MOISTURE AND HEAVY METAL STABILIZATION FOR COAL COMBUSTION RESIDUALS USING SODIUM POLYACRYLATE

by

Sai Sahithi Annamraju

A thesis submitted to the faculty of
The University of North Carolina at Charlotte
in partial fulfillment of the requirements
for the degree of Master of Science in
Civil Engineering

Charlotte

2018

Approved by:

____

Dr. Milind V Khire

____

Dr. William Langley

____

Dr. Mariya Munir

ABSTRACT

SAI SAHITHI ANNAMRAJU. MOISTURE AND HEAVY METAL STABILIZATION FOR COAL COMBUSTION RESIDUALS USING SODIUM POLYACRYLATE.
(Under the guidance of DR. MILIND. V. KHIRE)

Due to the recent (2015) federal regulations pertaining to disposal of coal combustion residuals (CCR) from electric utilities, methods to dewater the CCR impoundments, establish structural stability, and mitigate the leaching of heavy metals from CCR leachate into ground water has become a pressing issue in the industry. In order to contribute towards easing the challenges in CCR excavation and groundwater contamination risk, this research aimed at evaluating the use of a super absorbent polymer (SAP) sodium polyacrylate, as an additive in moisture stabilization of saturated coal ash, to increase its mechanical strength, and to evaluate uptake of heavy metals from coal ash leachate. Undrained shear strength of coal ash samples containing 1% to 4% weight fractions of SAPs was measured by Pocket Penetrometer, Torvane, and Unconfined Compression Strength device. During the two phases of this project, up to five ponded ash samples collected from coal ash ponds located in the southeastern region of the U.S. were evaluated. The samples were compacted at standard Proctor effort at water contents ranging from 58% to 70%. The addition of the SAPs improved the undrained cohesion from 0 to 3 psi for selective SAP mixes at weight fractions as little as 1%. In order to evaluate the stabilization or uptake of heavy metals by the SAP, aqueous solutions of arsenic, barium, cobalt, selenium and vanadium at 0.5 mg/L initial concentration were mixed with SAP formulations containing sodium polyacrylate, bentonite clay, and wood flour. After a contact time of 24 hours or more, the leachate was analyzed. The SAPs were able to uptake

50% to 80% of cobalt and barium. The SAPs did not uptake arsenic, selenium and vanadium. The state or valency of the heavy metal ion or complex it forms was the key factor that influenced the effectiveness of the SAP uptake of heavy metals. The weight fractions of the SAPs had no influence on the uptake efficiency for the weight fractions assessed in this research.

ACKNOWLEDGEMENTS

I acknowledge first and foremost, Dr. Milind V Khire for guiding me throughout this research project. I thank him particularly for his confidence that I would complete this project successfully. I will be indebted to him for his mentorship in both academic, professional, and personal setting. I am thankful to Zappatec for providing funding for the Phase I of this project. I would like to acknowledge the support provided by the Coal Ash and Liquid Management (CALM) Office at the University of North Carolina at Charlotte in assisting me in securing the ash samples and super absorbent polymers to carry out the research experiments. I want to thank Quint Barefoot, Chris Hardin, and Ric Traver for all the support during the Phase I of this project.

I wish to thank Robert Raab for helping me with laboratory experiments during the Phase I research. I owe a special thanks to Dr. William Langley for trusting and letting me use his laboratory apparatus, expensive rotary tumbler etc., Dr. Langley has been my second mentor throughout my research in analytical chemistry. He has been kind, patient, and helpful in many ways.

This thesis would not have been possible without the patient and frequent emotional support of Sharath Chandra, my significant other. Thousands of miles away from me, and he has been my rock throughout the three years of graduate studies.

Finally, to the most important people in my life, my mom Sridevi and my dad Ramesh, I cannot express my gratitude in words. My dad has been my inspiration in many ways: ethics, morals, determination, and aspiration towards better world. Without him, I

wouldn’t have chosen this field. My mother is the reason I was able to finish my graduate studies. She trusts me and stays by my side through thick and thin. I never told you both, but I love you.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ACAA = American Coal Ash Association

BFS = Blast Furnace Slag

CCP = coal combustion products or Coal Ash

CPR = Contamination Potential Ratio

XPAA = Cross-linked Poly Acrylic Acid

ESP = Electro Static Precipitators

EPA = Environmental Protection Agency

FAAS = Flame Atomic Absorption Spectrophotometer

FA = Fly Ash

FDA = Food and Drug Administration

ICP-OES = Inductively Coupled Plasma- Optical Emission Spectrometer

LEAF = Leaching Evaluation and Assessment Framework

MCL = Maximum Contaminant Level

MDD = Maximum Dry Density

MSDS = Material Safety Data Sheet

OECD = Organization for Economic Co-operation and Development

OMPS = Organic Polymer Modified Kaolinite NA-PS

OMC = Optimum Moisture Content

PAA = Poly Acrylic Acid

PA_m = Polyacrylamide

PAA = Polyacrylic acid

PEG = Polyethylene Glycol

PEGDA = Poly Ethylene Glycol Diacrylate

PVA = Polyvinyl alcohol

RCRA = Resource Conservation and Recovery Act

PAA_{NA} = Sodium polyacrylate

SAP = Super Absorbent Polymer

UCS = Unconfined compressive strength

XRD = X-ray Diffraction

LIST OF SYMBOLS

γ_d = dry unit weight

μ = micro

Ω = ohm

γ = unit weight

1. INTRODUCTION

According to the Organization for Economic Co-operation and Development (OECD), coal accounts for about 34% in United States (OECD 2015). According to American Coal Ash Association (ACAA) ‘Production & Use Survey’ data, in the U.S. 117.3 million tons of coal combustion products (CCPs) or coal combustion residuals (CCRs) were produced and about 52% (61.1 million tons) were reused (ACAA 2015). There are several applications where CCPs can be utilized to reduce the waste disposal and land utilization. Silicon dioxide, aluminum oxide and calcium oxide are the primary constituents in coal ash. CCP can be divided into two broad categories, Class C and Class F, depending on the nature of coal that is burnt. Class C is produced when lignite or sub-bituminous coal is burnt and Class F is produced when anthracite or bituminous coal is burnt. Class C contains about 20% or more Calcium Oxide than Class F. When coal burns, heavier particles settle down and lighter particles are suspended in the air. Heavier coal ash is termed as the bottom ash and lighter coal ash as fly ash. Bottom ash is collected at the bottom, while fly ash is collected in different ways. Commonly used methods involve Electro Static Precipitators (ESP), filter bags, and wet scrubbing. ESPs use charged plates: one positive and the other negative and flue gas containing combustion particles passes through the negative plate first where the particles are induced with the negative charge. Then, the air is directed towards the positively charged plate where the negatively charged particles are attracted. Filter bags are made up of different fabrics in various shapes such as round and pleated. When the flue gas passes through the filter bags, the suspended particles are caught by the fabric. Continuous flue gas flow creates a cakey particle layer which in turn functions as a porous filter bed where finer particles are trapped. Both methods, ESPs and filter bags release cleaner air into the atmosphere. Wet scrubbing is another method where a liquid, mostly water or water mixed with lime, is sprayed into the flue gas. When the particulates come in contact with the scrubber liquid, they are adsorbed into the liquid. The effluent or the waste water is now directed to the collection/settling ponds and treated before releasing into river waters. Class C fly ash is a valuable resource and is used in applications such as concrete due to its cementitious properties, as a filler in embankments, and in highway subgrades. Class F fly ash, which has little or no cementitious properties has commonly been dumped into unlined ponds in the past.

1.1 Federal Regulations

According to the Resource Conservation and Recovery Act (RCRA), coal ash is classified under subtitle D instead of subtitle C which is for hazardous waste. Even though coal ash is not considered a potential threat, infiltration from ash ponds into ground water can hold serious contamination problems where the heavy metal concentrations can exceed the maximum contaminant levels (MCL). Hence, in the recent years, proper disposal of coal ash has become an important subject. Environmental Protection Agency's (EPA 2009) policy states that pond ash from unlined impoundments, if have impacted or are expected to impact the groundwater adversely, should be moved into lined landfills to mitigate the leaching of harmful constituents from the discarded ash. After the disposal of coal ash into the ponds for a long period of time, storm water infiltrates into the ponds often saturating the coal ash. Higher water content of ash makes it hard to excavate and transport the ash because wet coal ash has relatively lower shear strength. In addition, the vibration and surcharge imposed by the heavy equipment results in liquefaction of the saturated coal ash and that creates a safety and operational challenge for the ash contractors.

1.2 Moisture Removal Methods

The most common methods for dewatering coal ash ponds are shallow wells and rim ditches. Moisture control/stabilization and achieving sufficient shear strength are key for excavation and transport of coal ash from coal ash ponds. This thesis evaluates an emerging technology where additives can provide both moisture control and improvement in the shear strength and stabilization or uptake of heavy metals in ponded coal ash.

1.3 Objectives

This research thesis explores the use of sodium polyacrylate $(C_3H_3NaO_2)_n$ as a polymer additive. Industry refers to the polymer additives such as sodium polyacrylate as super absorbent polymer (SAP) due to the use of the polymer in medical and hygiene products to stabilize excess moisture.

The key objectives of this research thesis are as follows.

1. Evaluate the moisture stabilization capabilities of the SAP when used for coal ash at relatively high water contents;
2. Evaluate the shear strength of wet coal ash after excess moisture has been stabilized by the SAP; and

3. Evaluate stabilization or uptake of heavy metals by the SAP when used as an additive in the fly ash. The key purpose of exploring this objective is to alleviate the leachability of heavy metals from coal ash into ground water.

2. BACKGROUND

This section provides background information generated from literature review on additives used in soils and coal ash to improve the performance of these materials.

2.1 Use of Additives for Waste Solidification

Usage of polymers in fully saturated geotechnical embankments has been a practice for a long period. The polymers used for geotechnical stabilization of embankments can be classified as: organic & inorganic. Organic polymers are produced from naturally occurring materials like quarry fines, lime, agricultural products etc. Inorganic polymers are the ones manufactured from chemicals such as organo-silane, sodium polyacrylate etc. These additives serve various functions such as moisture stabilization, reduction in leaching of undesirable constituents into groundwater etc. SAP such as sodium polyacrylate is a hydrophilic material manufactured from polymerization of acrylic acid and sodium hydroxide, which absorbs and retains moisture under moderate pressure conditions.

2.2 Super Absorbent Polymer

Hydrophilic additive was first produced by polymerizing acrylic acid and divinylbenzene in an aqueous medium in 1938. Hydrogels are the materials that are hydrophilic in nature that has network of polymer chains in its structure. Hydrogel was first produced in 1950 using monomers such as hydroxyalkyl methacrylate with swelling capacity of 50%. Major commercial production took place in 1978 in female hygiene industry. This was a huge revolution in the field of absorption materials because the materials also had other characteristics that stood out like retention of water under confining pressure and relatively high absorption capacity.

2.2.1 Types of Super Absorbent Polymers

SAP can be classified based on three criteria: nature of occurrence, presence of charge in the polymer network, and type of repeating monomer unit in the polymer structure.

a. Natural of occurrence: Natural SAP are hydrogels produced from polysaccharides (carbohydrate) and polypeptides (proteins). Starch is an example of this type. Synthetic SAP is based on petrochemicals. However, most of the SAP are a combination of both.
b. Presence of charge in the polymer network: Four types can be considered based on this norm; non-ionic, ionic, amphoteric electrolyte, and zwitterionic. Ionic SAPs can have both anionic or cationic polymer network. Amphoteric electrolyte type contains both acid and base groups while zwitterionic contains both anionic and cationic groups in the repeating monomer unit of polymer structure.
c. Type of repeating monomer unit of the polymer structure: Most conventional SAPs have three types of repeating monomers such as, cross-linked polyacrylates & polyacrylamide, hydrolyzed cellulose/starch-polyacrylonitrile, and cross-linked copolymers of maleic anhydride.

Most commonly used and produced SAPs are synthetic anionic acrylic that is neutralized by acrylic acid or acrylamides or its salts.

2.2.2 Characteristics of Super Absorbent Polymers

The key characteristics of SAPs that enable potential use of SAPs for coal ash include absorption capacity, rate of absorption, absorption capacity under load, biodegradability and non-toxicity, and pH neutrality in aqueous medium. In order to use an SAP in the dewatering of coal ash ponds, above listed characteristics play a key role. A majority of the ash ponds are saturated and have an excessive amount of water. In commercial settings, in the view of applicability and time and the rate at which the moisture is absorbed is significant. Most contractors prefer quick results. SAP has the capacity to withhold moisture and hold it under confining pressures because of the surface cross-linking of the polymeric chains. Even though, most of the SAP is synthetic, it has been approved by the U.S. Food and Drug Administration (FDA). Long before the application of SAP in environmental field, the material has been in use in the food and personal hygiene industry for decades. Research related to the toxicology of the material in the environment states that there are no harmful effects and that it is mostly biodegradable. All of these characteristics make it ideal to use in the moisture stabilization of ponded coal ash.

2.2.3 Structure of Super Absorbent Polymers

Hydrophilic nature of SAP is attributed to the carboxylic acid group present in the polymer network (Figure 2-1), which has an affinity for water. Sodium polyacrylate is the anionic acrylic SAP that was used for this research. Polymer network has cross-links that prevent the polymer from infinite swelling i.e. dissolving in the medium. Positive sodium ions and the negative carboxylic acid group attract the water molecules into the network. Repulsion between the similar polarity ions causes the network to expand causing the hydrogel to swell. Sodium trapped inside the polymer network maintains electric neutrality.

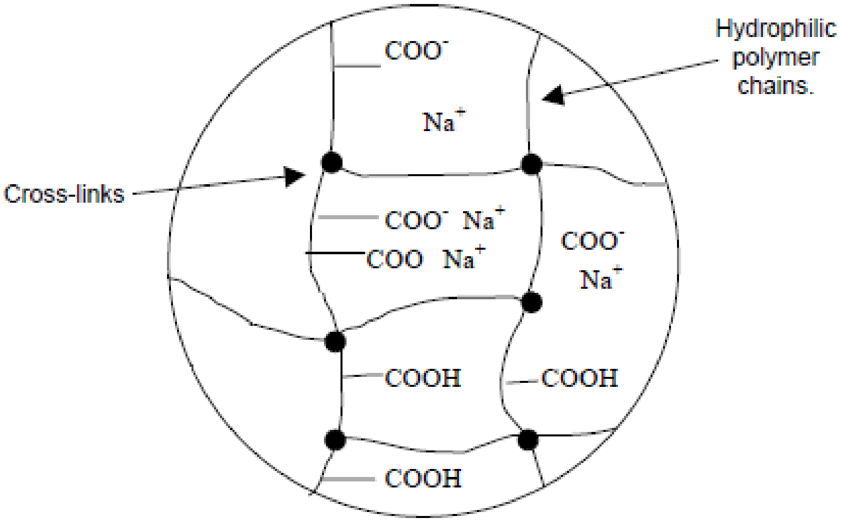

Figure 2-1 Structure of SAP (Mark 2004)

2.2.4 *Mechanism of Super Absorbent Polymers*

Both physical and chemical interaction takes place in the working of SAP. Sodium ions inside the polymer network increase the osmotic pressure inside the gel. When polymer is added to the aqueous medium (e.g., wet coal ash), hydration and hydrogen bond formation takes place.

It is important to discuss the polar nature of water molecule to understand the SAP mechanism. Water molecule has covalent bonding between the oxygen and hydrogen atoms. Electron configuration of elements, hydrogen and oxygen, is written as $1s^1$ and $1s^22s^22p^4$. Electrons in the outermost orbit are the valency electrons which indicate the bonding ability of an element with other atoms. In water molecule, one atom of oxygen bonds with two atoms of hydrogen. Valency of hydrogen is 1 and oxygen is 6. Oxygen and hydrogen bond by sharing electrons. However, since oxygen is more electronegative than hydrogen, shared electrons move closer to oxygen atom in the molecule. This uneven distribution of shared electrons causes partial negative charge to oxygen and partial positive charge to hydrogen. Further, the two lone electron pairs of oxygen atom repel from each other decreasing the bond angle between the two covalent bonds of hydrogen atoms and oxygen atom. Due to this non-linear molecular shape, charges in the covalent bonds do not cancel each other and makes water a polar molecule.

Water molecule dissociates into negative hydroxide ion (-OH) and positive hydrogen ion (+H). In the SAP, carboxylic acid group dissociates in water as carboxylate ion and hydronium ion.

$$\mathrm{RCOOH} \leq == > \mathrm{RCOO}^{-} + \mathrm{H}^{+}$$

a. Hydration: Water is a polar solvent which gets attracted to positive or negative charges, or both. COO- attracts the H+ ions of water and Na+ attracts the OH- ions of the water molecule (Figure 2-2).

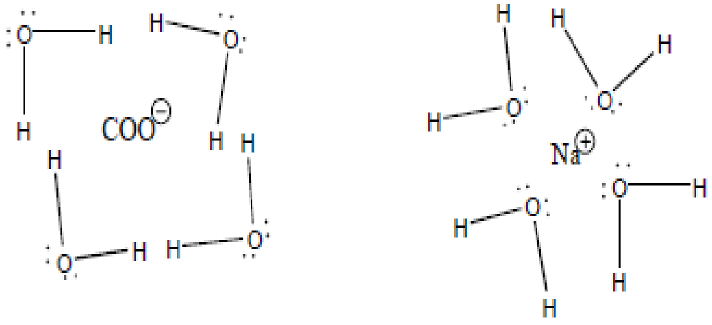

Figure 2-2 Hydration (Mark 2004)

b. Hydrogen Bond Formation: Interaction of hydrogen with any electronegative element like oxygen results in hydrogen bonds (Figure 2-3). Re-stating the electron configuration of oxygen, $1s^2 2s^2 2p^4$, there are two lone electron pairs in the outer orbit of the atom. Now, hydrogen atoms get attracted to the lone electron pairs on the electronegative oxygen atom since hydrogen in the dipolar water molecule has positive charge to it.

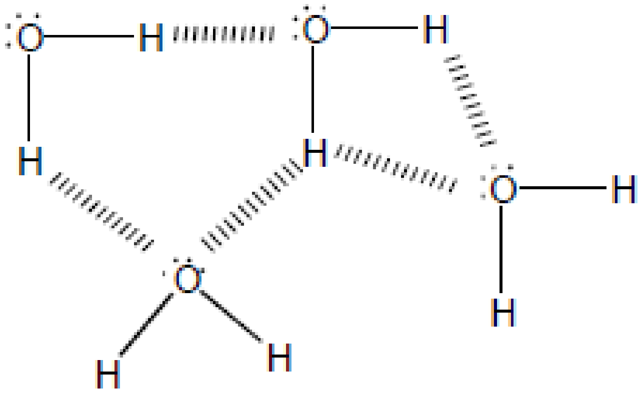

Figure 2-3 Hydrogen bond formation (Mark 2004)

2.2.5 *Cross-linking*

SAP, having carboxyl (carbonyl -C=O and hydroxyl -OH) acid group is a weak acid group but soluble in water. What makes the SAP not soluble in water is the cross-link structure. Polymer chains in the network are present as entangled coils. When polymer is placed in the water, the network expands to dissolve. But, cross links present in the network stop the infinite swelling due to the elastic refractive force in the coiled chains. The disorder of the system's entropy is also reduced when the coiled chains straighten out and form hydrated chains. Swelling force and the retractive force balance each other, stopping the polymer from dissolving. The higher the cross-linking density, the greater the strength of the polymer gel.

Cross-linking of SAP is of two types; core cross-linking and surface cross-linking.

a. Core cross-linking: A repeating monomer unit of the polymer is bonded with a double-bonded organic molecule using covalent bonding (Figure 2-4).

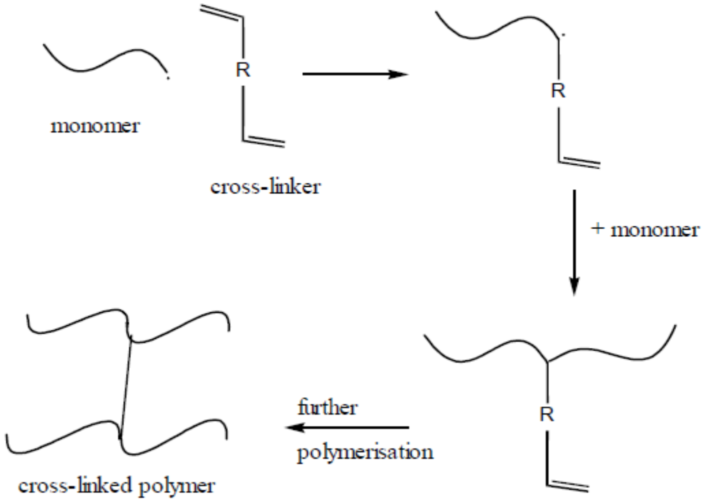

Figure 2-4 Core cross-linking (Mark 2004)

Cross-linker is introduced into the polymer backbone during the three-dimensional polymerization of the network. Example of cross-linker chemicals include tetraallyl ethoxy ethane and trimethylolpropanetrictylate.

b. Surface cross-linking: SAP absorbs high amounts of water relative to its weight but without the surface cross-linking, the swollen polymer gel doesn't have the strength to withstand the external pressure. Surface cross-linking is achieved by applying surface cross-linking solution to the dry polymer particles and then curing is done by conventional heating, thereby enhancing the polymer strength (Figure 2-5). Examples of surface cross-linking solution included glycerin which has functional group to bond with the polymer backbone. Any chemical group with minimum two functional groups can be used.

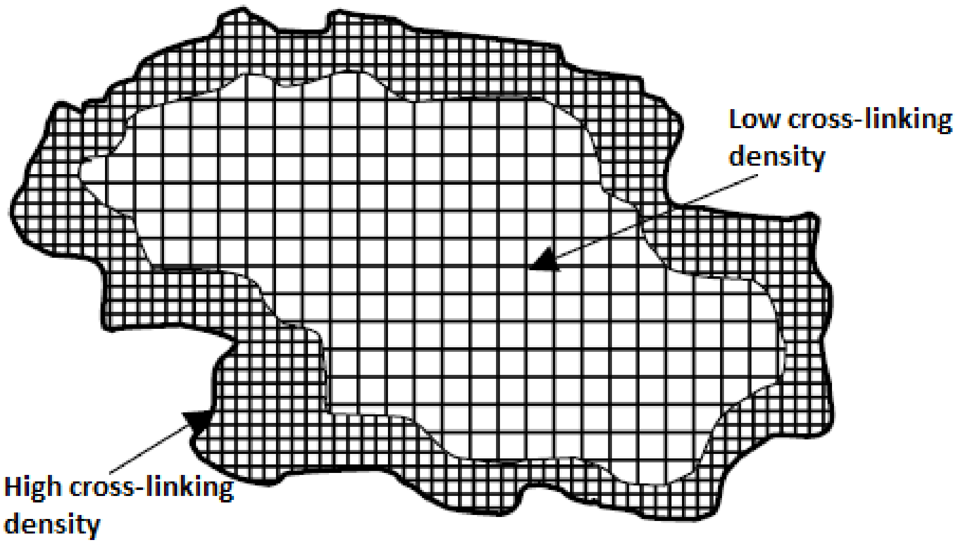

Figure 2-5 Surface cross-linking (Mark 2004)

It is important to balance the core cross-linking and surface cross-linking density in the polymer. Often, to increase the swelling capacity of the gel, core cross-linking is compromised. While there is a significant increase in the swelling capacity, the gel strength against confining pressure decreases.

2.3 Mechanical Strength

2.3.1 Optimum Moisture Content

Das et al. (2015) conducted studies on stabilization of ponded ash from steel plants using two biopolymers, Guar Gum, and Xanthan Gum. Different percentages of the biopolymers were added to three samples of ponded ash, RSP1, RSP2 and ADN, and were compacted to find the Optimum Moisture Content (OMC) and the Maximum Dry Density

(MDD). OMC of the samples increased as the dosage of biopolymer increased, while MDD decreased (Table 2-1).

Table 2-1 OMC and MDD of Pond Ash and Modified Pond Ash Samples (Das et al. 2015)

Pond Ash	**Pond Ash + XG/GG (%)**	**OMC (%)**	**MDD (kN/m^3)**
RSP 1	Pond Ash	40.93	10.80
	Pond Ash + XG (2%)	55.69	9.11
	Pond Ash + GG (2%)	48.34	9.58
RSP 2	Pond Ash	38.13	11.57
	Pond Ash + XG (1%)	44.79	10.36
	Pond Ash + XG (2%)	42.86	10.33
	Pond Ash + XG (3%)	43.55	9.86
	Pond Ash + GG (0.5%)	43.83	10.47
	Pond Ash + GG (1%)	46.95	10.34
	Pond Ash + GG (2%)	41.40	10.59
AND	Pond Ash	38.66	11.30
	Pond Ash + XG (2%)	44.79	10.11
	Pond Ash + GG (2%)	42.35	9.31

2.3.2 Effect of Additives on Unconfined Compressive Strength

Unconfined compressive strength (UCS) tests were conducted on the samples at their respective OMCs. The specific gravity ranged from 1.4 to 2.4 and had more than 75% fines (Das et al. 2015). Biopolymers, Guar Gum, and Xanthan Gum, are composed of pentasaccharide containing glucose, mannose, and glucuronic acid (R. Chen et al. 2013). These biopolymers work as thickening agents. When mixed with polar solvents like water, they swell and form strong hydrogen bonds. Based on observations that Guar Gum is viscous than Xanthan Gum, dosages of the biopolymers were decided. Solutions were made by mixing 0.5%, 1% and 2% of Guar Gum, and 1%, 2% and 3% of Xanthan Gum to the water, which were then mixed with the ponded ash prior to compaction. It was observed that the specific gravity of the samples increased with an increase of biopolymer dosage.

Unconfined compression strength (UCS) tests conducted at OMC showed that compressive strength increased with increase in biopolymer percentage of both the gums. However, when curing period is considered, sun-drying the samples (RSP 2) for a day showed greater compressive strength than the samples that were cured in moist state for 7 days (Table 2-2). Considering RSP 2 sample and RSP 2 sample mixed with 3% Xanthan Gum, strength of the ponded ash increased from 102 kN/m^2 to 154 kN/m^2 without curing, 28 kN/m^2 to 99 kN/m^2 with 7-day moist curing, and 126 kN/m^2 to 221 kN/m^2 with 1-day sun drying.

X. Chen et al. (2014) studied the effect of sodium polyacrylate and polyacrylic acid on the mechanical properties of iron and steel slag which has about 40% calcium oxide by weight. Size of the slag particles was about 80 microns. Slag was initially grinded and mixed with sodium silicate which is an alkali-activator that acts as a catalyst when a material is mixed with silica based polymer (Abdulkareem et al. 2015). Slag was then molded (ISO 2002) and compressive strength and rupture strength were measured for curing periods of 3 and 28 days. Sodium polyacrylate at weight fractions of 0.25%, 0.5%, 0.75% and 1%, was mixed with the slag before testing. It was found that 28-day curing was better than 3-day curing for both rupture strength (tensile strength) and compressive strength (Table 2-3).

Table 2-2 Unconfined Compressive Strength of Pond Ash and Modified Pond Ash Samples (Das et al. 2015)

Pond Ash	**Pond Ash + XG/GG (%)**	**UCS (kN/m^2) 0 day**	**UCS (kN/m^2) 7th day**	**UCS (kN/m^2) 1st day (sun dried)**
RSP 2	Pond Ash	102	28	126
	Pond Ash + XG (1%)	140	87	210
	Pond Ash + XG (2%)	149	91	216
	Pond Ash + XG (3%)	154	99	221
	Pond Ash + GG (0.5%)	98	92	199
	Pond Ash + GG (1%)	160	147	202
	Pond Ash + GG (2%)	169	149	204

This phenomenon was attributed to the hydration process. Initially, when sodium polyacrylate is added, hydration rate decreases with increase in the consistency of the material. With time, hydration rate increases and the strength increases. Greater fraction of sodium polyacrylate resulted in higher strength. However, the strength gain was marginal compared to the increase in dosage and strength of the samples did not increase linearly with increasing dosage. This was ascribed to the challenge in molding a sample when high dosage of sodium polyacrylate was used. The reason for improvement in strength was attributed to the formation of strong bonded molecular links of sodium polyacrylate in alkaline conditions.

Table 2-3 Influence of Sodium Polyacrylate Dosage on Slag-Based Geopolymer’s Rupture Strength and Compressive Strength (X. Chen et al. 2014)

Dosage of sodium polyacrylate	**3-day compression strength /Mpa**	**3-day rupture strength /Mpa**	**28-day compression strength /Mpa**	**28-day rupture strength /Mpa**
Blank sample	19.85	5.2	44.24	7.4
0.25%	18.6	4.65	42.72	8.5
0.50%	17.9	4.85	46.82	9
0.75%	18.1	5.35	45.07	8.9
1%	18.9	5.3	46.95	9.2

Numerous synthetic geopolymers have been studied to test its influence on soil properties. Zhang et al. (2004) focused on testing the influence of five types of water soluble organic polymers on the mechanical and physical properties of uncalcined-kaolinite geopolymer. Polyacrylic acid (PAA), Sodium Polyacrylate (PAA_{NA}), Polyethylene Glycol (PEG), Polyvinyl alcohol (PVA) and Polyacrylamide (PA_m) were the geopolymers tested in this study. Geopolymer are produced in two key steps: activation and poly-condensation

(Davidovits et al. 1985). Activation step includes dissolution of materials and formation of orthosialate acid in high pH base solution. Second step includes large poly-condensation between this orthosialate acid and silanol groups (Si-O-H). This high poly-condensation leads to the formation of 3-D cross link structure, which makes the material excellent for improving mechanical properties, temperature tolerance, durability, acid resistance, and heavy metal ions fixation (Zhang et al. 2004). Kaolinite (Kaolinite Na-PS) of particle size 1.5 µm was initially dried at 105 ˚C and mixed with water, activator, and the organic geo-polymer to make a slurry (OMPS- Organic Polymer Modified Kaolinite NA-PS) which was then molded in 20 x 20 x 20 mm steel molds. After an 8-hr curing period, samples were demolded and dried before analyzing. Ratio of water to solids, ratio of activator to kaolinite, curing temperature and curing time were the key aspects that influenced the mechanical properties of the testing material. Consistent with field operational practice, water to solid ratio of 0.5 was adopted. Compressive strength of all of the samples increased to reach a greatest value after which it dropped except for PVA-OMPS which was attributed to the high viscosity of this sample. PAA and PAA_{NA} worked better than the rest of the samples (Figure 2-6).

