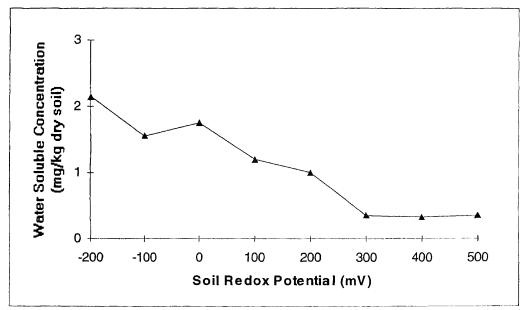


Figure 2.2 Critical Soil Redox Potential for Chromate, Iron, and Nitrate



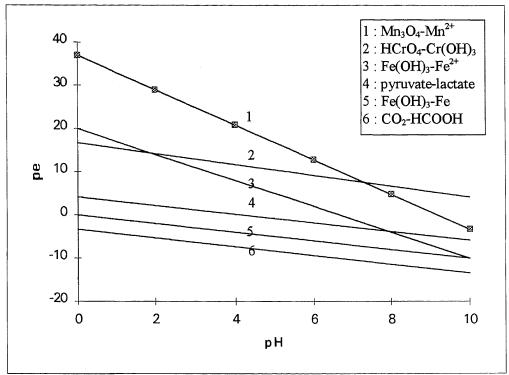
Source: Maascheleyn, P. H., J. H. Pardue, R. D. Delaune, and W. H. Patrick. "Chromium Redox Chemistry in a Lower Mississippi Valley Bottomland Hardwood Wetland." *Environ. Sci. Technol.* 26 (1992): 1217-1226

Figure 2.3 Critical Soil Redox Potential for Manganese

competed with chromate to react with organic matter. Therefore, the anaerobic condition might prefer the reduction of Cr(VI).

Organic matter might have the potential to cause indirect reduction of Cr(VI). It could promote the reduction of Fe(III) in the mineral phase into dissolved Fe(II). Then, the dissolved Fe(II) reduced Cr(VI) to Cr(III). From the literature [14], it was found that the excess reduction of Cr(VI) by dissolved Fe(II) occurred. The amount of dissolved Fe(II) accounted for only 20-40% of the Cr(VI) reduction. The activity of microorganisms was taken into account first, but it was objected because of the unmatched time scale. The organic reduction was also impractical since there was no reduction of the Cr(VI) that occurred when using the organic exclusively. Therefore, the hypothesis that Fe(II) dissolved from the soil mineral was taken into account [14].

2.1.4.3 Redox Potential. Redox potential of soil is also effected by microbial activity, organic matter, and reactivity of electron donor, and acceptor [15]. Maascheleyn, et al., [15] studied the ability of wetland soil to assimilate and retain chromium and found that redox status of soil could be used to determine the activity of chromium in soil. In wetland soil redox chemistry study [15] it was found that soil lacked in ability to oxidize Cr(III) to Cr(VI) even in the oxidizing condition (+500 mv), while Cr(VI) reduction occurred both in reduced and oxidized soil suspension with the different pathways. In the oxidizing to slightly reducing environment, +200 to +500 mv, aerobic condition, the dominant reaction was Cr(VI) reduction and sorption. When the redox level decreased to +300 mv it was found that Cr(VI) reduction was complete and none of sorbed Cr(VI) was



Source: James, B. R. "Hexavalent Chromium Solubility and Reduction in Alkaline Soils Enriched with Chromite Ore Processing Residue." *J. Environ. Qual.* 23 (1994): 227-233

Figure 2.4 The pE-pH Diagram for HCrO₄-/Cr(OH)₃ and Reducing Agents

detected. In the reducing environment, Eh <+200 mv, anaerobic condition, Mn(IV) and Fe(III) were reduced to soluble Fe(II) and Mn(II). As a result of both diffusion and advection the soluble ions leached into the aqueous medium. The dominant reaction was reduction of Cr(VI) by Fe(II) and Mn(II), catalyzed by microorganism activity. The relationship between redox potential and the dissolved ion concentration of Fe, Cr, Mn, and NO₃ in the soil suspension is shown in Figure 2.2 and 2.3. We might be able to conclude that the reaction governing the chromium speciation in soil is Cr(VI) reduction, except when an oxidizing agent is present.

2.1.4.4 Reducing Agent. Reduction can occur by reducing agents, such as Ferrous ion (Fe[II]), reduced sulfur, and organic compounds as represented in equation 2.5 and 2.6. Chromium reduction by Ferrous ion is the effective pathway for reducing Cr(VI) to Cr(III) [3]. From equation 2.5 [8, 16], three moles of Fe(II) is equivalent to one mole of Cr(VI), but in general the amount of Fe(II) required is higher because of its potential oxidation by atmospheric oxygen [8].

$$3Fe^{2+} + HCrO_4^- + 7H^+ \rightarrow 3Fe^{3+} + Cr^{3+} + 4H_2O$$
 (2.5)

$$2HCrO_4 + 4HSO_3^- + 6H^+ \rightarrow 2Cr^{3+} + 2SO_4^{2-} + S_2O_6^{2-} + 6H_2O$$
 (2.6)

Surprisingly, Mn(II) was found to be able to reduce more than 50 percent of soluble Cr(VI) at pH 8 and tended to be better at higher pH. Mn(II) induces the reduction at pH higher than 7.2, while Mn(III) induces oxidation at pH lower than 7.2 [3]. The oxidizing reducing potential of chromium with manganese could also be predicted from the pE-pH diagram as shown in Figure 2.4.

Barlett and James [10] suggested that once Cr(VI) was reduced it would not significantly oxidize except under certain limited conditions, essentially when large quantities of Mn(III) or Mn(IV) are present.

2.1.4.5 Oxidizing Agent. The most common oxidizing agents for oxidation of Cr(III) to Cr(VI) are Mn(III) and Mn(IV). In the atmospheric aerosols and droplet at pH less than 7, it was found that the oxidation of trivalent chromium was slow, while the reduction of hexavalent chromium was faster. Therefore, the trivalent chromium should be the dominant species in the acidic condition [16]. One oxidation reaction equilibrium is represented in equation 2.7.

$$2Cr^{3+} + 6Mn^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 6Mn^{2+} + 14H^+$$
 (2.7)

The oxidation of trivalent chromium to hexavalent chromium is also found to be slow in the high pH range since 1) the adsorption of trivalent chromium increases when pH decreases, 2) higher pH will promote the precipitation of trivalent chromium as chromium hydroxide, 3) the available soluble trivalent chromium in the organically complexed ligands are less prone to be oxidized than their original forms.

Oxygen is the ubiquitous oxidizing agent. The oxidation of Cr(III) to Cr(VI) by oxygen is found to be very slow and negligible at earth surface condition [17]. James [3] ran the tests on the reoccurring of blush by putting the surface soil in the oxygen and nitrogen atmosphere. The blush reoccurred regardless of the presence of oxygen. However, oxygen does effect the reduction of Cr(VI) to ion Cr(III) since it will compete with Cr(VI) for the ion [3, 8].

We might be able to conclude that in the alkaline pH range of chromite ore residue the reaction is inert and the oxidation of Cr(III) to Cr(VI) generally does not occur, but the chromate salt leftovers in the residue continually dissolves and threaten the adjacent environment. The slow dissolution of calcium chromate salt could last for decades. Therefore an effective treatment technology is required to permanently remediate these contaminated sites.

2.2 Vitrification

Vitrification is an innovative technology that converts the hazardous contaminated waste into a chemical durable glass-like product. Vitrification was first used to treat radioactive waste and was successfully demonstrated in bench and pilot scale studies by Pacific Northwest Laboratory [18]. The advantages of vitrification could be recognized by its long-term durability of waste, applicability to many kinds of waste and soil, volume reduction, and cost effectiveness. The process consists mainly of vitrification and off-gas treatment.

The theory of vitrification is based on the natural occurring obsidian (silicate glass), originated from the rapidly solidified magma. Because of the rapid cooling rate and high liquid viscosity of oxide and silicate, the molecule cannot move sufficiently to form crystalline structure. The glass-like structure is formed. The atomic of glass-like product is random, thus there is no preferential planes of weakness as in the crystalline structure.

Durability tests of vitrified products were performed on the In-situ Vitrification (ISV) by Pacific Northwest Laboratory (PNL) and the result from the 24-soxhlet tests in

99 deionized water indicated that leach rate of vitrified products were comparable to pyrex and granite [18]. The durability of vitrified product might be indicated by a mean life time of 18 million years of obsidian [19], which has the similar chemical and physical properties.

The temperature required for vitrification depends upon the fusion temperature of soils, mostly consisting of silicondioxide and aluminumoxide, which ranges from 1100°C to 1400°C, about 200°C increment might be necessary to get the complete fusion. The high temperature used in the process is advantageous as [18];

- 1. Organic matter will be decomposed through pyrolysis into combustible gas and moves upward through the melting mass, reducing environment. When exposed to the oxygen-containing environment the combustible gas will be oxidized.
- 2. The extensive convective mixing patterns will evenly distribute the contaminant in soil into the uniform concentration throughout the vitrified mass.
- 3. The inorganic and toxic heavy metals will be encapsulated or incorporated into the glass during solidification.
- 4. Volume reduction, which depend upon the difference of initial soil density and vitrified product density. From the ISV, performed by PNL, the vitrified mass density remained quite constant, at about 2.2-2.5 g/cu.cm [18], regardless of the original soil density. Volume reduction of the vitrification of sludge was found equal to two third of the initial volume [18].
- 5. The inclusion metals will be liquefied when the heating temperature reaches their melting point. Higher density than soils, liquefied metal will move downward and solidify

separately. In the electric arc furnace, the liquefied metal can be recycled by draining the bottom part of the molten mass.

