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**THE CHEMICAL FIXATION AND SOLIDIFICATION
OF A CHROMIC ACID WASTE
USING TYPE I PORTLAND CEMENT
AND FLYASH**

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A thesis submitted to the Faculty and Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science (Environmental Science and Engineering).

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ABSTRACT

Chromium is toxic to humans in the hexavalent form and must be treated prior to disposal in order to meet very stringent regulatory concentration disposal limits. The chromic acid waste used in this research had a Cr(VI) concentration in excess of 30,000 parts per million (ppm). The purpose of this research was to determine a solidification/stabilization process to immobilize the hexavalent chromium present in a beryllium metal electropolishing chromic acid solution. The ultimate goal of this research was to fix the Cr(VI) to 0.5 ppm or less as measured by the Toxicity Characteristic Leaching Procedure (TCLP). A stepwise experimental approach was taken to empirically determine the best process to meet this goal. In order to stabilize the toxic chromic acid waste, it was necessary to convert the Cr(VI) to Cr(III) prior to solidification using Type I Portland cement and flyash. A treatment scheme was developed using metal filings as the reducing agent. One hundred-ten percent of the stoichiometric amount of iron required to reduce the hexavalent chromium in solution was added to the waste acid. A precipitation phase using 50% sodium hydroxide (NaOH) by weight followed reduction to raise the pH of the highly acidic waste above pH 7 and to precipitate out the Cr(III) present. The optimum water:waste:cement/flyash loading was determined in order to reach the ultimate goal of 0.5 ppm Cr(VI) in the final TCLP leachate. TCLP extract concentrations were measured for Cr(VI) using a Dionex Ion Chromatograph and EPA Method 218.6 for dissolved hexavalent chromium. Three sets of solidification/fixation

experiments were conducted resulting in a formulation which completely fixed the hexavalent species in the cement monolith. The stabilized samples were evaluated on ease of mixing, slowest initial set up time, uniformity of cured sample, and ability to stabilize the Cr(VI). A cement:flyash:waste ratio of 1.5:1.5:1 using 40% water by weight and an industrial water reducing agent, PSI 300N, was determined to yield the best TCLP results combined with the best sample characteristics. Recommendations to eliminate the waste drying step and redesign the stabilization process such that it could be conducted in-situ in 55 gallon drums were made to optimize this stabilization process in future research for implementation on an industrial scale.

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Chapter 1

INTRODUCTION

During the 1970-1980 time period, the electropolishing of beryllium parts at a local manufacturing facility generated thirty 55 gallon drums of a hazardous chromic acid waste. The liquid waste stream consists of a spent milling solution used to finish the beryllium parts. The waste contains total chromium in excess of 30,000 parts per million (ppm) and has a pH below 1.0. In addition, the waste also contains trace amounts of selenium, cadmium, lead, arsenic, beryllium, and silver. The chromium content of the waste exceeds the present Toxicity Characteristic Leaching Procedure (TCLP) allowable chromium concentration of 5 ppm by nearly five orders of magnitude. The waste can not be disposed of until the concentration of chromium is reduced to 5 ppm or less.

1.1 Motivation for Research

Due to the inherent toxic characteristics of the waste (Table 1.1), the waste-filled drums can not be disposed of given current disposal regulations as discussed in Chapter 2. As a result, it is necessary to reduce the hexavalent chromium-Cr(VI)-to-its-less-toxic valence state, Cr(III), and determine a means to stabilize the waste such that it can pass the TCLP test. The generator must determine an ultimate disposal method resulting in a final wasteform that is not hazardous to human health or the environment.

Table 1.1
Chomic Acid Waste Characteristics

METAL	CONCENTRATION (ppm)
Arsenic	153
Cadmium	9
Chromium	30,000
Lead	478
Selenium	less than 1
Silver	17
Beryllium	less than 1

1.2 Objectives

The objective of this research was to determine a practical on-site ultimate disposal method which successfully solidified and stabilized the Cr(VI) in a cement monolith. A surrogate waste was prepared containing approximately 30,000 ppm total

chromium according to specifications provided by the waste generator. For the purpose of this study, the trace metals listed in Table 1.1 were neglected.

1.2.1 Goal

The overall goal of this project was to determine a stabilization process which could fix the Cr(VI) concentration of the waste acid such that it measured below 0.5 ppm using approved Environmental Protection Agency (EPA) ion chromatography methods.

1.2.2 Specific Objectives

The specific objectives of this study were to investigate methods with engineering promise which could accomplish the following:

1. Determine a practical, inexpensive method to reduce Cr(VI) to Cr(III),
2. Determine a practical, inexpensive method to precipitate out Cr(III) solids at an alkaline pH,
3. Determine a workable stabilization process using Type I Portland cement and flyash which could be implemented on an industrial scale, and
4. Determine a stabilization waste loading formulation which resulted in Cr(VI) concentrations below .5 ppm in the final TCLP leachate.

Type I Portland cement was initially used as the Chemical Fixation and Solidification (CFS) reagent. Subsequently, flyash was included in the process as a stabilization aid to improve the performance of the process.

Chapter 2

BACKGROUND and LITERATURE REVIEW

For many decades, it was common industrial practice to landfill any waste generated despite the nature of the waste's constituents. With the advent of the Resource Conservation and Recovery Act (RCRA), Superfund Amendment and Reauthorization Act (SARA), and other EPA regulations, these practices are gradually being phased out. This change in mindset and in practice is forcing the development of new treatment and disposal technologies. In response to this pressing challenge, the EPA's Office of Research and Development (ORD) and Office of Solid Waste and Emergency Response (OSWER) created the Superfund Innovative Technology Evaluation (SITE) Program in the late 1980's. SITE is "a formal program [created] to accelerate the development, demonstration, and use of new or innovative technologies that offer permanent, long term cleanup solutions for hazardous wastes" (EPA, 1990). This program encourages both individuals and industries alike to set the precedent with improved technologies. Regulations such as the "landbans" passed on May 8, 1985 which prohibit "the placement of bulk or noncontainerized liquid hazardous waste or free liquids contained in hazardous waste in any landfill" (Hazardous Substances and Waste Act (HSWA) Section 3004(c)(1)) promote more stringent disposal methods.

Today, it is clear to industries nationwide that the land disposal of hazardous

wastes is not the method of choice from an environmental standpoint and occupies the lowest position in the EPA's hierarchy of methods (Conner, 1990). Thus, industries are forced to comply with these stricter disposal regulations in order to remain in operation. Because of this change in mindset and in practice, these "landbans" have created a multitude of new waste streams which require either pretreatment or complete treatment prior to final land disposal. One such treatment method which has found increasing applications because of these newer, stricter regulations is CFS - Chemical Fixation and Solidification. CFS was selected as the ultimate disposal method to resolve this study's spent chromic acid disposal issue.

2.1 What is CFS?

CFS was originally used prior to the 1970's to solidify radioactive waste, mine backfilling, soil stabilization and grouting, and for the production of stabilized base courses for road construction (Conner, 1990). Solidification and stabilization are designed to:

- improve handling and physical characteristics of the waste by producing a "solid" from liquid or semi-liquid,
- reduce contaminant solubility in the treated waste, and
- decrease the exposed surface area across which transfer or loss of contaminants may occur (EPA,1991).

Solidification refers to techniques "that encapsulate the waste in a monolithic solid of high structural integrity" (Conner, 1990). Solidification alone, is typically not sufficient to meet RCRA regulations because the hazardous properties of the waste are still present and are not sufficiently immobilized. As a result, chemical stabilization (i.e., fixation) is needed in conjunction with solidification to prevent unwanted mobilization of contaminants. Stabilization refers to techniques which "reduce the hazard potential of the waste by converting the contaminants into their least soluble, mobile or toxic form" (Conner, 1990). This occurs by altering the pH of the waste, altering the form of the contaminant or complexing the contaminant in a solid matrix (Bishop, et al, 1982). Stabilization is classified as a Best Demonstrated Available Technology (BDAT) method by the EPA and has been used to delist several RCRA wastes from their original RCRA classifications to classifications with a less stringent disposal requirements.

According the Jesse Conner (1990), one of the foremost experts of the CFS technology, "the potential market for CFS services, technology, and equipment in the United States is estimated to be at least 5 to 10 million metric tons (wet) or about 1 to 2 billion gallons per year." This market will continue to grow as stricter regulations are passed forcing more industries to comply with waste disposal regulations. CFS is considered an ultimate disposal method which implies "the final deposition of [a] waste which, for either technical or economic reasons, may not be recycled or further reduced in volume by conventional treatment processes" (Conner, 1990). Once a waste has been processed using CFS, it should never pose a threat and can be classified as

"nonhazardous" indefinitely. CFS is the preferred method for treating many hazardous waste releases or sites because it provides the opportunity for on-site treatment and eliminates the transportation step inherent in off-site disposal (Conner, 1990).

According to the EPA, "the final product [of CFS] should be a monolithic mass with good dimensional stability, high freeze-thaw resistance, low permeability, high strength, and resistant to biological and chemical attack" (EPA, 1979; Bishop, et al, 1982). Presently, there are numerous technologies, ranging in both cost and proven effectiveness, trying to achieve the EPA's aforementioned CFS criteria. These methods include variations of cement based systems, thermoplastic encapsulation processes, macroencapsulation, organic polymerization systems, and other systems such as the Chemfix[®] and SolidTek[®] Processes which are patented technologies (Conner, 1990). Because of the uniqueness and relatively small volume of waste of concern in this project, the initial research objective was to determine an effective CFS formulation using Type I Portland cement. An effective process is one that is reasonable both in terms of cost and final monolith volume which immobilizes the Cr(VI) species both in the laboratory and at the generator facility. As determined through experimentation, this scope was later modified to design a Portland cement/flyash process to meet the research objective. Both types of systems are discussed in detail below.

2.1.1 Portland Cement Based Systems

Portland cement is the most common cementitious additive used in CFS technology.