Ionization of organic geo-polymers in activator solution, produces positive and negative ions that neutralize the negative charges on the kaolinite particles. This decreases the repulsive forces and increases the compressive strength and cross bending strength (Table 2-4). Furthermore, samples were boiled for 2 hours in distilled water and tested. It was noted that PAA-OMPS achieved 61.2% increase in the compressive strength after boiling. Boiling increases the viscosity which in turn improves the mechanical property of the material.

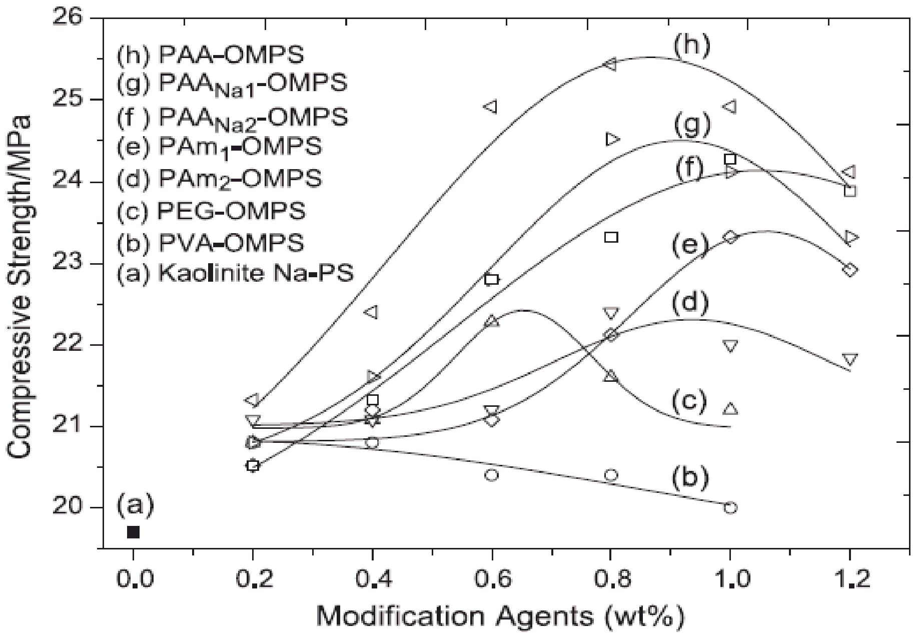

Figure 2-6 Comparison of compressive strength of kaolinite and modified kaolinite samples (Zhang et al. 2004)

Table 2-4 Physical and Mechanical Properties of Kaolinite and Modified Kaolinite Samples (Zhang et al. 2004)

OMPs	**Compressive strength (Mpa)**	**Increment of compressive strength (%)**	**Cross-bending strength (Mpa)**	**Increment of cross-bending strength (%)**
Na – PS	19.7	-	3.7	-
PAA - OMPS	25.4	29	5.4	45.7
PAA Na 1 - OMPS	24.5	24.4	6.1	64.9
PAA Na 2 - OMPS	24.3	23.4	-	-
PAm 1 - OMPS	23.3	18.3	-	-
PAm 2 - OMPS	22.4	13.7	-	-
PEG - OMPS	22.3	13.2	3.6	-3.2
PVA - OMPS	20.8	5.6	-	-

Chand et al. (2007) conducted experiments on in-place stabilization technique using hydrated lime columns on large-scale laboratory prototypes of ash ponds. In-situ water content of ash varied from 10 to 110 %. Ponded ash was seen to have reduced pozzolanic effects and lower bearing capacity when saturated. Ash F fly ash was obtained from 1 m depth from a thermal power station ash pond. Calcium hydroxide (68% pure) was used for the stabilization method. Slurry formed from ponded ash and water (Solid to liquid ratio of 1:2 by weight) was placed in circular tanks with drain (Figure 2-7). Test samples were obtained from tanks with the hydrated lime column. Settlement and curing process was allowed at room temperature of 30 ˚C and samples were obtained at three-time periods from 3 radial distances from the center and at three depths using sampling tubes of 38 mm diameter and 250 mm height. As the depth increases, reduction in water content and increase in dry density was seen in both stabilized and unstabilized tanks due to higher consolidation at greater depths caused by the overburden pressure. Samples obtained at 90-day period from stabilized tanks showed lower dry density and higher water content compared to the samples obtained at the same time from unstabilized tanks due to the extra moisture seeping from the lime column. With time, consolidation and lime pozzolanic reaction resulted in gradual decrease of water content and increase in dry density. pH decreased as radial distance from the lime column increased. However, after the stabilization periods of 180 days and 365 days, increase in the pH was seen at all locations indicating the migration of lime.

Unconfined compressive strength decreased with the increase in radial distance and increased with curing time. Samples obtained at different depths showed that compressive strength was higher for top samples and lower for mid samples. Top sample strength can be attributed to the evaporation of moisture resulting in the strength increase. Bottom samples strength can be attributed to the consolidation effect resulting in the lower moisture content and hence higher compressive strength. However, at all depths, compressive strength values increased with the stabilization period showing that lime and ash pozzolanic reaction was a slow process.

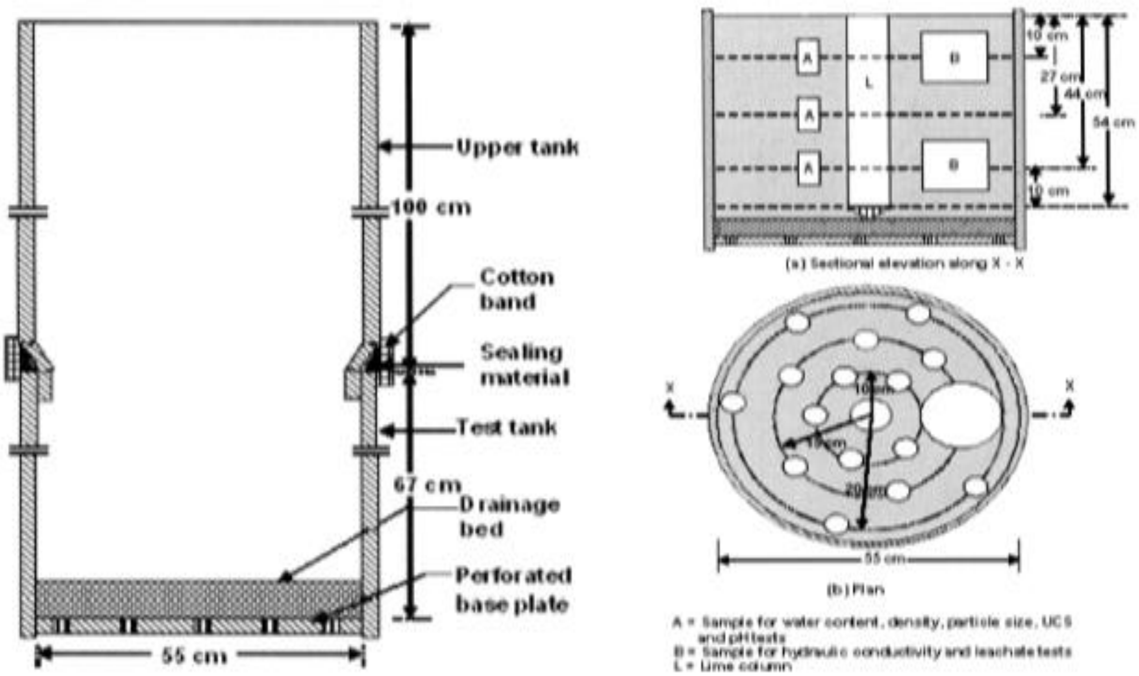

Figure 2-7 Tank setup of ash slurry (Chand et al. 2007)

Albino et al. (1996) studied the stabilization of residue from municipal solid waste incinerator that had heavy metals, calcium trisulphoaluminate and silicate hydrates. Alumina and silica present in the residue generate C-S-H (calcium silicate hydrate). Binding matrices form Ettringite, which has good binding properties. Ettringite and C-S-H together contributes to the mechanical strength of the residue. Curing temperature was the key aspect in reaching strong mechanical strength. Both mechanical and chemical properties of the residue were studied. Residue from incinerator was mixed with water and cured for 28 days at 25 ˚C and 100% humidity in 5 cm high and 3 cm diameter molds. Residue was a mixture of acid components formed during the flue gas desulfurization process at the absorption lime column of the incinerator and fly ash. After removing the organics by heating the sample at 105 ˚C for 2 hours, chemical composition of the residue was analyzed, which had toxic levels of heavy metals. Different percentages of blast furnace slag (BFS) and fly ash (FA)were used along with the binding matrices for testing; 0%, 20%, 40%, 60% and 80% weight fractions. Calcium Oxide in BFS and FA was 41.1% and 4.8%, respectively (Table 2-5).

Table 2-5 Chemical Composition of Blast Furnace Slag and Fly Ash by Weight Percentage (Albino et al. 1996)

Chemical Composite	**Blast Furnace Slag**	**Fly Ash**
SiO_2	33.2	56.8
CaO	41.1	4.8
Al_2O_3	14.1	25.5
TiO_2	0.5	2.2
Fe_2O_3	1.6	4.2
MgO	7	1.5
Na_2O	-	3
K_2O	0.4	0.2
SO_3	2.6	0.4

X-ray Diffraction (XRD) analysis showed the formation of Calcium sulfate dihydrate that converts into ettringite in the case of FA at 0%, 20% and 40%. FA 60% and 80% did not show ettringite formation. In the case of BFS, ettringite formation was seen in samples containing up to 60% waste. BFS samples showed higher ettringite formation despite lower gypsum content because of less conversion of hemihydrate to dihydrate. Hemihydrate attributes to the rapid setting strength (Valenti et al. 1984). Compressive strength of the samples decreased with an increase in waste content. BFS samples showed higher strength than the FA samples (Figure 2-8). C-S-H formation favors the mechanical strength in case of slag based residue but not in fly ash based residue.

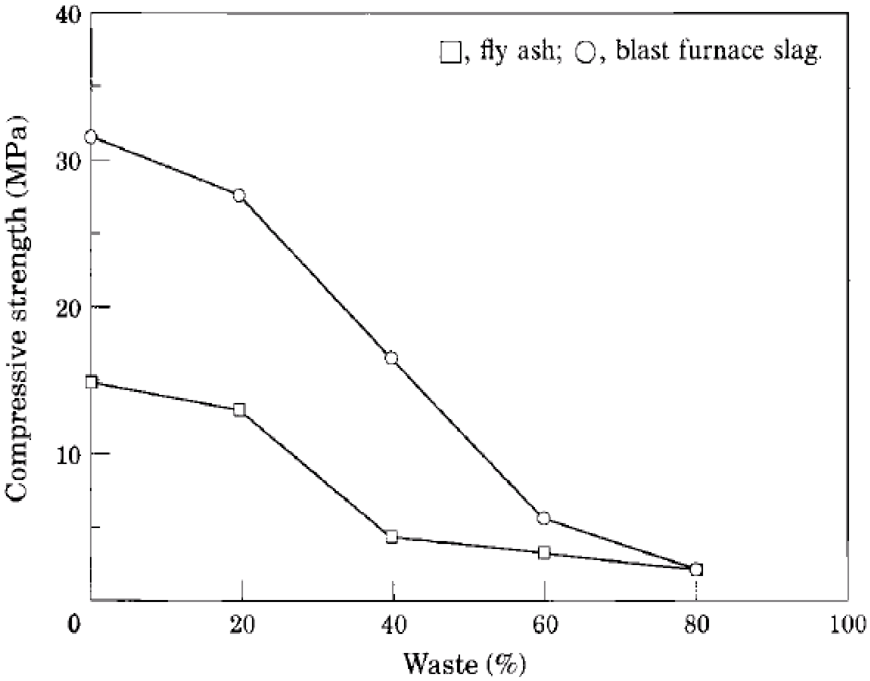

Figure 2-8 Compressive strength of cured samples (Albino et al. 1996)

2.4 Leaching

Albino et al. (1996) carried out leaching tests for heavy metals. There was no statistically significant variation between leached metal concentration and the waste content

(Table 2-6). This is explained by the authors as the outcome of physical trapping of metals in the cured samples since metals are present as oxides, which are stabilized by high temperature incineration process in the waste. Stabilized metal oxides do not re-speciate in the hydration process and the increase of leachability with an increase of waste content may be due to the decrease in the compressive strength.

Table 2-6 Results of US. EPA Leaching Tests in mg/L (Albino et al. 1996)

Element	**Raw waste**	**FA 20**	**FA 40**	**FA 60**	**FA 80**	**BFS 20**	**BFS 40**	**BFS 60**	**BFS 80**	**Legal limit (mg/L)**
Cr	0.05	0.11	0.12	0.22	0.28	0.06	0.05	0.09	0.15	0.20
Cd	0.20	BD[1]	BD	BD	0.03	BD	BD	BD	0.03	0.02
Pb	0.25	0.12	0.09	0.20	0.25	0.13	0.14	0.16	0.17	0.20
Cu	0.07	BD	0.01	BD	0.10	0.01	0.01	0.01	0.01	0.10
Zn	1.89	BD	BD	BD	0.09	BD	BD	BD	0.15	0.50
Mn	1.00	0.01	0.01	0.01	0.36	0.01	0.01	0.01	0.59	2.00
Fe	0.18	BD	BD	0.01	BD	0.01	BD	0.02	0.02	2.00

BD[1] = Below Detection Limit i.e. < 0.01 mg/L

Chand et al. (2007) collected leachate samples from single radial distance of 15 cm from top and bottom locations and tested for arsenic, chromium, copper, mercury, magnesium, lead, and zinc using Flame Atomic Absorption Spectrophotometer (FAAS). Samples were extracted using special mold and water flow under constant head pressure of 1.5 m was setup for 7 days. On the 7th day, samples were analyzed for metals using FAAS. Samples were below detection limit (Abdulkareem et al.) for chromium, mercury, and lead. Leaching of elements doesn't correlate with the depth of the sample extractions (Table 2-7).

Table 2-7 Concentration of Metals in Leachate Samples in mg/L (Chand et al. 2007)

Sample designation	**Position**	**As**	**Cr**	**Cu**	**Hg**	**Mg**	**Pb**	**Zn**	**Ca**
90 - N	Top	0.118	BD[1]	0.023	BD	3.771	BD	0.048	70
	Bottom	0.129	BD	0.029	BD	4.053	BD	0.109	65
90 - LC	Top	0.207	BD	0.019	BD	3.785	BD	0.039	65
	Bottom	0.143	BD	0.017	BD	3.947	BD	0.099	75
180 - LC	Top	0.219	BD	0.016	BD	3.681	BD	0.036	90
	Bottom	0.198	BD	0.018	BD	3.826	BD	0.107	85
365 - LC	Top	0.248	BD	0.019	BD	3.900	BD	0.027	100
	Bottom	0.210	BD	0.013	BD	4.069	BD	0.069	98
Permissible limits (mg/L)		0.01	0.05	1.30	0.001	150	0.01	3.00	-
Threshold limits (mg/L)		1.00	5.00	130	0.10	15,000	1.00	300	-

Note: number of pore volumes of flow after seven days varies from 70 to 142 for top level samples and 175 to 455 for bottom level samples

BD[1]: below detection limit

Contamination Potential Ratio (CPR) was calculated by conducting hydraulic conductivity tests. Combining the concentration and hydraulic conductivity, CPR was calculated using Eq. 1. CPR less than 1 is desirable because that shows that amount of metal is lower in the tested material than in the control material at the specific time.

$$CPR = \frac{K * C}{K_0 * C_0} \tag{1}$$

where K is the hydraulic conductivity of test sample, C is the concentration of metal in the test sample leachate and K_0 is the hydraulic conductivity of control sample, and C_0 is the concentration of metal in the control sample leachate.

Arsenic, copper, magnesium, zinc had CPR less than 1. CPR for the metals further decreases with the stabilization period showing the effectiveness of the lime ash reaction that's preventing the leaching of the metals (Table 2-8). This can also be due to the precipitation of metals due to the high alkaline pH of the stabilized ash. CPR values of arsenic for samples obtained from the top is greater than 1, while for the samples collected from the bottom are lower than 1. But, the top and bottom sample As CPR show a decreasing trend with increasing stabilization period. Bottom sample for Ca is nearly 1 during 90-day stabilization period because of the slow pozzolanic reaction due to which the lime leaches out and moves down. With longer time periods, pozzolanic reaction takes place and CPR gradually decreases, showing that cementitious products trap the metals from leaching.

2.4.1 Effect of pH on Leaching of Metals

Izquierdo et al. (2012) discuss the various factors that affect the leachability of metals present in the coal fly ash. Leaching depends on the speciation of the element in coal fly ash. Mobility of the metals is also pH sensitive. Release of the metals such as cobalt, copper, mercury, nickel, lead, tin, and zinc is reduced when pH ranges between 7 and 10. While release of oxy-anionic species like arsenic, boron, chromium, molybdenum, antimony, selenium, vanadium increases when pH ranges between 7 and 10. Calcium concentration in the coal fly ash also has great role in the leaching of the metals.

Table 2-8 Contamination Potential Ratio (CPR) for Metals (Chand et al. 2007)

Sample designation	**Position**	**Contamination Potential Ratio (CPR)**				
		As	**Cu**	**Mg**	**Zn**	**Ca**
90 - N	Top	1[a]	1	1	1	1
	Bottom	1[b]	1	1	1	1
90 - LC	Top	1.62	0.77	0.92	0.74	0.85
	Bottom	0.94	0.50	0.83	0.77	0.99
180 - LC	Top	1.08	0.40	0.57	0.43	0.74
	Bottom	0.71	0.30	0.44	0.46	0.61
365 - LC	Top	1.02	0.41	0.50	0.27	0.69
	Bottom	0.62	0.17	0.39	0.24	0.58

[1] 90 - N-T is control samples for all top - level samples

[2] 90 - N-B is control samples for all bottom - level samples

Izquierdo et al. (2012) state that it is not right to decide the degree of risk based on the element concentration but on the leachability of the metal. Solubility of the elements varies after condensing onto the coal fly ash particles during desulfurization process. Most of the times, these elements form compounds with the available calcium which in turn affects the degree of leachability. Jones (1995) reports that elements such as barium, cobalt, chromium, manganese, nickel, and lead are distributed in between the surface of the particle and the matrix which makes them unavailable for leaching. Leaching of such metals would depend on their solubility. Elements that are associated on the surface such as cadmium, copper, molybdenum, vanadium, and zinc are more leachable. Concentration of calcium and sulfur affects the pH of coal fly ash because these oxides neutralize the pH of the coal fly ash leachate (Izquierdo et al. 2012). Strongly alkaline fly ash has pH range of 11-13, where Ca/S >>1. Mildly alkaline fly ash with low Ca contents has pH between 8 and 9. Acidic fly ash has no oxides of calcium and magnesium. pH of the coal fly ash is dynamic in the environment. Both alkaline and acidic fly ash, over time, reach neutral values, which affects the release of elements. Fly ash rich in calcium and sulfur forms ettringite ($Ca_6Al_2(SO_4)_3$(Zohuriaan-Mehr et al.)$_{12}$.26H_2O) when alkaline fly ash (pH>11) is combined with water. Ettringite captures the trace elements and hence reduces the leachability.

General trends of elements leachability are presented against pH (Figure 2-9). Arsenic is a surface associated element and its release is pH dependent. Over a range of pH 7 to 11, arsenic has high solubility and hence high leachability. In fly ash with low levels of calcium, leachability decreases over time. Precipitation of element doesn’t occur in low calcium fly ash. Barium leachability depends on the ratio of Ca and S, but not on the pH. Higher sulfur levels in combination with higher calcium levels tend to precipitate by the formation of compounds with barium such as $BaSO_4$, which is insoluble. Large part of boron is present in soluble form in coal fly ash. Solubility of boron depends less on pH when pH is greater than 6. Ettringite formations in alkaline fly ash binds boron but acidic fly ash does not. Chromium is present abundantly as Cr^{3+} in coal fly ash and is less soluble. Leaching of chromium is pH dependent. High and low level of pH achieves great release of element while near neutral pH achieves less than 0.02 mg/kg. Cobalt leachability is higher at lower pH levels and is least when pH is between 9 and 10. Leachability of cobalt again increases when pH is greater than 12. When the coal fly ash has higher iron content, cobalt associates with Fe species and is less leachable throughout the pH range. Selenium has complex leaching behavior dependent on pH. At neutral pH, selenium is least soluble. Solubility increases as the pH increases and hence alkaline coal fly ash has higher leachability of selenium. Selenium is available abundantly as Se^{4+} in coal fly ash. Vanadium is readily leachable in fly ash with low calcium. Vanadium tends to compound with calcium, forming calcium vanadate. Higher calcium concentration in alkaline fly ash attenuates the release of vanadium since calcium vanadate precipitates. But, in acidic fly ash leachate, calcium available is dissolved and hence vanadium is soluble.

2.4.2 Effect of Contact Time on pH

W. R. Roy et al. (2011) studied the factors that influence the pH of coal fly ash leachate since it is important in the assessment of environmental impacts in the long run. In order to understand the potential buffering processes that influence the pH of coal fly ash leachate, kinetic-geochemical models were developed using the software, REACT®. Research investigations found that 70% of all fly ashes produce leachate of alkaline pH (Spears et al. 2004). pH of CCPs ranges from 4 to 12, when combined with water depending on the constituents of the CCPs. Leachate is alkaline when oxides of calcium and magnesium are hydrolyzed during the coal combustion, and acidic when sulfuric acid or sulfur dioxide from flue gas entry is adsorbed on the CCP particles. Another possibility could be the hydrolysis of Al^{3+} ion due to the aluminum sulfates (Spears et al. 2004). Roy et al. (1984) conducted experiments on initially acidic fly ash and reported that the pH increased from 4.1 to 7 in 21 to 36 days. This phenomenon was attributed to neutralization of sulfuric acid. It was seen that the concentrations of aluminum, cadmium, chromium, copper, iron, nickel, and zinc decreased as the pH increased.

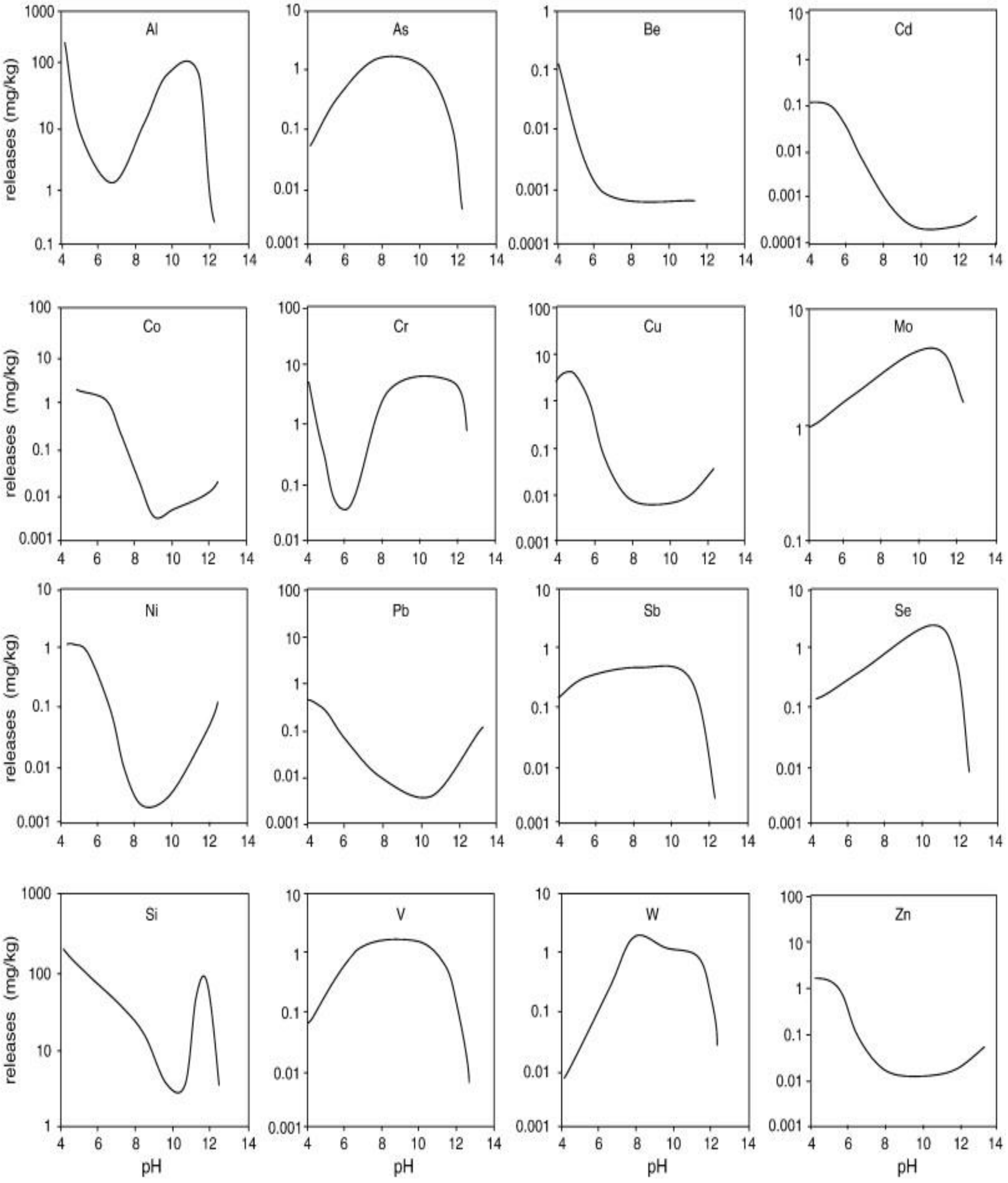

Figure 2-9 Leachability of metals vs. pH (Izquierdo et al. 2012)

Schramke (1992) showed that decrease in pH can also occur when carbon dioxide is introduced into alkaline fly ash leachate that has calcite (Eq. 2).

$$Ca2+ + CO2 + H2O \text{----}\rightarrow CaCO3(s) \downarrow + 2H+ \tag{2}$$

Water was synthesized to simulate the storm water and mixed with the fly ash samples. Two fly ash samples, Ash 159, and Ash I7, were prepared following the procedure mentioned in Schramke (1992) and Roy et al. (1984). Ash 159 was prepared by mixing 50 g of ash with 1 Liter of deionized water for 600 days at 25 ˚C. Ash I7 was prepared by adding 3,400 g of ash into 19 Liters of deionized water and mixed for 106 days at 22 ˚C in a vessel which was open to the atmosphere. Ash samples were synthesized using right amounts of solutes based on literature and mineralogical composition. pH results of Ash 159 showed an increase of pH to 10.3 after a 3-hour contact period indicating calcium oxide present in the ash reacted with water producing calcium and hydroxyl ions resulting in a pH decrease (Figure 2-10).

Carbon dioxide was introduced to the experiment which decreased the pH. Experimental results and REACT$^{®}$ software results followed the same trend (Fig. 2-1). As the contact time increased, pH drop was seen and after 80 hours, pH remained constant at 8.8. REACT $^{®}$ model was not able to simulate the same trend with the calcium which was accounted to precipitation of calcite preventing the model from detecting it. REACT $^{®}$ model showed similar trend with sulfate concentration. High initial concentration of sulfate was ascribed to the dissolution of calcium sulfate and the later constant concentration was credited to the lower solubility of gypsum (Figure 2-11).

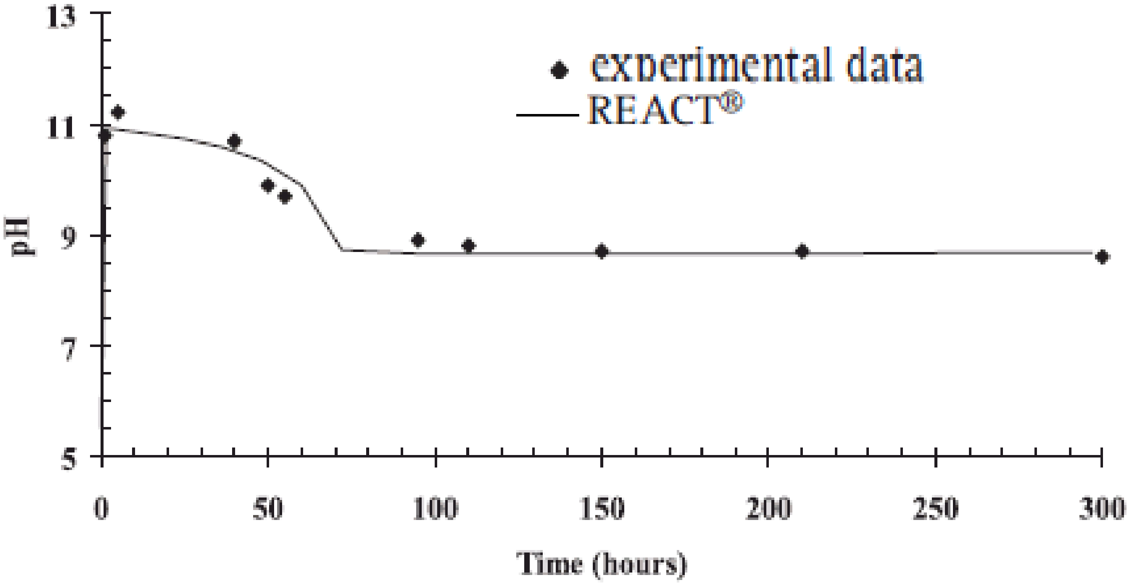

Figure 2-10 Change in pH for Ash 159 (W. R. Roy et al. 2011)

W. R. Roy et al. (2011) showed that the initial acidic or alkaline pH value is subjected to change in the environment due to geochemical buffering. Carbon dioxide can buffer the alkaline coal ash pH by producing H^+ ions that result in reduced pH. pH of acidic fly ash can be neutralized with the dissolution of oxides of calcium and magnesium. It was also found that alkaline fly ash leachate, when open to atmospheric carbon dioxide, its pH decreases to 8-9 due to carbonate buffering and calcite precipitation. Based on these results, REACT ®, can be used to simulate the field conditions and asses the pH changes of the leachate in the environment.