6. The hazardous organic and its secondary products will be efficiently destroyed within the vitrified temperature range. From the engineering-scale ISV, performed by PNL, the destruction efficiency of PCBs was found to be 99.9%, and 99.9999 % inclusion off-gas treatment. The concentration level of PCBs in vitrified mass was nondetectable and the mass released to off-gas treatment was 0.05 % by weight, with the initial concentration of 500 ppm [18]. Furan and dioxin, secondary products of fired PCBs, were also found to be very small in quantities and represented no hazardous operation control. It might indicate that the diffusion rate of hazardous organic in soil was slower than the destruction rate [18].

Vitrification is also known as the high efficiency pathway for nitrate destruction. Within the vitrified temperature range, nitrate will be decomposed into mostly nitrogen and carbon dioxide, which represent the dominant species of the gas bubble occurring during the vitrification [18]. Fluoride is found to be retained in the vitrified sample while sulfur dioxide will escape and be treated in the off-gas treatment. The element retention is found to be related to the melting depth and cold cap residence. Deeper in depth and occurring of cold cap will enhance the element retention [18].

Ex-situ vitrification will be performed on the cold-top design electric furnace. The operating feature of cold top electric furnace is the same as cold cap in ISV, and can be accomplished by feeding the materials or soils from the top of the furnace. The thickness of unmelted layer of feeded materials will be maintained at about 6 to 12 inches [20]. The

advantages of cold-top design include insulation for the molten zone and therefore a saving of energy, increasing the element retention in the same pattern as cold cap ISV [18], filtering the fume and gas produced during the vitrification, lowering the exhaust gas temperature and heating the feeding materials.

2.2.1 Cost of Operation

The major costs of operation are electrical power, labor, and consumable materials. Cost from ISV performed by PNL was 227-259 \$/cu.m for transarunic contaminated soils, 183-247 \$/cu.m for hazardous chemical, and 70 \$/cu.m for 70 % moisture content industrial sludge, the unit volume represented the volume of initial soils [18]. The decreasing cost resulted from the less constrained of off-gas treatment and the qualifies labors when dealing with less hazardous substances. The operation cost for ex-situ vitrification for combustion residue MSW in the electric arc furnace was 116 \$/dry ton of residue for production rate of 300-350 tons per day, 130 \$/ton for 150-175 tons per day production rate, and 206 \$/ton for 50-60 tons per day production rate.

2.2.2 Chemical Composition of Soils

The chemical composition of soils in ISV, by PNL, was mainly SiO₂ and Al₂O₃, accounting for 70-80%. The higher level of these oxides tended to increase the durability of vitrified product while increasing viscosity and decreasing electric conductivity [18]. The vitrification was also performed on the combustion residue MSW, which contained Si from 10 to 21 %, and Fe from 5 to 17 %. The crystalline structure was detected when the

Si concentration was reduced to 10 %, P₂O₅ increased to 8 %, and when the sample contained greater iron concentration since that reduces the melting temperature and viscosity [20]. It was found that at 6.2 % of carbon concentration in the MSW residue the erratic furnace operation was detected due to the accumulation of carbon on the surface of molten mass, which initiated arcing , provided a short circuit path. Carbon also reacted with metal oxides to form CO and further reacted with moisture to form H₂, which caused a bridging problem with cold top design of the furnace [20].

2.2.3 Vitrified Products

The vitrified products from the ISV were found to have compressive and tensile strengths one order of magnitude higher than that of unreinforced concrete [18]. The vitrified products from the combustion MSW residue also satisfied the ASTM test requirements for aggregates in asphalt, concrete and portland cement; and potential usage as grit for sandblasting [20]. The leachate was measured for eight TCLP metals and was below the EPA regulatory limits [18, 20].

2.3 Vitrification of Chromium Contaminated Soils

The molten temperature of pure chromium and chromite ores are higher than the vitrified temperature, but before reaching their melting point chromium can be affected by the oxidation and reduction reaction. Impurities in the chromium mixture could lower the melting temperature to a range of 1513°C to 1920°C [23]. Based on the reducing environment of melting soils, the reduction of hexavalent chromium to trivalent chromium

and/or elemental chromium should occur. The potential chromium reduction in the presence of aluminum, silica, and carbon could be represented in equation 2.8 to 2.10 [23] and is similar to chromium reduction in Ferrochromium process.

$$Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3 \tag{2.8}$$

$$2Cr_2O_3 + 2Si \rightarrow 4Cr + 3SiO_2 \tag{2.9}$$

$$Cr_2O_3 + 2C \rightarrow 2Cr + 3CO \tag{2.10}$$

Combustible gases produced by the pyrolysis of organic, CO and CH₄, also promote the reducing environment. Methane is the most active gaseous reducing agent on chromite [23]. It was found that about 70 percent of FeO was reduced in less than a second in the presence of 75 percent CH₄ [23]. Carbon is an effective reducing agent at high temperature for chromite (FeO.Cr₂O₃). At 1200°C FeO and Cr₂O₃ were rapidly reduced to iron and chromium carbide, at 1400°C iron was rapidly decarburized while most chromium was still in the carbide form [23].

From the microwave treatment test of hexavalent-chromium-impregnated soil, the x-ray diffraction results showed that before treatment iron and chromium in soil were segregated but after treatment the chromate phase disappeared, iron and chromium were no longer segregated, and the chromite (FeCr₂O₄ or FeO.Cr₂O₃) and chromic oxide (Cr₂O₃) were formed [21]. The chromite formed is the same form as mineral chromite ore, with its octahedral crystalline structure. The maximum temperature in this experiment was 1175°C. The leachate EP toxicity test found that chromium concentration in the leachate was less than 5 ppm, the regulatory limit [28]. The total chromium concentration

in the vitrified products and milled soils were found to be in the impregnated concentration range, proving the effective element retention.

Clark [22] also found that CaCrO₄, the hexavalent dominant species in Jersey City contaminated soils, began to loose its oxygen when heated above 800°C, which is still lower than the vitrified temperature.

After the reduction reaction, trivalent chromium which has a similar ionic radius (0.64 A) to aluminum (0.54 A) and titanium (0.68 A) is believed to be able to form the tetrahedral coordination bonding in silicate glass, the same manner as the other two elements do, at the concentration less than 7 % by weight. Aluminum ion in silicate glass serves to raise the melting temperature and viscosity, stabilize and strengthen the glass, and lower solubility for alkali metal compound. Similar results are expected from the substitution of Al by Cr.

From the x-ray diffraction study on the treated sample, chromium was found in the chromite or chromic oxide forms [21], which are crystalline structures. This result might indicate that chromium did not substitute aluminum or silica in the silicate glass, but it solidified into the crystalline structure, and was encapsulated or bonded to the glass matrix. In the electric arc vitrification of combustion residue MSW the crystalline structure also occurred in some samples. The leach rate from the crystalline products from ISV were found to be less than from the vitrified products [18].

The TCLP chromium concentration results from both crystalline and glass-like products were far below the regulatory limit. Element retention was proved by the higher concentration of chromium in vitrified mass and milled soils [20, 21]. From literature, the

fume accounted for only 0.8 to 4.4 % by weight of the feed material and its chromium concentration was 20 to 52 % less than the feed chromium concentration [20].

From the above discussion it proves that vitrification is a viable technique for effective remediation of chromium contaminated soils. In this research nine chromium contaminated soils were vitrified and the properties of vitrified products were tested for use as construction material.

CHAPTER 3

EXPERIMENTAL METHODS

3.1 Experimental Program

The experimental procedure consisted of two steps. In the first step, physical and chemical analyses of soil samples were conducted, and in the second step, the vitrified products were analyzed. Soil samples were analyzed for the TCLP chromium concentration to evaluate the potential hazard, the chemical composition and physical characteristic to determine the suitability for vitrification process. Total and hexavalent chromium concentrations were determined to evaluate the element retention.

In the second step, original soils adjusted with additives were vitrified by Corning Incorporated, and were subjected to physical and chemical analyses. The physical characteristics were determined to assess the reuse value. The feasibility of the remediation was supported by the chemical characteristics; i.e., TCLP chromium concentration.

3.2 Soil Sample Collection

Nine contaminated sites in Hudson County were selected to perform the feasibility study of ex-situ vitrification, engineering and pilot scale. Soil samples were taken from nine different sites by personnel from New Jersey Department of Environmental Protection (NJDEP) accompanied by students and faculty from New Jersey Institute Technology and

Stevens Institute of Technology. The soil samples were collected within six inches from the surface. Five gallons containers with waterproof lids were used to store the samples. The external chains of custody were generated to keep track of the hazardous soil samples. Sites name, and NJDEP site number selected were shown in table 3.1.