The advantages of cement-based systems are as follows:

1. Additives are available at a reasonable price,
2. The composition is consistent from source to source,
3. Equipment and cement mixing techniques are well developed and readily available,
4. The strength and permeability of the final product can be varied by controlling the amount of cement added, and
5. Good data on modeling of environmental effects from the leaching of cement-based waste forms are available from the nuclear waste field (Conner, 1990; Pojasek, 1979).

The ASTM Type I Portland cement is a general all-purpose cement, and is typically the most inexpensive type of cement. Type I is most commonly used in CFS work and is referred to as "CSA Normal" in industry (Conner, 1990). This study used only Type I cement manufactured by the Southwestern Portland Cement Company in Lyons, Colorado in order to maintain a consistent source.

Portland cement consists of a calcium silicate mixture containing primarily di- and tricalcium silicates. The process of cementation itself is quite complex and there are three models to explain the behavior of cement particles when mixed with water. What happens when a hazardous waste is added to cement is best explained by Conner (1990)

who states:

"water in the waste reacts chemically with Portland cement to form hydrated silicate and aluminate compounds. Solids in the waste act as an aggregate to form a 'concrete,' although the types of solids encountered in wet wastes may produce a concrete of low strength. The optimum combination of waste and Portland cement, the type of Portland cement chosen, and any additives, will vary with the waste type and its composition. This minimum water to cement ratio is approximately 0.40 by weight for Portland cement, but will also depend on the waste itself, since some waste solids may absorb large amounts of water. The addition of too much water may result in a layer of freestanding water on the surface of the solidified product, as well as reduction in strength and increase in permeability of the final product."

2.1.2 Portland Cement/Flyash Based Systems

Another commonly used fixation additive used in CFS technology is flyash. Flyash is a solid waste product of coal combustion. Nearly 50 million tons of flyash is generated annually in the United States, 80% of which is discarded into landfills or disposal ponds (American Coal Ash Association, 1991). The most common usage of flyash in industry is to make flyash cement. According to Conner (1990), "flyash imparts many desirable properties to concrete for certain usages, the most important of which is significant economy because it replaces 25-35 percent of the Portland cement normally used." These cost savings could be passed on to solidification/fixation processes by substituting a portion of the Portland cement with an equal portion of flyash. The downside to this, however, is the larger monolith volume and weight increase than with

a Portland cement system.

Flyash acts as a bulking agent and as a pozzolan (i.e., reacts chemically with the cement and water at room temperature to form a slow-hardening cement) in a Portland cement/flyash process. It is composed primarily of silica, alumina, iron oxide and calcium oxide (Conner, 1990). The presence of alumina and silica reduce the amount of residual Ca(OH)_2 typically found in cured cement. Flyash has been known to act as a fixing agent for chromium in solidification/fixation processes and has also led to significant increases in monolith strength (Conner, 1990). This increased strength can be attributed to the improved solid particle packing brought about by the increased surface area available given the mean particle size of flyash is less than 5 microns (Glasser, 1993). Flyash reacts more slowly than Portland cement and causes some changes in the composition of hydration products common to cement (Batchelor and Wu, 1993). As a result, it takes longer for the cement-flyash-waste mixture to reach equilibrium allowing the bulk composition of the hydrated portions of the slurry to slowly change (Glasser, 1993). This slow process allows for most of the early-formed crystalline phases to undergo ion exchange thereby causing fixation to occur. Flyash is reported to cause a decrease in hydroxide and chloride in the cement pore water when added to Portland cement (Batchelor and Wu, 1993). Like Portland cement, this additive is readily available and very inexpensive.

2.1.3 Waste Loading Criteria

Whether a cement based or cement-flyash based system is used, the key to the proper solidification and fixation of the waste is to determine effective water-to-cement/flyash and waste-to-cement/flyash ratios that can immobilize the high concentration of chromium. As the water-to-cement/flyash ratios increase, the permeability of the waste form increases due to a higher percentage of large pores formed in the monolith. Water-to-cement/flyash ratios in excess of 0.5 cause bleed water to form on the surface of the waste form. In a pure water-cement system, the solidified wasteform approaches zero at a water-to-cement ratio of 0.32 and increases exponentially as the water-cement ratio increases to 0.70 (Conner, 1990). Given these factors, the waste-to-cement/flyash ratio will depend on the amount of water in the waste itself which will bind with the cement's silicate matrix during hydration. The four stages of hydration of Portland cement are as follows:

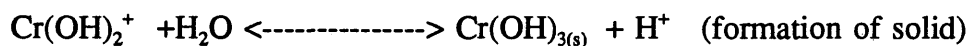
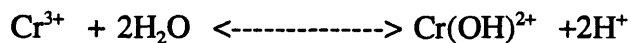
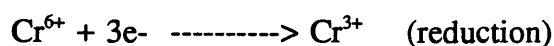
1. Time = 0 minutes (min): Cement grains are dispersed in the aqueous waste
2. Time = 2 min: Calcium sulfoaluminate hydrate forms on surfaces
3. Time = 2 hours (hr): Sulfoaluminate hydrates and other hydrates form an intermeshing network that causes setting
4. Time = 2 days: Network develops further resulting in wasteform hardening (Conner, 1990).

Proper hydration and sample mixing characteristics were two criteria used to evaluate this study's CFS process design. These criteria are discussed in Section 2.5.

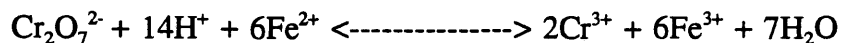
2.2 Can CFS Technology Fix Chromium?

As previously stated (Table 1.1), the waste of interest was a spent acid mixture with high chromium concentration. According to Sandesara (1980), "a spent acid with high heavy metal content makes the problem of disposal more hazardous than just disposal of heavy metals alone. Spent acids are water-soluble, which makes almost all the heavy metals which they contain water soluble." The hexavalent form of chromium is very mobile in the environment and is both an acute and chronic hazard (Jacobs, 1992). Most Cr(VI) solids are expected to be relatively soluble under normal environmental conditions. Because of its soluble nature, Cr(VI) compounds have a high leach potential (i.e., the rate at which the hazardous or undesirable constituents are removed from the waste and passed into the environment via the leachate is relatively easy). Given the high chromium concentration associated with this spent waste, one would assume the Cr(VI) would resolubilize if it came in contact with the environment. This could jeopardize both wildlife and human health considering the toxicity of Cr(VI) as discussed in Section 2.3. Conner (1990) notes "metals are the only really hazardous constituents that cannot be destroyed or altered by chemical or thermal methods, and so must be converted into the most insoluble form possible to prevent their re-entry into the environment." The trivalent species of chromium is much less soluble and toxic than the Cr(VI) and is readily

fixed with Portland cement. According to Conner, "the only practical way to fix hexavalent chromium when it is present in substantial amounts is to reduce it to the trivalent state" (Conner, 1990). Given the concentration of Cr(VI) in this waste, reduction must occur if the Cr(VI) is to be successfully fixed in the final wasteform. The critical chemical reduction reactions of concern are as follows:



Eary and Rai (1988, 1989) found that Cr(VI) is reduced in seconds by reaction with Fe^{2+} ions and in a matter of hours to days by ferrous-iron-containing oxides and silicate minerals. Ferrous ammonium sulfate (FAS) and sodium bisulfate are also known reducing agents (Jacobs, 1992). Reduced electrolytic iron filings were selected as the primary reducing agent for this research project due to availability. The governing equation for Cr(VI) reduction using iron is:



$$\text{Log } K_{\text{eq}} = 57 \quad (\text{Saleh, et al., 1989})$$

Bishop (1988) found that Cr(III) was easily immobilized in cement-based CFS systems and hypothesized that the chromium respeciated as a silicate causing it to become strongly bound in the CFS product matrix. The rate of chromium dissolution was almost identical

to the rate of silicon dissolution in the matrix. This research reaffirms the need to reduce the Cr(VI) to Cr(III) in order to stabilize the final wasteform.

2.3 Is the Stabilization of Chromium Important?

In 1797, Nicolas-Louis Vauquelin discovered chromium in the Siberian red lead ore known as crocite, PbCrO_4 (National Academy of Sciences, 1974). Unlike many metals, chromium was unknown to ancient peoples prior to this time. During the early 1800's, the first commercial process of manufacturing chromates by roasting chromite with lime and soda ash was developed in Great Britain. This process was then followed by technological advances including: bichromate and chromium pigment production, mordant dyeing, chrome tanning, metallurgy production and chrome plating.

These enormous technological gains, however, were not without detrimental human health effects. As early as 1827, only seven years after dyeing processes became industrialized, cases of skin ulceration and dermatitis in British dye workers that handled potassium dichromate were reported (Gad, 1989). 57 years later, Mackenzie did a study which reported nasal septum perforations in workers exposed to potassium dichromate (Gad, 1989). Despite such evidence that Cr(VI) related industrial processes were harmful to humans, such processes continued to flourish even though more cases were reported. The first study of lung cancer in chromate workers in the United States was made in 1948 by Machle and Gregorius at the request of the chromate-producing industry. This report confirmed Gross and Kosch's 1943 findings in their epidemiology study that identified

8 cases of pulmonary carcinoma at three chrome pigment plants in Germany (National Academy of Sciences, 1974, Gad, 1989).

As data from numerous related cohort studies became available, the processes by which chromium salts were produced were changed and working conditions at production facilities were significantly improved. Although certain forms of Cr(VI) are noncarcinogenic (i.e., monochromates and dichromates of the Group IA elements), most airborne forms of Cr(VI) are known to cause an increased risk of respiratory cancer (Sitting, 1979). Whereas airborne Cr(III) has not been proven to be carcinogenic, Cr(VI) is classified as a "probable human carcinogen" (i.e, Group A) and is known to be mutagenic (Goldhaber and Vogt, 1989). The carcinogenic potential of Cr(VI) depends on the stoichiometry, morphology and solubility of its compounds. Finely powdered metals are most soluble and can be readily absorbed by the human body. Numerous studies have been done proving the deadliness of Cr(VI) via the inhalation pathway. Today, chromium is still used at chromic acid anodizing facilities, for electropolishing processes (such as this study), and as a corrosion inhibitor for cooling towers (Alexeeff et al., 1989). CrO₃ is the typical industrial form with an enforceable Maximum Contaminant Level (MCL) of 0.05 mg/L as total chrome in drinking water (Goldhaber and Vogt, 1989).