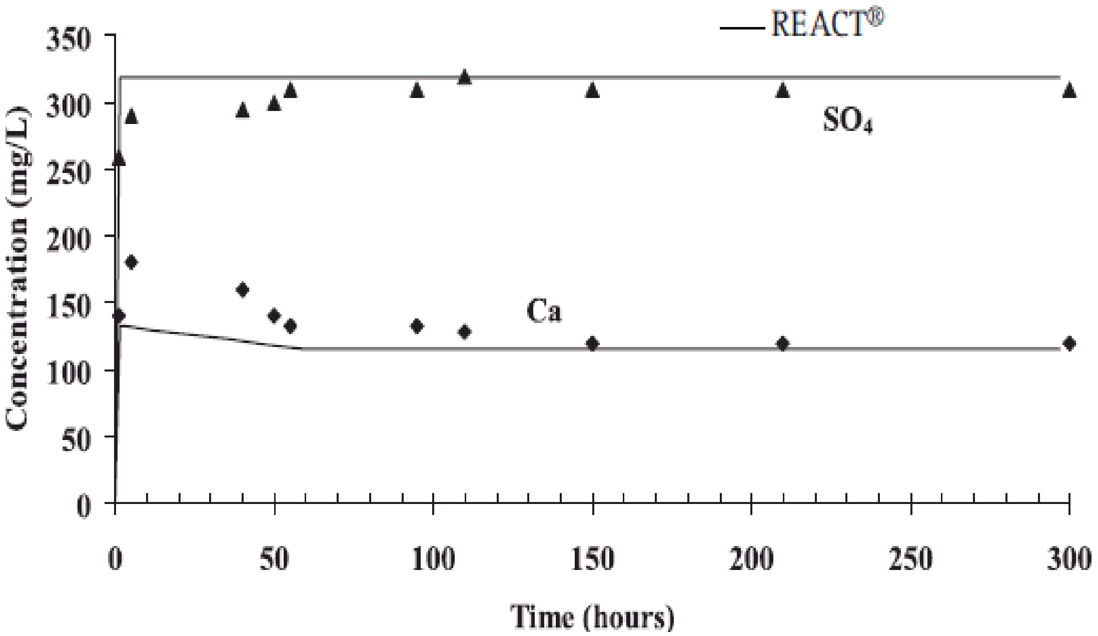

Figure 2-11 Concentration of calcium and sulfate of Ash 159 leachate against time (W. R. Roy et al. 2011)

2.4.3 *Effect of pH on Sorption*

P. Roy et al. (2011) investigated the removal of toxic metals such as chromium (Cr^{6+}), nickel, lead, and copper using Poly Acrylic Acid (PAA) and cross-linked Poly Acrylic Acid (XPAA). PAA forms complexes with divalent cations and cross linking the PAA i.e. XPAA removes the disadvantage of infinite swelling of PAA in aqueous solutions. This paper discusses the effect of pH, concentration, and interference of other ions, on the uptake of metals. PAA is one of the hydrogels that forms chelating groups that can uptake metal ions. Hydrogels have polymeric network with many adsorption sites. XPAA is stable in both acidic and basic solutions. To test the uptake of metal ions using the hydrogel polymers, 100 ppm standard stock aqueous solutions of chromium (Cr^{6+}), copper, nickel and lead were prepared by dissolving potassium dichromate, copper nitrate, nickel nitrate, and lead nitrate in ultrapure water separately. Different cross-linking PAAs were prepared with varying amounts of poly ethylene glycol diacrylate (PEGDA) which is the cross-linking agent. 50 mg of dried hydrogel polymer was mixed with 50 ml of metal solution with 100 ppm metal concentration and shaken for 2-hrs. Buffer solution was used to adjust the pH to 5. After the contact time, amount of metal ion in the extractant was tested. Even though XPAA had higher sorption capacity than PAA, increasing cross-linking agent further resulted in decreasing sorption of the metal ions. pH studies were done to show its effect on the sorption of metals on XPAA-10, limiting to a range of 2 to 8. Metals formed insoluble hydroxides at pH greater than 8. Within the tested range of 2-8, sorption increased with increasing pH (Figure 2-12).

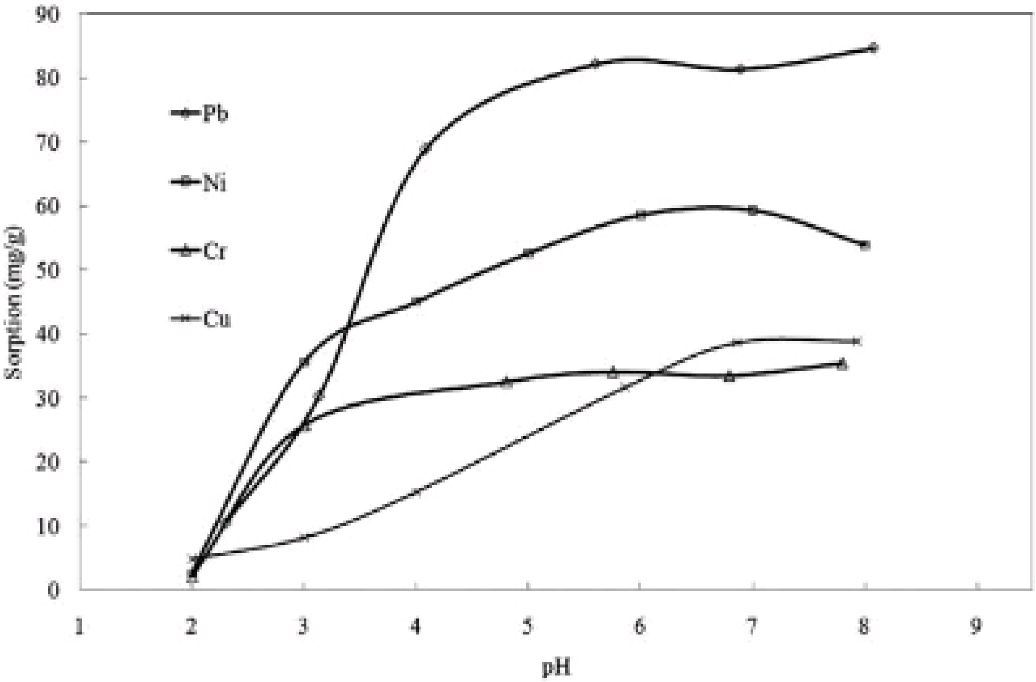

Figure 2-12 Effect of pH on sorption of metal ion (P. Roy et al. 2011)

2.4.4 *Adsorption Isotherm*

Different concentrations of metal ion solutions were mixed with 50 mg of dried hydrogel polymer for 24-hour at 30 ˚C at target pH of 5. The mixture was then filtered and extractant was analyzed for the metal ion concentration on ICP-OES (Inductively Coupled Plasma- Optical Emission Spectrometer). Adsorption isotherms were made by plotting the metal ion absorbed onto the hydrogel against the total metal ion concentration in the solution. Isotherm constants and the correlated coefficients of the plots were then calculated as per Langmuir and Freundlich isotherms.

Langmuir isotherm model uses the following equation (Equation 3).

$$\frac{C_e}{q_e} = \frac{1}{k_b} + \frac{C_e}{b} \qquad (3)$$

Freundlich model isotherm uses the following equation (Equation 4).

$$\log q_e = \log k_f + \frac{\log C_e}{n} \qquad (4)$$

where C_e is total metal concentration in the solution (mg/L), q_e is the absorbed metal concentration (mg/g), k and b are langmuir model constants, and k_f and n are Freundlich isotherm constants. Both Langmuir and Freundlich isotherms fit the data well and show the effect of positive sorption of the metals (Table 2-9).

Batch tests were performed with increasing amount calcium ranging from 10 to 200 ppm in the samples that had a 100 ppm of lead. Results show that sorption capacity remained constant with increasing calcium concentration. The reason was attributed to the stronger interaction of the hydrogel with the lead ions compared to the calcium ions.

Table 2-9 Langmuir Isotherm Model Coefficients for Metals (P. Roy et al. 2011)

Metal	**Langmuir Equation**		**K (mol^{-1})**	**b (mg/g)**	**R^2**
Cu	C_e / q_e	$0.33 + 0.01\, C_e$	0.043	68.96	0.94
Ni	C_e / q_e	$0.18 + 0.009\, C_e$	0.049	111.11	0.97
Pb	C_e / q_e	$0.25 + 0.01\, C_e$	0.040	99.00	0.97
Cr	C_e / q_e	$0.47 + 0.02\, C_e$	0.041	50.00	0.97

3. MATERIALS AND INSTRUMENTS

3.1 Materials

The raw materials used in this research included ponded coal ash, SAPs, ultra-pure water, standards for heavy metals, nitric acid, and sodium hydroxide. Testing was done in the Environmental Research Laboratory located in the at Energy Production & Infrastructure Center (EPIC) of the University of North Carolina at Charlotte.

3.1.1 Coal Combustion Residual Ponded Ash

Five wet CCR ash samples were collected from four unspecified coal ash impoundments in the southeast region of the U.S. The samples were collected and stored in five-gallon containers with lids. Two 5-gallon containers of each ash sample were collected.

3.1.2 Super Absorbent Polymers (SAP)

Total five SAP formulations supplied by Zappatec and Power Pellets supplied by Martlin Distributing were used the additives in the wet ponded ash. The key difference in the six SAPs used was the weight fractions of sodium polyacrylate, Portland cement, wood flour/fiber, and bentonite clay. Table 3-1 summarizes the compositions.

According to the manufacturer's Material Safety Data Sheet (MSDS), in 1% water, the pH of crosslinked sodium polyacrylate is 5.5-6.5, Specific Gravity is 0.4-0.7, and melting point is above 390 F. None of the polymers used in the testing had odor.

Table 3-1 Composition of the Polymers Used in the Testing

Polymer	**SAP (%)**	**Bentonite (%)**	**Portland Cement (%)**	**Wood Flour (%)**	**Wood Fiber (%)**
P100	100	-	-	-	-
P2	50	50	-	-	-
P4	50	25	25	-	-
P6	75	8.33	8.33	8.33	-
P7	25	-	-	-	75
Power Pellets	5	-	-	-	95

Polymer P100, which is 99% pure crosslinked sodium polyacrylate, is clear white in color, looks and feels like granular salt powder. Polymer P2 contains 50% Bentonite and has light grey color to it. Polymer P4 contains 50% SAP and equal quantities (25%) of Bentonite and Portland cement. Hence, it is grey in color and feels granular. Polymer P6 contains 75% SAP and equal amounts (8.3%) of Bentonite, Portland cement, and Wood Flour. P6 has a distinct wood dust texture and color. Power Pellets looks like wooden pellets with 5% SAP and 95% wood fibers. Polymer P7 contains 75% wood fiber with 25% SAP. Fig. 3-1 shows a photo of each of the six polymers evaluated in this study.

Super Absorbent Polymer (SAP) can be described as a unique hydrogel that is used in various industries. SAP can absorb relatively large quantities of water, compared to its mass. In comparison to other water absorbing materials like filter paper, polyurethane sponge, wood pulp, and cotton ball, absorbency capacity of SAP based on the percentage of weight is higher (Table 3-2). SAP absorbs water but does not dissolve in water.

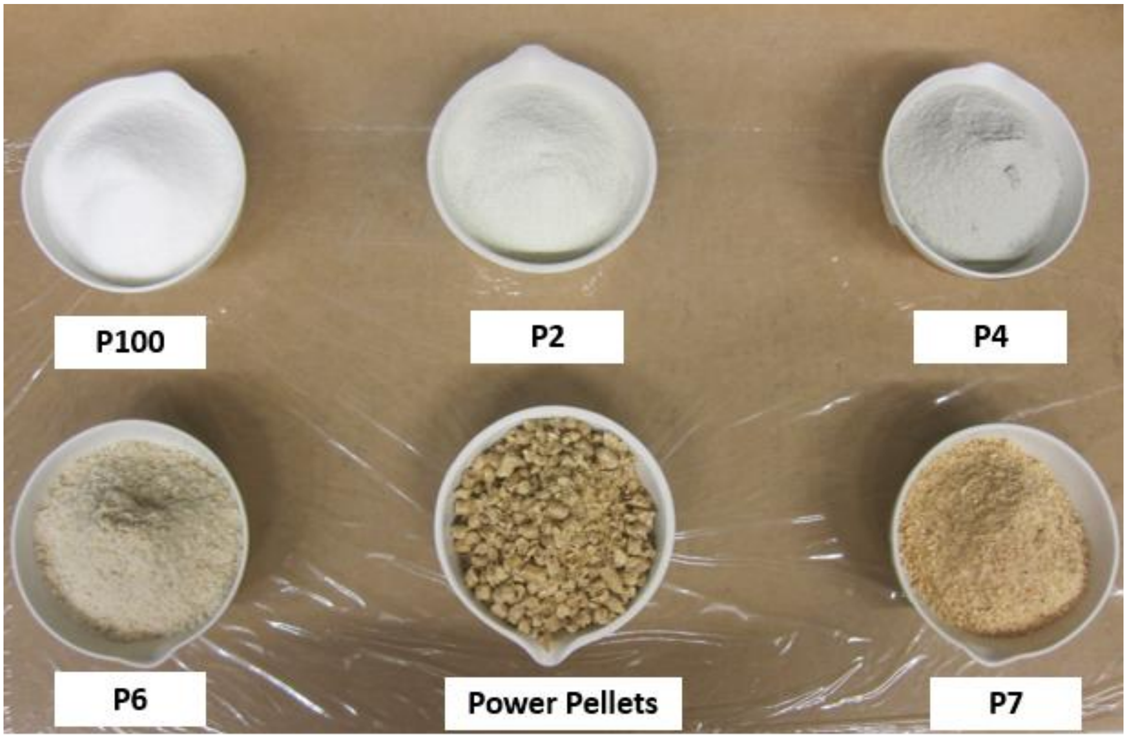

Figure 3-1 Visual representation of the polymers used in the testing

3.1.3 Ultrapure Water

Ultrapure water generated by Thermo Scientific™ Barnstead™ E-Pure™ Ultrapure Water Purification System was used for all test. Resistivity of the ultrapure water is ~ 18.2 M ohm-cm. All experiments were designed with the ultrapure water since this four-module filter system achieves total organic carbon level below 10 ppb and removes the particulates using 0.2 μm filter.

Table 3-2 Comparison of Water Absorbency Capacity

Absorbent Material	**Absorbency Capacity (% weight)**
Filter Paper	180
Polyurethane Sponge	1,050
Wood Pulp	1,200
Cotton Ball	1,890
SAP	20,200

3.1.4 Nitric Acid (HNO_3)

Nitric acid of 68-70% trace metal grade, concentrated nitric acid solution was obtained. Diluted acid solution was prepared with ultrapure water as needed. Various concentrations of the acid were used for different purposes. During the sample pH titration, 1N nitric acid was used. Concentrated nitric acid was used to digest the samples after extraction before running them on ICP-OES system. 2% nitric acid was prepared for usage as ICP-OES system rinse solution.

3.1.5 Potassium Hydroxide (KOH)

Potassium hydroxide solution at 1N strength was prepared using 56.11 g of solid potassium hydroxide in one liter of ultrapure water. 1N potassium hydroxide solution was used during the sample pH titrations.

3.1.6 Standard Trace Metals

1,000 µg/mL single element standard solutions prepared by Inorganic Ventures were obtained. Heavy metals that were used in the chemical analysis included arsenic, barium, boron, chromium, cobalt, selenium, and vanadium. These standards come in aqueous form dissolved in a matrix solution for stability. 2% Nitric acid is the most commonly found matrix but there are exceptions for elemental standards, for example boron, where water is the matrix.

3.2 Instruments and Equipment

The instruments and equipment used for sample preparation, testing, and analysis are described in this subsection.

3.2.1 Laboratory Apparatus and Equipment

For coal ash sampling, ceramic cubicles, and weigh machine AND GX-800 were used to weigh the exact amounts of coal ash. 100 ˚C oven was used to oven dry samples to measure moisture content. Large plastic trash bags were used to mix the coal ash with the ultrapure water to get the desired molding water content. For determining the mechanical strength parameters, standard proctor mold, Standard Proctor hammer, leveling tool, and plastic wrap were used. Compaction tools included Standard Proctor setup and Humboldt’s H-4165 Harvard Miniature setup. Shear strength measuring devices included Geo-Tester Pocket Penetrometer, ELE International Torvane, and Geo-Tac’s GeoJac Digital Unconfined Compression Testing System. Nalgene 250 mL and 2500 mL capacity HDPE plastic bottles and Bodine Electric Company’s gear motor tumbler at 28 rpm were used for mixing. For filtering the samples. conical flasks, funnel base, and GH polypro 47 mm, 0.45 µm hydrophilic polypropylene membrane filter were used. For samples with less solids concentration, Thermo Scientific 30 mm polypropylene syringe filters with 0.45 μm membrane was used to directly extract filtered samples without vacuum filtration apparatus. For chemical analysis, Agilent's 5100 Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES) was used to quantify the metal concentration in the samples. To test and store the extracted sample solutions, 15 mL and 50 mL plastic centrifuge tubes from VWR were used.

4. METHODOLOGY

The methodology used to execute the experiment is presented in two phases: Phase I - Mechanical Strength Analysis, and Phase II – Heavy Metals Stabilization Analysis. Sample preparation and testing procedures followed are presented in this section.

4.1 Phase I – Index and Mechanical Properties Evaluation

First phase of this research focused on the evaluation of shear strength of coal ash samples amended with SAPs and samples without SAP used as controls.

4.1.1 Coal Ash Classification

All the five coal ash samples obtained from undisclosed coal ash impoundment sites were of Class F type and have been hydrated in the field for many years. Exact age of the ash is unknown.

4.1.2 Moisture Content

Moisture content of the coal ash samples was determined according to ASTM-2216 (2010).

4.1.3 Specific Gravity

Specific gravity of the coal ash samples was determined according to ASTM-D854 (2014).

4.1.4 Paint Filter Liquids Test

The paint filter liquid test was done according to the guidelines of P. F. L. EPA (2004) to determine the free liquids present in the wet coal ash samples. Results of the paint filter test are used to assess disposal of the waste in a solid waste landfill. A plastic funnel was placed on a 50mL measuring cylinder and a filter paper with mesh number 60 was placed in the funnel. Representative coal ash sample passing through 0.375-inch sieve weighing 100 g was placed in the funnel carefully. Sample was then allowed to drain for 5 minutes. If any liquid drained from the sample into the measuring cylinder in that 5-minute time period, it was noted that the sample had free draining liquids. If liquid collects in the cylinder, then the sample has failed the paint filter liquids test.

4.1.5 Compaction Methods

Coal ash samples were compacted before shear strength tests were performed. Two methods for compaction were used: Standard Proctor Test using 4” by 4” molds; and Harvard Miniature Compactor; H-4165 Humboldt using 1.26” by 2.8” sample mold.

a. Standard Proctor Compaction

Coal ash samples were compacted at the Standard Proctor effort as per (ASTM-D698 2012). The samples compacted in the Standard Proctor molds were subjected to the Pocket Penetrometer and Torvane tests to measure the undrained compressive and shear strengths. The ash sampled blended with the SAPs at the desired mass fractions were compacted in 3 lifts, each lift subjected to 10 blows of the 5.5-lb drop hammer.

b. Harvard Miniature Compaction

Harvard Miniature Compaction Apparatus is a mini-scale compaction device used for compacting smaller samples having dimensions 1.25” x 2.8” (volume ~ 1/450 ft^3) using a 20-lb spring-loaded hammer. Similar to the procedure outlined for Standard Proctor compaction effort in the previous section, coal ash was filled in the Harvard miniature mold in 3 lifts. Each lift was compacted using 12 blows of the spring-loaded hammer to achieve about the same density as the samples compacted using the Standard Proctor effort. The samples compacted using the Harvard Miniature device were subjected to the unconfined compressive strength tests.

4.1.6 Sample Preparation and Testing

All coal ash samples arrived at in-situ water contents that ranged from moist to soaking wet. The minimum water content at which each ash sample fails the paint filter test was obtained by subjecting the sample to increasing water contents using tap water. Once that water content was established, additional 10% tap water was added to make the sample extremely wet to simulate a conservative field scenario. SAPs were added to the ash samples at various weight fractions and mixed thoroughly using a spatula. Due to moisture adsorption, most samples after mixed with SAPs visible “dried up” and met the paint filter test (Figure 4-1). The samples were then compacted in the Standard Proctor and Harvard Miniature molds for running shear strength tests.

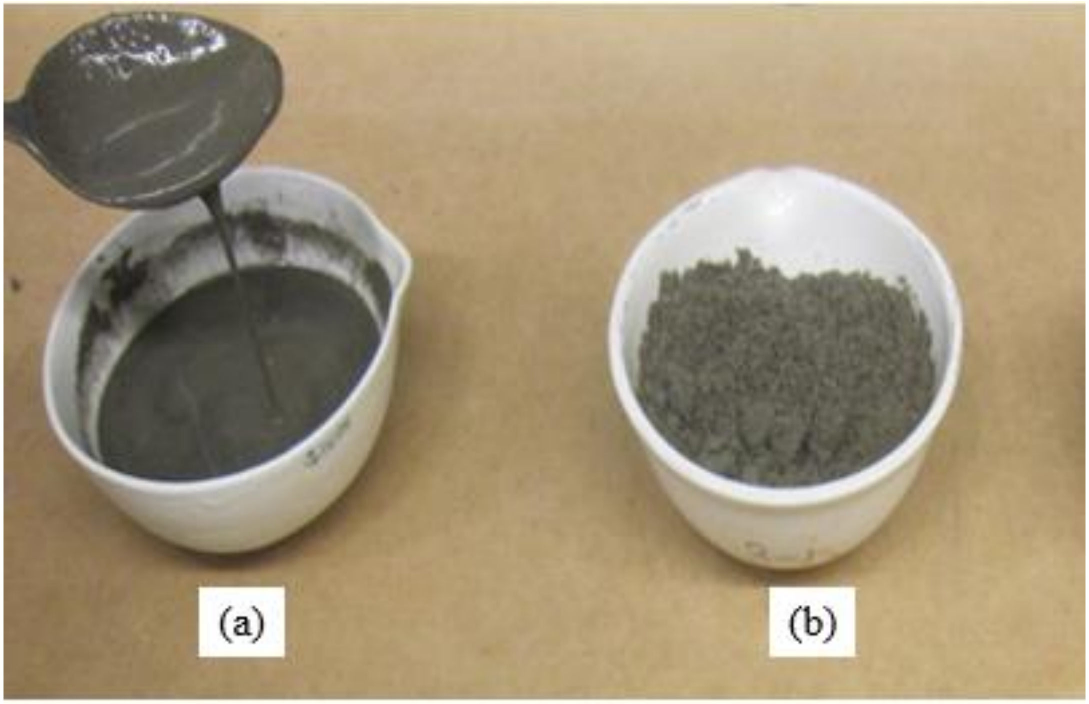

Figure 4-1 Coal ash sample failing Paint Filter Liquids Test (a); and passing paint filter test 15 minutes after mixing the SAP (b).

The following mass fractions of SAPs were added to the wet ash samples.

a. SAPs P100, P2, P4, and P6 at 1% and 2 % of dry mass fraction of the wet coal ash;
b. Power Pellets were evaluated at 2%, 4%, and 6% of dry mass fraction of the wet coal ash; and
c. SAP P7 was evaluated at 2% and 4% of dry mas fraction of the wet coal ash.

The samples were compacted in Proctor mold and Harvard Miniature molds. The samples in the Proctor molds were used for the measurements of undrained cohesion and shear strength using Geo-Tester Pocket Penetrometer and ELE International Torvane shear device.

Smaller Harvard Miniature samples tested for unconfined shear strength using Geo-Tac's GeoJac Unconfined Compression Testing device.

Both larger and smaller samples were tested using the above-mentioned methods after a pre-determined curing time as summarized in Table 4-1.

Table 4-1 Frequency of Testing Protocol

Polymer	**Curing Time After Polymer Addition**
P100	1 hour
P2	1, 24, 48, 72 hours
P4	1, 24, 48, 72 hours
P6	1, 24, 48, 72 hours
P7	1, 24, 48, 72 hours
Power Pellets	1, 4 hours

a. Pocket Penetrometer

A Geo-Tester Pocket Penetrometer was used to measure the unconfined compressive strength using the 15-mm diameter or 10-mm diameter stainless steel foot. The device the resistance to penetrating the surface of the sample for a fixed distance using the selected foot. Pocket Penetrometer is equipped with various sized penetrating foots. However, 15 mm and 10 mm were used to test samples. Fig. 4-2 shows the use of

Pocket Penetrometer on the surface of a coal ash sample mixed with an SAP compacted in a Proctor mold.

Figure 4-2 Pocket Penetrometer

b. Torvane Shear Device

ELE International Torvane Shear device (model number 26-2261 CL-600A) was used to measure the undrained cohesive strength of the compacted samples using the most sensitive vane (largest vane). The instrument has the capacity to measure shear strength up to 1 Kg/m.^{2} During the measurement, Torvane was gently inserted into the sample perpendicular to the surface. With constant pressure, the handle was rotated clockwise until the rotation does not yield any further gain on the dial gauge reading. Fig. 4-3 shows how the Torvane was used in this project.

Figure 4-3 Torvane Shear Device

c. Unconfined Compression Testing

Geo-Tac’s GeoJac Digital Unconfined Compression Testing System was used to test the smaller samples (1.28” x 2.6) compacted using the Harvard Miniature device for measuring unconfined compressive strength. Figure 4-4 shows a sample compacted and extracted using the Harvard Miniature device. Figure 4-5 shows the sample being tested for Unconfined Compression strength.

The instrument’s software allows the user to define the strain limit to end the test run automatically or to run the test manually so that the test can be ended after visible sample failure. After few trial and error experiments, the strain limit for the coal samples of this research was set to 15%. The strain rate for loading was maintained constant for all tests at 0.05 inch/min.

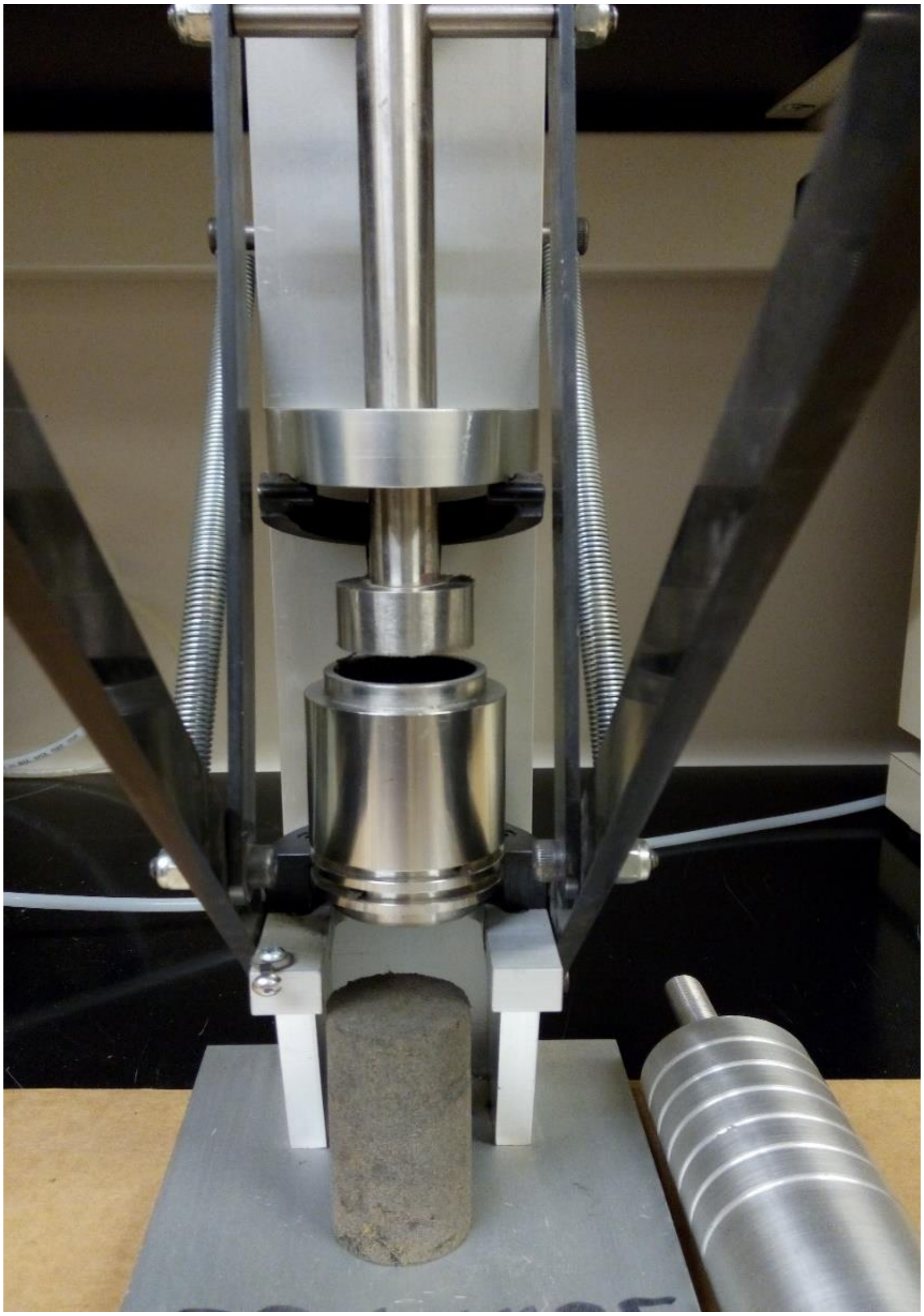

Figure 4-4 Harvard Miniature samples extraction for Unconfined Compression Testing

Figure 4-5 Unconfined Compression Testing

4.2 Phase II – Heavy Metal Stabilization Evaluation

Second phase of this research focused on the stabilization or uptake of specific heavy metals using the SAP added to the coal ash samples to explore reduction in leaching of heavy metals from the coal ash into the ground water.

Phase-II analysis includes series of batch tests to simulate liquid to polymer and coal ash to polymer partitioning of selective heavy metals. These batch tests will be discussed in this sub section. While there were variations among various batch tests carried out, the liquid to solid ratio was 10 mL extractant per gram of dry solids (about 10 to 1).

4.2.1 Synthetic Leachate Preparation

In order to evaluate the stabilization of uptake of heavy metals by the SAPs, one set of tests were carried out with synthetic leachate containing heavy metals listed in Table 4-2. The other set of tests consisted of using ponded coal ash from an undisclosed site which contained some of the heavy metals. The synthetic leachate was prepared using 18 M-ohm ultrapure water and standard trace elements bought from Inorganic Ventures were added to target aqueous phase concentration of 0.5 mg/L. Volumes of stock solutions used to prepare the synthetic water is mentioned in Table 4-2.

Table 4-2 Preparation of 1 Liter of 0.5 mg/L Synthetic Leachate

Element	**Stock Concentration (mg/L)**	**Volume Used (mL)**
Arsenic	1001 ± 5	0.499
Barium	996 ± 4	0.502
Boron	1002 ± 6	0.499
Cobalt	998 ± 3	0.501
Selenium	1003 ± 4	0.498
Vanadium	1000 ± 5	0.500

4.2.2 Effect of pH

The mobility of heavy metals is dependent on the pH of the environment surrounding the heavy metals. Hence, in order to evaluate how the SAPs, influence the pH of the mix, samples were prepared by mixing 20 g of environmental grade dry Ottawa sand with 200 mL of synthetic leachate containing arsenic, barium, boron, cobalt, selenium, and vanadium at 0.5

mg/L. This sample preparation is similar to Vanderbilt's Leaching Evaluation and Assessment Framework test 1313 (EPA 2009). For this phase of work only two SAPs, P100 and P7, were evaluated due to the results from Phase of the project and due to budget constraints. P100 was added to the Ottawa sand – synthetic leachate mix at 0.5%, 1%, and 2% and P7 was added at 1%, 2%, and 4% of the dry weight of sand. After the addition of the polymer for three identical samples for a given weight fraction of the polymer, the pH of mix was targeted to reach 4, 7, and 10 by adding acid, base or both. After recording the initial pH within 0 to 15 minutes of the mix, the mix was placed on a tumbler for 24 hours and pH was recorded after 24 hours.