Table 3.1 Site Name, NJDEP Site Number, and Responsible Party

Site name	NJDEP number	Abbreviation	Responsible Party
Roosevelt Drive-In	115	RDI	Allied Signal Inc.
Colony Diner	070	CD	Allied Signal Inc.
Garfield Avenue	114	GAR	PPG Inc.
Liberty State Park	015	LSP	Allied Signal Inc.
Hackensack River Road	131	RR	Maxus/Occidental Chem. Corp.
Diamond Shamrock	113	DS	Maxus/Occidental Chem. Corp.
NJ Tumpike Bayview	020	TPR	Unknown
Green Acres	008	CPR	PPG Inc.
Reed Mineral	041	RM	Maxus/Occidental Chem. Corp.

Allied Signal Inc., responsible party for RDI, CD, and LSP, operated the chromate production facility from 1905 to 1954. During that period the chromate manufacturing process was high-lime process (55 % of lime) [1]. From 1942 to 1964, PPG Inc., the responsible party of CAR and GAR operated chromate extraction facility by low-lime process (15 % of lime) [1].

3.3 Chemical Characteristic Tests for Soil Samples

Approximately one hundred gram samples from each site were sent to a certified laboratory within 48 hr. to analyze for the hexavalent chromium concentration, using EPA method 3060A (alkaline digestion followed by colorimetric method) for identification.

Approximately one pound sample from each site was sent to Stevens Institute of Technology to perform the following chemical analyses; TCLP chromium leachate by inductively coupled plasma (ICP) spectrometer, total chromium concentration by soft and hydrofluoric digestion, and soil pH.

3.4 Physical Characteristic Tests for Soil Samples

Physical characteristic tests were performed on soil from each site to determine the following properties;

- 1. Moisture Content (standard method in ASTM D2216)
- 2. Liquid and Plastic Limit (standard method in ASTM D4318)
- 3. Grain Size Analysis (standard method in ASTM D421 and D422)
- 4. Specific Gravity (standard method in ASTM D854)

All wasted soil was collected in a waterproof container and will be vitrified.

3.5 Soil Sample Preparation for the Vitrification

The samples for vitrification were prepared using the following recipe; 75 % by weight of soil with 5 % moisture content, 25 % by weight of sand (SiO₂), 2 gms of carbon per 5 lbs of sample. SiO₂ was added to compensate for the low concentration of Si in most of soil samples. Carbon was added to ensure that the reduction of hexavalent to trivalent chromium was complete. Samples from all nine sites were vitrified, except for RM, since its hexavalent concentration was below the detectable limit.

Soil samples weighing approximately 5 pounds, except for CD, LSP, and GAR, which were 10 lb, were sent to Corning Inc. for vitrification, accompanied with the external chain of custody. Soil samples from RDI was duplicated, one with 10 percent moisture content and 4 gms of carbon, the other was 5 percent moisture content and 2 gms of carbon, both were sent to Corning Inc. for vitrification.

3.6 Vitrification Process

The prepared soil samples, 5 lbs each, were put into double silica crucibles, 600 cc inside and 1800 cc outside, to prevent possible melt-through of one crucible inside the furnace. The 10 lbs size samples were also placed into double crucibles, 1800 cc inside and 3500 cc outside. The samples were subjected to 1590°C for 3 hours and then were poured into the other crucibles to make an observation of glass viscosity. These crucibles were then held at 1350°C for 1 hour. The crucibles were then transferred to another furnace set at 1250°C, held for 1 hour and then the temperature was set at 1000°C. It took 1 hour and 20 minutes to cool from 1250° C to 1000°C. Finally, the crucibles were transferred to a furnace set at 1000°C, held for 1 hour and then shut off to slowly cool to room temperature. All samples experienced heavy foaming and weight loss, which might due to volatilization.

3.7 Chemical Characteristic Tests for Vitrified Samples

After receiving the vitrified samples, the samples were then cleaned to remove the crucibles chips. Each sample was crushed by the electric grinder, two dust and very small

particles weighing 50 gms were sent to Stevens Institute of Technology and to an Independent Laboratory. The vitrified samples were analyses for hexavalent chromium concentration. Stevend Institute of Technology was responsible for the TCLP chromium concentration and total chromium. The TCLP chromium concentration were determined by using inductively coupled plasma (ICP) spectrometer. The amount of chromium was determined by hydrofluoric digestion followed by ICP spectrometer analysis.

3.8 Physical Characteristic Tests for Vitrified Samples

All the remaining crushed samples were tested to determine their physical properties.

These tests are required by NJDOT to evaluate the suitability of using the aggregates as highway construction material. The brief experimental procedures are shown in appendix D. The required tests include;

- 1. Specific Gravity and Adsorption of Aggregates (ASTM C-127, ASTM C-128)
- 2. Moisture Content (ASTM C-2216)
- 3. Unit Weight and Void Ratio in Aggregates (ASTM C-29)
- 4. LA Abrasion (ASTM C-131)
- 5. Soundness of Aggregates by Use of Sodium Sulfate (ASTM C-88)
- 6. Organic Impurities in Aggregates-Colorimetric (ASTM C-40)
- 7. Sieve Analysis (ASTM C-136 and ASTM C-117)
- 8. Clay Lumps and Friable Particles (ASTM C-142)

Since the melting temperature was as high as 1590°C, the organic compound and water should be totally pyrolyzed and/or evaporated, thus the organic content and moisture content could be negligible.

All the available sample sizes were too small and less than that required to follow the ASTM standard, therefore the same aggregates were subjected to series of different test methods. The test methods were performed in the following order: moisture content, grain size distribution, unit weight, specific gravity, friable material, sodium sulfate soundness and then LA abrasion.

The maximum size of crushed aggregate was restricted by the sample size and the electric grinder. The maximum size of crushed aggregates for RDI was 3/8", 3/4" for CD, GAR and LSP, and 1/2" for RR, TPR, DS and CPR. The inadequate sample size made it impossible to perform the all required experiments for coarse aggregates. Therefore only CD GAR and LSP have their coarse aggregates test results. Due to the limitation of amount of aggregates a broadened range of sizes were used for testing, deviating from the ASTM standard procedure, which may introduced small error for coarse aggregate tests.

3.9 Quality Control

Quality control checks were conducted during the tests by specifying the control limits between the duplicated tests, and following the control limits indicated in ASTM standard methods for each physical property test. Any pairs of results that were not within the control limits were redone. The ASTM specified limits were shown in table 3.2.

All the tests performed were duplicated for each samples, except for LA abrasion tests that could not be duplicated as once the sample was tested, the sample was destroyed. The quality control checks for friable material and sieve analysis tests were ignored as the reuse of the same samples made the duplicated result less reliable than the first result. For friable materials, since all friable parts were removed after the first test, second test results had no meaning. The sodium sulfate soundness test should also belong to this category where the duplicated test is less reliable than the first test, but if the sample structure was uniformly distributed and the degradation continued in the same manner, it will provide reasonable results when expose the same sample twice.

Table 3.2 Control Limits for Physical Property Tests.

Parameter	QC Check	Control Limits (single Operator Prec.)
Specific Gravity		
: Fine Aggregates		
- SSD	Duplicate	0.027 (D2S)
- Dry	Duplicate	0.032 (D2S)
: Coarse aggregates		
- SSD	Duplicate	0.020 (D2S)
- Dry	Duplicate	0.025 (D2S)
Absorption		
-fine aggregates	Duplicate	0.31 (D2S)
-coarse aggregates	Duplicate	0.25 (D2S)
Unit Weight	Duplicate	40 kg/cu.m (D2S)
Sodium Sulfate Soundness	Duplicate	68% (D2S%)

D2S = Different between two tests, calculated from the specified % average

Source: ASTM standard

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Test Results and Discussions of Soil Samples

Chromium concentration, chemical composition, and physical characteristic of soils are determined and are shown in table 4.1, 4.2, and 4.3, respectively. Grain size analysis results for each soil sample is represented in appendix A.

From the physical characteristic test results for soils, it can be concluded that all soil samples consisted mostly of silt since they all had no plastic and liquid limits. The specific gravity of the contaminated soils are higher than regular specific gravity of regular soils, which lie between 2.65 to 2.72; these results imply the impregnation of heavy metal in soil, which should be mostly iron and chromium according to the chemical composition. Moisture content varied depending on the location of the original soil and weather condition on the day sampling was performed. The vitrification process is not affected by moisture content [18], only higher energy is required for higher moisture. In this research, moisture content was controlled at 5 percent to accommodate the furnace cold top design. If the moisture content is high it will generate large quantities of air bubbles which can form bridging between molten and unmelted zone, it might also carry the feed material over into the off-gas treatment, resulting in less treatment efficiency. The behavior of heavy foaming also occurs in the presence of high carbon concentration.

Grain size distribution results of the soil samples are considered acceptable for the vitrification, the maximum cumulative weight percent finer at 0.15 mm opening sieve is less than 30 percent. From the literature, cumulative weight percent of 34.9 percent finer than 0.15 mm size was successfully vitrified [20]. Low percentage of fines results in low fume production and enhances the life of off-gas treatment system.