It is clear the industrial use and disposal of chromium over the past 150 years has been detrimental to both human health and the environment. The level of Cr(VI) present in the waste of concern in this study is clearly a health concern if appropriate stabilization

and disposal is not achieved. The waste's total chromium concentration was previously measured by the generator using the EPA's TCLP and Environmental Protection (EP) Toxicity methods and is nearly five magnitudes larger than the 5 ppm TCLP limit for chromium. It is imperative to determine a realistic CFS process which can be implemented by the generator to eliminate the existing hazard potential associated with storing 30 drums of chromic acid waste and preventing a release to the environment.

2.4 How are CFS Processes Investigated in the Laboratory?

The following sections discuss in detail the physical and chemical testing procedures performed on the initial liquid and solidified wasteforms. These procedures are the standard methods used by industry today and those which can successfully be done in the laboratory.

2.4.1 Physical Test

The paint filter test is a physical test used to determine the presence of "free liquids" in a representative sample of bulk waste. The test is required by RCRA's 40CFR§264.314 and §265.314, and is used to determine if a material releases free liquid. The equipment needed to perform this test is a paint filter, ring stand and funnel.

The waste is placed in the suspended filter and allowed to sit for 5 minutes. If any liquids drip from the filter, the waste fails the test and is deemed to contain free liquids (EPA, 1989). The term "free" liquid refers to water which is chemically unbound

or that which has not been immobilized in hydrating particle surfaces during the cementation process (Conner, 1990). The HSWA Land Ban Section 3004(c)(1) prohibits hazardous wastes containing free liquids from being landfilled. Thus, it is imperative that the cemented waste mixture can pass this test.

2.4.2 TCLP: Toxicity Characteristic Leaching Procedure

The TCLP is the EPA's basis for the promulgation of BDAT treatment standards for its land disposal restrictions program. According to Anderson et al. (1979), an ideal leaching test can determine:

- the highest potential pollutant concentration in the leachate
- the factors controlling pollutant concentration
- the total amount of pollutant releasable from a given amount of waste, and
- the release pattern of the contaminant with time.

This study utilized the TCLP as its sole leaching procedure to investigate the aforementioned criteria. An EPA (1989) TCLP summary follows:

"Waste samples are prepared by crushing the wastes to pass through a 9.5 mm screen, and liquids are separated from the solid phase by filtration through a 0.6 - 0.8 micron borosilicate glass fiber filter under 50 psi pressure. Two choices of buffered acidic leaching solutions are offered under TCLP, depending on the alkalinity and the buffering capacity of the

wastes. Both are acetate buffer solutions. Solution No. 1 has a pH of about 5; Solution No. 2 has a pH of about 3. The leaching solution is added to a filtering apparatus at a liquid:solid ratio of 20:1, and the sample is agitated with a National Bureau of Standards (NBS) rotary tumbler at 30 rpm for 18 hours. The leaching solution is filtered and combined with the separated liquid waste fraction for analysis."

The analysis for chromium was performed using the Dionex Ion Chromatograph and Spectrophysics 3500 Autosampler to determine the Cr(VI) concentration in the leachate. Figures 2.1 and 2.2 depict the TCLP process and following sample analysis. A thorough methods description is provided in Chapter 3.

The purpose of performing the TCLP test was not only to determine the final concentration of Cr(VI) in the leachate but also to calculate the percent reduction of chromium capable by the different stabilization formulations. By determining both the "before stabilization" and "after stabilization" concentrations of contaminants, we can determine if the cement-to-waste ratio was successful in immobilizing the Chromium.

The "Percent Reduction" is calculated as follows:

$$(1 - a/b) \times 100 = c \quad \text{where}$$

a = pollutant concentration in TCLP extract of treated sample

b = pollutant concentration in TCLP extract of untreated sample

c = percent removal

This value "indicates the stabilization efficiency; i.e., how effectively the stabilization treatment sequestered or bound the pollutant, thereby yielding a TCLP leachate with a lowered concentration of the pollutant" (Alvarez, et al., 1990). The primary variables that

affect the outcome of leaching tests are:

- temperature
- chemical composition of waste and leaching medium
- timing and number of extractions
- physical and engineering properties of the waste and surrounding materials
- agitation technique (EPA, 1989; Tittlebaum, et al., 1985).

These factors were monitored as discussed in Chapter 4 to determine an ideal cement matrix which stabilized the chromium.

2.5 What Criteria are Used to Evaluate CFS Processes?

According to Conner (1990), there are 5 basic steps in choosing the proper CFS system. These are:

1. Definition of the problem and collection of data on the important design parameters and project considerations,
2. Data analysis and comparison with past experience,
3. CFS process testing. In the laboratory, possible test formulations hypothesized in step 2 are applied to actual waste samples using efficient, well-established test protocols. This fine-tunes the process for a particular waste stream and verifies that proposed formulations will meet the waste fixation/stabilization objectives,
4. Regulatory interaction and approval, and
5. Implementation of the solution.

This research project focuses primarily on the first 3 steps. In addition, one must also consider the waste source in terms of:

1. The holding facility,
2. Transport to the CFS system,
3. Process mode, and
4. Waste removal system (Conner, 1990).

Given the relatively small quantity of waste (6 cubic meters), this study proposed to design a practical and inexpensive on-site treatment process. Section 121 of SARA promotes on-site treatment that "permanently and significantly reduces the volume, toxicity, or mobility of [the] hazardous substances" (SARA, Section 121). The process steps (reduction, precipitation and fixation) were evaluated against three criteria to optimize the stabilization process in the laboratory for future scale up using process equipment (i.e., tanks, mixers, etc.). These criteria are:

1. The consistency of the waste, water, and fixing agent slurry must have good mixing characteristics such that the ingredients can be thoroughly mixed by hand with no difficulty.
2. The slurry must have a realistic set up time such that the slurry does not harden too rapidly to either immobilize the mixing apparatus or prevent proper cement hydration (Section 2.1.3).
3. The final wasteform must be able to undergo the TCLP test and yield Cr(VI) concentrations below 0.5 ppm in the leachate.

Details of the experimental methods and materials are given in the next chapter.

Chapter 3

METHODS & MATERIALS

The following text describes the methods and materials used in this study to meet the research objectives stated in Chapter 1. All experiments were conducted in the Colorado School of Mines environmental science and engineering stabilization laboratory.

3.1 Waste Preparation and Evaluation

The surrogate was prepared in one liter quantities as needed. Table 3.1 lists the constituents and corresponding amounts needed to make up a batch. The ingredients were added in the order listed in the table. The solution was continuously stirred using a teflon stir bar and Fisher Scientific stir plate to ensure complete dissolution of the chromium trioxide crystals and complete mixing after each acid addition.

3.2 Reduction Investigation

As previously discussed in Chapter 2, Cr(VI) must be reduced to Cr(III) prior to solidification in order to stabilize the chromium in the final cement monolith. Three reduction experiments were conducted using Mallinckrodt reduced electrolytic iron filings. The reduction reaction is very exothermic, thus the rate of Fe addition was important to control the reaction. The iron was weighed using an Ohaus Model TS400S Balance and

Table 3.1
Surrogate Waste Recipe

Constituent	Quantity
200 +/- 15 ml/L	Deionized Water
71 +/- 2 g/L	CrO ₃
750 +/- 15 ml/L	H ₃ PO ₄
30 +/- 2 ml/L	H ₂ SO ₄

added to various sized aliquots of waste acid contained in Kimax beakers. One hundred-ten percent of the stoichiometric amount of iron was added each time to ensure complete Cr(VI) reduction. Each of the experiments was conducted in a laboratory hood on a 9" Pyrex pie plate which rested on top of the Fisher Scientific stir plate. The beakers containing the waste were placed on the pie plate; the pie plate served as spill containment in case the reactions overflowed. The mixture was stirred for 5 minutes using a teflon stir bar and as expected, the filings clung to the magnetic stir bar. Table 3.2 is a reduction experiment summary that details the iron filing doses and beakers used.

Table 3.2
Summary of Reduction Experiments

Reduction Experiment	Approximate Fe Dose (grams)	Beaker Volume (ml)
1	2	100
2	1	100
3	.5	250

3.2.1 Reduction Experiment #1:

In experiment #1, 5.60 grams of the iron filings was added to a 30 ml aliquot of waste acid.

3.2.2 Reduction Experiment #2:

A second identical experiment was performed except that the Fe was added in much smaller doses. The end result, however, was similar to the first and is discussed in Chapter 4.

3.2.3 Reduction Experiment #3:

A third experiment was conducted using a larger beaker. As previously, 5.6 grams of iron was added in extremely small increments to the 30 ml of waste acid contained in the beaker.

3.3 Precipitation Investigation

The solubilities of most heavy metals are influenced by the pH of leaching solutions with the exception of some amphoteric metals. In general, solubilities of metals are low when leaching solutions have a high pH and vice versa. Alkaline materials, like cement, have high neutralization potentials. The intent of this experiment was to precipitate the Cr(III) in the reduced waste acid and to raise the pH of the waste such that it could be easily mixed with the Portland cement/water which was measured to have a pH above 12.0. It was thought that by raising the waste pH to neutral or alkaline values would prevent the Cr(III) from reoxidizing to Cr(VI). $\text{Cr}(\text{OH})_3$ is the dominant aqueous species in 7 - 10 pH range (Rai, et al, 1989). Calcium hydroxide ($\text{Ca}(\text{OH})_{2(s)}$) and sodium hydroxide (NaOH) were selected as precipitation agents. Three precipitation experiments were conducted using these agents. All solid precipitation agents added were weighed using an Ohaus Model TS400S Balance. Experiments #2 and #3 used the following equipment to titrate the 50% NaOH solution into the waste acid: Orion Model 420A pH meter, Orion pH (91-57) probe, 50 ml Kimax buret, buret stand, miscellaneous glassware, Fisher Scientific magnetic stir plate and teflon-coated stir bars. pH was measured using

a calibrated Orion 420A pH Meter; the meter was calibrated using pre-made Cole Parmer Standard Buffer Solutions, pH 4.01 and 7.00. Table 3.3 summarizes the 3 precipitation experiments.