4.2.3 Individual Heavy Metal Evaluation

The set of tests carried out used only one heavy metal at a time in the synthetic leachate. Ottawa sand was not added to the mix either. Thus, separate aqueous solutions were prepared for arsenic, barium, boron, cobalt, selenium, and vanadium, each at 0.5 mg/L. 200 ml of synthetic leachate was mixed with following mass of P100 and P7: 0.1, 0.2, and 0.4 g of P100 and 0.2, 0.4, and 0.8 g of P7.

4.2.1 Heavy Metal Stabilization Evaluation with Coal Ash

These tests consisted of using ponded as from one of the undisclosed sites and carrying out heavy metal extraction tests with and without the SAPs. The tests were carried out by mixing 829 g of oven dried ponded coal as with 1171 mL of 18 M-ohm ultrapure water in a 2 L HDPE container and placing it on a rotation tumbler for 3 days.

Solutions were then extracted and filtered to separate the coal ash from the leachate. The solution served as a stock of leachate from the coal ash. To this leachate, P100 and P7 were added at 0.5%, 1%, and 2% and 1%, 2%, and 4% of dry mass fraction of coal, respectively. The mix containers were subjected to thorough mixing by placing on the tumbler for 3 days. After 3 days, the solutions were filtered to remove the polymer in gel form, suspended particles, and precipitates from the aqueous solution. The aqueous solution was subjected to analytical testing to quantify the concentration of heavy metals using ICP-OES.

4.2.2 Contact Time and Extraction

It was observed during the initial testing phase that the pH of the solution changes after the SAPs are added. However, the pH change was time dependent and it took anywhere from few minutes to few hours for the pH to stabilize. Hence, for all tests, "initial" pH was measured and it refers to the pH measured within 15 minutes after the SAP was added and manually mixed. The pH was also measured after 24 hours or 3 days depending the test after the mix was placed on a tumbler to allow the reactions to occur and the pH to stabilize (Figure 4-6).

4.2.3 Preparing Standards

Standards were used to calibrate the analytical equipment (ICP-OES) that was used to measure the concentrations of arsenic, barium, boron, cobalt, selenium, and vanadium. For each heavy metal, five standard solutions were prepared at concentrations ranging from low to high. 2% nitric acid solution was used to dilute the 0.5 mg/L stock of the heavy metal and prepare the standards.

4.2.4 Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES)

ICP-OES was used to measure the concentrations of heavy metals in the aqueous solutions of samples extracted from the mixes (Figure 4-7). The samples were tested as per the procedure presented in the equipment manual. System was flushed with 10% nitric acid before each of the test run. All standards, method blanks, and samples were all run in a batch mode. ICP-OES analysis was carried out both in axial and radial mode of wavelength detection and the average value of the heavy metal concentration was calculated and presented in Section 5 of this thesis.

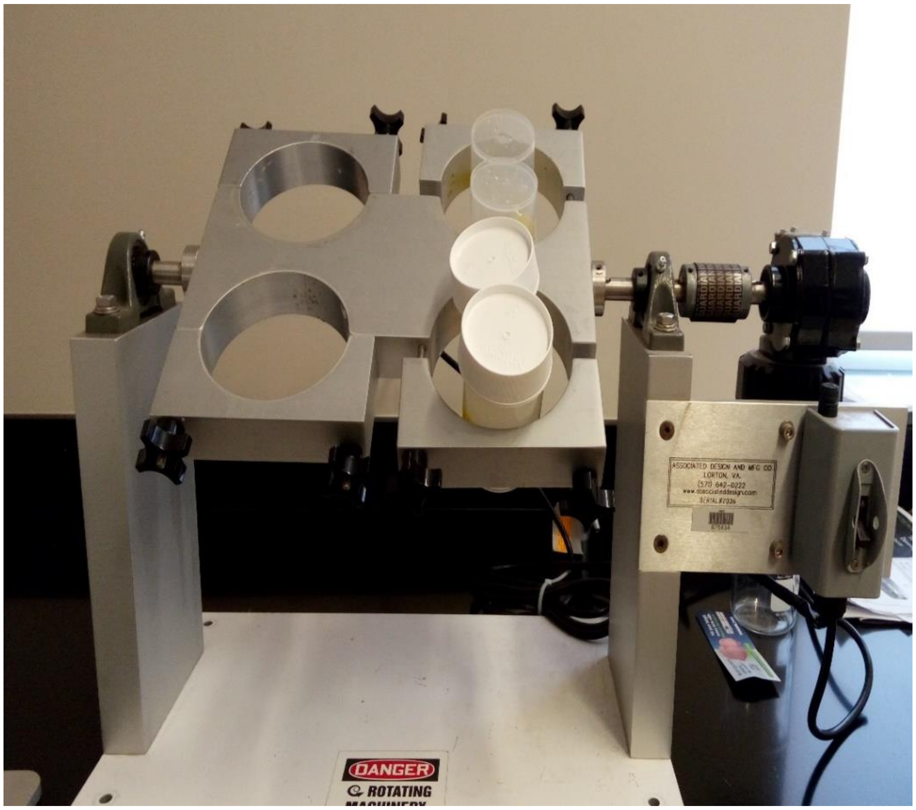

Figure 4-6 Rotating tumbler to mix the samples

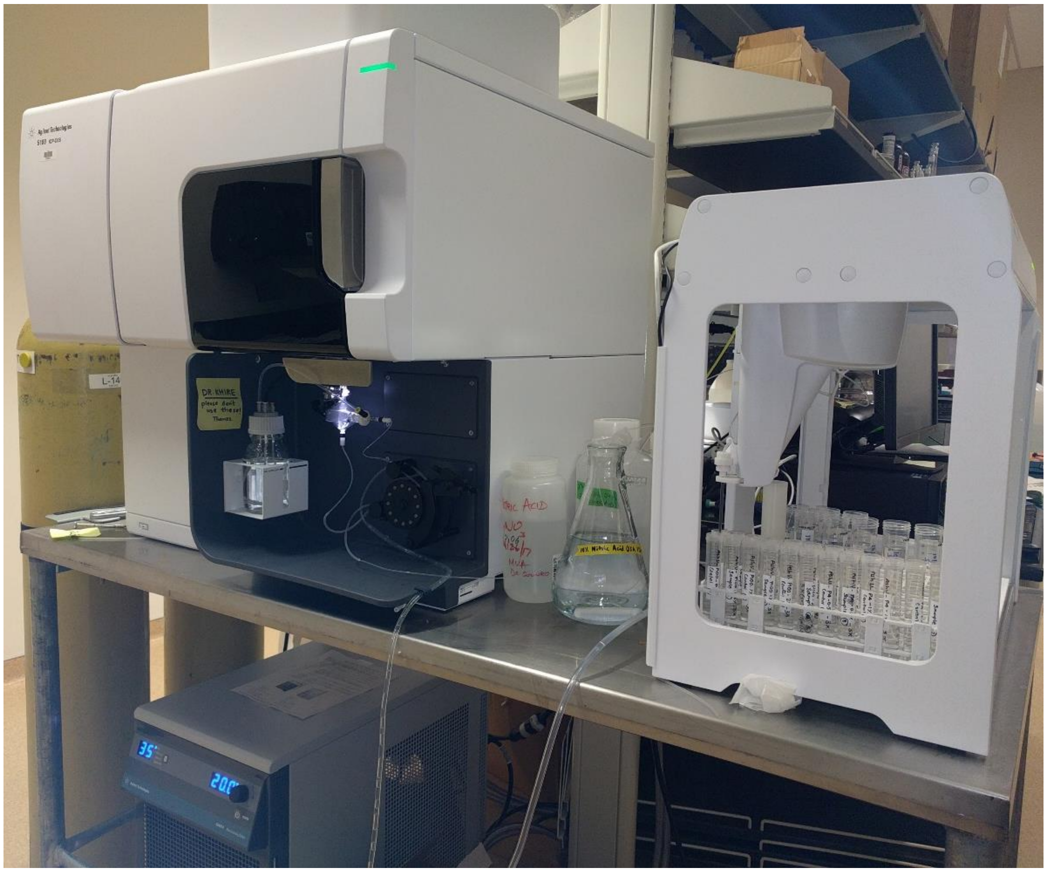

Figure 4-7 Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES)

5. RESULTS AND DISCUSSIONS

The results of Phase I (index and mechanical properties) and Phase II (heavy metal stabilization evaluation) are presented in this section.

5.1 Phase I – Index and Mechanical Properties Evaluation

5.1.1 Moisture Content

The “as delivered” or initial water contents of all ponded ash samples were measured. The water contents at which the samples failed the paint filter tests were also measured. The molding water content is the water content at which the ash samples were stabilized with the addition of SAPs. The molding water content is 10% greater than the water content at which the wet ash failed the paint filter test. The initial and molding water contents for the five ponded ashes are presented in Table 5-1. These water contents are reported as gravimetric water contents calculated based on the dry basis.

Table 5-1 Initial and Molding Water Content of Coal Ash Samples

Coal Ash Sample	**Initial Water Content (%)**	**Molding Water Content (%)**
Coal Ash C	37 %	70%
Coal Ash A	48%	65%
Coal Ash M1	37%	60%
Coal Ash M2	34%	58%
Coal Ash U	34%	70%

All SAPs except the power pellets stabilized the moisture in the ash samples to meet the paint filter test at the weight fractions tested in this study. Power pellets non- uniformly absorbed the excess moisture. Hence, while portions of the samples were free of excess water, the over sample did not meet the paint filter test. Hence, power pellets were eliminated in further testing during this study.

5.1.2 Specific Gravity

Specific gravity of coal ash samples measured in accordance with ASTM-D854 (2014) are presented in Table 5-2.

Table 5-2 Specific Gravity of Coal Ash Samples

Coal Ash Sample	Specific Gravity
Coal Ash C	2.39
Coal Ash A	1.80
Coal Ash M1	2.33
Coal Ash M2	2.24
Coal Ash U	2.08

5.1.3 Compaction Properties

Table 5-3 presents the unit weights at which the coal ash samples blended with the SAPs were compacted for performing all strength tests using Standard Proctor and Humboldt Harvard Miniature devices. These unit weights correspond to the Standard Proctor effort.

Table 5-3 Dry Unit Weight of Compacted SAP Blended Coal Ash Samples

Coal Ash Sample	**Dry Unit Weight (lb/ft^3)**
Coal Ash C	60
Coal Ash A	50
Coal Ash M1	54 – 58
Coal Ash M2	55 – 58
Coal Ash U	44 - 50

5.1.4 Pocket Penetrometer

Undrained cohesion measured using Pocket Penetrometer for Ash A and C mixed with SAPs P100, P2, P4 & P6 are presented in Fig. 5-1. Among the SAPs tested, P4 and P6 yielded the greatest undrained cohesion and the values improved as the samples cured Both P4 and P6 contained the Portland cement and cement tends to gain strength as it cures. Nevertheless, the 1-hr undrained cohesion of all samples ranged from 1 to 2 psi and it increased to 3 to 4 psi for P4 and P6 in additional 2 to 3 days of curing. This is a significant gain in the shear strength of the ash when compared to the slurry state of the ash just before the SAP was added.

Undrained cohesion measured using Pocket Penetrometer for Ash M1, M2, and U mixed with SAPs P100, P4 & P7 are presented in Fig. 5-2. Among the SAPs tested, P7 yielded the highest undrained cohesion and the values improved as the samples cured Both P4 and P7. Curing time has no effect on the undrained cohesion of ash mixed with P100. P7 contains 75% wood flour. Wood flour slowly absorbs the excess moisture and expands. This time dependent phenomenon helps in rise the undrained shear strength as a function of curing time.

Nevertheless, the 1-hr undrained cohesion of all samples ranged from 2 to 4 psi and it increased to 4 to 6 psi for P7 in additional 2 to 3 days of curing.

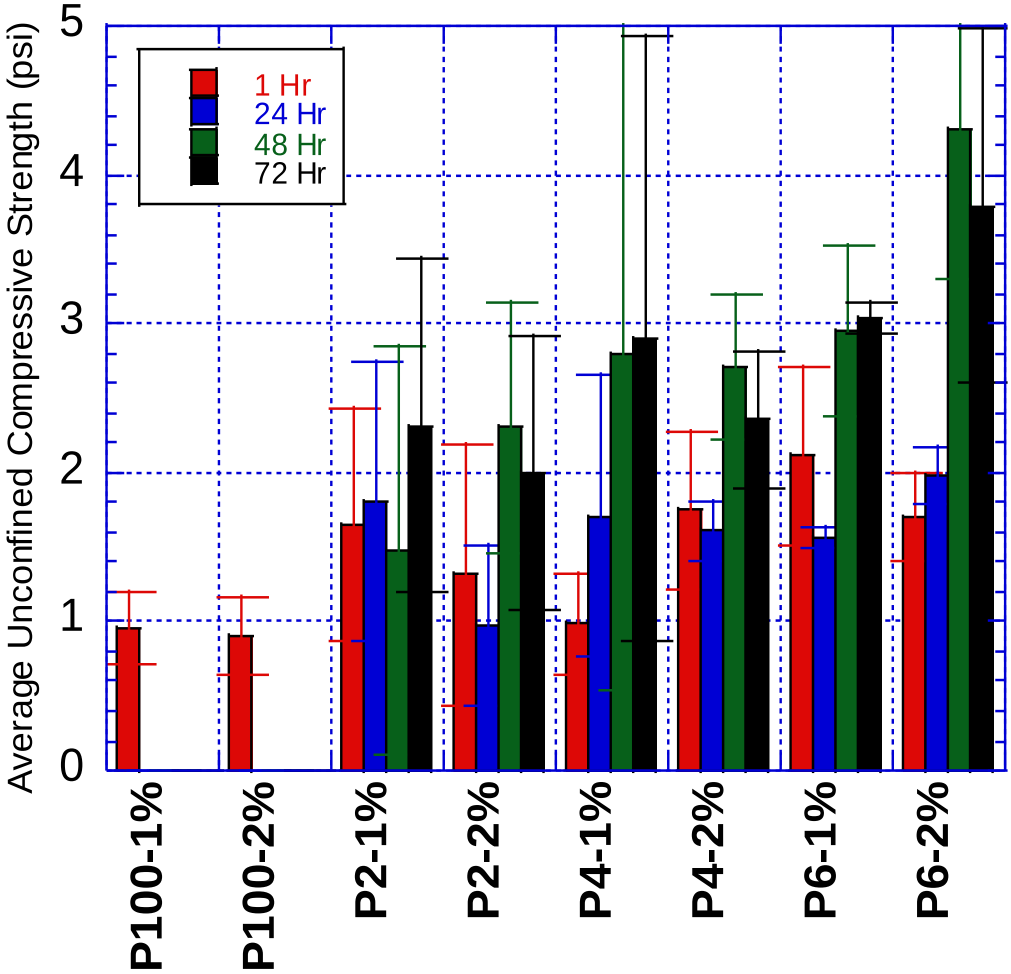

Figure 5-1 Average unconfined compressive strength measured by Pocket Penetrometer for Ash A & C

The results presented in Figs. 5-1 and 5-2 also indicate that increasing the weight fraction of the active polymer sodium polyacrylate does not necessarily yield greater shear strength.

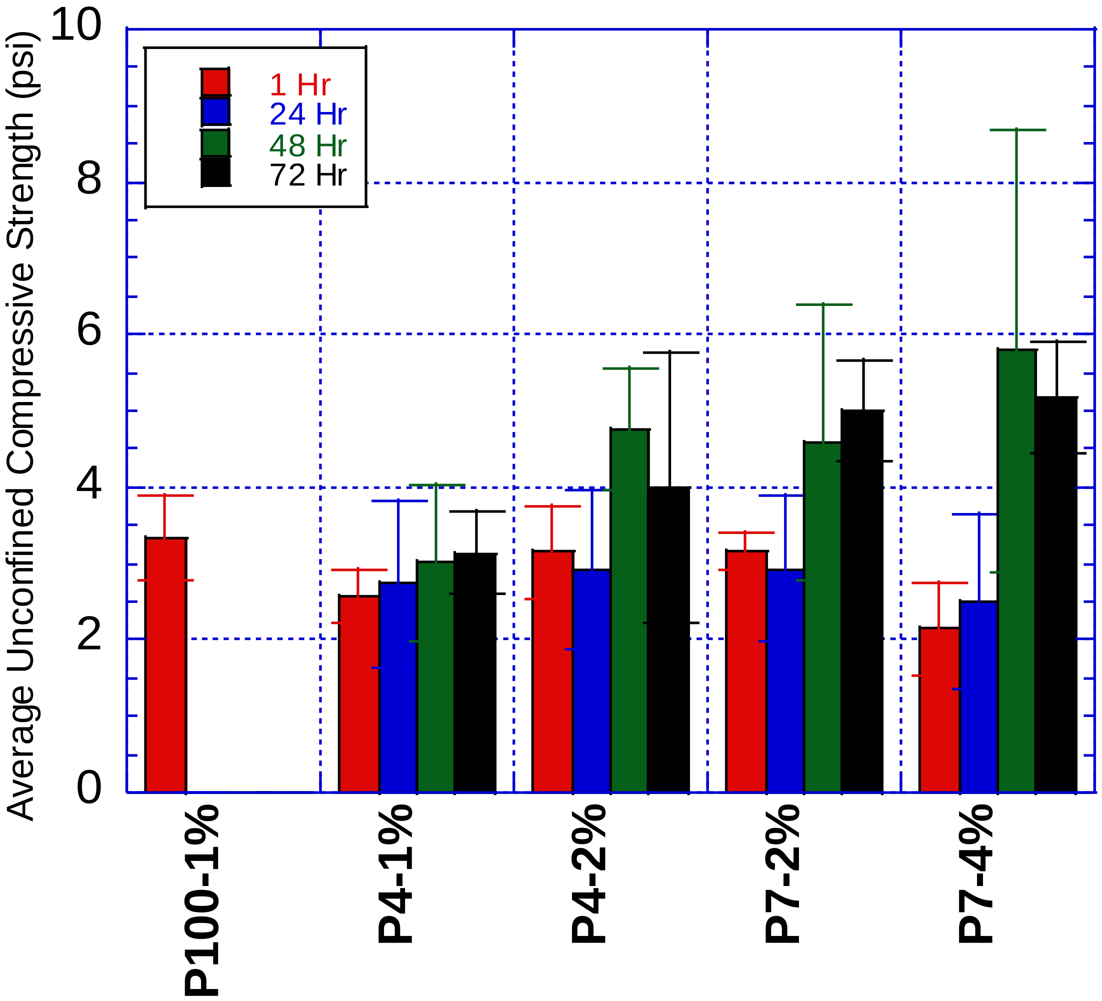

Figure 5-2 Average unconfined compressive strength measured by Pocket Penetrometer for Ash M1, M2 & U

5.1.5 Torvane Shear Device

Fig. 5-3 shows the average undrained cohesion measured by Torvane for Ash A and C. For coal ash samples A & C, the average undrained cohesion is about 0.5 to 1 psi and maximum undrained cohesion is about 2 psi. There is very little or no difference and no trends in undrained cohesion due to the duration of curing. Wood flour in P6 composition may have helped in achieving slightly higher undrained cohesion for P6 compared to the other SAPs.

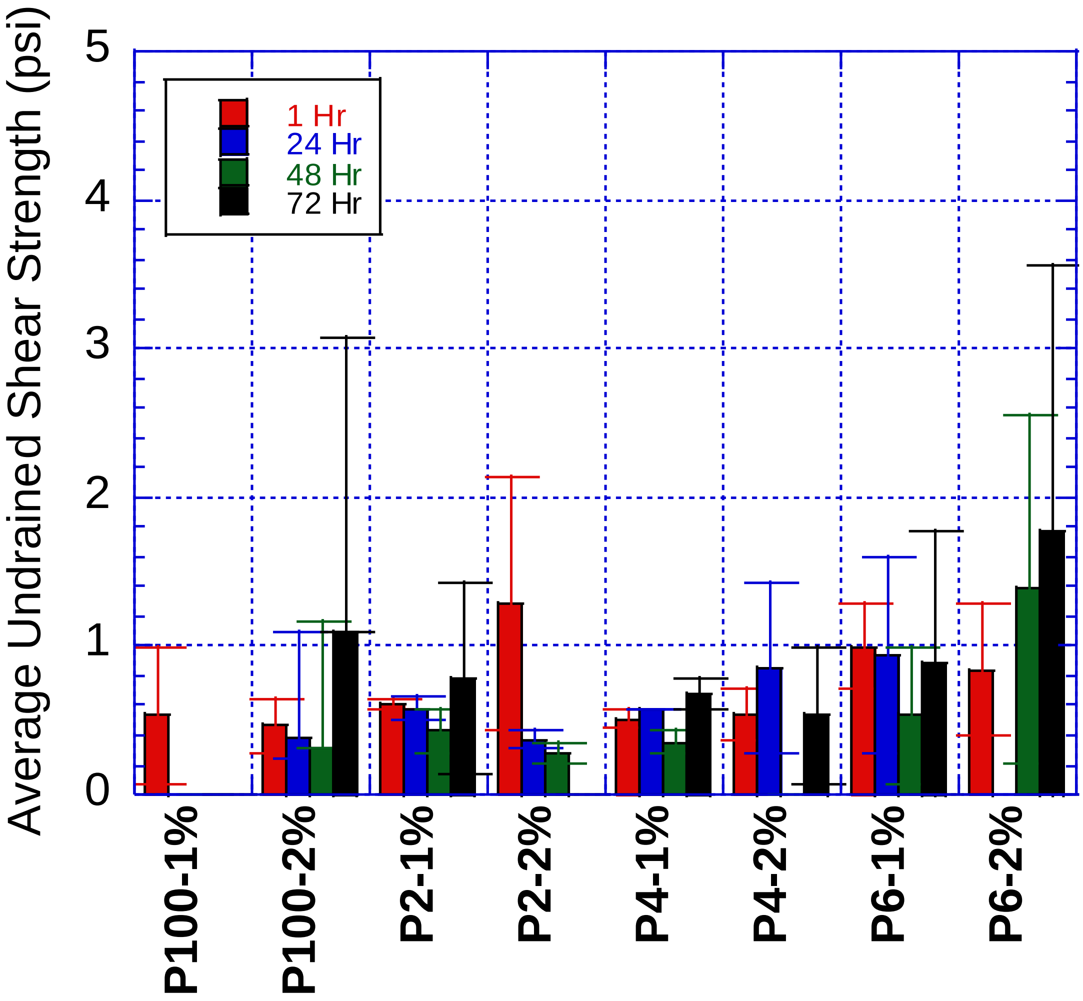

Figure 5-3 Average undrained shear strength measured by Torvane for Ash A & C

Similar to Ash A and C, averaged undrained cohesion for ash samples M1, M2 and U measured using Torvane show no significant gain in shear strength due to the SAP (Fig. 5-4). Moreover, samples containing higher polymer content showed lower cohesion.

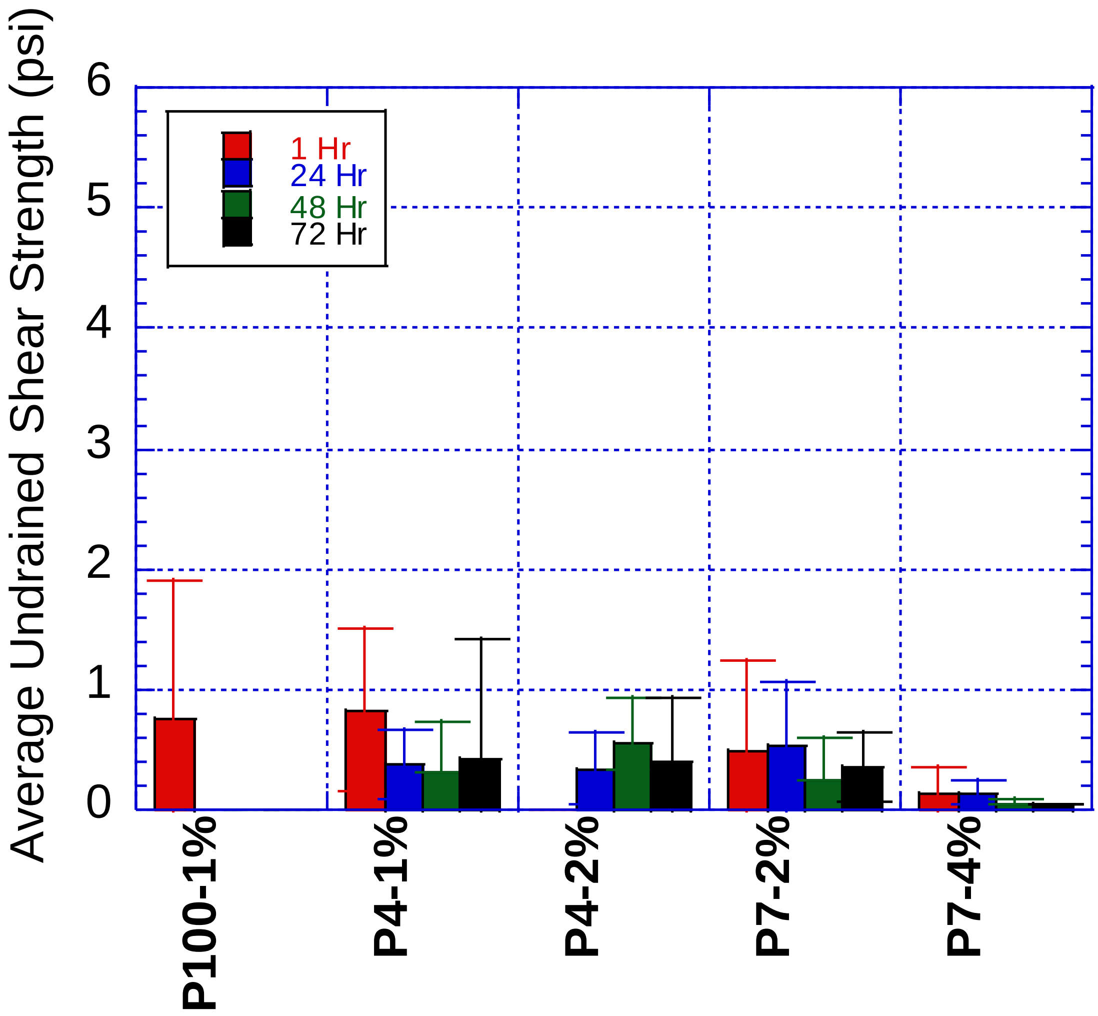

Figure 5-4 Average undrained shear strength measured by Torvane for Ash M1, M2 and U

Unconfined compression strength measured using the loading frame is considered as the industry standard for assessing undrained or short-term shear strength of soils or soil-like materials (Valenti et al. 1984). However, usually the UC strength is measured on samples having diameter of ≥ 2.8 inches. In this research, due to the limitation associated with the quantities of ash that was obtained for testing allowed smaller samples.

Fig. 5-5 shows the average UC strength for Ash A and C. The UC strength ranged from 1 to 2 psi. These values are similar to those measured by the Pocket Penetrometer. Curing time did not influence the UC strength. There was very little to no difference in the UC strengths due to various SAPs.

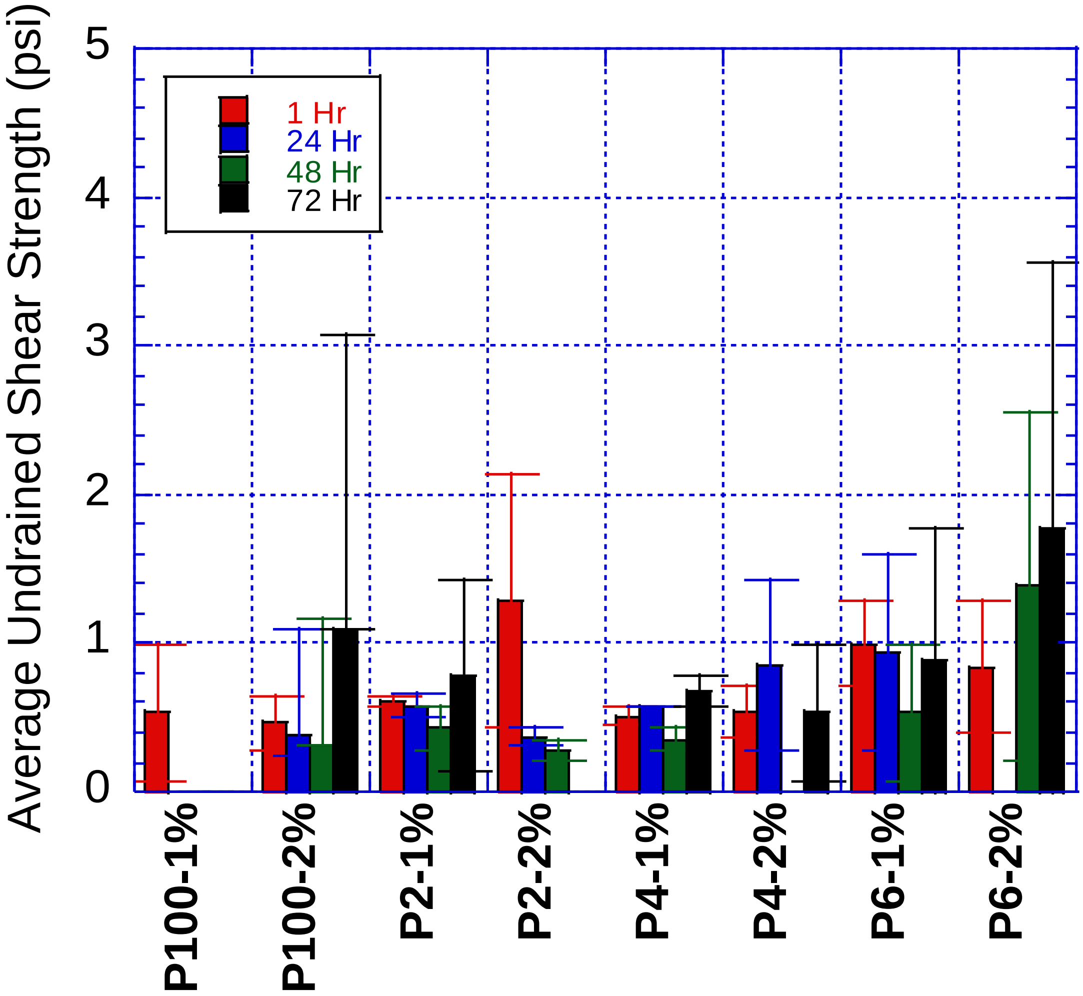

Figure 5-5 Average unconfined compression strength for Ash A & C

Fig. 5-6 shows the average UC strengths for Ash M1, M2 & U. For these Ash, SAP P4 and P7 yielded higher UC strengths (2 to 3 psi) compared to SAPs P2, P4 and P6 yielded for

Ash A and C (1 to 2 psi). P4 and P7 yielded similar UC strengths. While the weight fractions of P7 were greater than P4, P4 contains about 2 times more sodium polyacrylate. Hence, P4 and P7 were compared at the same weight fraction of sodium polyacrylate. Both P4 and P7 performed better than P100. This indicates that the wood flour combined with sodium polyacrylate helps in improving the shear strength of the ash.