Table 4.1 Chromium Concentration in Soil Samples

Site	Total Cr	Total Cr	Hex.	TCLP	Soil pH	TCLP
	soft	HF	Chromium	Leachate	_	pH
	digestion	digestion				
	(mg/kg)	(mg/kg)	(mg/kg)	(mg/l)		
Roosevelt Drive-in	20275	4600	4440	46.74	12.22	9.8
Colony Diner	25573	5294	4800	68.58	11.52	7.88
Garfield Avenue	11729	1821	246	8.67	9.16	6.94
Liberty State Park	16125	1544	1240	32.41	10.18	7.24
Hackensack River Road	2853	587	19.7	3.83	8.88	5.61
Diamond Shamrock	8086	950	61.7	1.65	8.99	5.48
NJ Tumpike Bayview	12228	544	29.2	2.09	9.71	7.11
Green Acres	17738	1268	29.2	5.81	8.95	6.37
Reed Mineral	1936	455	-	4.624	9.25	4.41

The chemical analysis for chromium concentration in soil samples showed high concentrations of Cr(VI), as high as 4800 ppm in Colony Diner with 68.6 ppm TCLP leachate concentration. Concentration of chromium ranged from 0.2 to 2.5 %, with 0 to 22 % of total chromium was in the hexavalent form. Soil pH range lied within the alkaline range, 8.9 to 12.2. The concentration of chromium also indicated some relationship with pH, higher pH associated with higher chromium concentration. The relationship might be based on the fact that chromite ore residue was alkaline, while the

Table 4.2 Chemical Compositions of Soil Samples

Site	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	Total
Roosevelt Drive-in	3.74	5.4	30.76	3.96	21.51	28.95	3.14	100.46
Colony Diner	3.88	4.88	22.60	3.55	13.06	23.53	2.84	74.33
Garfield Avenue	1.66	5.55	23.64	7.23	6.84	13.42	1.63	59.97
Liberty State Park	26.89	5.44	39.85	8.59	13.16	11.33	5.91	111.18
Hackensack River Road	0.48	4.59	41.6	1.97	4.89	10.95	1.85	66.32
Diamond Shamrock	0.47	5.13	100	2.58	3.98	17.11	2.06	131.32
NJ Tumpike Bayview	0.82	5.5	32.46	7.8	6.73	36.36	4.06	93.72
Green Acres	0.14	5.43	40.68	9.16	6.44	12.16	6.31	80.31
Reed Mineral	0.06	4.27	7.31	1.75	1.60	7.23	1.17	23.38

 Table 4.3 Physical Characteristics of Soil Samples

Site	Specific Gravity	Water content %	Liquid Limit	Plastic Limit	D 10	D30	D60	Cu	Сс
Roosevelt Drive-in	2.76	22.00	None	None	0.11	0.29	0.73	6.63	1.05
Colony Diner	2.72	29.60	None	None	0.056	0.19	0.55	9.8	1.17
Garfield Avenue	2.98	24.60	None	None	0.056	0.178	1.3	23.2	0.44
Liberty State Park	3.21	14.70	None	None	0.049	0.17	1	20.4	0.59
Hackensack River Road	3.02	14.70	None	None	0.15	0.65	3.2	21.3	0.088
Diamond Shamrock	2.78	16.65	None	None	0.042	0.18	0.54	12.9	1.43
NJ Tumpike Bayview	2.76	32.46	None	None	0.01	0.075	0.4	40	0.01
Green Acres	3.12	25.40	None	None	0.038	0.16	0.8	21	0.84
Reed Mineral	2.9	6.09	None	None	0.077	0.48	1.9	24.7	1.57

regular pH of soil is near neutral. Therefore the higher concentration of the chromite ore residue, the higher soil pH, and also higher concentration of chromium. From the literature [3], in the soils pH range, chromate is stable, therefore the concentration of Cr(VI) should be close to the amount of Cr(VI) imparted in the dumped chromite ore residue, which remained in its slowly soluble chromate compound.

Chemical composition of contaminated soils was rather different from the regular soil. Silica and aluminum are the major components of soil but the results showed that only LSP had 26.99 percent of silica while the other contained less than 4 percent silica. The iron fraction was also high as were Na and Ca. Chromite ores consists of two major parts; spinel fraction and gangue. The spinel fraction contains isomorphous mixture of mineral that constitute a group crystallizing in the isometric system. The common chemical formular of mineral in spinel is RO.R₂O₃; i.e. FeO.Cr₂O₃ (chromite), MgO.Cr₂O₃ (picrochromite), and FeO.Al₂O₃ (hercynite). Gangue is a minor portion consisting mostly of magnesium silicates. Natural chromite (FeO.Cr₂O₃) ore consists of 30 to 50 percent Cr₂O₃; 10 to 25 percent of FeO, Al₂O₃, and MgO; 2 to 10 percent of SiO₂, and less than 2 percent of CaO. From chromite ore composition, contaminated sites are mostly chromite ore processing residue, not regular soils. The high concentration of Na and Ca is possible since Na₂CO₃ and CaO were the essential mixture in chromate production.

The calculation of Ca in soils from LSP, CD and RDI were higher than the others which is due to the high-lime chromate manufacturing process. Hexavalent chromium and TCLP leachate concentration from LSP, RDI, and CD were distinguished from the other. Hexavalent chromium concentrations ranged from 7.7 to 22 % of total chromium and

TCLP leachate concentrations were 32.41-46.74 mg/l, while the other were less than 2% and 8.67 mg/l, respectively. CaCrO₄ was a slow dissolving chromate and it should prevail in chromite ore residues leftover from the high-lime process. We may conclude that the high different hexavalent in LSP, CD and RDI might relate with the manufacturing process.

4.2 Physical Identification of Vitrified Samples

Roosevelt Drive-in; The sample size after vitrification was 0.670 kgs for RDI-1 and 0.602 kgs for RDI-2. The surface of the sample is slightly shiny. There were some small air bubbles at the top and bottom and a small hole in the middle. The color of the sample was dark brown with some yellowish stains beneath the surface. The surface of crushed aggregate looked smooth.

Colony Diner; The sample size after vitrification was 1.75 kgs. The surface of the sample was very shiny like the surface of a metal. There are some air bubbles beneath the surface and at the very bottom, with a hole in the middle. The color of the sample was dark gray, except beneath the surface and around the air bubble the color seem to be yellowish. The surface of crushed aggregates were rather rough.

Garfield Avenue; The sample size after vitrification was 1.67 kgs. The surface of the sample was slightly shiny. There are some air bubbles beneath the surface and at the very bottom, with a very small hole in the middle. The color of the sample was dark gray. The surface of crushed aggregates were smooth and there were shiny metalike stains. At

the bottom of the sample there were some small metal particles, spherical in shape, that could be separated from the sample.

Liberty State Park; The sample size after vitrification was 1.75 kgs. The surface of the sample was slightly shiny and some areas were shiny as Colony Diner. The sample was already broken into quite a few pieces in the crucible. There are more air bubbles beneath the surface and at the very bottom than the other samples. This sample sticked strongly to the silica crucible parts and was very hard to clean up. The color of the sample was dark gray. The surface of crushed aggregates was smooth but some areas look porous.

Hackensack River Road; The sample size after vitrification was 0.46 kgs. The surface of the sample was shiny. The sample was already broken into quite a few pieces in the crucible. There were air bubbles beneath the surface and at the bottom with a hole in the middle. Within 1 cm from the surface there were white spot distributed all over the area, the color of the sample was dark gray. The surface of crushed aggregates was smooth.

NJ Turnpike Bayview; The sample size after vitrification was 0.6 kgs. The surface of the sample was shiny. There were air bubbles beneath the surface and at the bottom with a big hole in the middle. The surface of crushed aggregates were quite smooth, and gray in color. The sample was magnetic.

Diamond Shamrock; The sample size after vitrification was 0.58 kgs. The distinguishing feature of this sample was the white spots distributed all over the sample, denser in the upward direction, while the sample color was dark gray. Crushed surface

was smooth and shiny. Also, there were air bubbles in the top and bottom with a hole in the middle. The metalike particle were found at the bottom, separated from the sample.

Green Acres; The sample size after vitrification was 0.72 kgs. This sample had the hardest, strongest and heaviest properties. Only few air bubbles were found instead there was a lot of porous areas, which was rough, hard, shiny and rust-like in color, that occupied almost 30 percent of the specimen. The surface was shiny and the color was gray. The sample was magnetic.

Most of the vitrified products were identified by their shiny surface, like hematite, which may be due to the presence of Fe₂O₃. FeO in the chromite ore will oxidize from FeO to Fe₂O₃ when exposed high temperature [23].

Vitrified samples were found to contain air bubbles at the top, bottom parts, and a hole in the middle. Gas bubbles in vitrified sample may have originated from pyrolized gas of organic matters, nitrate destruction, moisture, and also oxidation of carbon.

4.3 Test Results and Discussions of Vitrified Samples

The vitrified samples were subjected to the series of tests for chemical and physical characteristics. The chemical and physical characteristics are shown in tables 4.4 and 4.5, respectively.

4.3.1 Chemical Test Results and Discussions

From the results, it might be concluded that all hexavalent chromium were reduced and the vitrified samples were not further hazardous as confirmed by TCLP leachate results, which revealed less than 5 ppm of chromium, the regulatory limit [28]. There were no further analysis of chemical composition of vitrified samples, the speciation of reduced chromium, and the concentration profile of chromium. The hexavalent concentration in the vitrified samples were below the detectable limit, confirming the complete reduction. The hydrofluoric digestion tests were conducted to analyze for total chromium concentration and the results indicated the significantly lower chromium concentration, which is opposed to other literature. From the literature, the hydrofluoric digestion was found not to be an effective way to analyze the chromium in vitrified products. The Bergdorf pressure digestion cell incorporated with multiple reagents can be used instead [21]. The x-ray diffraction is also an effective way for analysis [20]. The literature review showed element retention, chromium concentration in vitrified products was higher than the feed concentration [20, 21].