Table 3.3
Summary of Precipitation Experiments

Experiment/ Dilution	Reagent	Reagent Concentration	Reagent Volume/Mass	Reduced Waste Mass	Mass of Water Added
1	Ca(OH) ₂	100%	30.8 g	154.2 g	0
2	NaOH	100%	33.3 g	100 g	0
3/1:1	NaOH	50%	23.5 ml	100 g	100 g
3/2:1	NaOH	50%	23.5 ml	100 g	200 g
3/3:1	NaOH	50%	N/A	100 g	300 g
3/4:1	NaOH	50%	23.0 ml	100 g	400 g

3.3.1 Precipitation Experiment #1

In the first precipitation experiment, 30.8 grams of Baker Analyzed reagent grade calcium hydroxide added to 154.2 grams of reduced waste acid. An excess of 10% extra Fe filings were added to the waste acid in the previous reduction step to ensure maximum Cr(VI) reduction. The $\text{Ca(OH)}_{2(s)}$ was added very gradually to the beaker containing the waste acid. The mixture was stirred using both a teflon stir bar/magnetic stir plate set up and intermittently by hand using a Kimax stir rod. The beaker walls, stir rod, and teflon spatula were rinsed off using deionized water.

3.3.2 Precipitation Experiment #2

In light of the difficulties (described in Chapter 4) when using $\text{Ca(OH)}_{2(s)}$, the neutralization experiment was repeated using Aldrich ACS reagent grade sodium hydroxide pellets. NaOH was selected due to its availability and known ability to neutralize very strong acids via simplistic laboratory titrations. In this experiment, 33.3 grams NaOH was added to 100 gram of waste acid in small, non-uniform increments. One hour after the onset of this experiment (i.e., from the time of Cr(VI) reduction), the pH was 2.2.

3.3.3 Precipitation Experiment #3

To determine if the pH could be raised further, a 50% NaOH solution (by weight) was made using NaOH pellets and 17.8 ohm Nanopure water. An unmeasured amount

of the 50% NaOH solution was added to the waste acid mixture using a 250 ml low density polyethylene (LDPE) Nalgene squeeze bottle.

Given the dramatic effects of using the 50% NaOH solution versus both the solid pellet version and the Calcium Hydroxide solid, it was decided to repeat the experiment but strictly use the NaOH solution. The 50% NaOH was titrated into the waste acid. Four waste acid dilutions (1:1, 2:1, 3:1, and 4:1) were titrated. Due to the rock-like mass created by adding the NaOH solution to the concentrated acid mixture, diluting the waste with Nanopure seemed appropriate from an end product result stand point as well as for safety purposes.

For each dilution, 100 gram aliquots of waste acid were reduced with 3.69 grams of Fe filings as described in the reduction experiments. After the reduction reaction occurred, an additional .36 grams (10% by weight) of Iron was added to ensure complete Cr(VI) reduction had taken place. Each sample was diluted as previously stated. The purpose of dilution was to determine a reduced waste mixture which would not form solids when concentrated NaOH was added. It was believed that in the previous experiment the concentrated acid combined with the concentrated base did not contain enough water to prohibit such an end product. The dilutions would reduce the intensity of the reaction by diluting the acid and provide the water of reaction needed. By determining a dilution in which the acid did not spatter as the caustic was added, a safer process could be designed on a larger scale and be successfully implemented.

Two additional titrations were performed using dilutions of 1.5:1 and 2.5:1 to

monitor both pH and NaOH usage. These results are given in tabular form in Appendix A.

3.4 Stabilization

The final phase of sample preparation involved stabilizing the dried waste. The success of the formulations was evaluated based on the ability of each mixture to produce a solid wasteform which insolubilized the Cr(VI). The goal of the fixation experiment was to devise a waste:water:cement/flyash ratio which minimized Cr(VI) solubility and fixed all the Cr(VI) in the monolith. In addition, this formulation must produce a solidified monolith that met the aforementioned fixation criteria and could be physically reproduced on a larger scale using industrial mixers and mixing vessels. The following text describes the three sets of experiments performed to reach a successful mixture ratio which completely fixed the Cr(VI). Type I Portland cement was the solidification/fixation agent used for the first and second set of experiments; Type I Portland cement and flyash were the solidification/fixation agents used in the third experiment.

The sample preparation for these experiments was perhaps the most critical aspect of the project. The reduced and neutralized waste was combined with varying amounts of cement, flyash and water and allowed to cure. The variables in this process were:

- Volume of waste added
- Volume of cement added

- Volume of water added
- Time of sample cure (5, 7, and 14 days)
- Weight of retardant added (if any)
- Ambient temperature
- pH of reduced waste

Constants in the process were:

- pH of cement (12.45)
- Source of cement
- Mixing procedure
- Sample mold

Table 3.4 summarizes the 3 stabilization experiments conducted in this research. All samples were prepared and cured using the same methodology. Variations in laboratory ambient temperature (14 - 28°C) occurred throughout the research project. Each sample was prepared in 4 basic steps: dry, mix, cure and evaluate. These steps are discussed in the following section.

3.4.1 Drying

Once the samples had been reduced and titrated as outlined above, the remaining liquid was poured into an 8" teflon skillet and dried overnight in a Fisher Isotemp® Series 500 drying oven at 105°C. Dried samples were removed from the oven and allowed to

Table 3.4
Summary of Stabilization Experiments

Sample	pH	% Water	Days Cured	Cement:Fly- ash: Waste	PSI 300N
A	7	40%	7	1:1	none
B	7	35%	8	1:1	none
C	7	40%	8	3:2	none
D	8	35%	10	1:1	none
E	8	40%	14	3:2	none
F	10	40%	12	2:1	none
G	10	35%	13	1:1	none
H	10	40%	14	1:1	none
I	9	35%	13	1:1	none
M	10	35%	7	1:1	3 oz less
N	10	40%	7	1:1	3 oz less 20%
O	9	35%	7	1:1	6 oz less 20%
P	9	40%	7	1:1	6 oz less 20%
Q	9	40%	7	1:1	6 oz
R	10	40%	5	1:1:1	6 oz
S	10	35%	5	1:1:1	6 oz
T	10	40%	5	1.5:1:1	6 oz
U	10	40%	5	2:2:1	6 oz
V	10	40%	5	1.5:1.5:1	6 oz

cool in a 4 tiered desiccator. Once the sample had cooled, the dried waste was removed from the skillet and ground up using a ceramic mortar and pestle until the fines could pass through an A.S.T.M.E. - 11 Specification #40 brass sieve. The skillet, mortar and pestle were acid washed using a 10% nitric acid bath to prevent cross contamination of different samples.

3.4.2 Mixing

Each sample was mixed using a small stainless steel spoon and teflon spatula. Varied proportions of dried waste and cement (and flyash) were measured and poured into 250 ml double lined truncated, cone-shaped plastic cups. The purpose of using two cups was to prevent the leaking or drying out of samples in case the innermost cup cracked. The waste and cement were mixed together using the small spoon to ensure the dry components were completely mixed prior to liquid addition. Chilled nanopure water (and PSI 300N Water Reducing Add-Mixture) was then added and stirred together with the small teflon spatula.

3.4.3 Sample Cure

Once mixed, the samples were allowed to set up for approximately 5 to 10 minutes. The sample was then covered with a loose fitting piece of parafilm; a moist paper towel was laid on top of the parafilm and the entire unit was sealed with one large piece of parafilm. The samples were checked on a daily basis to ensure the paper towel

was still moist and provided adequate moisture for the cure. The second and third sets of samples were prepared in the same manner. These latter samples, however, were placed in a large LDPE plastic tub containing two 250 ml beakers filled with water. The samples were placed inside the tub which was sealed using Reynolds® aluminum foil. The purpose of this modification was to provide a more uniform curing environment (i.e., uniform humidity amongst samples and no draft from ambient laboratory conditions). The temperature could not be controlled in this chamber and was the same as that in the laboratory (20+/-8°C). According to Jacobs (1992), samples can easily be tested after 3 days of curing; at that time most or all of the chrome which will be fixed in the monolith has been fixed. All the samples were cured for 5 to 14 days, thus the curing times were assumed to be adequate and the curing time variations were assumed to be insignificant.

3.4.4 Stabilization Experiment #1

The first series of samples prepared for TCLP analysis consisted of 9 samples ranging in pH (7 to 10), water content (35 to 40%) and cement: waste loading (1:1 to 2:1). The pH range was selected given the previous work done with NaOH precipitation. Because the waste acid could be reduced and easily raised to pH 10, it was decided to vary samples from the neutralization point (i.e., pH 7) to the maximum pH 10. The water loading was varied at each pH to be either 35% or 40% by weight of the total sample. Finally, the waste loadings were modified to determine if the proportion of cement had

any impact on the fixation of the Cr(VI).

3.4.5 Stabilization Experiment #2

The second batch of samples were prepared as previously discussed in Sections 3.4.1 through 3.4.3. These samples, however, were modified slightly by adding a water reducing agent to the formulation. PSI 300N, a common water reducing agent manufactured by Cormix Construction Chemicals and used in the construction industry, was added to the chilled Nanopure in measured doses per the manufacturers specifications. A PSI 300N specification sheet is included in Appendix C. The manufacturer recommended 3 ounces of PSI 300N per 100 pounds of cement; 6 ounces per 100 pounds could also be used if cement mix was not of the desired consistency. The amount of water needed is intended to be reduced by 20% by using this reducing agent. The water reducing agent was selected in an attempt to retard the setting time of the initial sample set up in order to fix more of the Cr(VI) in the cement matrix. Three samples at pH 9 and 2 samples at pH 10 were mixed using this reducing agent. Once again, water volumes of 35% and 40% by weight were used.