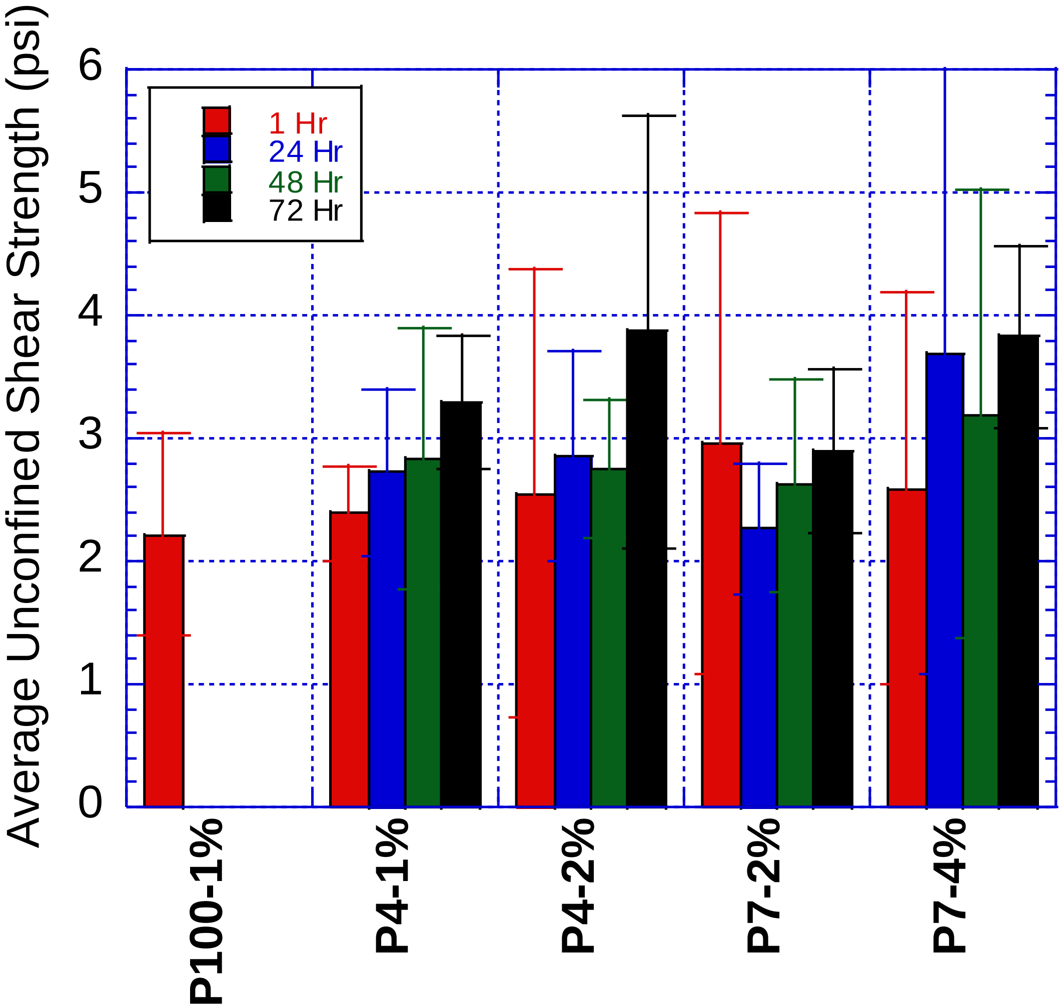

Figure 5-6 Average unconfined compression strength for Ash M1, M2 & U

5.1.6 Unconfined Compressive Strength vs. Molding Water Content

UC strength of Ash U was measured without the addition of any SAP at water contents 36% and higher till the sample had no strength. Fig. 5-7 shows the results. As the molding water content was increased, the shear strength decreased. The highest UC strength was 6 psi at water content equal to 36%. The UC strengths presented in subsection 5.6 for ash blended with the SAPs were all considerably less than 6 psi. Thus, further testing is needed to optimize the strength of the ash if greater shear strengths are desired.

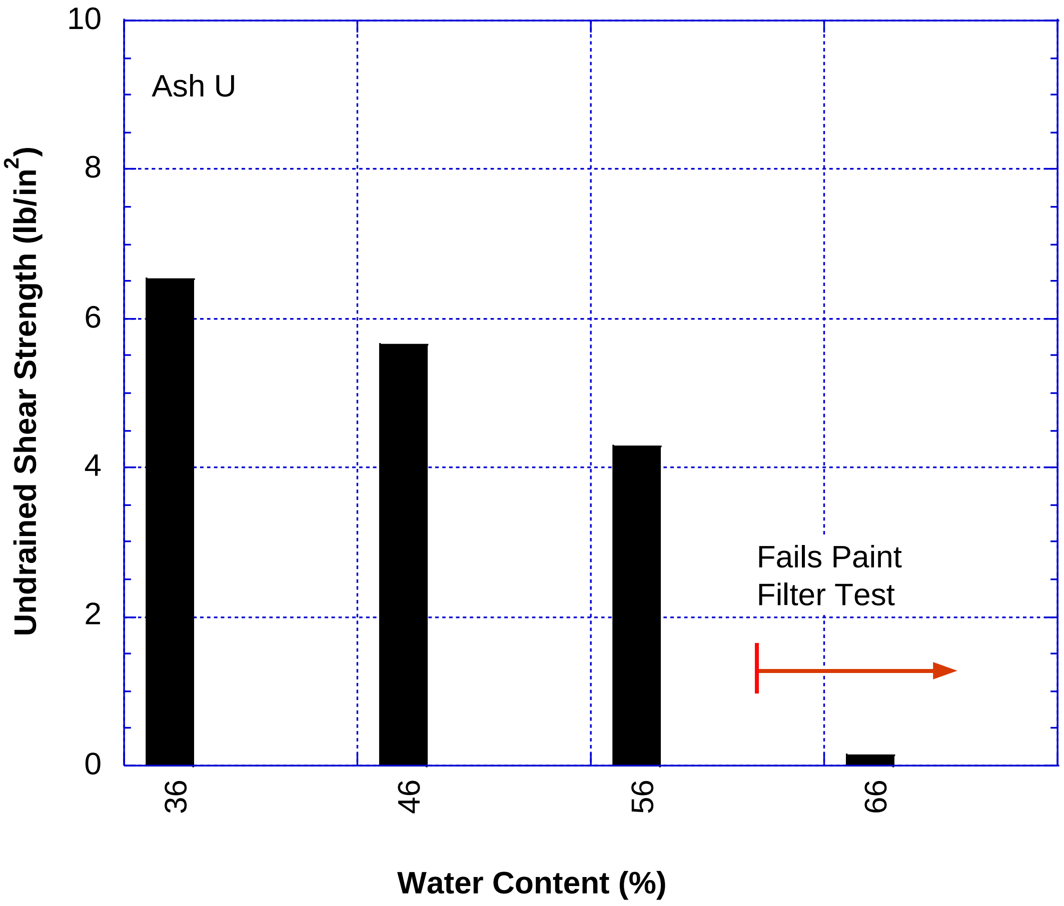

Figure 5-7 Unconfined compressive strength vs molding water content for Ash U without the addition of SAP

5.2 Phase II – Heavy Metal Stabilization Evaluation

5.2.1 Effect of pH

Figure 5-8 shows the pH of the samples containing synthetic leachate, Ottawa sand and SAP P100 at 0 to 2%. The target pH of the samples was 4, 7 and 10. The target pH was achieved by adding 1N nitric acid and/or 1 N potassium hydroxide. The pH immediately after mixing (within 15 minutes) vs. after 24 hours on a rotating tumbler are presented in Fig. 5-8. When P100 is present, irrespective of the weight fraction of P100 and the initial pH, after 24 hours pH of all the samples was 7 ± 1. SAP in the samples appears to have high buffering capacity which neutralizes the pH of the samples. Average pH of the samples after the batch tests is 7.2.

Similar pH trend was seen in samples with polymer P7 (Figure 5-9). Though the initial pH of samples before the contact time was set to different values 4, 7, and 10, average pH of samples after the contact time is 7.8. Initial pH of samples was recorded without any addition of acid or base. The initial pH of samples increased with increasing polymer content. pH after the contact time for all the samples was within 7 ± 1.5.

5.2.2 Mixed Heavy Metal Evaluation with Ottawa Sand

The subsection presents the results of tests carried out with aqueous solution of arsenic, barium, cobalt, selenium and vanadium each heavy metal added to the solution at a concentration of 0.5 mg/L. The heavy metal solution also referred to as synthetic leachate was mixed with a predetermined weight fraction of P100 or P7 and with and without Ottawa sand used the as the solid matrix. Figs. 5-10 to 5-14 show the results for P100 and Figs. 5-15 to 5-19 show the results for P7.

The target concentration of the heavy metal in the aqueous solution before the SAP was added was 0.5 mg/L. For each heavy metal, the tests were carried out at these four pH values: natural pH of the solution (which was predominantly 3.5 as the stock metals were digested in nitric acid), 4, 7, and 10.

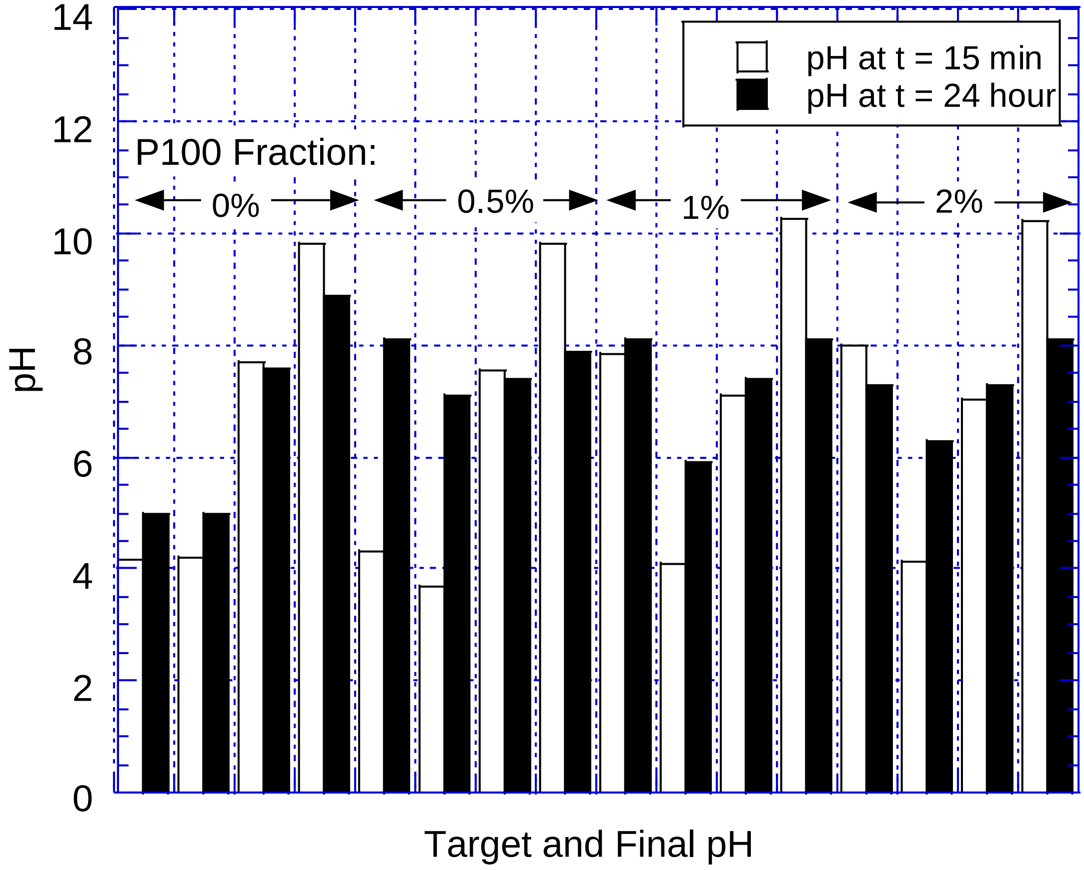

Figure 5-8 Effect of pH due to the addition of P100 at t = 15 min and 24 hours

No uptake of arsenic was observed in any of the samples irrespective of the pH and the amount of polymer in it. Controls did not contain P100. Reduced arsenic in the controls can be attributed to adsorption or precipitation of arsenic due to Ottawa sand.

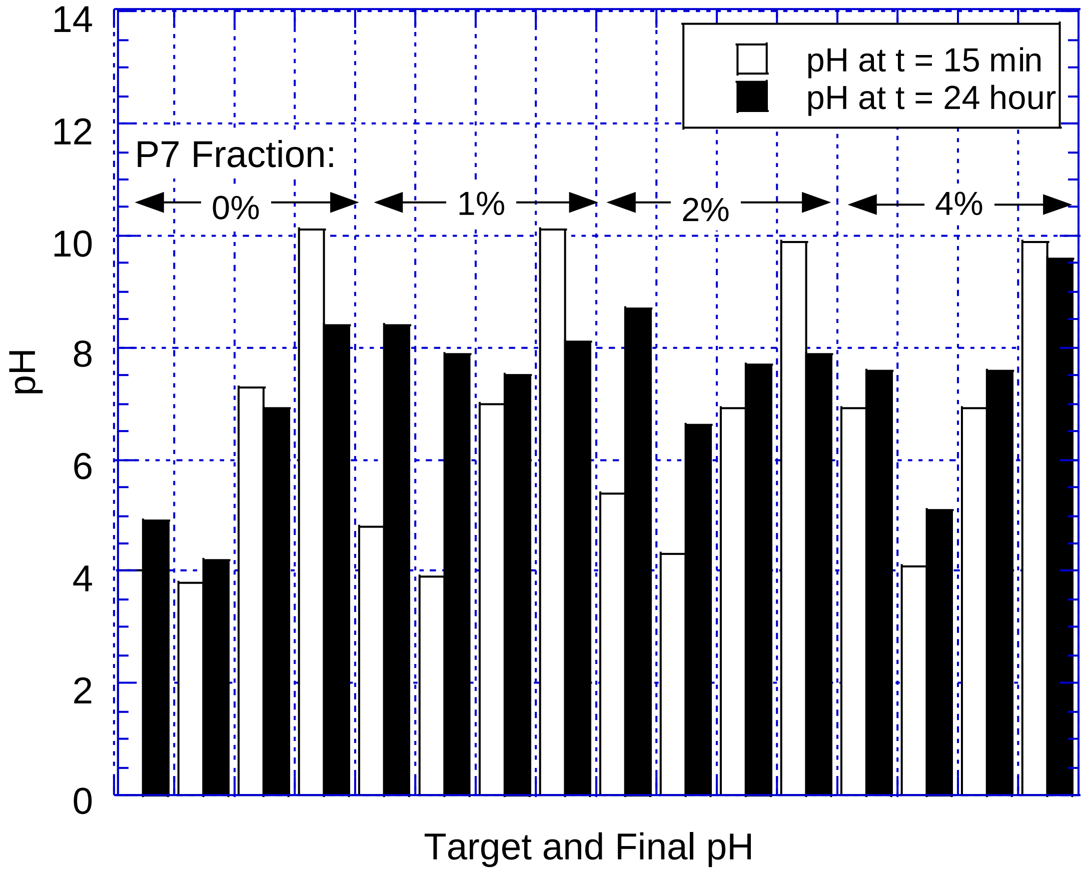

Figure 5-9 Effect of pH due to the addition of P7 at t = 15 min and 24 hours

Sand seems to be adsorbing arsenic when initial pH is 3.5 and at pH 4 (Fig. 5-10). Speciation of arsenic at near neutral pH (pH= 7 ± 1) which is the average pH range of all samples with P100 is a critical factor in determining the uptake (W. R. Roy et al. 2011). SAP P100 works on the principle of hydrogen bonding and osmosis of ions (Mark 2004). Speciation of arsenic in the standard stock solution is H_3AsO_4 and $HAsO_2$ both of which are compounds with no charge. This might be the reason why there is no uptake of arsenic with P100.

Figure 5-11 shows the concentration of barium for various initial or target pH when P100 was used. The controls indicate there was no reduction or uptake of barium. However, when P100 was added, the concentration of barium decreased from 0.5 mg/L to 0.15 mg/L to 0.3 mg/L in a majority of the samples. However, couple of samples containing P100 did not show any reduction or uptake. The reduction is most likely due to uptake by sodium polyacrylate.

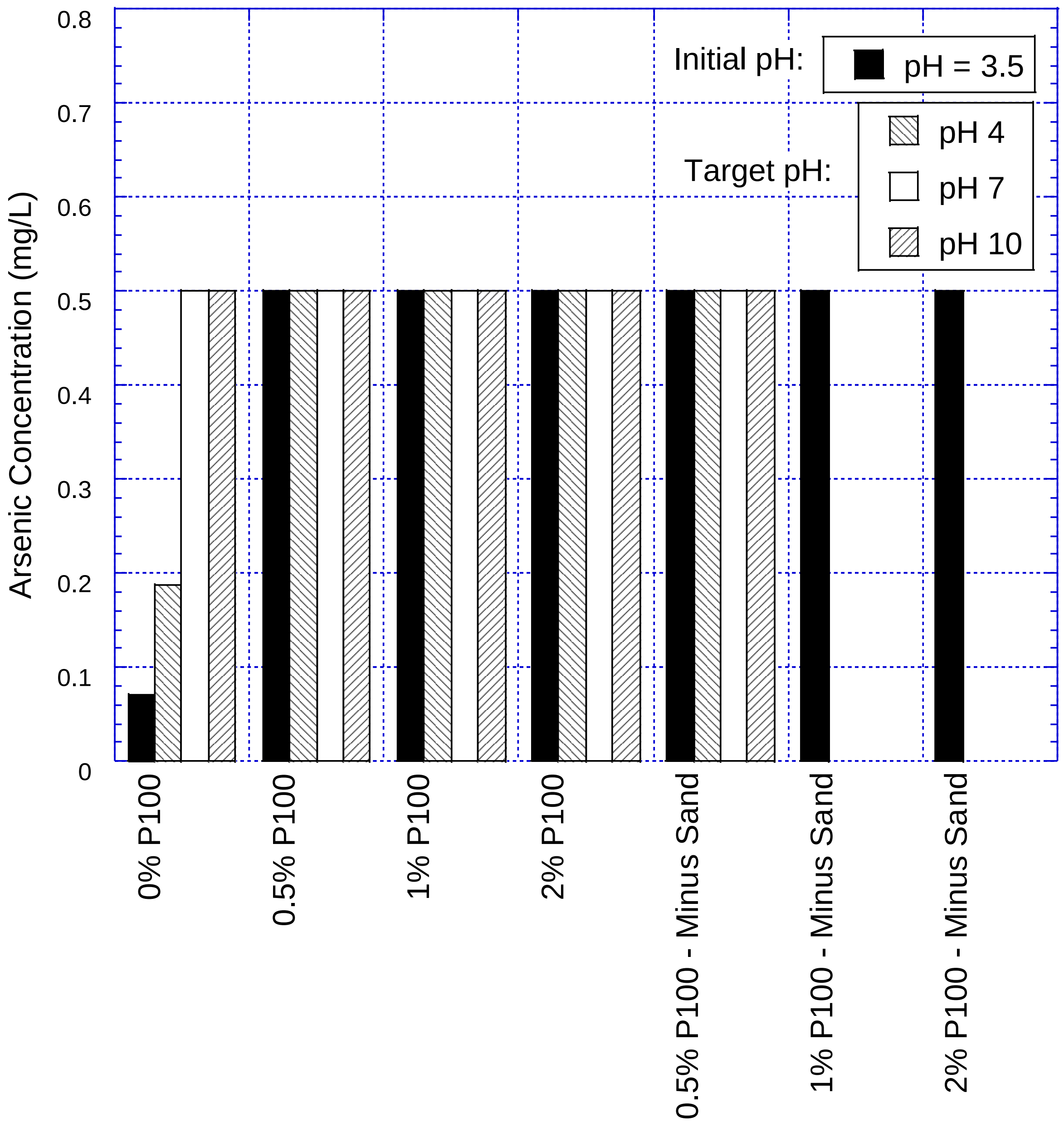

Figure 5-10 Arsenic stabilization using P100 with mixed heavy metal synthetic leachate

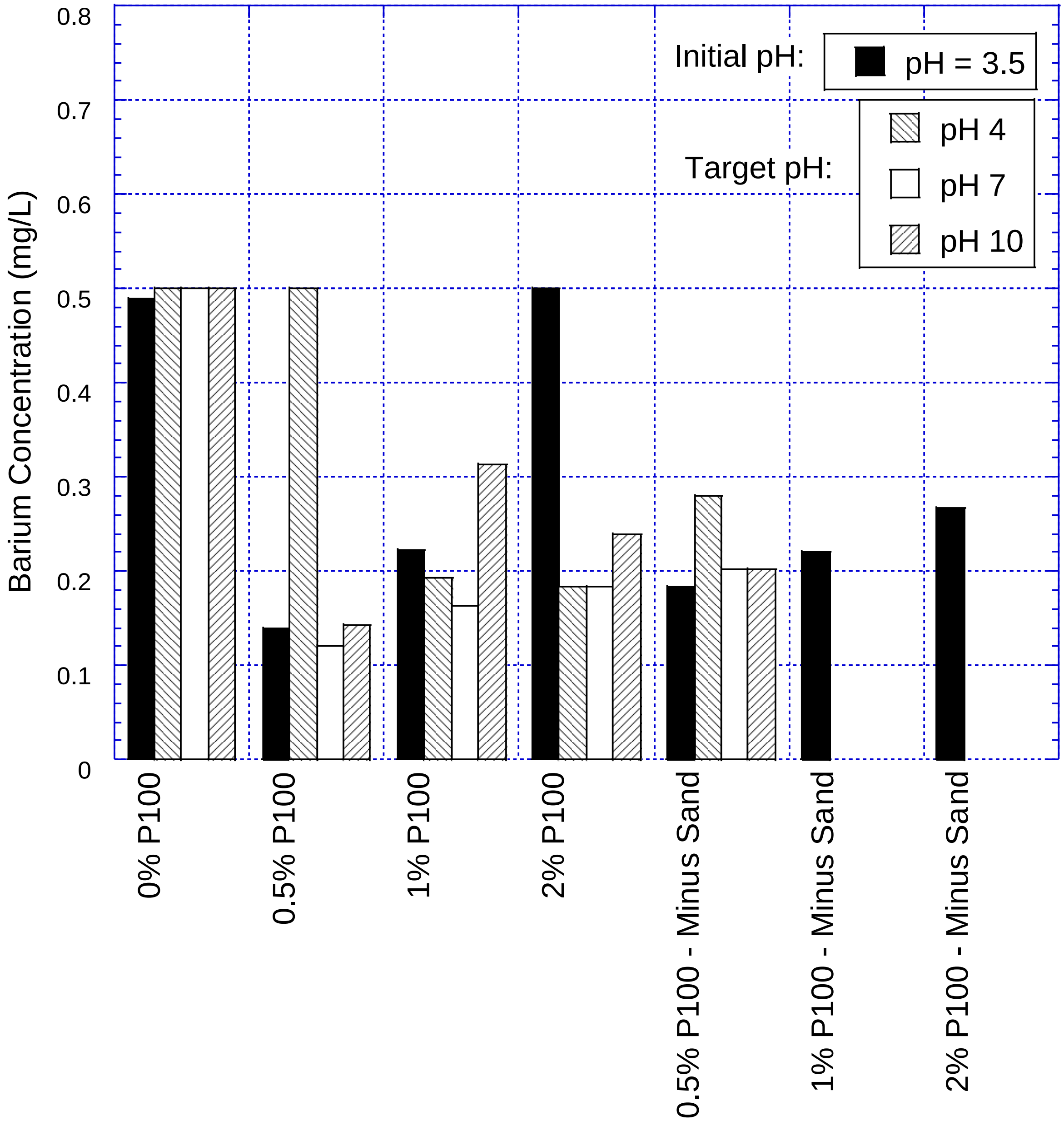

Figure 5-11 Barium stabilization using P100 with mixed heavy metal synthetic leachate

Figure 5-12 shows the concentration of cobalt for various initial or target pH when P100 was used. The controls indicate there was no reduction or uptake of cobalt. However, when P100 was added, the concentration of cobalt decreased from 0.5 mg/L to 0.2 mg/L. When sand was not added, the cobalt concentration was slightly higher ~ 0.25 mg/L. This indicates that sand was adsorbing about 0.05 mg/L of cobalt from the aqueous solution. Similar to barium, cobalt is a divalent cation. The polymer with net negative charge seems to be adsorbing divalent cations.

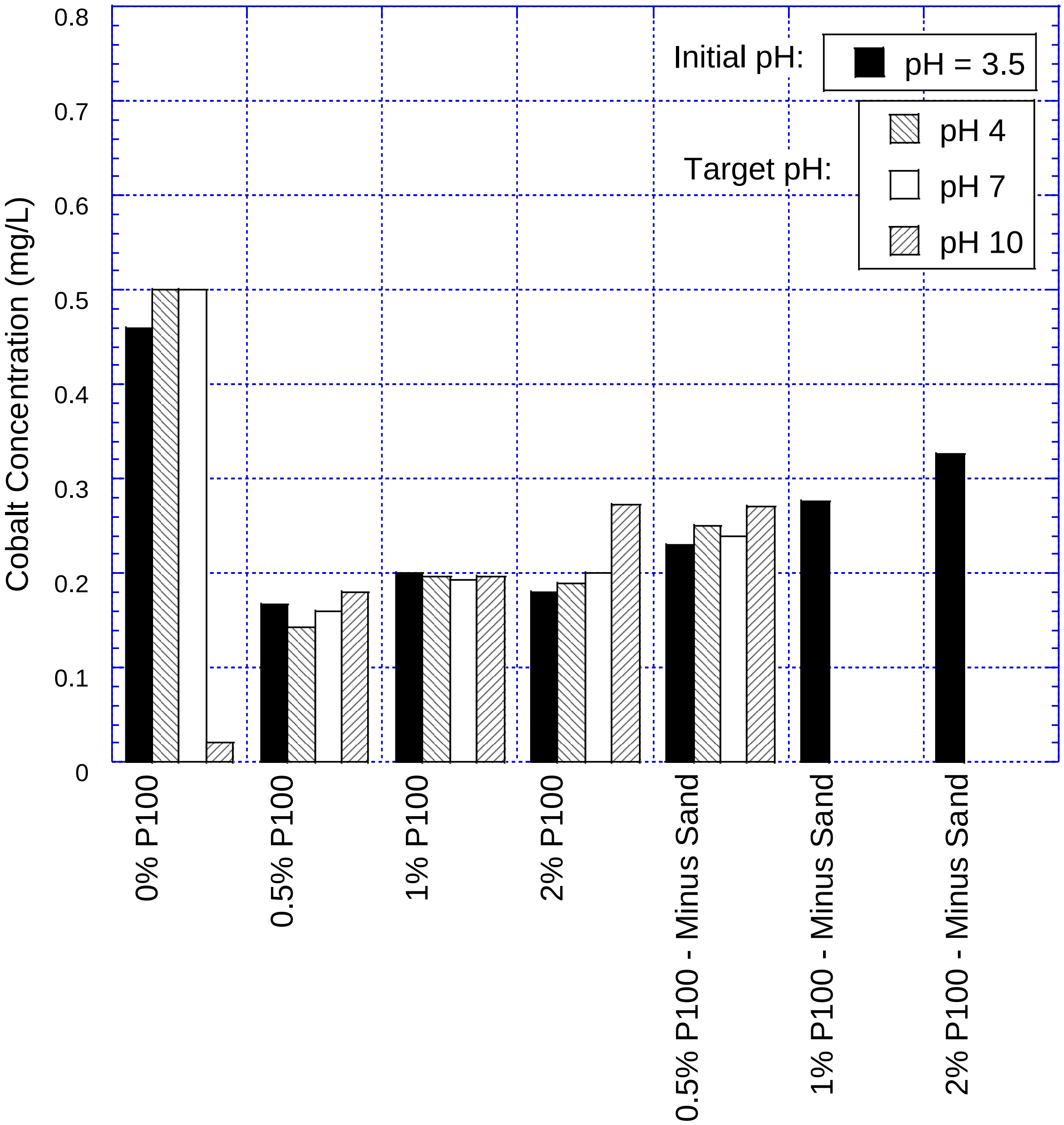

Figure 5-12 Cobalt stabilization using P100 with mixed heavy metal synthetic leachate

Figure 5-13 shows the concentration of selenium for various initial or target pH when P100 was used. There was no reduction in selenium concentration in most of the samples. This maybe because selenium or selenium complexes firmed is not a cation in the pH range developed due to the presence of SAP.