Table 4.4 Chromium Concentration of Vitrified Samples

Site	TCLP Cr	Total Cr	Hexavalent
	Leachate	Soft	Chromium
	(mg/l)	Digestion	
		(mg/kg)	(mg/kg)
Roosevelt Drive-in	0.015	0.061	<5.2
Colony Diner	0.0254	15.2	<5.2
Garfield Avenue	0.542	15.5	<5.2
Liberty State Park	0.0934	111.2	<5.2
Hackensack River Road	0.233	47.5	<5.2
Diamond Shamrock	1.649	46	<5.3
NJ Tumpike Bayview	0.213	153	<5.4
Green Acres	2.239	423.4	<5.1

Table 4.5 Physical Characteristics of Vitrified Samples

	Bulk SG		Bulk	Bulk SG		Adsorption		<u></u>	
Site	(Dry	Basic)	(SSD	Basic)			Unit Weight	% Void	% Porous
	Fine Agg.	Coarse Agg	Fine Agg.	Coarse Agg	Fine Agg.	Coarse Agg	(kg/cu.m)		
Roosevelt Drive-in 1	3.16	2.99	3.20	3.01	1.29	0.77	1759.61	41.04	5.32
Roosevelt Drive-in 2	3.20	3.02	3.24	3.04	1.29	0.77	1757.82	41.71	5.46
Colony Diner	3.21	2.91	3.25	2.94	1.39	1.20	1721.79	40.72	9.29
Garfield Avenue	3.12	3.00	3.16	3.03	1.34	0.94	1820.58	39.25	3.66
Liberty State Park	3.33	3.15	3.39	3.17	1.66	0.67	1784.58	43.16	5.53
Hackensack River Road	2.89	2.87	2.89	2.88	0.29	0.28	1743.91	39.11	0.52
Diamond Shamrock	2.63	2.55	2.64	2.56	0.40	0.74	1567.17	38.42	3.06
NJ Tumpike Bayview	3.13	2.94	3.15	2.97	0.59	0.79	1702.93	42.04	5.94
Green Acres	3.40	3.26	3.43	3.28	0.87	0.71	1868.50	42.52	4.28

Table 4.5 Physical Characteristics of Vitrified Samples (continued)

Site	Colorimeric	Friable	Material	Na ₂ SO ₄	Soundness	LA	LA abrasion	
		Fine Agg.	Coarse Agg	Fine Agg.	Coarse Agg	% Loss	Uniformity	Adj.% Loss
Roosevelt Drive-in 1	lighter	0.25	-	2.02	_	47.29	0.25	21.7
Roosevelt Drive-in 2	lighter	0.13	-	1.82	-	47.29	0.25	21.7
Colony Diner	lighter	0.85	0.08	1.64	2.36	53.82	0.25	30.1
Garfield Avenue	lighter	0.39	0.18	1.39	3.79	32.01	0.23	17.9
Liberty State Park	lighter	0.80	0.06	1.64	2.61	30.04	0.23	18.0
Hackensack River Road	lighter	0.80	0.23	1.67	-	78.51	0.26	24.3
Diamond Shamrock	lighter	1.20	0.29	2.05	-	78.51	0.19	20.4
NJ Tumpike Bayview	lighter	0.40	0.24	1.68	-	99.46	0.41	44.2
Green Acres	lighter	0.00	0.07	1.48	_	53.64	0.22	18.8

4.3.2 Physical Test Results and Discussions

All the test results are presented as the average of two tests (shown in table 4.5) except for the results from sieve analysis, friable material and LA abrasion tests (because the less reliable duplicated results were ignored), and 2) sodium sulfate soundness for coarse aggregates and unit weight for RDI, CD, GAR, and LSP (since the specified sample size was not available after Abrasion test). Table 4.6 shows the physical property requirements comparing with the test results.

Table 4.6 Physical Property Requirements

Tests	Max. results from all sample	Max. Allowable by NJDOT(1)	Max. Allowable by ASTM(2)
For Coarse Aggregates			
-LA Abrasion	99.46	40*	50*
-Sodium Sulfate Soundness	3.79	10*	12*
-Friable&Clay LumpMaterial	0.29	0.5*	2*
-Absorption	1.2	1.7**	-
For Fine Aggregates			
-Sodium Sulfate Soundness	2.05	5*	10*
-Friable&Clay LumpMaterial	1.2	5 (AASHTOT88)	3*
-Absorption	1.66	2*	_

(*): Mimimum values from all categories

(**): 1.2 % for boiler slag, 1.7 % for other categories

(1): from ASTM C33

(2): from NJDOT section 901.03-901.13, 1989

4.3.2.1 Specific Gravity and Adsorption. Specific gravity, dry basic, for coarse aggregates ranged from 2.55 to 3.26. Water adsorption ranged from 0.28 to 1.20 % by weight. For saturated surface dry basic, specific gravity for fine aggregate ranged from 2.63 to 3.40, and their absorption ranged from 0.29 to 1.66 % by weight. Specific gravity

of vitrified product was mostly higher than the original soil which may be due to by volatilization of organic matter, volume reduction due to the rearrangement of their structures. The percent adsorption could also identify the potential susceptibility of the vitrified products to hydration when they presented in the unsaturated environment. All the adsorption test values were less than that specified by New Jersey Department of Transportation (NJDOT) as shown in the table 4.6. The porosity of the samples which can be estimated by comparing the specific gravity of both fine and coarse aggregates of each samples ranged from 0.52 to 9.29 %.

- 4.3.2.2 Unit Weight. These test results are subjected to change when the maximum aggregates size and sample size are different. Unit weight ranged from 1567.7 to 1868.5 kg/m³.
- 4.3.2.3 Moisture Content and Colorimetric Test. All samples had no moisture content and were free of injurious organic impurities, determined by the lighter color compared to the standard solution in colorimetric test.
- 4.3.2.4 Friable Material. All samples possessed low percentage of friable material, which indicated the high durability and also the uniformity of vitrified products. The test results for the fine aggregate tests were quite sensitive to the weight measurement, and even the discrepancy of 0.01gm, the accuracy of the scale, could make the result

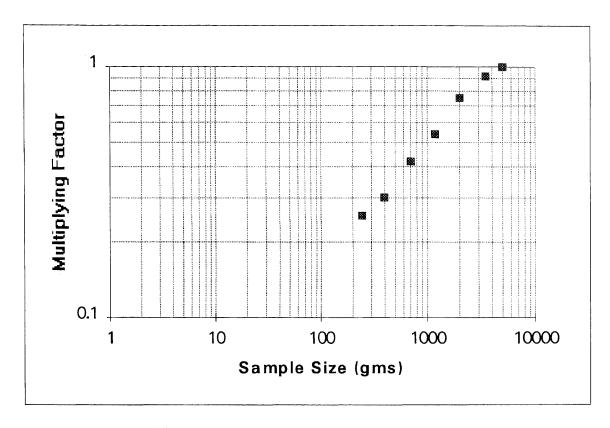


Figure 4.1 Multiplying Factors for LA Abrasion Test

significantly different. The results were not the average but the first test results since all the friable material were already removed after the first test.

4.3.2.5 Sodium Sulfate Soundness. Sodium sulfate soundness test was used to determine the resistance of aggregate to the weathering, which build up the stress in aggregates. The results showed the values that are much less than that specified by NJDOT (10 percent).

4.3.2.6 LA Abrasion Test. Due to the insufficient sample size, this was a difficult test to conduct. However the abrasion tests are performed on all samples. The number of revolutions and charges were remained the same as that was specified in the standard method in ASTM. This condition should be the worst case.

Table 4.7 Adjusted Percent Weight Loss in LA Abrasion Tests

Site	Sample weight (gms)	% weight loss after 500 rev.	Uniformity	Multiplying factor	Adjusted percent weight loss
Roosevelt Drive-in	714.8	47.29	0.25	0.46	21.75
Colony Diner	1192.6	53.82	0.25	0.56	30.14
Garfield Avenue	1170.1	32.01	0.23	0.56	17.93
Liberty State Park	1441.4	30.04	0.23	0.60	18.02
Hackensack River Road	328.1	78.51	0.26	0.31	24.34
Diamond Shamrock	253.6	78.51	0.19	0.26	20.41
NJ Tumpike Bayview	315.5	171.8*	0.41	0.30	51.54
Green Acres	411.8	53.64	0.22	0.35	18.77

^{*} Adjusted value using the average uniformity

From the results, DS, 0.32 kgs in tested weight, possessed the most severe degradation, it should be higher than 100% since the percent weight loss after 500 revolution was 99.46 % and the uniformity was 0.4, while the average uniformity was 0.24. If we kept the uniformity at 0.24, the percent weight loss increased to 170 percent, which would be the reasonable number.

From table 4.7 we can notice that the results also depend on the sample size. Therefore, we developed a model to show the effect of sample size on the degradation rate. The control samples were aggregates used in mixing asphalt concrete. A series of control samples different in size were subjected to the test. The percent weight loss of each samples were recorded. Multiplying factor are determined from the fraction of percent weight loss at each sample sizes to the percent weight loss of the standard sample size (5 kg). Multiplying factors and sample sizes were plotted in Fig. 4.1. The linear relationship was assumed. Adjusted percent weight loss were obtained from multiplying the observed percent weight loss with the multiplying factor as shown in table 4.7. From the adjusted results we can conclude that all sample was satisfied the 40 percent weight loss limitation established by NJDOT, except for DS which had 53.64 percent weight loss. However, the different samples had different structures and degree of degradation, therefore we must bare in mind that this adjusted values represent the potential values and are subjected to change when actual samples were tested. The correct results will be further determined in the full-scale test.