3.4.6 Stabilization Experiment #3

Given the results of Experiments #1 and #2, it was not clear as to what steps to take next to further fix the Cr(VI) in the final monolith. Conner's text (1990) suggests the usage of jet cement, a high alumina content cement which has been used in other

chrome stabilization/fixation research projects. This type of cement, however, was not available in the Denver area. Per personal communication with Jesse Conner (1994), Conner suggested repeating the experiment using a mixture of Type I Portland Cement and flyash. Like jet cement, a high alumina content specialty cement, flyash has also been found to readily fix chrome contaminated wastes. Flyash was obtained from a local Quickrete® vendor in the Denver area. A specification sheet for the flyash is included in Appendix C. 5 samples were prepared using pH 10 dried waste, 35% and 40% by weight water volumes, full strength PSI 300N (i.e., 6 ounces per 100 pounds cement without the 20% manufacturer's suggested water reduction) and varying waste:cement:flyash loadings.

3.5 Evaluation

Once the samples had cured, each sample was removed from its plastic mold and broken into pieces small enough to pass through an A.S.T.M.E. - 11 Specification 9.5 mm brass sieve. A standard size hammer was used to break the samples. The samples were placed in the bottom pan of the sieve apparatus and struck with the hammer until the pieces were small enough to pass through the sieve. Samples were then sieved. The hammer was acid washed and air dried between uses to prevent cross-contamination of samples.

Hundred gram samples were weighed out using an Ohaus Model TS400S balance and poured into the two liter TCLP extraction bottles. All samples were measured for pH

per the EPA TCLP guidelines to determine whether to use Extraction Fluid #1 or 2. Sample pH values were between 9.0 and 12.9. All samples used the #2 Extraction Fluid. This fluid was made up fresh for each sample using Nanopure water and reagent grade glacial acetic acid. The samples were prepared and agitated using a Lars Lande Rotary Extractor for 18 +/- 2 hours. The samples were analyzed again for pH after the tumbling period and filtered through a .45 micron pore size Whatman (934-AH) glass microfibre filter. A 1000 ml Millipore vacuum borosilicate glass filtering apparatus was used to collect the filtrate. The filtrate was then acidified with 18 M HCl and stored in a laboratory refrigerator for a maximum of two days prior to analysis. Figure 3.1 depicts this sequence of events in a flowchart.

The Variable Wavelength Detector (VDM) of the Dionex Ion Chromatograph was used to analyze the samples for Cr(VI). EPA Method 218.6 *Determination of Dissolved Hexavalent Chromium in Drinking Water, Groundwater and Industrial Wastewater Effluents by Ion Chromatography* was used. The Dionex AS-7 column and NG-1 guard columns were used as recommended by the vendor. The ion chromatograph (IC) was used in conjunction with a Spectraphysics 3500 Autosampler. Compressed helium and nitrogen, grades 5.0 and 4.8 respectively, were employed with this method. Figure 3.2 depicts the Ion Chromatograph sample analysis in a flowchart. Samples for Stabilization Experiments #1 and #2 were diluted 10:1 with Nanopure water to ensure detectability by the IC (i.e., IC calibrated to 10 parts per million, ppm). The IC was recalibrated with a series of Cr(VI) standard solutions (0, 1, 5, 10 ppm) for each experiment. A sample

standard curve is included in Appendix B.

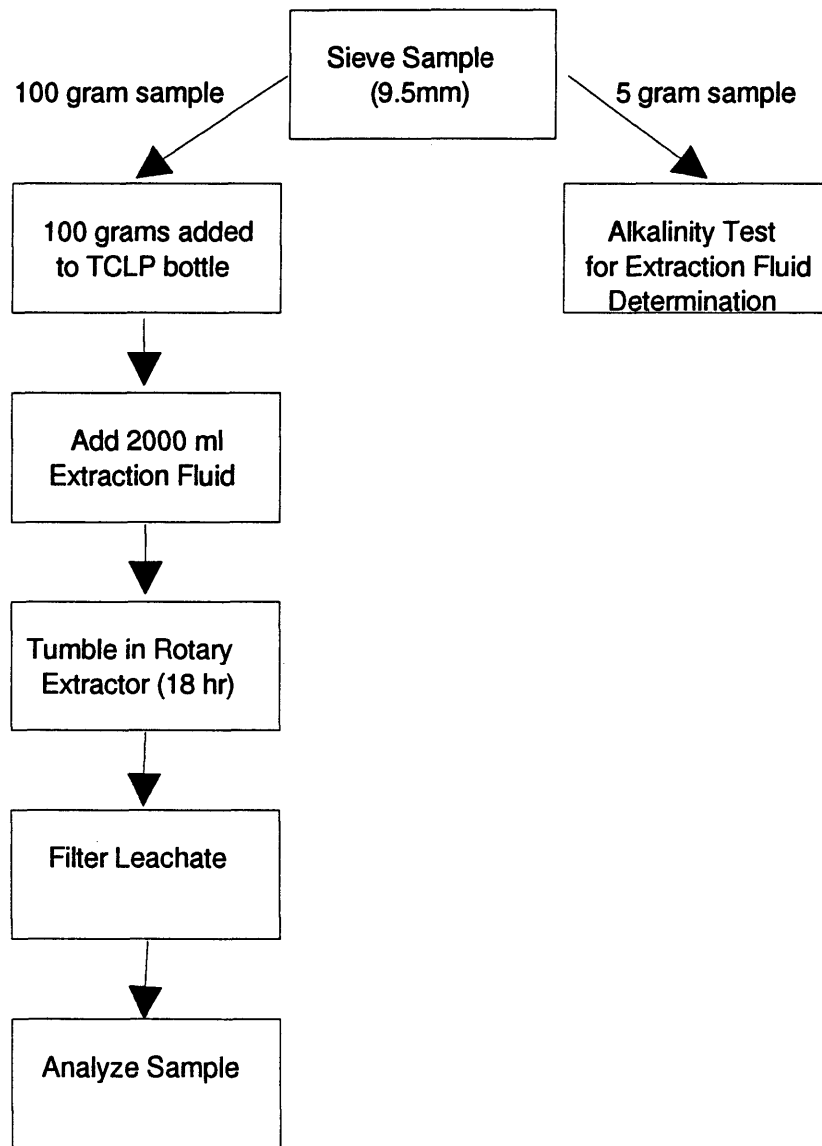


Figure 3.1: Sample Preparation Flowchart

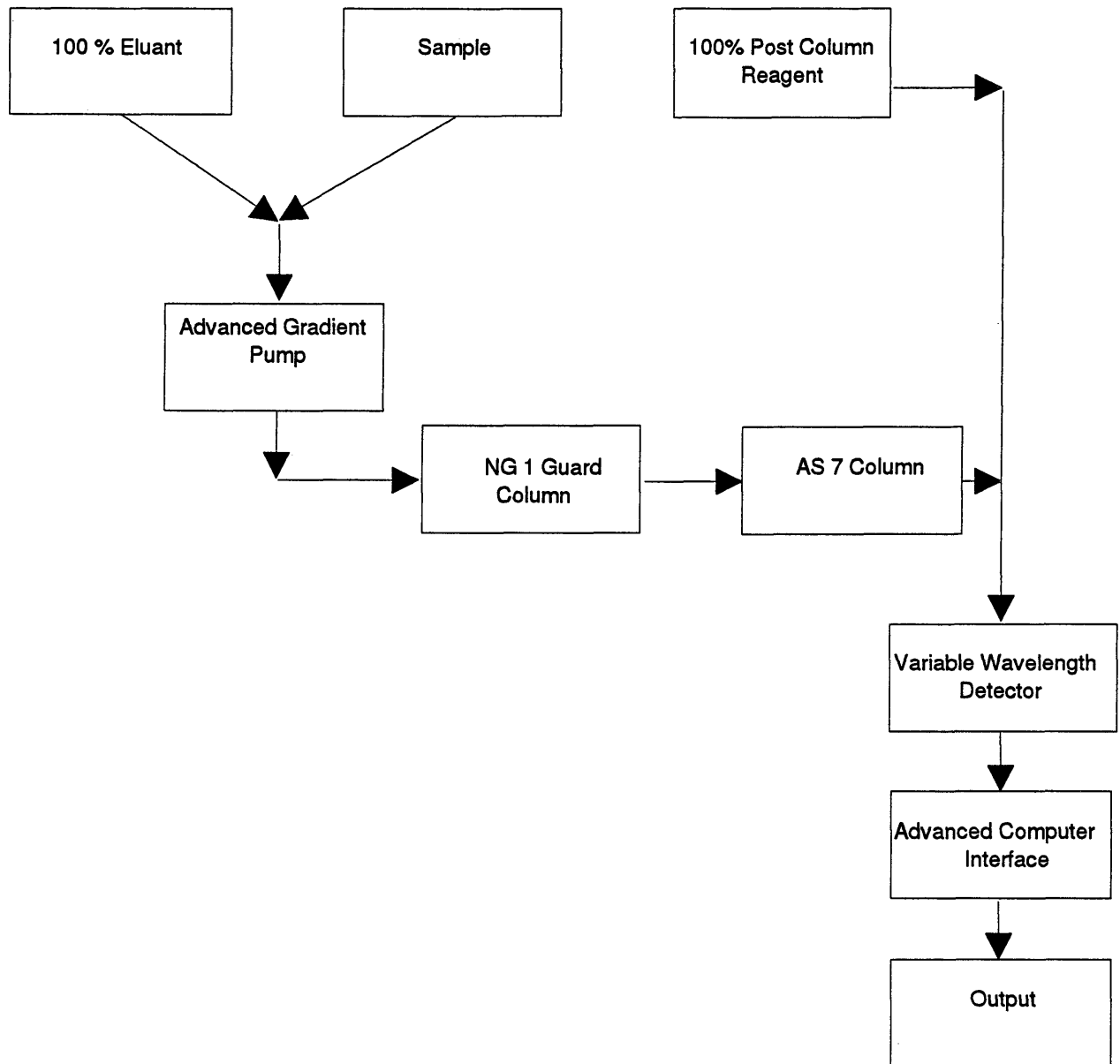


Figure 3.2: Dionex Ion Chromatograph Flowchart

Chapter 4

RESULTS and DISCUSSION

The following chapter discusses the results of the experiments previously described in Chapter 3.