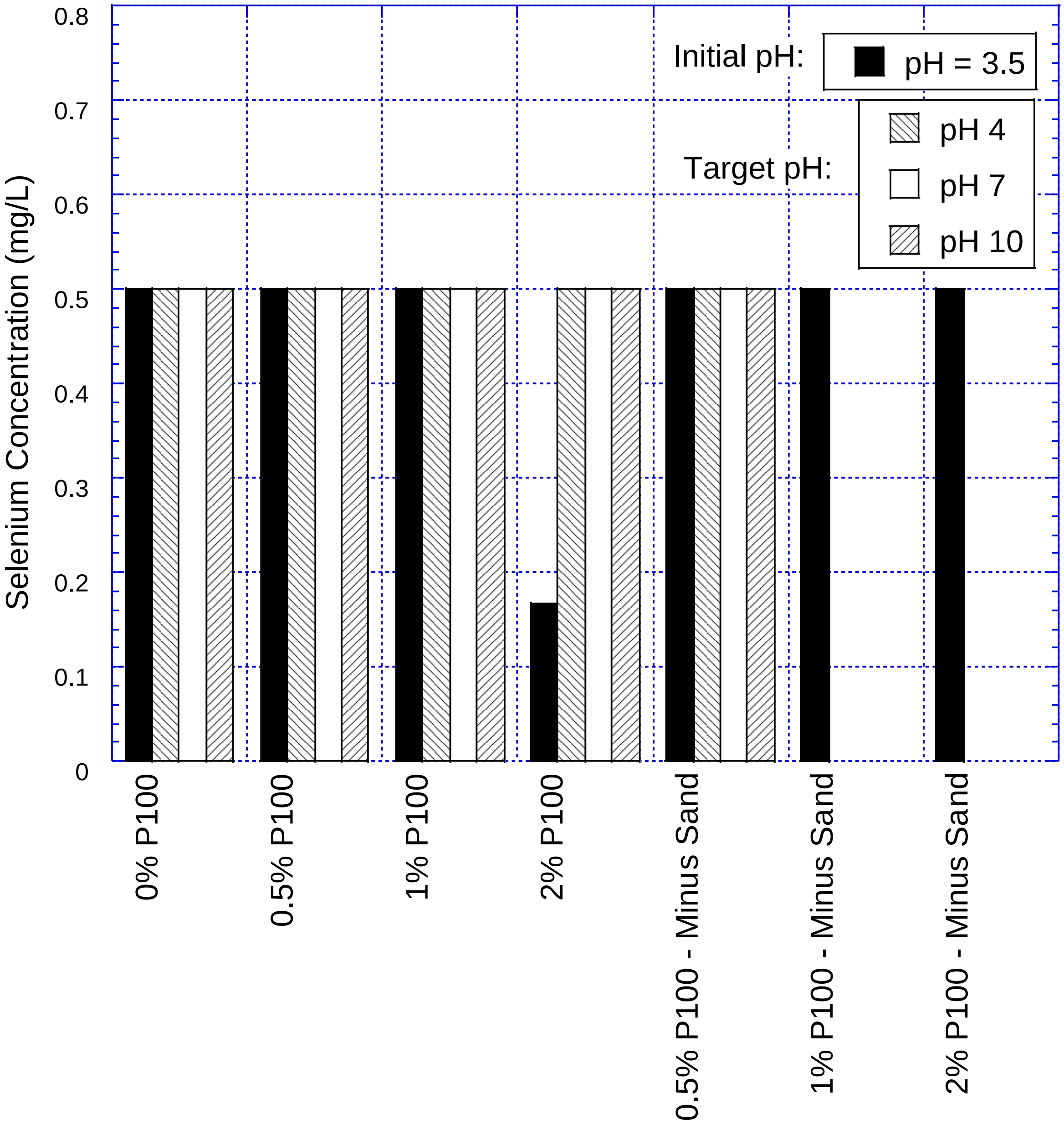

Figure 5-13 Selenium stabilization using P100 with mixed heavy metal synthetic leachate

Figure 5-14 shows the concentration of vanadium for various initial or target pH when P100 was used.

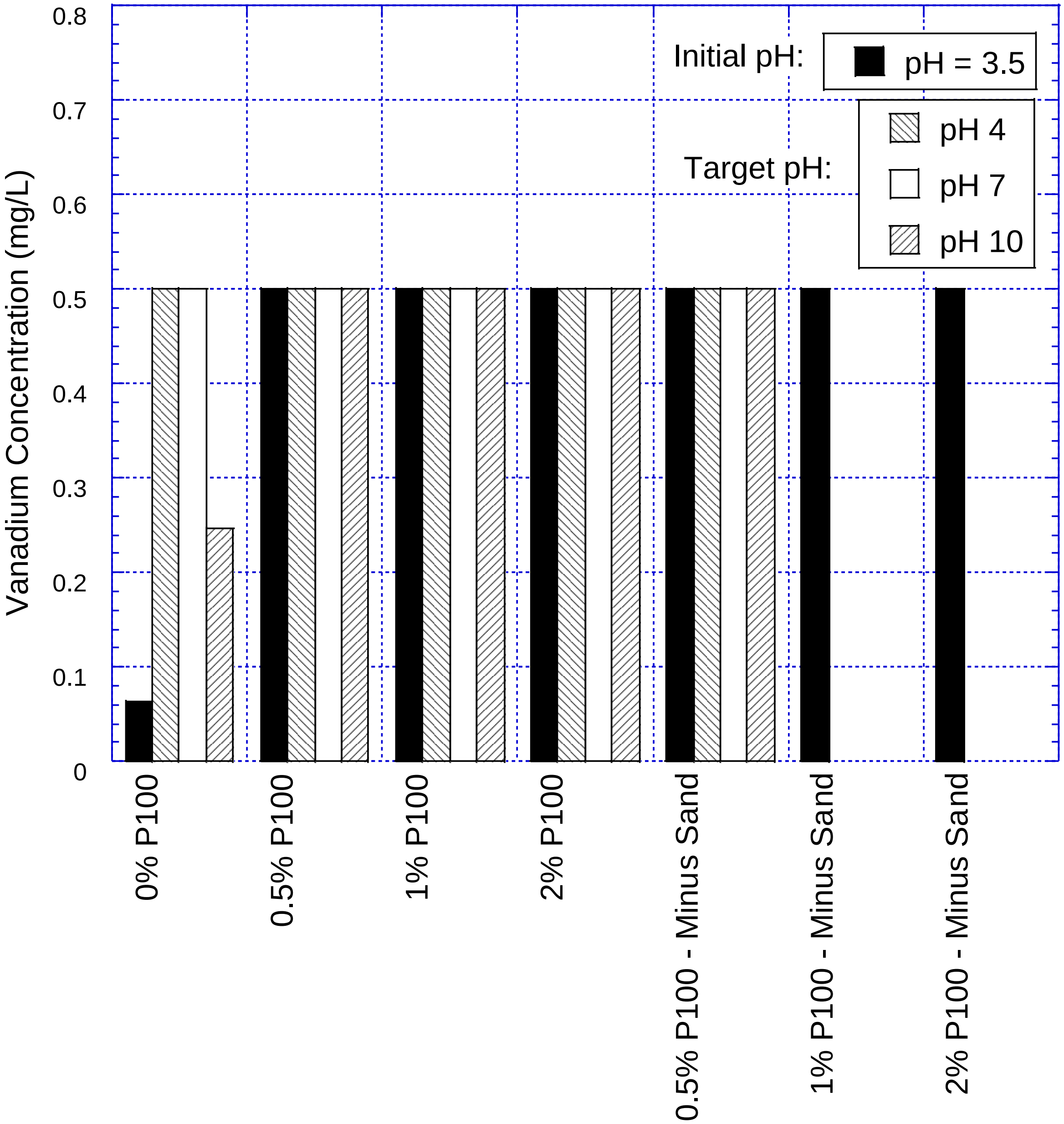

Figure 5-14 Vanadium stabilization using P100 with mixed heavy metal synthetic leachate

There was no reduction in vanadium concentration in most of the samples. This maybe because vanadium in the standard stock solution used is $H_2V_{10}O_{28}^{4-}$ (Ventures 2016), which is a poly-anion at pH 6.5 (Bard 2017) which is within the average pH range (7 ± 1) of all the samples and controls.

Figure 5-15 shows the concentration of arsenic for various initial or target pH when P7 was used. No uptake of arsenic was observed in most of the samples irrespective of the pH and the amount of polymer in it. Controls (without P7) showed reduction in arsenic. This observation was also made when P100 was used (Fig. 5-10). It can be attributed to adsorption or precipitation of arsenic due to Ottawa sand.

Figure 5-16 shows the concentration of barium for various initial or target pH when P7 was used. Barium uptake in samples containing P7 is higher than when P100 was used. With P7, barium concentration reduced from 0.5 mg/L to 0.05 mg/L whereas, it reduced to 0.5 mg/l when P100 was used. Thus, the wood flour present in P7 maybe providing some level of adsorption. None of the control samples (without P7) showed reduction in barium concentration.

Figure 5-17 shows the concentration of cobalt for various initial or target pH when P7 was used. Cobalt behaves similar to barium. Both are divalent cations. None of the control samples (without P7) showed reduction in cobalt. All samples showed up to 80% uptake of cobalt after a contact time of 24 hrs.

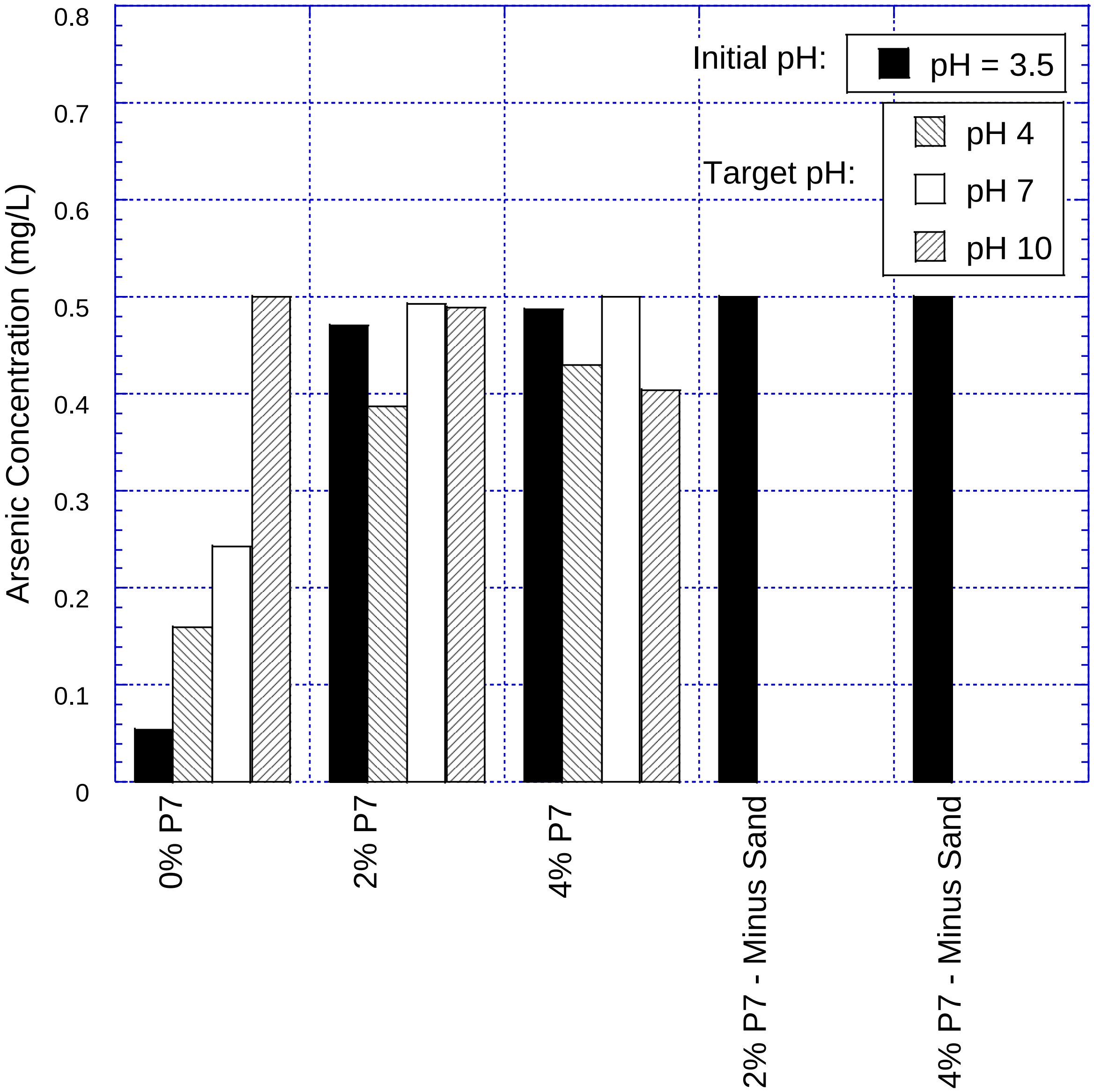

Figure 5-15 Arsenic stabilization using P7 with mixed heavy metal synthetic leachate

Figs. 5-18 and 5-19 show the concentration of selenium and vanadium for various initial or target pH when P7 was used, respectively. There was no reduction in selenium or vanadium for most of the samples. Thus, the wood flour did not influence the adsorption of the heavy metals.

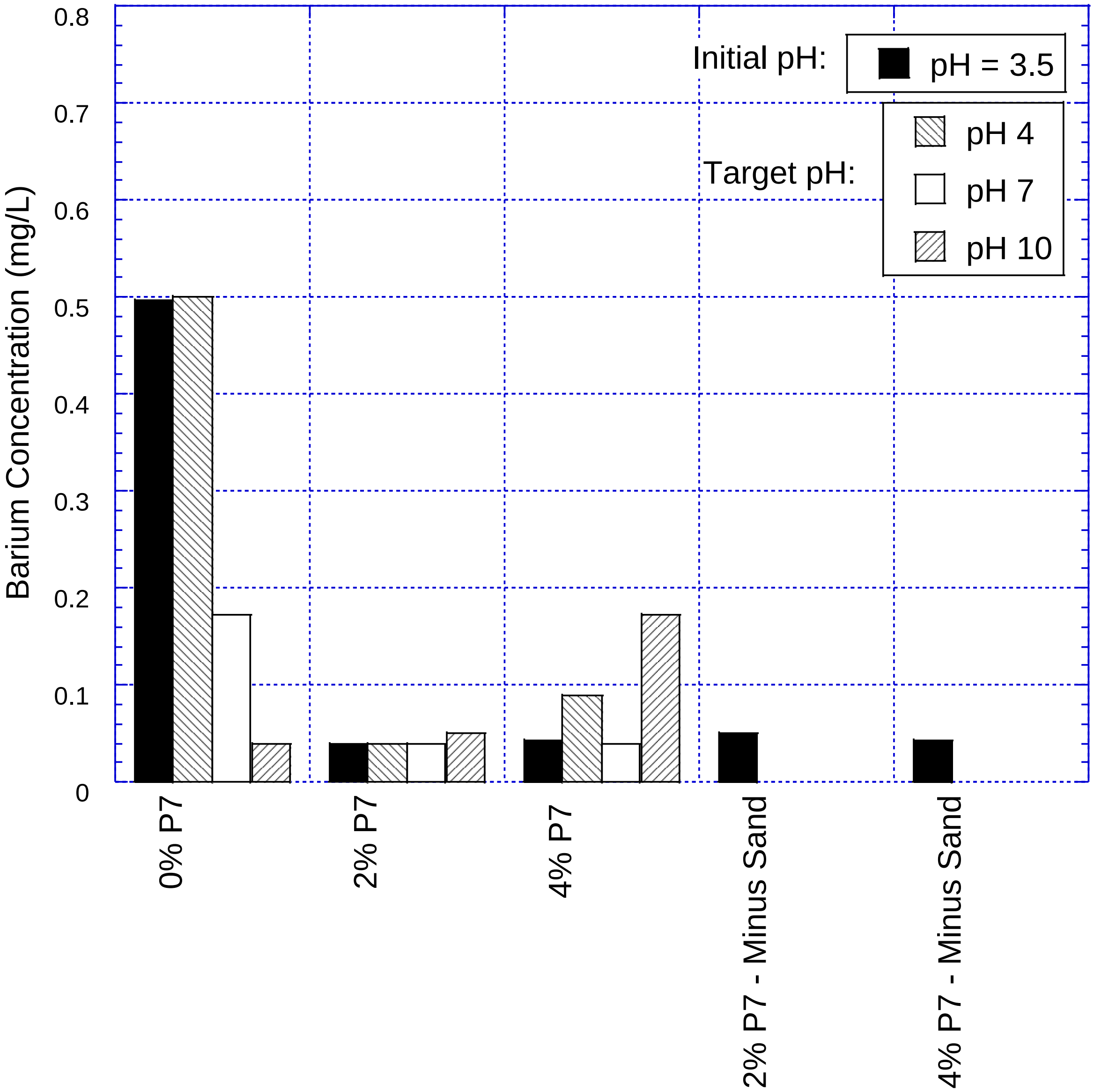

Figure 5-16 Barium stabilization using P7 with mixed heavy metal synthetic leachate

5.2.3 Individual Heavy Metal Evaluation

The subsection presents the results of tests carried out with aqueous solution of arsenic, barium, cobalt, prepared separately for each heavy metal and mixed with a predetermined weight fraction of P100, P4, or P7 and without the Ottawa sand. Figs. 5-20 to 5-22 show the results for arsenic, Figs. 5-23 to 5-25 for barium and Figs. 5-26 to 5-25 for cobalt. These tests allowed isolating the adsorption or precipitation that may have been caused by the presence of Ottawa sand and when multiple heavy metal species competed for adsorption or uptake by the SAP.

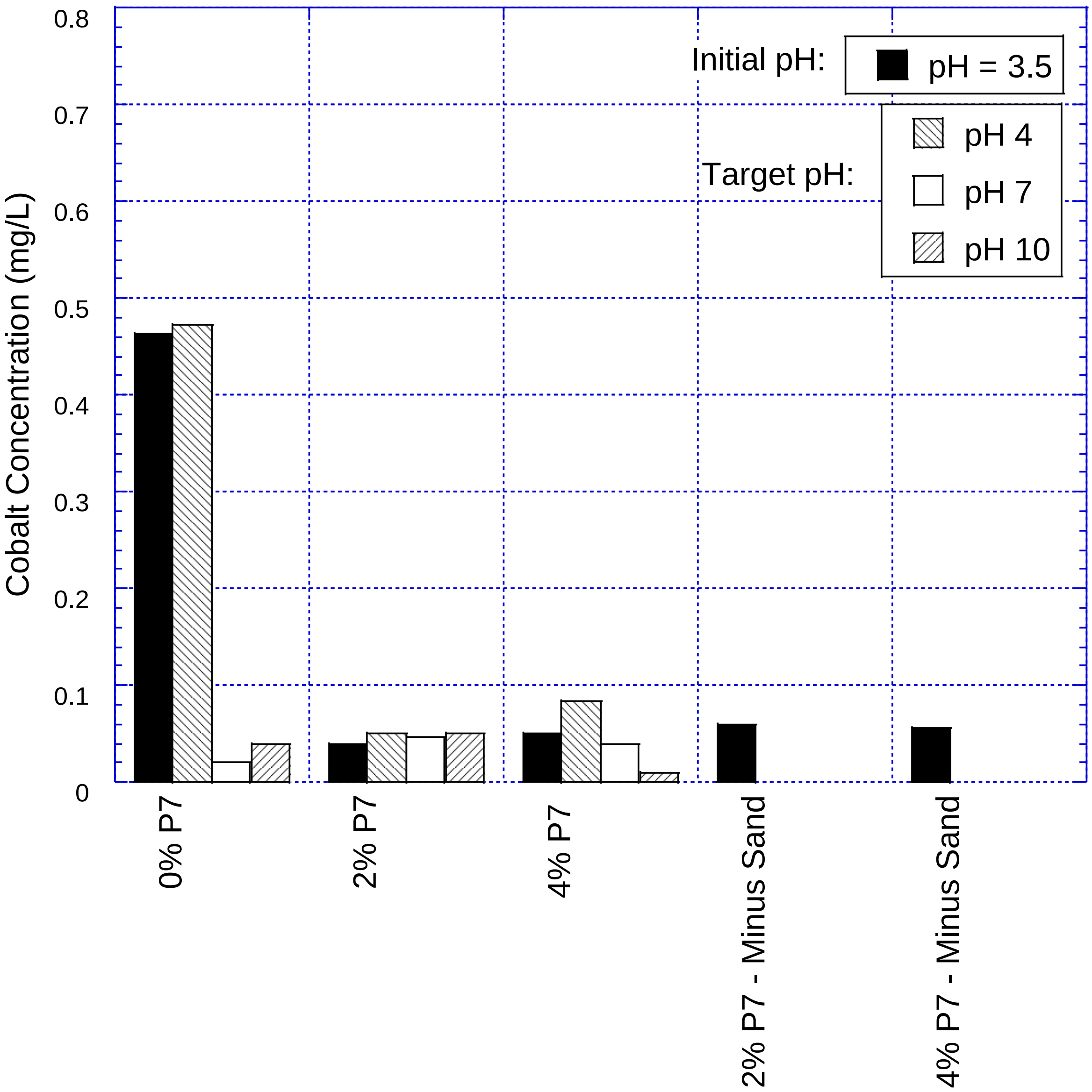

Figure 5-17 Cobalt stabilization using P7 with mixed heavy metal synthetic leachate

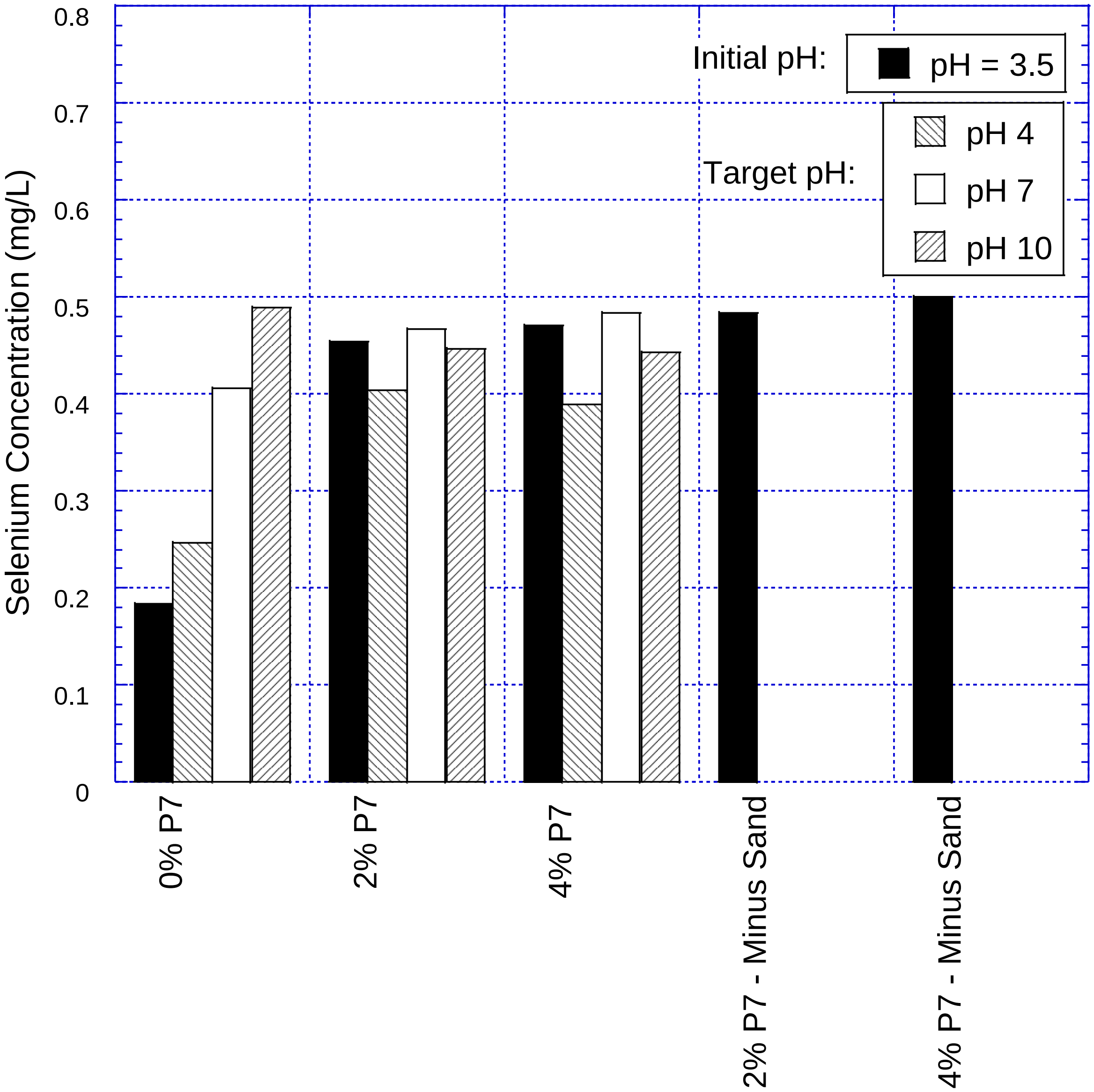

Figure 5-18 Selenium stabilization using P7 with mixed heavy metal synthetic leachate

Samples with P100 and P4 were tested at weight fractions equal to 0.5%, 1%, and 2% of 20 g, and samples with P7 were tested at weight fractions equal to 1%, 2%, and 4% of 20 g. These weight fractions are same as those used when all heavy metals were present in aqueous solution and the results were presented in 5.2.2.

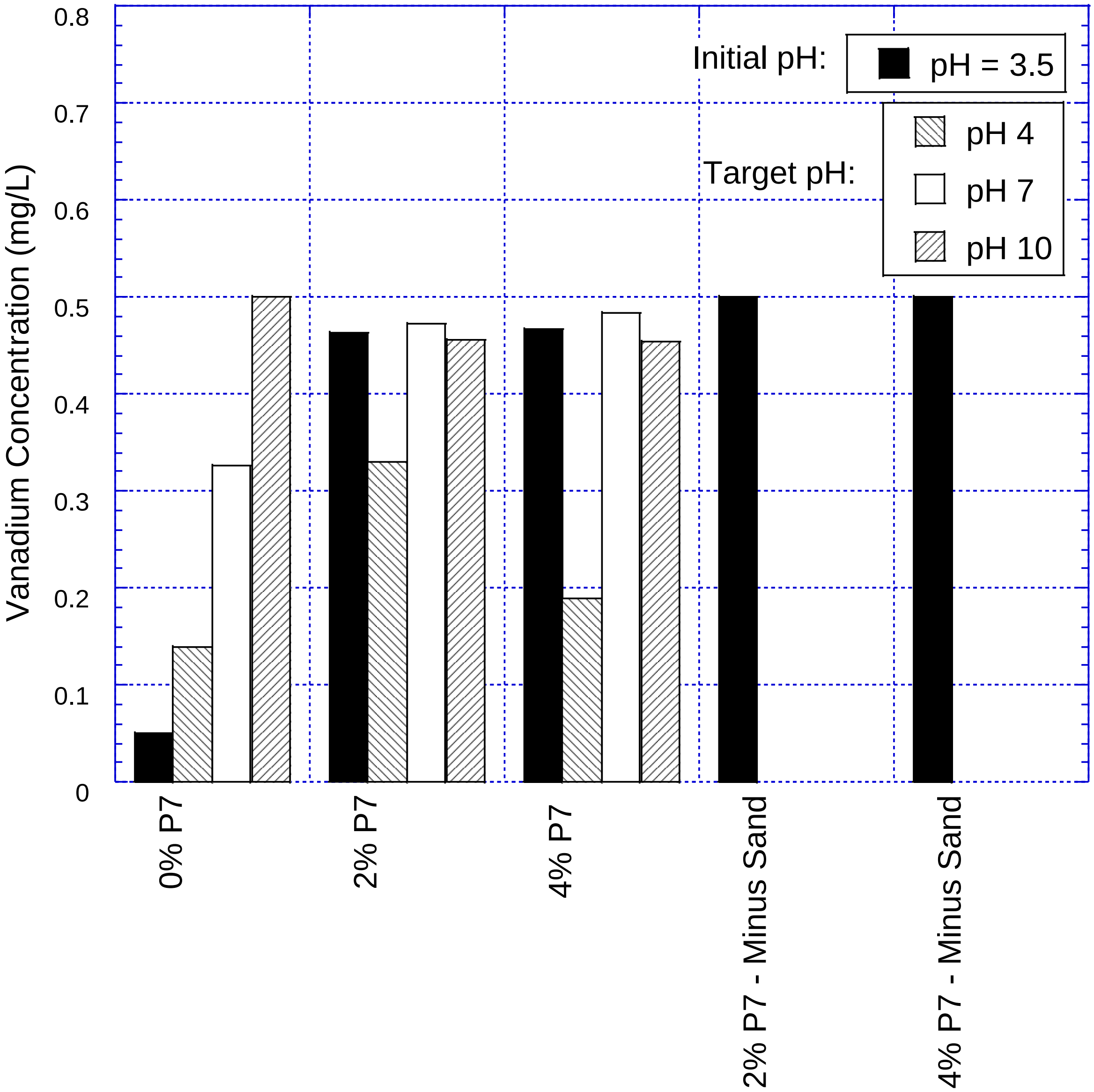

Figure 5-19 Vanadium stabilization using P7 with mixed heavy metal synthetic leachate

Figures. 5-20 to 5-22 confirm that none of the SAPs (P100, P4 or P7) were able to uptake arsenic. Hence, arsenic concentrations did not decrease. Figs. 5-23 to 5-25 and 5-26 to 5-28 show that all SAPs were successful in the uptake of barium and cobalt, respectively.