4.4 Volume Reduction

The potential volume reduction was also determined. In fact, volume reduction should be calculated from the different density between the in-situ soil and vitrified products, but we had not collected the data on in-situ soils density, therefore the difference between soil and vitrified products specific gravity were used to determine the potential volume reduction, which is shown in table 4.8.

Table 4.8 The Potential Volume Reduction from Vitrification

Site	Specific	Specific	Specific	Volume	Volume
	Gravity of	Gravity of	Gravity of	Reduction	Reduction
	Soil	Vitrified	Vitrified	(Fine)	(Coarse)
		Soil	Soil		
		(Fine)	(Coarse)		
Roosevelt Drive-in 1	2.76	3.16	2.99	14.5	8.3
Roosevelt Drive-in 1	2.76	3.20	3.02	15.9	9.4
Colony Diner	2.72	3.21	2.91	18.0	6.9
Garfield Avenue	2.98	3.12	3.0	4.7	0.7
Liberty State Park	3.21	3.33	3.15	3.7	*
Hackensack River Road	3.02	2.89	2.87	*	*
Diamond Shamrock	2.78	2.63	2.55	*	*
NJ Tumpike Bayview	2.76	3.13	2.94	13.4	6.5
Green Acres	3.12	3.40	3.26	8.9	4.5

^{*:} The results shown the decreased values

All vitrified samples had higher specific gravity than original soil specific gravity, except for DS and RR. The physical identification of both samples were different from the other, by the occurrence of white spots, especially in RR the white spots distributed throughout the samples. It might relate with iron concentration which is very high, 100 % for DS and 41.6 % for RR. From the iron concentration, we might assume the high specific gravity in DS but in fact when the molten mass solidified the molten metal moved

downward and solidified separately, which caused the lower specific gravity. On the other hand, specific gravity of CPR with 40.68 % iron concentration turned out to be higher than the original soil. The significant property of CPR is its magnetic property throughout the sample which might imply the incorporation of iron throughout the sample mass, resulting in higher specific gravity. Other noticeable difference between CPR, and RR and DS is that CPR was the higher concentration of MgO. Volume reduction is another advantage for in-situ vitrification, but is not significantly important in ex-situ vitrification.

CHAPTER 5

SUMMARY AND CONCLUSIONS

Vitrification process is an innovative remediation technology purposed to stabilize hazardous waste besides the solidification/stabilization by chemical reagents. It also has the other advantages such as volume reduction, reusable products, durable and long-life products, and cost effective.

The feasibility study of remediation and reuse of chromium contaminated soils was conducted. The effectiveness of remediation was determined by the hexavalent chromium reduction and the trivalent chromium retention, which was verified by the TCLP leachate test results and hexavalent chromium concentration analysis. If the physical properties of the vitrified products are comparable to the aggregates properties set forth by NJDOT and ASTM, then the vitrified products can be used as aggregates in construction. From the physical test results, all the samples were acceptable as aggregates in construction. The LA abrasion tests results show high values because of the smaller sample size used in the experiments. The results were corrected to account for the sample size. The adjusted values were satisfied the requirement except for sample from DS.

The heterogeneity of soil might have some effect on the vitrified sample properties, however vitrification has been performed on many types of waste and has been found to be an effective remediation technology.

Therefore we can conclude that the chromium contaminated soil can be remediated and reused by vitrification. However, further investigation is needed to develop the cost of treatment, and to determine the effect of the aggregates incorporated into concrete and asphalt cement. The above will be evaluated during the second phase (the pilot-scale test) of the project in 1996.