4.1 Reduction Experiment

The addition of iron to the waste acid caused a violent exothermic reaction to occur roughly 12 min after the iron was added. During the reaction, condensation formed quickly on the interior beaker walls from the heat given off by the reaction. The color of the waste acid-iron mixture changed from orange-red to an intense emerald green which was taken as presumptive evidence that Cr(VI) had been reduced to Cr(III). In both Reduction Experiments #1 (2 gram dose) and #2 (1 gram dose), the beakers were undersized causing the resulting green liquid to overflow the 100 ml beaker onto the 9" Pyrex pie plate beneath it.

In Experiment #3 (0.5 gram dose), the violent reaction occurred as expected but was contained in the larger sized beaker. After the reaction had ended, the resulting liquid was emerald green in color and appeared to have a slippery, viscous consistency. The excess iron filings clung to the stir bar; the stir bar was removed taking the iron with it. The final pH of the mixture was below pH 1.0.

Given the success of this reaction, it was decided to continue to use Fe filings as the reducing agent for the duration of the research project. Each time the experiment was conducted, it was apparent that an undetermined amount of activation energy was necessary before the iron would react with the chromic waste acid. An average induction period of 12 minutes was determined.

4.2 Precipitation Experiment

4.2.1 Precipitation Experiment #1

The $\text{Ca}(\text{OH})_{2(s)}$ did not mix well with the waste acid and tended to float in clumps on top of the acid surface. The waste bubbled slightly after each addition and moisture collected on the inner walls of the beaker from the steam given off by the reaction. After 13 minutes, approximately 50% of the $\text{Ca}(\text{OH})_{2(s)}$ had been added without any significant visible change in the waste or without a major reaction occurring; the remaining caustic was added in one dose and a vigorous reaction occurred. The final pH of the mixture was 1.9. This neutralization method was abandoned as ineffective (i.e., little change in pH, slow reaction time, and difficulty in mixing the $\text{Ca}(\text{OH})_{2(s)}$ with the waste acid).

4.2.2 Precipitation Experiment #2

Ten to twelve NaOH pellets were added at a time. Initially, no reaction occurred and no precipitants formed. Within a 5-10 minute time period, a violent reaction took place causing the acid to boil. 3 ml of deionized water was added to cool the acid and the beaker was placed in a lukewarm water bath. After 11 minutes, all the NaOH pellets

had been added and the green waste appeared much thicker than the original solution; the mixture did not contain any visible precipitants to attribute to this thicker, more viscous consistency. Addition of 50% NaOH caused the green liquid to react violently and form a greenish-brown rock-like mass in the bottom of the beaker. As the NaOH solution was added, the waste acid splattered. The pH prior to the addition of the NaOH solution was 2.2.

4.2.3 Precipitation Experiment #3

The following section describes each NaOH titration of the reduced, diluted waste in detail, including visible physical changes in the waste during the titration. Each diluted sample was titrated to pH 7.

4.2.3.1 1:1 Dilution

During the 1:1 dilution titration, only 3 to 5 drops of NaOH could be added at one time. Each time the NaOH came in contact with the reduced waste acid, the acid splattered. Where droplets touched the acid surface, brown specks appeared. Both the specks and splattering dissipated as the teflon stir bar thoroughly mixed the waste acid and caustic. Condensation appeared on the sides of the beaker as the NaOH was added. White precipitant formed after 8.5 ml of NaOH had been added. After 10 ml of NaOH had been added, the concentration of precipitant increased such that the mixture became much thicker and turned a light shade of green. Once the mixture became a milky green

color, each addition of NaOH thereafter caused brownish-black specks to form on the mixture surface. This reaction required 23.5 ml of NaOH to reach a final pH; the maximum temperature measured was 55°C. The NaOH was added slowly to avoid acid of 7.0. The spattering. Temperatures would probably rise much more quickly and to higher levels with a more rapid addition of base.

4.2.3.2 2:1 Dilution

The 2:1 dilution was much easier to manage. The acid did not spatter or form brown specks with the addition of the NaOH. Unlike the 1:1 dilution, ten or more drops of caustic could be titrated into the waste reaction without an adverse reaction from occurring. White precipitant began to form after the addition of 2 ml of NaOH. The mixture became a milky green color after 9 ml of caustic had been added. Additions of NaOH after this color change caused brown specks to form at the surface. As previously, the brown specks dissolved with continued stirring. This dilution took 23.5 ml of 50% NaOH to reach pH 7.0. The maximum recorded temperature was 51°C.

4.2.3.3 3:1 Dilution

The 3:1 dilution was discarded due to the fact that the buret was mistakenly refilled with Nanopure rather than caustic during the titration.

4.2.3.4 4:1 Dilution

The 4:1 dilution reacted similarly to the 2:1 dilution requiring 9.35 ml to induce the milky green color change and 23.0 ml to reach a final pH of 7.0. The maximum temperature recorded was 54°C.

Following these titrations, it was decided that the 1.5:1 was a workable dilution which minimally increased the volume of the waste. This dilution did not spatter and could be easily titrated in a relatively short time.

4.2.4 Additional Titrations

A 2.5:1 titration was taken to pH 10.0. Above pH 7.0, the waste became greenish-brown. Given this further color change, an additional dilution (1.25:1) was made and titrated. The acid spattered (confirming the decision to use the 1.5:1 dilution) and the sample also became greenish-brown above pH 7. The sample became more of a brown color as the pH exceeded 10.0. The sample could not be titrated past pH 11.7 because the addition of NaOH caused the formation of unknown crystals in the waste creating a solid. In light of this, it became apparent that it was not possible to bring the pH of the waste up to that of cement (pH 12.45). The incremental addition of NaOH versus increase in pH indicated that the mixture was saturated with OH⁻ ions and had reached a threshold. The pH 11.7 waste was a very dark brown color and when poured into an aluminum tin for drying, the waste mixture corroded the pan and disintegrated the pan bottom overnight in the drying oven. The experiment was not repeated and future

samples would only range in pH from 7 to 10 given these results.

4.3 Stabilization Experiment

4.3.1 Stabilization Experiment #1

As indicated in the last column of Table 4.1 neither initial pH, waste loading or the amount of water added (between 35 and 40%) had any significant effect on the fixation of the Cr(VI).

Table 4.1

Stabilization Experiment #1 Results

Sample	pH	% Water	Days Cured	Cement: Waste	Cr(VI) (ppm)
A	7	40%	7	1:1	6.60
B	7	35%	8	1:1	6.50
C	7	40%	8	3:2	6.83
D	8	35%	10	1:1	6.46
E	8	40%	14	3:2	6.62
F	10	40%	12	2:1	6.99
G	10	35%	13	1:1	6.52
H	10	40%	14	1:1	6.54
I	9	35%	13	1:1	6.46

All the TCLP leachate samples ranged from 6.46 to 6.99 ppm Cr(VI) when analyzed using the Dionex ion chromatograph. The TCLP extract had a yellowish tint after being tumbled for 18 hr and then filtered; this yellowish tint was indicative of the presence of Cr(VI) in the extract. The samples which used a 40% water loading were much easier to mix and set up more slowly than the samples with a 35% water loading. All of the samples, however, set up in less than two minutes, an unrealistically short amount of time for any industrial, large scale process. In addition, it was also evident that the samples at initial pH greater than 9 cured more slowly than those with an initial pH below 8. Each sample grew very warm when all the components were mixed together, especially those of lower pHs (i.e, pH 7 - 8). This heat of reaction eventually caused some of the plastic molds to crack, probably due to expansion of the slurry. The waste:cement loading did not effect the mixing process. It only affected the ease of breaking the samples for the TCLP test (i.e., the higher the cement content, the more difficult to break the sample). Visual sample results 3 days or more into the cure period are summarized in Appendix D. In general, these samples were very coarse in nature when broken apart and several were unevenly mixed. This unevenness of mixture can be attributed to the extremely quick set of the sample (i.e., insufficient time for complete sample mixing). Appendix E summarizes specific details about TCLP runs for these 9 samples. Sample ion chromatography output is included in Appendix F.

4.3.2 Stabilization Experiment #2

In light of the results from Stabilization Experiment #1, it was decided that the second set of samples should use the 1:1 cement:waste loading factor to minimize final monolith volume, a pH range of 9 - 10 to keep the pH of the sample and cement as similar as possible as well as retard the curing process by using a water reducing agent, and to use 35 to 40% water for better mixing characteristics. In addition, all the samples were cured for a uniform time period of 7 days.

The final concentration of Cr(VI) in the TCLP extract was not affected by sample pH or water loading. The water reducing agent (PSI 300N) did not help fix more of the Cr(VI) by slowing the sample set up time as desired. PSI 300N is used in industry to slow cement set up and strengthen the end product by providing a longer amount of time for the cement silicates to react with the available calcium hydroxide with the addition of water to the mixture. The range of Cr(VI) from the second batch of samples was consistent with the first with a range of concentrations of 6.46 - 6.57 ppm. As previously, the TCLP extract had a yellowish tint indicating Cr(VI) had leached from the crushed sample during the 18 hr tumbling period.

The process was remarkably improved and more realistic for its future scale up although the Cr(VI) stabilization results did not improve with Experiment #2. With the addition of the water reducing agent, samples became much easier to mix and the set up time improved slightly. Sample P which utilized 40% water and 6 ounces of water reducing agent per 100 pounds cement without decreasing the water content by 40%

resulted in the best mixing, slowest curing sample. The sample was like a loose slurry once all the ingredients had been added and thoroughly mixed. This sample took several minutes to set up. It should also be noted that none of these samples cracked their molds like samples from Experiment #1 and appeared to be better mixed and smoother in consistency upon examination once they were broken up with the hammer in preparation for the TCLP test. The water reducing agent, however, created a much stronger end product which is very difficult to physically break apart. Table 4.2 details the results of stabilization experiment #2. Visual sample results 3 days into the cure period are summarized in Appendix D. Appendix E summarizes specific details about TCLP runs for these 5 samples.