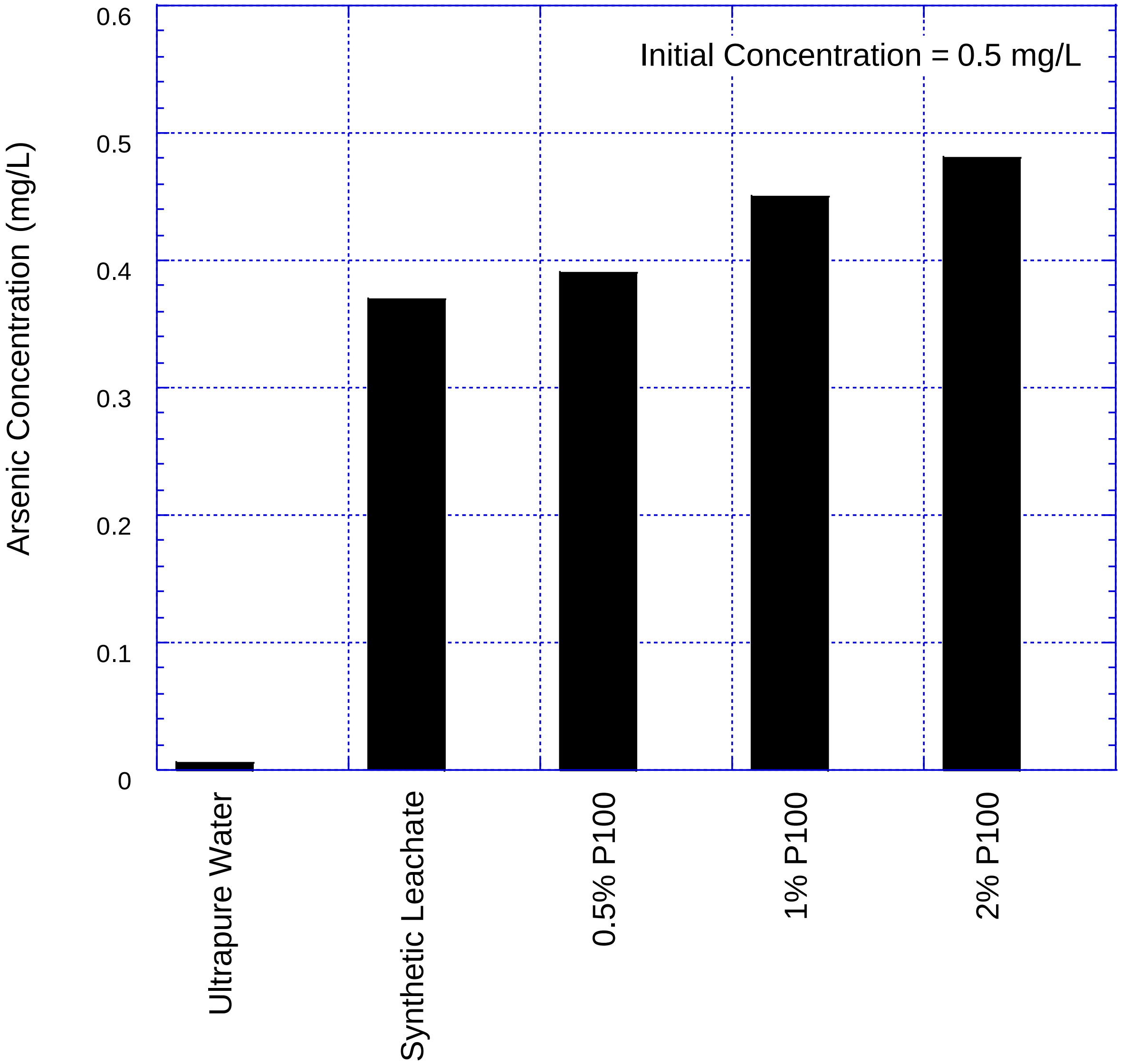

Figure 5-20 Arsenic stabilization using P100 with individual heavy metal synthetic leachate

There is no correlation between net uptake and SAP weight fraction for a given SAP. This may be because the lowest weight fraction of the SAP used provided ample sites for the heavy metal adsorption. This hypothesis can be confirmed if additional tests are conducted at significantly lower weight fractions of the SAPs until there is measurable reduction in the concentration of the heavy metal(s).

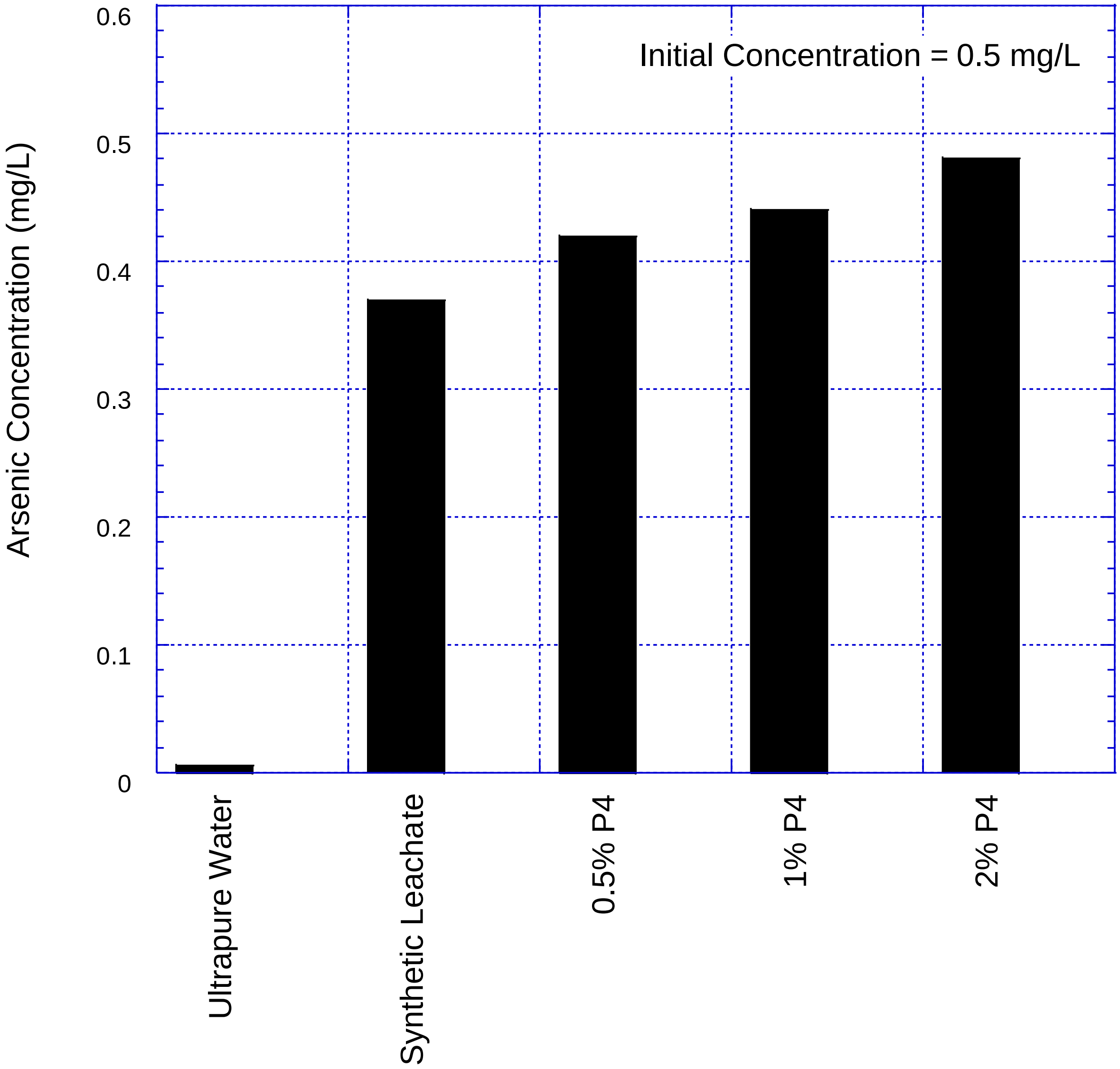

Figure 5-21 Arsenic stabilization using P4 with individual heavy metal synthetic leachate

Among the three SAPs, P7 showed the most reduction. P7 contains the least amount of the active polymer – sodium polyacrylate and contains wood flour. Thus, relatively small amount of sodium polyacrylate was sufficient to uptake the divalent cationic heavy metals.

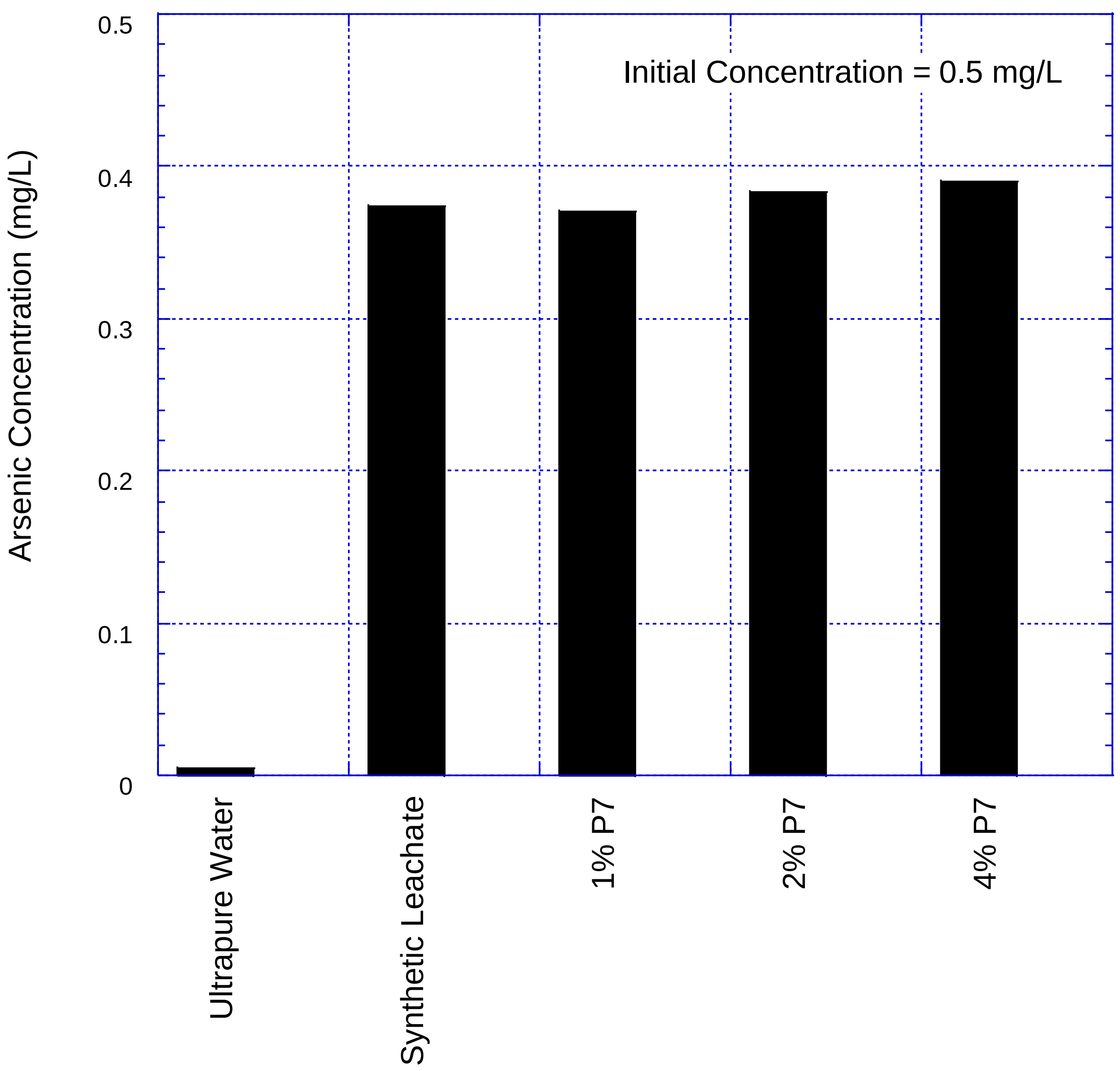

Figure 5-22 Arsenic stabilization using P7 with individual heavy metal synthetic leachate

5.2.4 Heavy Metal Stabilization Evaluation with Coal Ash

These tests consisted of mixing 829 g of dry ponded coal ash into 1170 mL of ultrapure water and allowing leaching of heavy metals from the ash into water by placing it on a rotating tumbler for 3 days. Because the concentration of heavy metals is not uniform across the mass in a coal ash sample, for each SAP weight fraction, a separate ash sample was used to establish the control (source concentration). Thus, three SAPs (P100, P4 and P7) and three weight fractions for each SAP resulted in total 9 ash samples (829 g of dry ash and 1171 mL of ultrapure water used for each of the 9 samples).

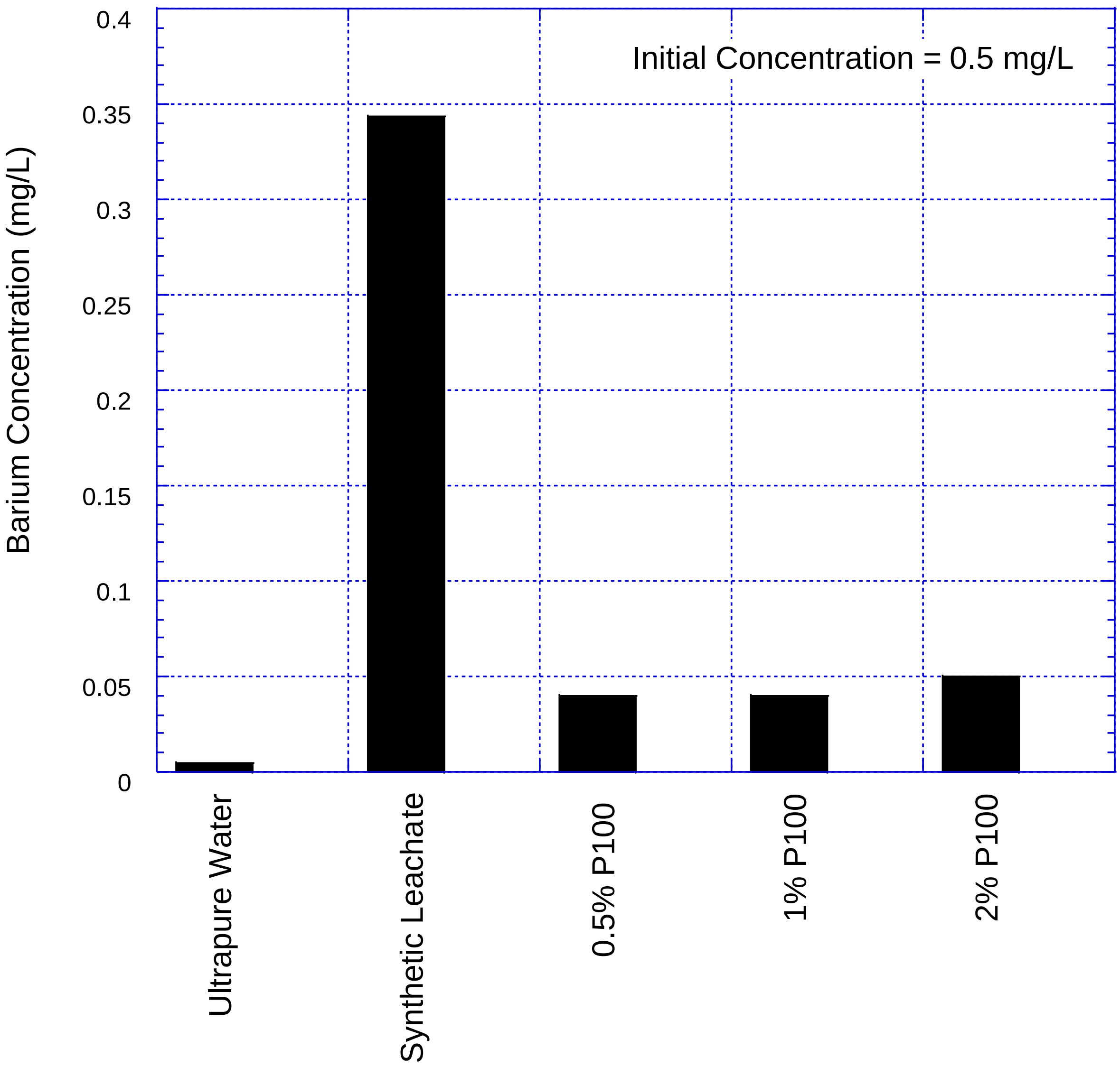

Figure 5-23 Barium stabilization using P100 with individual heavy metal synthetic leachate

Fig. 5-29 shows the concentration of arsenic in controls and samples containing SAPs P100, P4, and P7 at different weight fractions. Initial concentration of arsenic that leached out from the coal ash (control) was about 0.009 mg/kg. While few samples containing the SAPs show some decrease in the arsenic concentration, it is not consistent. The decrease could be an artifact of "noise" from the measurement device (ICP-OES). It can be concluded from this plot that none of SAPs were able to stabilize or uptake arsenic. These results are consistent with the results of experiments carried out without the ash (Sections 5.2.2 and 5.2.3).

Fig. 5-30 shows the concentration of barium in controls and samples containing SAPs P100, P4, and P7 at different weight fractions. Initial concentration of barium that leached out from the coal ash (control) was about 0.05 mg/kg. All samples except one, showed decrease in the concentration of barium of about 50%. It can be concluded from this plot that SAPs are able to stabilize or uptake barium. Increase in the SAP content did not result in greater uptake.

These results are consistent with the results of experiments carried out without the ash (Sections 5.2.2 and 5.2.3). The reason for concentration of the target heavy metal in sample being higher than in the control (for P100 at 2%) might be because of other interfering ions in the solution that have the same wavelength as the target heavy metal.

Fig. 5-31 shows the concentration of cobalt in controls and samples containing SAPs P100, P4, and P7 at different weight fractions. Initial concentration of cobalt that leached out from the coal ash (control) was about 0.042 mg/kg. All samples showed about 30% to 90% decrease in the concentration of cobalt. It can be concluded from this plot that SAPs are able to stabilize or uptake cobalt. Increase in the SAP content did result in greater uptake for P4 and

P7. However, the trend was opposite for P100. These results are consistent with the results of experiments carried out without the ash (Sections 5.2.2 and 5.2.3).

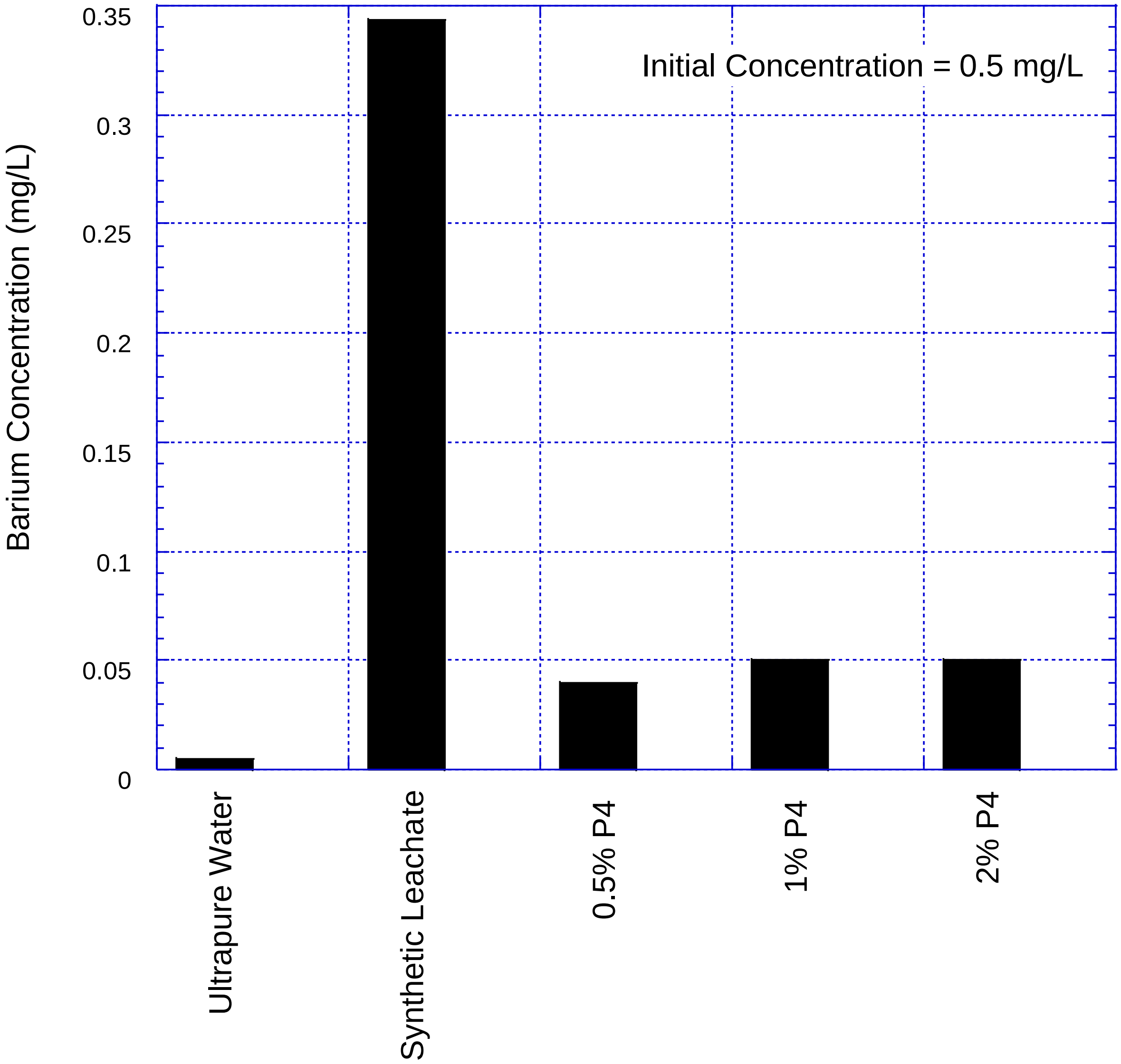

Figure 5-24 Barium stabilization using P4 with individual heavy metal synthetic leachate

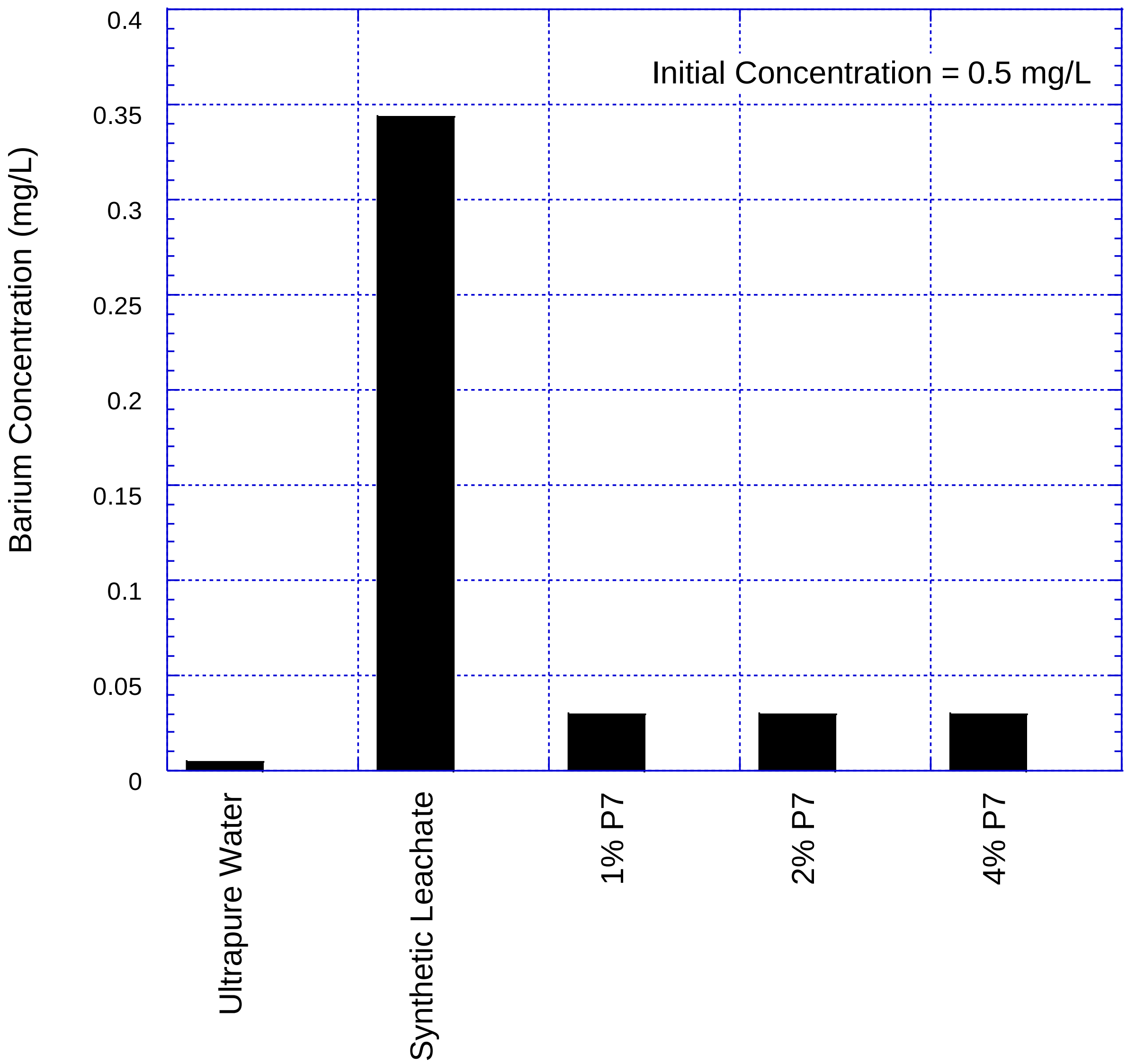

Figure 5-25 Barium stabilization using P7 with individual heavy metal synthetic leachate

Fig. 5-32 shows the concentration of selenium in controls and samples containing SAPs P100, P4, and P7 at different weight fractions. Initial concentration of selenium that leached out from the coal ash (control) was about 0.009 mg/kg to 0.024 mg/kg. While few samples containing the SAPs show some decrease in the selenium concentration, it is not consistent. It can be concluded from this plot that none of SAPs were able to stabilize or uptake selenium.

Similar pattern was observed for vanadium (Fig. 5-33). These results are consistent with the results of experiments carried out without the ash (Sections 5.2.2 and 5.2.3).

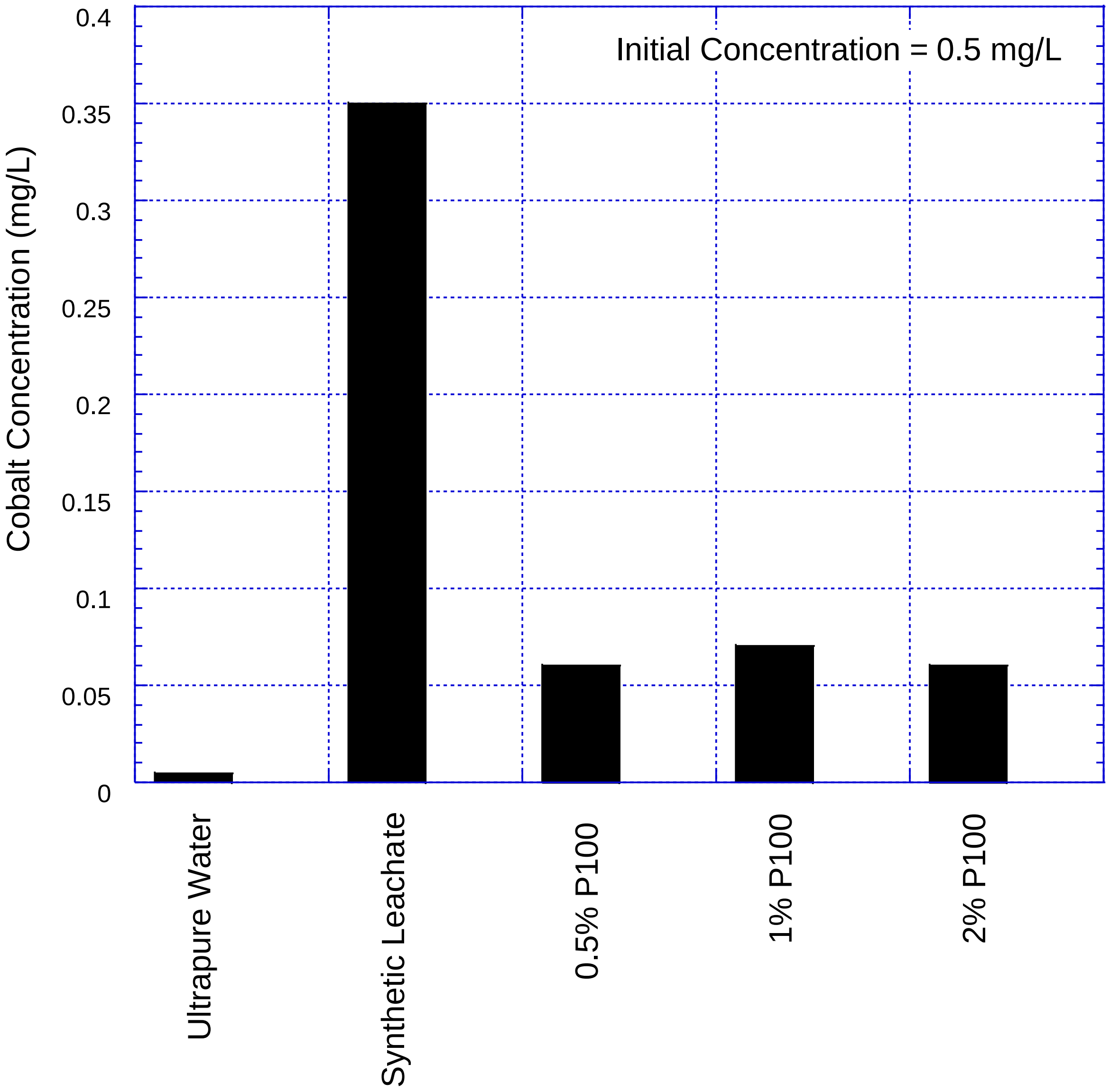

Figure 5-26 Cobalt stabilization using P100 with individual heavy metal synthetic leachate

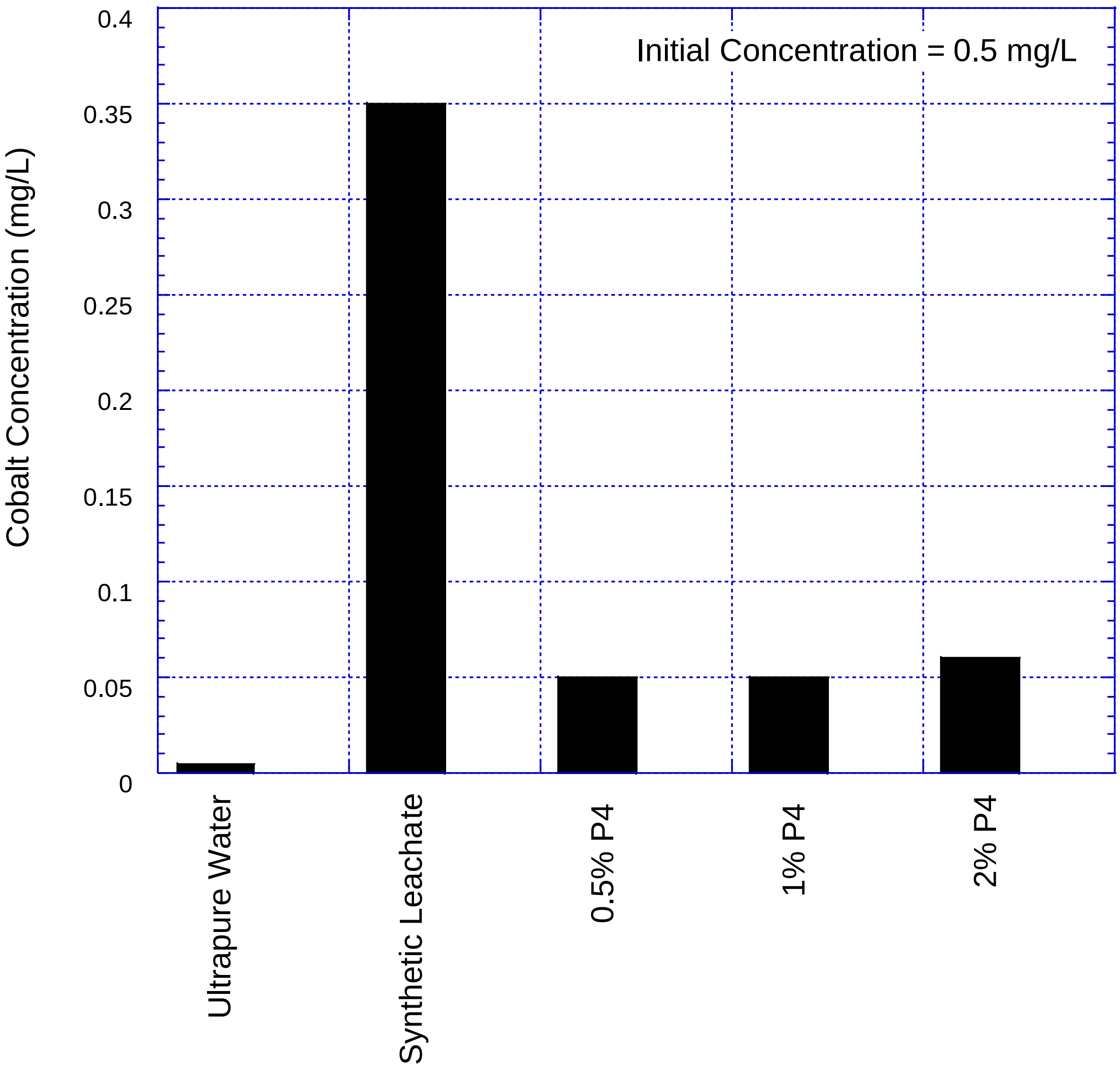

Figure 5-27 Cobalt stabilization using P4 with individual heavy metal synthetic leachate