APPENDIX A

GRAIN SIZE DISTRIBUTION CURVES OF SOIL SAMPLES

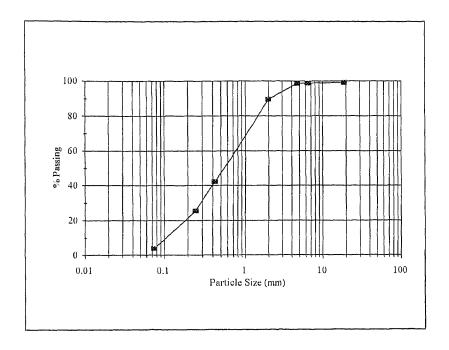


Figure A1 Grain Size Distribution Curve of RDI

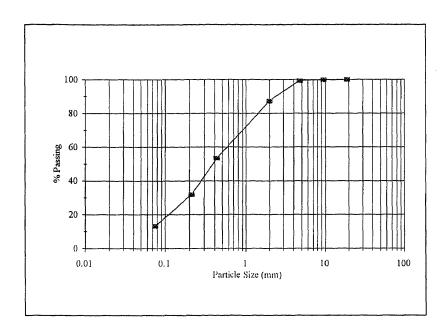


Figure A2 Grain Size Distribution Curve of CD

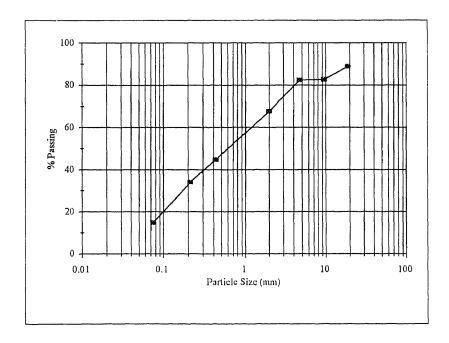


Figure A3 Grain Size Distribution Curve of GAR

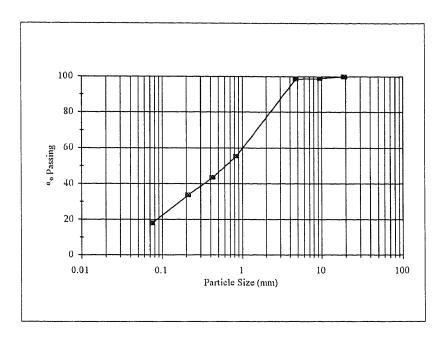


Figure A4 Grain Size Distribution Curve of LSP

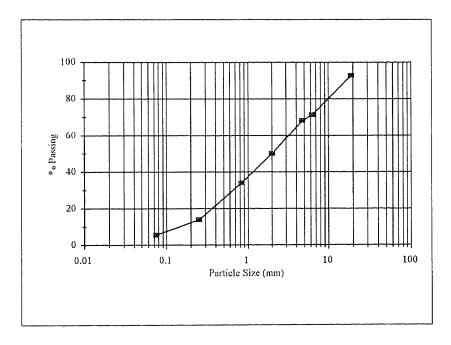


Figure A5 Grain Size Distribution Curve of RR

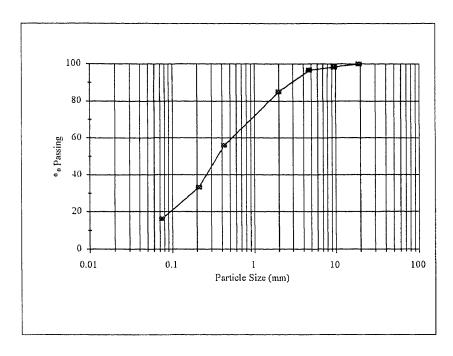


Figure A6 Grain Size Distribution Curve of DS

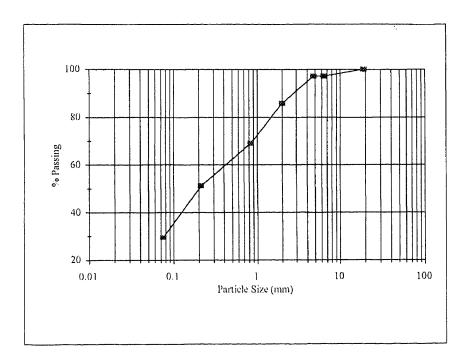


Figure A7 Grain Size Distribution Curve of TPR

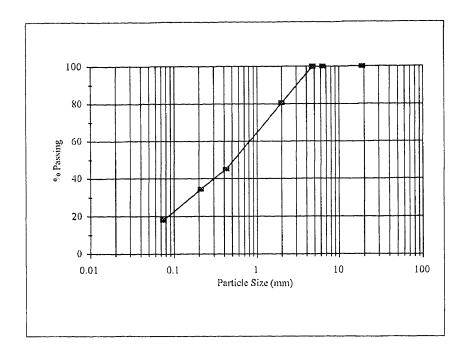


Figure A8 Grain Size Distribution Curve of CPR

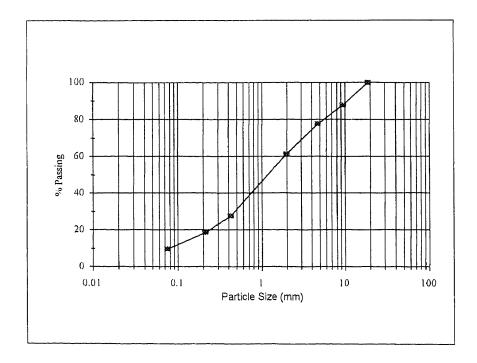


Figure A9 Grain Size Distribution Curve of RM

APPENDIX B

GRAIN SIZE DISTRIBUTION OF VITRIFIED SAMPLES

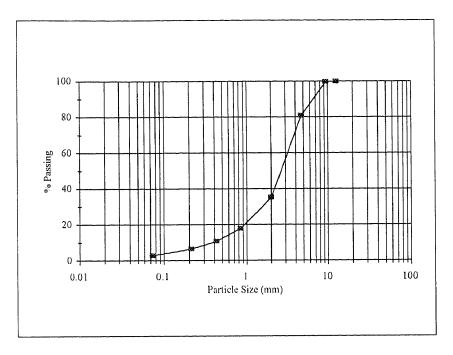


Figure B1 Grain Size Distribution Curve of RDI-1

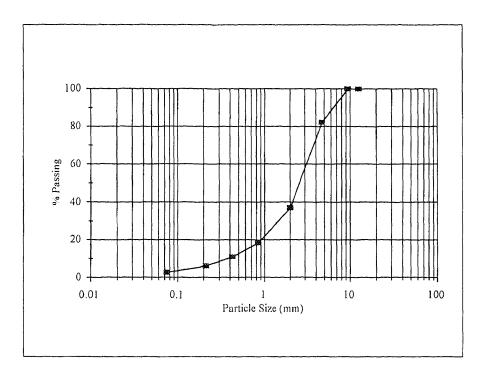


Figure B2 Grain Size Distribution Curve of RDI-2

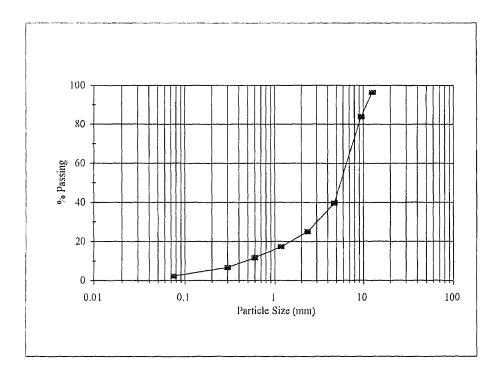


Figure B3 Grain Size Distribution Curve of CD

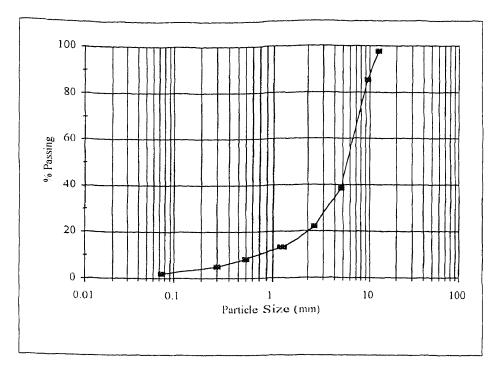


Figure B4 Grain Size Distribution Curve of GAR

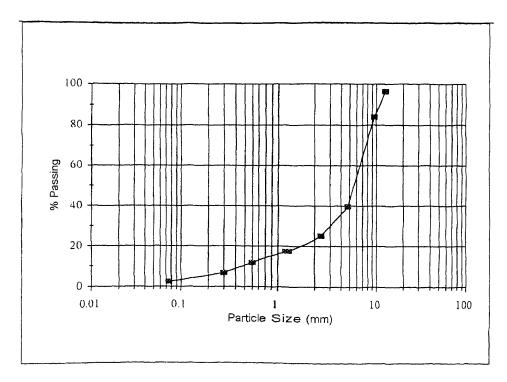


Figure B5 Grain Size Distribution Curve of LSP

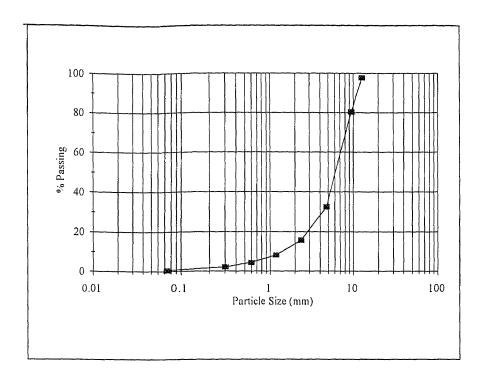


Figure B6 Grain Size Distribution Curve of RR

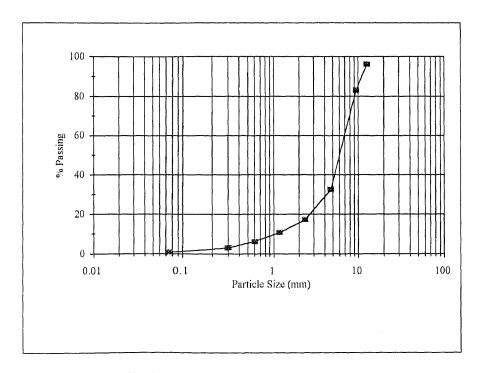


Figure B7 Grain Size Distribution Curve of DS

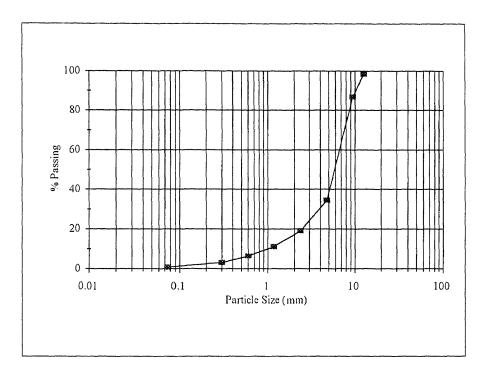


Figure B8 Grain Size Distribution Curve of TPR

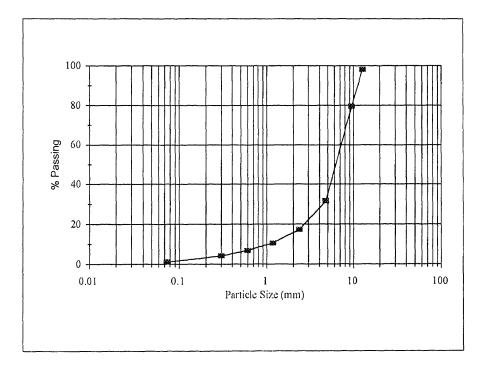


Figure B9 Grain Size Distribution Curve of CPR

APPENDIX C

QUALITY CONTROL CHECKS FOR VITRIFIED SAMPLE TESTS

Table C 1 Control Limits for Quality Control Checks

Table C1 Control Danies 10	T Quinty COZETEZ CARGO	
Parameter	QC Check	Control Limits (single Operator Prec.)
Specific Gravity		
: Fine Aggregates		
- SSD	Duplicate	0.027 (D2S)
- Dry	Duplicate	0.032 (D2S)
: Coarse aggregates		
- SSD	Duplicate	0.020 (D2S)
- Dry	Duplicate	0.025 (D2S)
Absorption		
-fine aggregates	Duplicate	0.31 (D2S)
-coarse aggregates	Duplicate	0.25 (D2S)
Unit Weight	Duplicate	40 kg/cu.m (D2S)
Sodium Sulfate Soundness	Duplicate	68% (D2S%)

D2S = Different between two tests, calculated from the specified % average

Source: ASTM standard

Table C 2 QC Checks for Specific Gravity (Dry), Fine Aggregates

			Fine Aggregates	
Site	Test	Test	Difference	Control
	no.1	no.2	between 2 tests	Limit
Roosevelt Drive-in 1	3.155	3.162	0.007	Acceptable range
Roosevelt Drive-in 2	3.181	3.211	0.030	of two tests
Colony Diner	3.204	3.213	0.009	must not differ
Garfield Avenue	3.123	3.111	0.012	by more than
Liberty State Park	3.325	3.335	0.010	0.032
Hackensack River Road	2.880	2.890	0.010	
Diamond Shamrock	2.645	2.616	0.029	
NJ Tumpike Bayview	3.143	3.117	0.026	
Green Acres	3.402	3.403	0.001	

Table C 3 QC Checks for Specific Gravity (Dry), Coarse Aggregates

	Coarse Aggregates				
Site	Test	Test	Difference	Control	
	no.1	no.2	between 2 tests	Limit	
Roosevelt Drive-in 1	2.981	3.00	0.019	Acceptable range	
Roosevelt Drive-in 2	3.027	3.016	0.011	of two tests	
Colony Diner	2.899	2.922	0.023	must not differ	
Garfield Avenue	3.001	3.005	0.004	by more than	
Liberty State Park	3.154	3.137	0.017	0.025	
Hackensack River Road	2.864	2.876	0.012		
Diamond Shamrock	2.539	2.55	0.011		
NJ Tumpike Bayview	2.952	2.936	0.016		
Green Acres	3.269	3.245	0.024		

Table C 4 QC Checks for Specific Gravity (SSD), Fine Aggregates

	Fine Aggregates				
Site	Test	Test	Difference	Control	
	no.1	no.2	between 2 tests	Limit	
Roosevelt Drive-in 1	3.198	3.201	0.003	Acceptable range	
Roosevelt Drive-in 2	3.224	3.250	0.026	of two tests	
Colony Diner	3.247	3.260	0.013	must not differ	
Garfield Avenue	3.168	3.150	0.018	by more than	
Liberty State Park	3.379	3.391	0.012	0.027	
Hackensack River Road	2.890	2.897	0.007		
Diamond Shamrock	2.654	2.628	0.027		
NJ Tumpike Bayview	3.159	3.138	0.021		
Green Acres	3.433	3.431	0.002		