4.3.3 Stabilization Experiment #3

The results of the last set of experiments (flyash addition) reached the desired objectives of this research project. Cr(VI) was 0 ppm in the TCLP extract for all 5 samples. The samples were analyzed twice and the ion chromatograph was recalibrated twice with new standards to ensure the 0 ppm reading was valid. Unlike the slightly yellow color of the TCLP extracts from the first and second batches of samples, the TCLP extract for all the samples in this last batch remained clear after the 18 hour tumbling period and did not discolor when acidified prior to testing. Table 4.3 denotes the ratios of waste loading, flyash and cement additions. Other sample details are provided in Appendices D and E. The addition of flyash not only proved to be an

Table 4.2
Stabilization Experiment #2 Results

Sample	pH	% Water	PSI 300N	Cement: waste	Cr(VI) (ppm)
M	10	35%	3 oz less 20% water	1:1	6.51
N	10	40%	3 oz less 20% water	1:1	6.57
O	9	35%	6 oz less 20% water	1:1	6.49
P	9	40%	6 oz less 20% water	1:1	6.52
Q	9	40%	6 oz	1:1	6.46

Table 4.3
Stabilization Experiment #3 Results

Sample	pH	% Water	PSI 300N	Flyash: Cement: Waste	Cr(VI) (ppm)
R	10	40%	6 oz.	1:1:1	0
S	10	35%	6 oz.	1:1:1	0
T	10	40%	6 oz.	1.5:1:1	0
U	10	40%	6 oz.	2:2:1	0
V	10	40%	6 oz.	1.5:1.5:1	0

effective method to fix the Cr(VI) but also produced monolithic like samples which were relatively easy to break apart with a hammer. The crushed samples had a sandy, clayey consistency and appeared to be evenly mixed with no cracks or clumps of cement as with the samples in experiments #1 and #2. The samples stayed relatively cool while being mixed unlike the samples in Experiments #1 and #2. The plastic cup was slightly warmer than room temperature while the sample was mixed. The most easily mixed samples (T, U, and V) all used 40% water by weight and 6 oz per 100 lb cement PSI 300N. The

slurries had a very runny consistency, one which could easily be mixed with an industrial mixer and the poured into a solidification vessel. Ideally, the samples could be mixed in the final solidification vessel (i.e, a drum).

4.4 Other Results

As described in Chapter 2, the Paint Filter Test was conducted for each of the cemented samples. By visual inspection, it was obvious that none of the samples contained free liquid and the test was not applicable.

Chapter 5

CONCLUSIONS

In conclusion, this research project successfully determined a formulation by which the Cr(VI) in a waste acid could be stabilized and fixed permanently. Although additional research needs to be conducted prior to implementing this process on an industrial scale, this project has confirmed previous CFS research results and has incorporated these findings into a 3 phase approach toward solving a real hazardous waste generation issue.

The key findings in this research were:

1. Elemental iron is an effective Cr(VI) reducing agent,
2. A 1.5:1 water to waste ratio provided a workable mixture for the precipitation of Cr(III),
3. Type I Portland cement is ineffective as the sole fixing reagent because the waste/cement mixture sets up too quickly for proper cement hydration or mixing to occur,
4. Type I Portland cement mixed with a water reducing additive yields a workable mixture but does not stabilize additional chromium, and
5. Type I Portland cement mixed with a water reducing additive and flyash yields a workable mixture which results in 100% fixation of the Cr(VI). A 1:1.5:1.5 waste to flyash to cement ratio with 40% water, full strength water reducing additive resulted in 0 ppm Cr(VI).

Technologies such as CFS must further be developed in research such as this project in order to determine realistic methods to process hazardous wastes in an attempt to solve

a very real problem that presently exists with finding hazardous waste disposal methods that are protective of both human health and the environment.

Chapter 6

RECOMMENDATIONS FOR FUTURE RESEARCH & INDUSTRIAL IMPLEMENTATION

Because Cr(VI) was successfully fixed in the flyash/cement samples, the experimenter has a high level of confidence that this experiment could be scaled up to an industrial process after the formulations were optimized through additional research efforts. The formulations from Stabilization Experiment #3 should be repeated to confirm the results of the research project as well as attempt other variations in the waste:cement:flyash ratio to minimize final monolith volume and increase the waste loading for consideration of final disposal.

In order to implement this process, however, care must be taken in equipment selection to ensure the safety of the individuals overseeing the reactions. The following section discusses key points which should be considered in taking this process from its current pilot-scale level to a full scale industrial process.

6.1 Laboratory Optimization

Prior to implementing this CFS process on an industrial scale, the reduced waste drying step should be eliminated. Although this step was used for convenience in this research, it would be infeasible to attempt to dry 6 cubic meters of diluted waste acid on

a large scale. Furthermore, it is hypothesized that this drying step may have caused the reoxidation of Cr(III) to Cr(VI) and should be eliminated to prevent oxidation from occurring.

Another reason to eliminate the drying step is to prevent the possibility of creating airborne Cr(VI) from the resulting grinding and sieving step. Airborne Cr(VI) is a known carcinogen and exposure should be avoided.

Sampling curing may be optimized by designing a temperature and humidity controlled chamber in which the samples can cure under uniform conditions. The effects of curing samples under ambient laboratory conditions is unknown, but given the variability in temperature as observed by this study, this is an area of research which needs further examination.

6.2 Industrial Optimization

Finally, this process should be optimized such that it can be completed in-situ in 55 gallon drums in preparation of its ultimate disposal.

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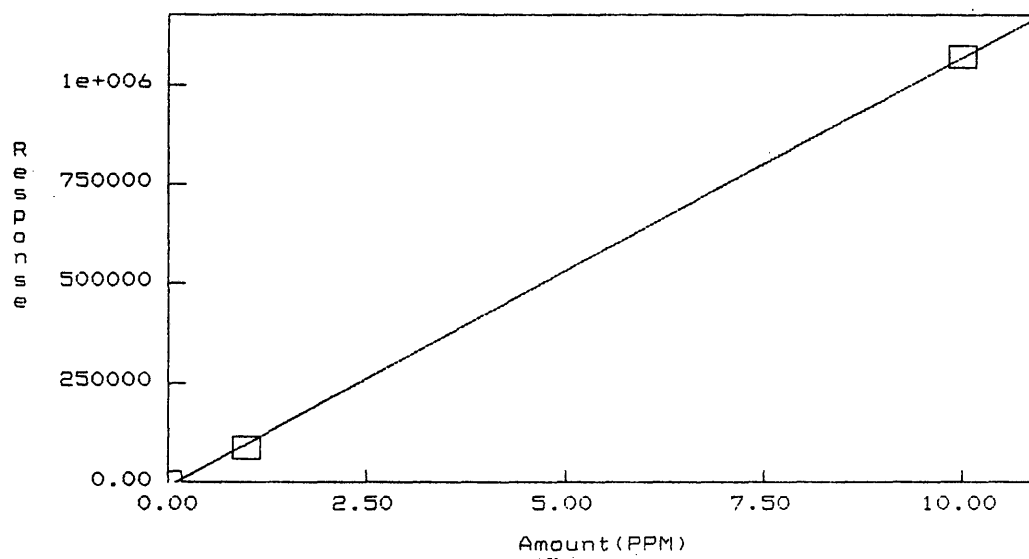
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APPENDIX A

Additional Titrations		
Dilution	Final pH	NaOH (ml)
1:1	6.95	23.5
2:1	7	23.5
3:1		
4:1	6.98	23
1.5:1	7.02	30.4
2.5:1	10	35.9

APPENDIX B

Component: CHROM (VI)
Fit Type: Linear
 $r^2 = 0.999722$
 $Amt = Resp * 9.264e-006 + 0.0875$
 $Resp = Amt * 1.079e+005 + -9454$
Standardization: External
Calibration: Area



APPENDIX C

PSI-300N

MAN 15 1994

PSI-300N is a normal setting, highly concentrated, multi-component, liquid admixture conforming to ASTM C 494, Type A. PSI-300N reduces the quantity of mixing water required to produce concrete of a given consistency while providing greater economy for a given strength. It increases strengths significantly and improves watertightness, workability and finishing characteristics.

PSI-300N does not contain calcium chloride in its formulation and is compatible with air-entrained or non air-entrained concrete mixes, as well as with concrete containing calcium chloride. Using only the finest raw materials, PSI-300N is manufactured in our own plants under rigid quality control standards.

ADVANTAGES IN PLASTIC CONCRETE

- Reduces plastic shrinkage cracking
- Decreases segregation
- Improves workability
- Reduces mixing water for a given consistency
- Provides improved placing and finishing characteristics
- Maintains normal setting times

ADVANTAGES IN HARDENED CONCRETE

- Increases compressive, flexural and bond strength to steel
- Reduces cracking and shrinkage
- Reduces permeability—increases watertightness
- Increases resistance to freezing and thawing
- Provides improved finished appearance

APPLICABLE STANDARDS

ASTM C 494, Type A
 CIRCA 27
 AASHTO M 194

DOSAGE RATES

3-4 fl oz per 100 lbs cement. For information on usage at higher rates, contact your Cormix Construction Chemicals representative.

TYPICAL COMPRESSIVE STRENGTH

517 lbs cement/cu yd
 Tested at same slump

	7 days (psi)	28 days (psi)
Plain	3125	3850
3 oz PSI-300N/ 100# cement	3615	4510
4 oz PSI-300N/ 100# cement	3915	5110

TYPICAL TIME OF SETTING

517 lbs cement/cu yd
 Tested at same slump

(ASTM C 403-Initial Set)

	Time of Setting at 73°F
Plain	4:45
3 oz PSI-300N/ 100# cement	4:45
4 oz PSI-300N/ 100# cement	5:15

COMPATIBILITY

PSI-300N is compatible with approved air-entraining agents, calcium chloride, stearates, and the like, but does not of itself entrain air significantly. It does not contain calcium chloride as a component.

TECHNICAL SERVICES

Our qualified representatives are available to all specifiers and users to assist and advise in specifications, dispenser installation and field service.

In no way is this service to be interpreted as supervision, which is the proper responsibility of others. Cormix Construction Chemicals is not responsible for conditions outside its control, including other materials, workmanship, design, inspection or ambient conditions.

PRECAUTIONS

PSI-300N can be used at temperatures as low as 23°F. Care should be exercised to prevent freezing below this temperature; however, freezing does not damage the material if thawed and mechanically agitated.