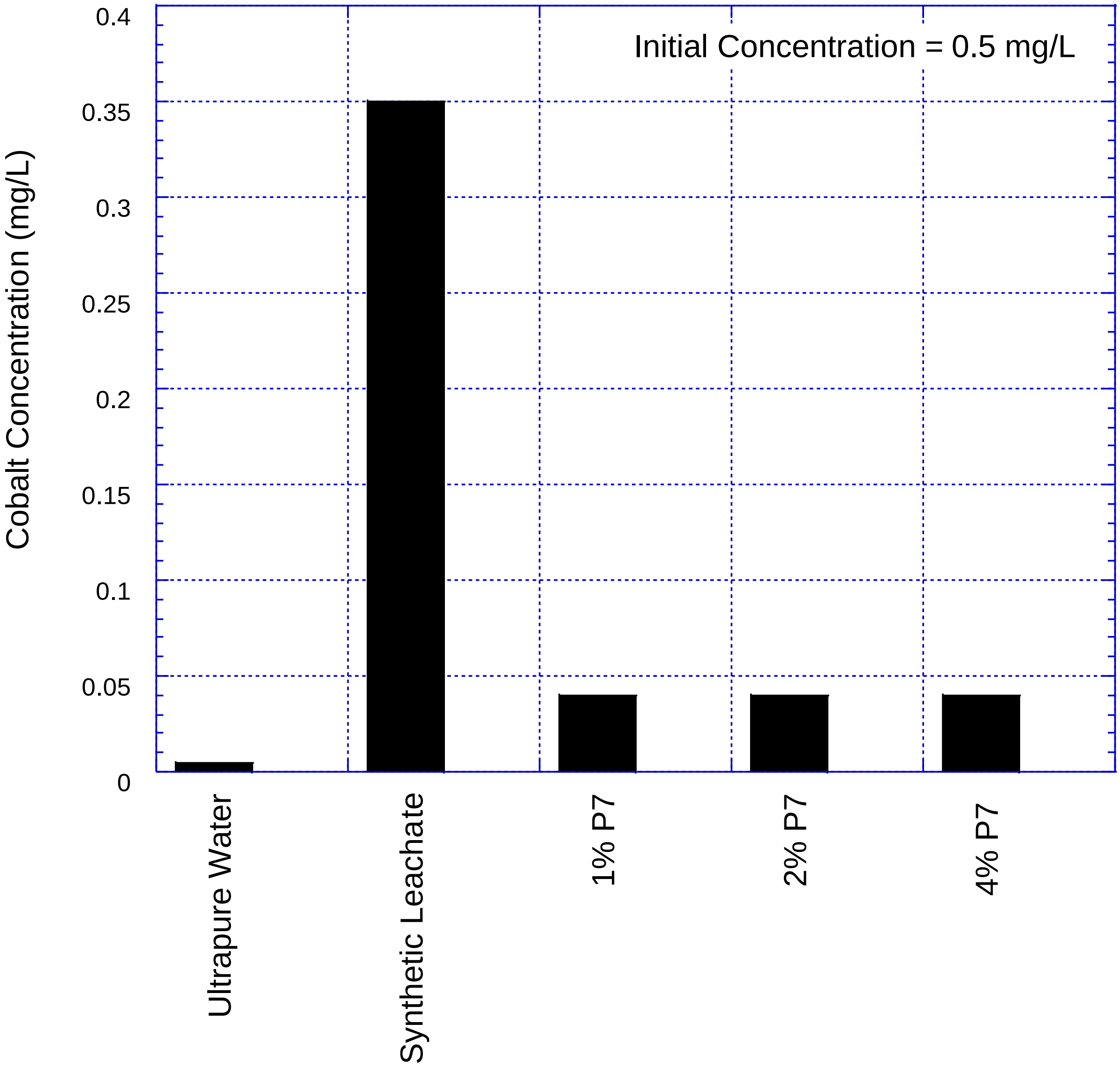

Figure 5-28 Cobalt stabilization using P7 with individual heavy metal synthetic leachate

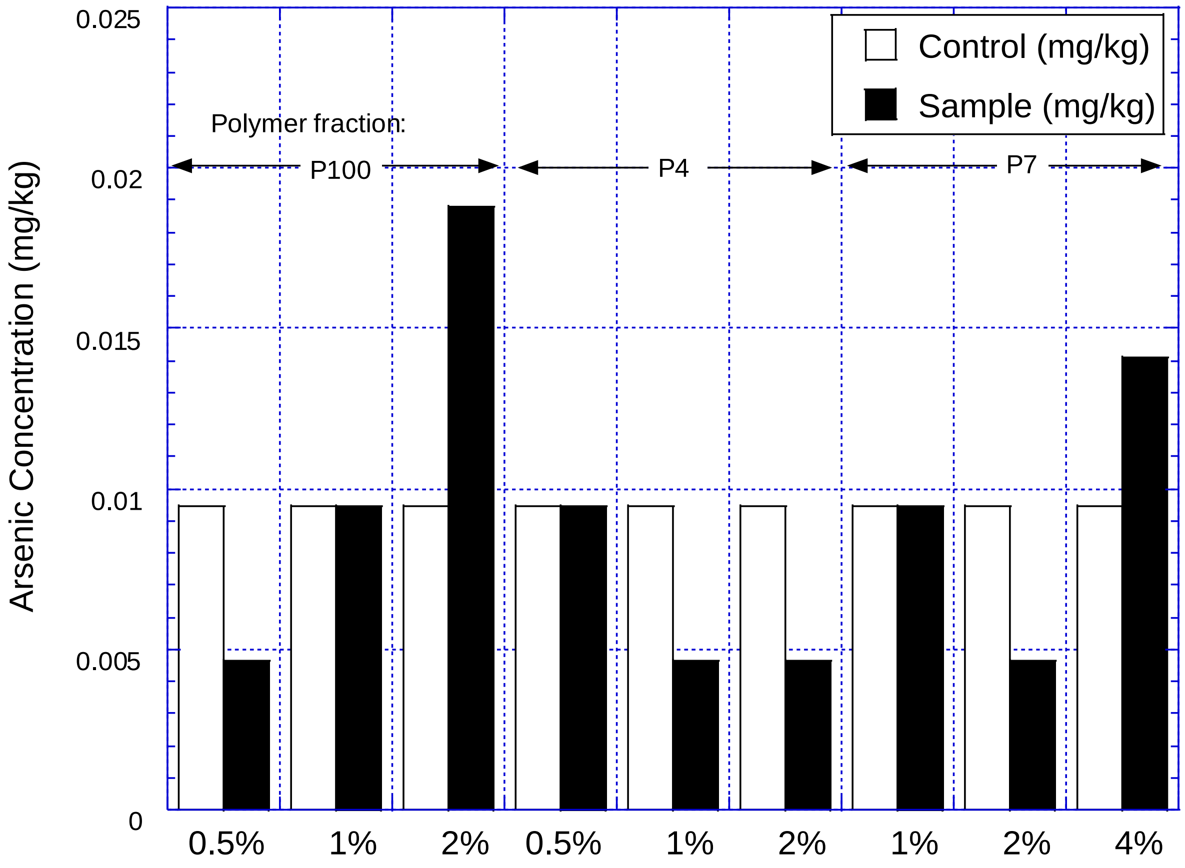

Figure 5-29 Arsenic concentration vs. polymer content in samples of coal ash

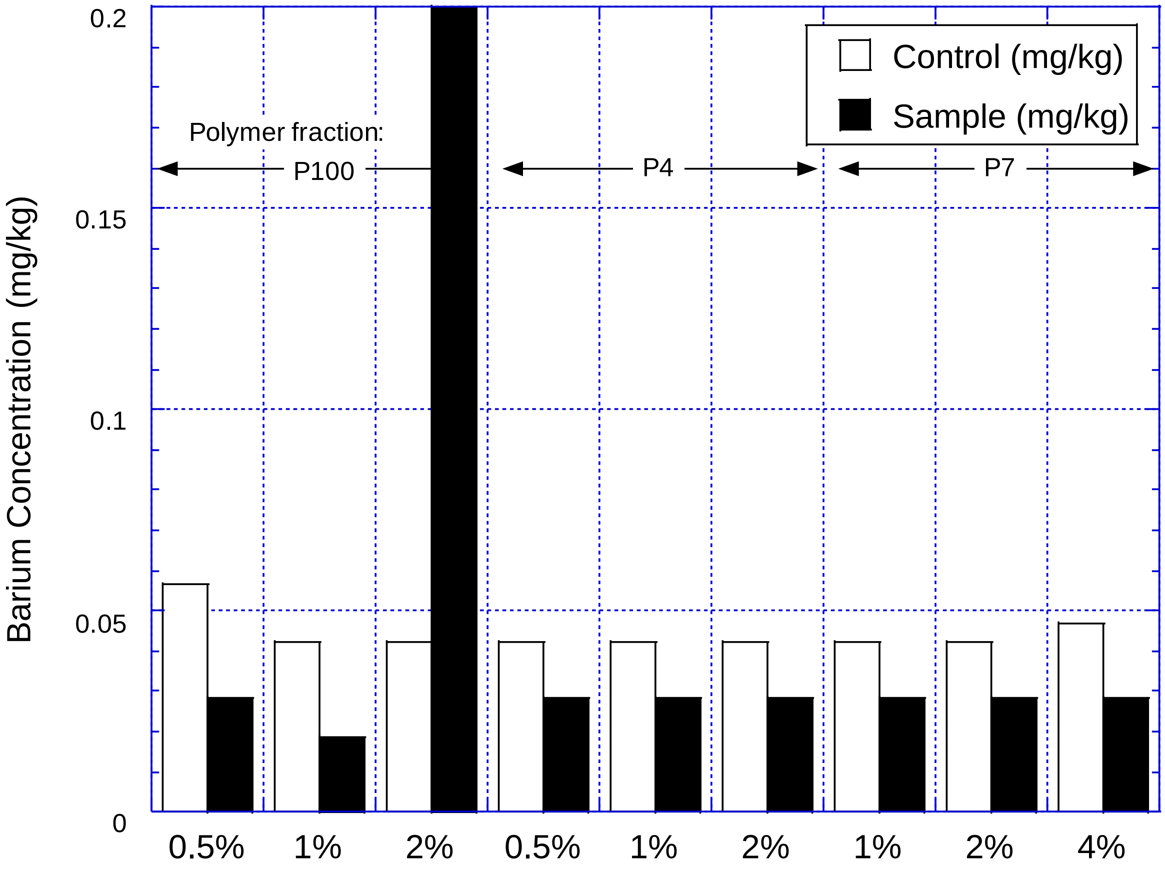

Figure 5-30 Barium concentration vs. polymer content in samples of coal ash

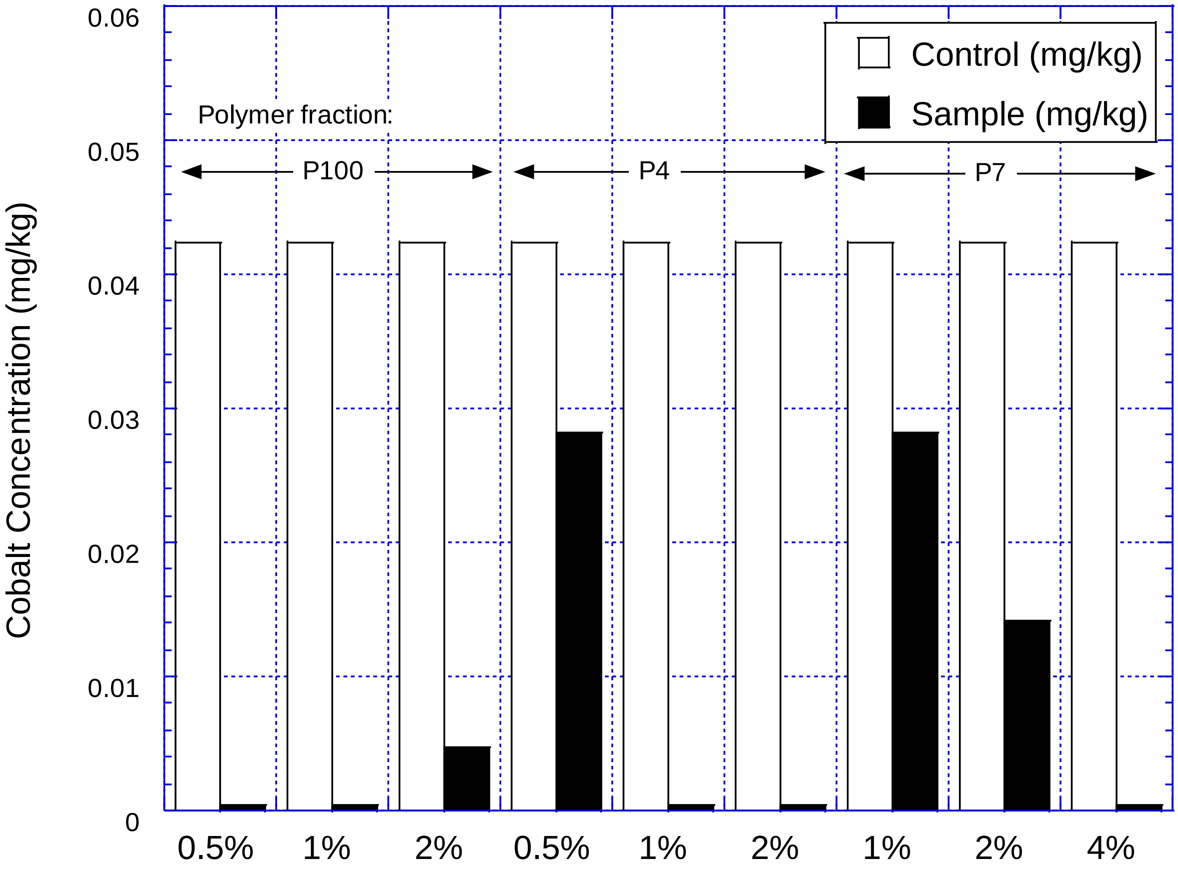

Figure 5-31 Cobalt concentration vs. polymer content in samples of coal ash

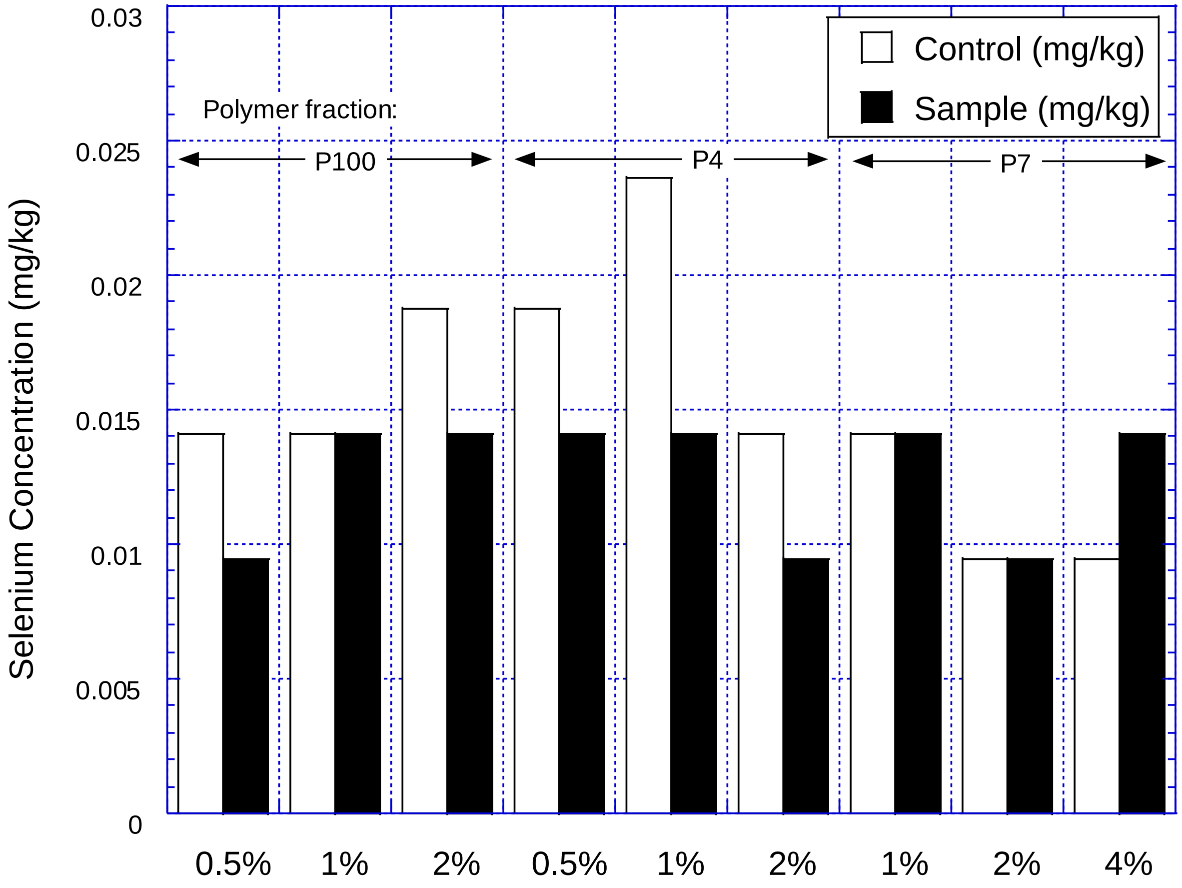

Figure 5-32 Selenium concentration vs. polymer content in samples of coal ash

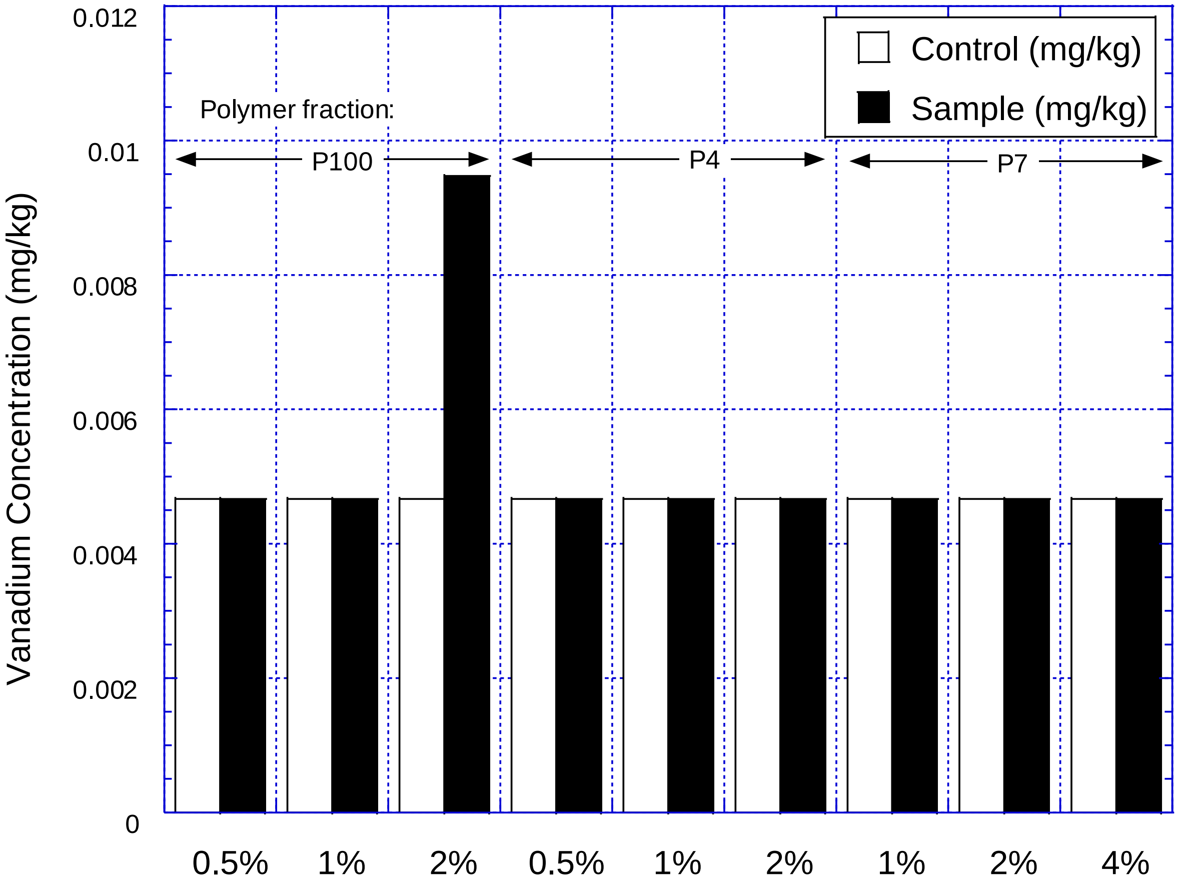

Figure 5-33 Vanadium concentration vs. polymer content in samples of coal ash

6. SUMMARY AND CONCLUSIONS

This research aimed at evaluating the use of an SAP - sodium polyacrylate and other additives mixed with sodium polyacrylate (cement, bentonite, wood fibers, wood flour), as an additive to stabilize excess moisture, improve shear strength and to evaluate the uptake of heavy metals from ponded coal ash. Five coal ash samples from undisclosed coal ash pond sites located in the southeastern U.S. were obtained and evaluated during this research.

All of the ash samples were tested for the moisture content at which they fail the USEPA paint filter liquids test. The water content at which the ash samples failed the paint filter test ranged from 48% to 60%. Tap water was added to increase the water content by an additional 10% and SAPs P100, P2, P4, P6, and P7 were added in weight fractions ranging from 0.5% to 4%. All SAPs were able to visually “solidify” the saturated ash samples. Selective samples were compacted to Standard Proctor effort and using Pocket Penetrometer, Torvane, and unconfined compressive testing device, shear strength parameters were measured. Addition of the SAPs improved the undrained cohesion from 0 to 2 psi to 10 psi with an average of 3 psi. SAP P7 which contains 25% sodium polyacrylate and 75% wood flour was the most effective considering it contained relatively small amount of sodium polyacrylate compared to other SAPs. In general, greater SAP fraction did not yield greater strength compared to the strength when the SAP content was 0.5% to 1%. Thus, large weight fraction of SAP is not required to achieve strength gain.

In order to evaluate the uptake of heavy metals when SAP is added to the ash, three sets of experiments were carried out:

1. SAPs P100 and P7 mixed with synthetic leachate containing 0.5 mg/L of arsenic, barium, cobalt, selenium, and vanadium, clean environmental grade Ottawa sand, and ultrapure water. Using nitric acid and/or potassium hydroxide, the pH of the solution was targeted to reach 4, 7 and 10 in separate titrations. The mix(es) was allowed a contact time of ≥ 24 hours on a rotating tumbler. After 24 hours, the leachate was analyzed for the heavy metals using an ICP-OES.
2. SAPs P100, P4 and P7 mixed with synthetic leachate containing 0.5 mg/L of arsenic, barium, and cobalt, in ultrapure water, only one element in the leachate at a time to ensure there are no competing ions. The mix(es) was allowed a contact time of ≥ 24 hours on a rotating tumbler. After 24 hours, the leachate was analyzed for the heavy metals using an ICP-OES.
3. SAPs P100, P4 and P7 mixed ultrapure water and oven dried ash from one of the ash pond sites. The mix was allowed a contact time of ≥ 3 days on a rotating tumbler. After 3 days, the leachate was analyzed for the heavy metals using an ICP-OES.

The results show that anionic sodium polyacrylate has buffering capacity to neutralize pH to 7 ± 1 no matter if the initial pH was 4, 7 or 10. Thus, after the addition of the SAP, within 24 hours the pH of the mix was 7 ± 1.

All three sets of tests indicated that the anionic SAP sodium polyacrylate was relatively effective to uptake divalent cationic barium and cobalt (uptake ≥ 50%). However, there was no measurable uptake of arsenic, selenium and vanadium. Thus, additional research would be needed to understand the state of valency of arsenic, selenium, vanadium, in the presence of the anionic SAP and study if there is a more favorable pH at which uptake is more likely.

REFERENCES

Abdulkareem, O. A., & Ramli, M. (2015). "Optimization of Alkaline Activator Mixing and Curing Conditions for a Fly Ash-Based Geopolymer Paste System." *Modern Applied Science*. Vol. 9, pp. 61.

ACAA, A. C. A. A. (2015). Coal Ash Reuse. Retrieved from https://www.epa.gov/coalash/coal-ash-reuse

Albino, V., Cioffi, R., Santoro, L., & Valenti, G. (1996). "Stabilization of Residue Containing Heavy Metals by Means of Matrices Generating Calcium Trisulphoaluminate and Silicate Hydrates." *Waste management & research*. Vol. 14, pp. 29-41.

ASTM-2216. (2010). Standard Test Methods for Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass. In.

ASTM-D698. (2012). Standard Test Methods for Laboratory Compaction Characteristics of Soil Using Standard Effort (12 400 Ft-Lbf/Ft3 (600 Kn-M/M3)). In.

ASTM-D854. (2014). Standard Test Methods for Specific Gravity of Soil Solids by Water Pycnometer. In.

Bard, A. (2017). *Standard Potentials in Aqueous Solution*: Routledge.

Chand, S. K., & Subbarao, C. (2007). "In-Place Stabilization of Pond Ash Deposits by Hydrated Lime Columns." *Journal of Geotechnical and Geoenvironmental Engineering*. Vol. 133, pp. 1609-1616.

Chen, R., Zhang, L., & Budhu, M. (2013). "Biopolymer Stabilization of Mine Tailings." *Journal of Geotechnical and Geoenvironmental Engineering*. Vol. 139, pp. 1802-1807.

Chen, X., Chen, L. S., & Xu, J. T. (2014). *Research on Sodium Polyacrylate and Its Effects on Mechanical Properties of Slag-Based Geopolymer*. Paper presented at the Applied Mechanics and Materials.

Das, S. K., Mahamaya, M., Panda, I., & Swain, K. (2015). "Stabilization of Pond Ash Using Biopolymer." *Procedia Earth and Planetary Science*. Vol. 11, pp. 254-259.

Davidovits, J., & Sawyer, J. L. (1985). Early High-Strength Mineral Polymer. In: Google Patents.

EPA. (2009). Method 1313 In *Leaching Test (Liquid–Solid Partitioning as a Function of Extract pH) of Inorganic Species in Solid Materials Using a Parallel Batch Extraction Test, US Environmental Protection Agency* (pp. 1-28).

EPA, P. F. L. (2004). Epa Method Sw - 846 9095b. In (pp. 1-4).

ISO. (2002). Iso/Dis 679, Methods of Testing Cement—Determination of Strength. In (pp. 29).

Izquierdo, M., & Querol, X. (2012). "Leaching Behaviour of Elements from Coal Combustion Fly Ash: An Overview." *International Journal of Coal Geology*. Vol. 94, pp. 54-66.

Jones, D. (1995). The Leaching of Major and Trace Elements from Coal Ash. In *Environmental Aspects of Trace Elements in Coal* (pp. 221-262): Springer.

Mark, E. (2004). "Superabsorbent Polymers." *Product development scentist for SAP. BASF Aktiengesellschaft ss*. Vol. 13, pp. 1-13.

OECD, I. S. (2015). Electricity Production from Coal Sources (% of Total). https://data.worldbank.org/indicator/EG.ELC.COAL.ZS?contextual=aggregate&locations=US

Roy, P., Swami, V., Kumar, D., & Rajagopal, C. (2011). "Removal of Toxic Metals Using Superabsorbent Polyelectrolytic Hydrogels." *Journal of Applied Polymer Science*. Vol. 122, pp. 2415-2423.

Roy, W. R., & Berger, P. M. (2011). "Geochemical Controls of Coal Fly Ash Leachate Ph." *Coal Combustion and Gasification Products*. Vol. 3, pp. 63-66.

Roy, W. R., & Griffin, R. A. (1984). "Illinois Basin Coal Fly Ashes. 2. Equilibria Relationships and Qualitative Modeling of Ash-Water Reactions." *Environmental science & technology*. Vol. 18, pp. 739-742.

Schramke, J. A. (1992). "Neutralization of Alkaline Coal Fly Ash Leachates by Co2 (G)." *Applied geochemistry*. Vol. 7, pp. 481-492.

Spears, D., & Lee, S. (2004). "Geochemistry of Leachates from Coal Ash." *Geological Society, London, Special Publications*. Vol. 236, pp. 619-639.

Valenti, G., Santoro, L., & Volpicelli, G. (1984). "Hydration of Granulated Blast-Furnace Slag in the Presence of Phosphogypsum." *Thermochimica acta*. Vol. 78, pp. 101-112.

Ventures, I. (2016). Interactive Periodic Table. Retrieved from https://www.inorganicventures.com/periodic-table

Zhang, S., Gong, K., & Lu, J. (2004). "Novel Modification Method for Inorganic Geopolymer by Using Water Soluble Organic Polymers." *Materials letters*. Vol. 58, pp. 1292-1296.

Zohuriaan-Mehr, M. J., & Kabiri, K. (2008). "Superabsorbent Polymer Materials: A Review." *Iranian Polymer Journal*. Vol. 17, pp. 451.