Table C 5 QC Checks for Specific Gravity (SSD), Coarse Aggregates

			Coarse Aggregate	es
Site	Test	Test	Difference	Control
	no.1	no.2	between 2 tests	Limit
Roosevelt Drive-in 1	3.003	3.023	0.020	Acceptable range
Roosevelt Drive-in 2	3.050	3.040	0.010	of two tests
Colony Diner	2.935	2.953	0.018	must not differ
Garfield Avenue	3.028	3.034	0.006	by more than
Liberty State Park	3.176	3.157	0.019	0.02
Hackensack River Road	2.874	2.882	0.008	
Diamond Shamrock	2.558	2.569	0.011	
NJ Tumpike Bayview	2.976	2.959	0.017	
Green Acres	3.289	3.269	0.020	

Table C 6 QC Checks for Adsorption, Fine Aggregates

Site	Test	Test	Difference	Control
	no.1	no.2	between 2 tests	Limit
Roosevelt Drive-in 1	1.35	1.22	0.13	Acceptable range
Roosevelt Drive-in 2	1.35	1.22	0.13	of two tests
Colony Diner	1.35	1.43	0.08	must not differ
Garfield Avenue	1.43	1.24	0.19	by more than
Liberty State Park	1.63	1.68	0.05	0.31
Hackensack River Road	0.33	0.24	0.09	
Diamond Shamrock	0.35	0.44	0.09	
NJ Turnpike Bayview	0.51	0.67	0.16	
Green Acres	0.89	0.84	0.05	

Table C 7 QC Checks for Adsorption, Coarse Aggregates

	Coarse Aggregates				
Site	Test	Test	Difference	Control	
	no.1	no.2	between 2 tests	Limit	
Roosevelt Drive-in 1	0.75	0.78	0.03	Acceptable range	
Roosevelt Drive-in 2	0.75	0.78	0.03	of two tests	
Colony Diner	1.08	1.32	0.24	must not differ	
Garfield Avenue	0.89	0.98	0.09	by more than	
Liberty State Park	0.75	0.58	0.17	0.25	
Hackensack River Road	0.34	0.21	0.13		
Diamond Shamrock	0.72	0.75	0.03		
NJ Tumpike Bayview	0.8	0.78	0.02		
Green Acres	0.7	0.71	0.01		

Table C 8 QC Checks for Sodium Sulfate Soundness, Fine Aggregates

	Fine Aggregates				
Site	Test	Test	Average	Difference	Control limit
	no.1	no.2		between 2 tests	68 % (D2S%)
Roosevelt Drive-in 1	2.70	1.35	2.02	1.35	1.38
Roosevelt Drive-in 2	2.26	1.38	1.82	0.88	1.24
Colony Diner	1.38	1.90	1.64	0.52	1.12
Garfield Avenue	1.54	1.24	1.39	0.30	0.95
Liberty State Park	1.85	1.43	1.64	0.42	1.12
Hackensack River Road	1.93	1.41	1.67	0.52	1.14
Diamond Shamrock	1.89	2.20	2.05	0.31	1.39
NJ Tumpike Bayview	1.86	1.50	1.68	0.36	1.14
Green Acres	1.50	1.45	1.48	0.05	1.00

Table C 9 QC Checks for Unit Weight

	Test	Test	Average	Difference	
Site	no.1	no.2		between	Control limit
				2 tests	
	(kg/cu.m)	(kg/cu.m)	(kg/cu.m)	(kg/cu.m)	
Roosevelt Drive-in 1	1759.61	*	-	-	Acceptable range
Roosevelt Drive-in 2	1757.82	*	_	-	of two tests
Colony Diner	1721.79	*	-	-	must not differ
Garfield Avenue	1820.58	*	-	_	by more than
Liberty State Park	1784.58	*	-	_	40 kg/cu.m
Hackensack River Road	1744.93	1742.89	1743.91	2.04	or
Diamond Shamrock	1564.86	1569.48	1567.17	4.62	25 lb/cu.ft
NJ Tumpike Bayview	1709.32	1696.54	1702.93	12.78	
Green Acres	1852.71	1884.29	1868.50	31.58	

^{(*):} There were no duplicated tests since the original grading were changed by LA Abrasion test.

APPENDIX D

EXPERIMENTAL PROCEDURE

The experimental procedures described herein are intended to give the brief information on the experimental method. The detailed procedure are fully described in ASTM standard.

D.1 LA Abrasion (ASTM C131-81)

This test method is used to determine the resistant to degradation by abrasion and impact of coarse aggregate. Los Angeles Machine is a rotating steel drum. Charges, metal spheres, and samples are put into the machine. Number of changes are determined from sample grading. The standard sample size is 5 kg for small size coarse aggregate. While the machine is rotating the charges are dropped to the sample, creating and impact crushing effect.

The machine are rotated 500 revolution at a speed of 30-33 rpm. After the test, processed sample is separated by the 1.7 mm (No.12 sieve). The material coarser than 1.7 mm. is washed and oven-dry at 105° C. Then, oven-dry at 105° C. Then, oven-dry the samples are weighed and the final weight as a percentage of the original weight is reported as percent weight loss. Uniformity is calculated from the ratio of weight loss at 100 revolution divided by percent weight loss at 500 revolution.

D.2 Specific Gravity and Adsorption of Aggregate (ASTM C127, ASTM C-128)

Specific gravity is defined as the ratio of solid density to water density. Specific gravity can be calculated from the weight ratio of solid divided by the water of the same volume. Volume of solid can be determined by the displacement of solid in water. The volume of water displacement is equal to volume of solid and the weight of water can be determined regarding with its density.

Specific Gravity (dry basic) is determined after the sample was oven-dried at 105 °C until the weight is constant.

Specific Gravity (saturated surface dry) is determined after the immersion of sample in water and air dry the sample. The saturated surface dry is reached when there is no film of water present on the aggregate surface. At saturated surface dry the permeable pores are filled with water.

Adsorption represents the weight percent of water that could be adsorbed on the permeable pore of aggregate to the sample weight. It can be calculated from the difference of specific gravity dry basic and saturated surface dry basic.

Porosity is defined as fraction of void volume to solid volume. It can be estimated from the difference of fine and coarse aggregate. In coarse aggregate the volume of water obtained includes the void volume and solid volume, while the volume of replaced water from fine aggregate represents only the volume of solid. The porosity can be determined from (volume of coarse aggregate-volume of fine aggregate)/ volume of fine aggregate at the same unit mass.

D.3 Soundness of Aggregates by Use of Sodium Sulfate (ASTM C 88-83)

This method is used to determine the soundness of aggregates when subjected to weathering action. This is accomplished by repeating immersion of aggregate in the saturated solution of sodium sulfate followed by oven drying to partially or completely dehydrated the salt precipitated in permeable pore spaces. The expansive force derived by the rehydration of the salt upon re-immersion is analogous to the expansion of water on freezing. The required sample size and sample grading for both fine and coarse aggregate is available in detail in ASTM standard. After five cycles of immersion and oven dry, weight loss is reported as a percentage of original weight.

D.4 Unit Weight and Void Ratio in Aggregates (ASTM C-29)

The unit weight are calculated from the compacted weight of sample in the measure divided by the measure volume. Measure is the cylindrical metal with the specified size depended upon the maximum size of aggregate available. Void ratio is calculated from the following formula;

$$% Void = [(S x W) - M)/(S x W)] x 100$$

where: M = Unit weight (kg/cu.m)

S = Bulk specific gravity (dry basic)

W = Density of water (kg/cu.m)

D.5 Sieve Analysis (ASTM C-136 and ASTM C-117)

This method is used to determine the particle size distribution of fine and coarse aggregate by sieving. The sample is dried at 105°C and then sieved by mechanical apparatus for a sufficient period of time. Suitable sieve size shall be selected to furnish the information required by the specifications covering the material to be tested. The percent finer at each specified sieve number is determined from the percentage by weight of sample that passes through that sieve.

D.6 Clay Lumps and Friable Particles in Aggregates (ASTM C-142)

This method is used to approximate the clay lumps and friable particles in aggregate. Clay lumps and friable particles are defined as the particles that can be broken by rubbing with finger into fine and removed by wet sieving. The percentage of clay lumps and friable particles is calculated as follows;

$$P = [(W - R)/W] \times 100$$

where P = Percent of clay lumps and friable particles

W = Weight of test sample

R =Weight of particle retained on sieve

D.7 Organic Impurities in Aggregates-Colorimetric (ASTM C-40)

This test is used to determine the presence of injurious organic compound in fine aggregates. The method is performed by adding 3% NaOH to the bottle filled with sample. After shaking the bottle vigorously and let it stands for 24 hr the color of sample

is observed and compared with that of the reference standard color solution. If the color of sample is darker than that of the standard solution, the fine aggregate may contain injurious organic compound. Full procedure and preparation of standard solution can be obtained from ASTM C-40.

D.8 Moisture Content (ASTM C 2216)

This test is used to determine the percentage by weight of water in the sample. The weight of sample before and after drying at 105° C are measured. The difference between these two value is the weight of water. The moisture content is the weight of water as the percentage of sample weight.

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