PSI-325

PSI-325 has been formulated to give a higher degree of set control in colder weather, in areas where prestressed or dissimilar metals aren't used.



RESOURCE MATERIALS TESTING, INC.

"Specialists in Fly Ash Testing"

REPORT OF FLY ASH ANALYSIS

TO: Western Ash Company
 Attn: Mr. Harry Roof
 4380 S. Syracuse St., Suite 305
 Denver, CO 80237

PROJECT NO.: RMT-048
 SAMPLE NO.: 5037
 DATE REC.: 02-02-94
 DATE REP.: 03-04-94

PROJECT NAME: Denver C Plant Fly Ash Q.A. Program
 SAMPLE ID: Class C Fly Ash Jan'94 QAP #62

CHEMICAL ANALYSES		
PARAMETER	RESULTS	ASTM C618 SPEC. F/C
Silicon Dioxide, SiO ₂ , %	31.66	---
Aluminum Oxide, Al ₂ O ₃ , %	21.40	---
Iron Oxide, Fe ₂ O ₃ , %	6.26	---
Sum of SiO ₂ , Al ₂ O ₃ and Fe ₂ O ₃ , %	59.32	70/50 min
Calcium Oxide, CaO, %	29.84	---
Magnesium Oxide, MgO, %	6.13	---
Sodium Oxide, Na ₂ O, %	---	---
Potassium Oxide, K ₂ O, %	---	---
Sulfur Trioxide, SO ₃ , %	2.85	5.0 max
Moisture Content, %	0.05	3.0 max
Loss on Ignition, %	0.22	6.0 max
Available Alkalies as Na ₂ O, %*	1.05	1.5 max
PHYSICAL ANALYSES		
Amount Retained on No. 325 Sieve, %	17.9	34 max
Strength Activity Index		
Portland Cement at 7 days, % of Control	109	75 min
Portland Cement at 28 days, % of Control	114	75 min
Water Requirement, % of Control	91	105 max
Autoclave Expansion, %	+0.03	0.8 max
Specific Gravity	2.78	---
Increase of Drying Shrinkage, %*	---	0.03 max
Reactivity with Cement Alkalies, %*	---	---
Reduction of Mortar Expansion, %	---	---
Mortar Expansion, %	---	0.020 max
Air Entrainment of Mortar, %	---	---

*Optional requirements applicable only when requested by purchaser.
 This material meets the requirements of ASTM C618 for the parameters tested.

By Robert L. Smith
 Robert L. Smith, Ph.D.

APPENDIX D

STABILIZATION EXPERIMENTS				
Sample	pH	Cr VI	Final Color	% Reduction
		ppm	of Extract	
A	7	6.60	yellow	
B	7	6.50	yellow	
C	7	6.83	yellow	
D	8	6.46	yellow	
E	8	6.62	yellow	
F	10	6.99	yellow	
G	10	6.52	yellow	
H	10	6.54	yellow	
I	9	6.46	yellow	
M	10	6.51	yellow	
N	10	6.57	yellow	
O	9	6.49	yellow	
P	9	6.52	yellow	
Q	9	6.46	yellow	
R	10	0.00	clear	100%
S	10	0.00	clear	100%
T	10	0.00	clear	100%
U	10	0.00	cloudy	100%
V	10	0.00	very clear	100%

Sample	pH before	pH after	pH of	Cr VI
	TCLP	TCLP	Extract	ppm
A	10.87	6.84	2.87	6.60
B	10.52	8.34	2.85	6.50
C	12.24	11.08	2.85	6.83
D	12.33	11.00	2.93	6.46
E	12.12	10.87	2.88	6.62
F	12.90	12.64	2.92	6.99
G	12.30	11.61	2.92	6.52
H	12.63	11.93	2.92	6.54
I	12.28	10.91	2.91	6.46
M	8.99	10.33	2.87	6.51
N	11.78	9.49	2.86	6.57
O	11.81	11.30	2.87	6.49
P	11.99	10.91	2.88	6.52
Q	11.87	10.96	2.86	6.46
R	11.38	11.22	2.87	0.00
S	9.20	11.42	2.87	0.00
T	11.54	10.57	2.86	0.00
U	11.85	10.86	2.87	0.00
V	11.33	10.53	2.86	0.00

Portland Cement/PSI 300N/Flyash Sample Characteristics			
Sample	Color of Uncured Mixture	Odor of Uncured Mixture	Time to Set (minutes)
A	army green	none	<1
B	army green	none	<1
C	army green	none	1
D	army green	none	<1
E	army green	none	1
F	army green	none	1
G	army green	none	1-2
H	army green	none	1-2
I	army green	none	<1
M	brownish green	none	<1
N	brownish green	none	1
O	army green	none	<1
P	army green	none	1-2
Q	army green	none	2
R	brown tint	none	1-2
S	brown tint	none	1
T	brown tint	none	>3
U	brown tint	none	>3
V	brown tint	none	>3

Portland Cement/PSI 300N/Flyash Sample Characteristics			
Sample	Ability to Break Sample	Sample Texture	Observations
A	easy	sandy	well mixed; light green color; small cracks
B	easy	sandy	poorly mixed; light and khaki green color
C	moderate	dry	well mixed; brown color; smooth surface; no cracks
D	very difficult	dry	well mixed; light green color; small cracks
E	easy	dry	well mixed; brown color; smooth surface; no cracks
F	very difficult	cement like	well mixed; light green color; no cracks
G	easy	very dry & crumbly	well mixed; light green color; large cracks; cracked plastic mold
H	easy	very dry & crumbly	well mixed; light green color; large cracks; cracked plastic mold
I	easy	very dry & crumbly	poorly mixed; medium green color; rough surface
M	difficult	very dry & crumbly	well mixed; green color; no cracks
N	easy	very dry & crumbly	well mixed; light green color; cracked plastic mold
O	very difficult	very coarse	well mixed; dark army green color; cracked plastic mold; rough surface
P	easy	chalky	not mixed at bottom; light green color
Q	easy	chalky	well mixed; light green color
R	easy	sandy, clayey	well mixed; brown color; very smooth texture; no cracks
S	easy	sandy, clayey	well mixed; brown color; very smooth texture; no cracks
T	easy	sandy	well mixed; brown color; very smooth texture; no cracks
U	moderate	sandy	well mixed; brown with grey tint
V	easy	sandy, clayey	well mixed; brown color; very smooth texture; no cracks

APPENDIX E

```

=====
Sample Name: F - A06                      Date: 12/10/1993 19:27:22
Data File :
Method   : c:\dx\method\chrom.met
ACI Address: 1 System: 1 Inject#: 6 Vial:A06 Detector:VDM-2
Analyst  :                               Column:
=====

```

```

-----
Calibration Volume Dilution Points Rate Start Stop Area Reject
-----
External          50           1 1800 5Hz  0.00  6.00   10000

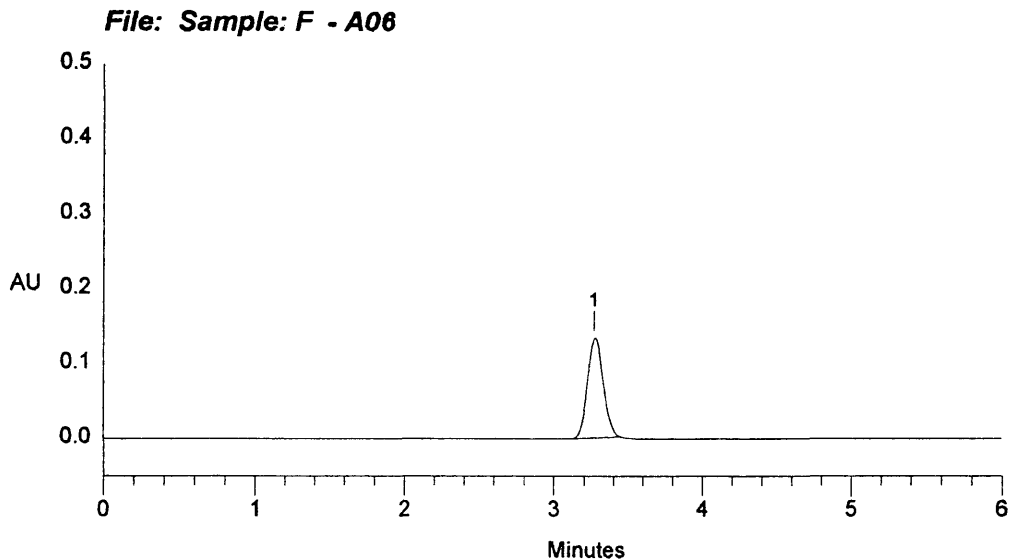
```

***** Component Report: All Components *****

Pk. Num	Ret Time	Component Name	Concentration PPM	Height	Area	Bl. Code	%Delta
1	3.27	CHROM (VI)	0.699	13161	99474	1	-0.51
Totals			0.699	13161	99474		

***** Peak Report: Unknown Peaks *****

Pk. Num	Ret Time	Component Name	Concentration PPM	Height	Area	Bl. Code	%Delta
Totals			0.000	0	0		



```
=====
Sample Name: V - A05                               Date: 02/27/1994 10:41:31
Data File  : c:\dx\data\cfs00031.D05
Method     : c:\dx\method\chrom.met
ACI Address: 1 System: 1 Inject#: 5 Vial:A05       Detector:VDM-2
Analyst    :                                       Column:
=====
```

```
-----
Calibration Volume Dilution Points Rate Start Stop Area Reject
-----
External          50           1 1800 5Hz 0.00 6.00      10000
-----
```

***** Component Report: All Components *****

Pk. Num	Ret Time	Component Name	Concentration PPM	Height	Area	Bl. Code	%Delta
0	0.00	CHROM (VI)	0.000	0	0	0	0.00
Totals			0.000	0	0		

***** Peak Report: Unknown Peaks *****

Pk. Num	Ret Time	Component Name	Concentration PPM	Height	Area	Bl. Code	%Delta
Totals			0.000	0	0		

File: cfs00031.D05 Sample: V - A05

