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United Arab Emirates University Deanship of Graduate Studies M.Sc. Program in Environmental Science

# REMOVAL OF SELECTED HEAVY METALS FROM WASH WATER GENERATED FROM READY-MIX CONCRETE TRUCKS, DUBAI, U.A.E.

By

## Imad Juma Mohammed Abungira

## A thesis

# Submitted to

United Arab Emirates University In partial fulfillment of the requirements For the Degree of M.Sc. in Environmental Sciences

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# DEDICATION

This thesis is dedicated to my great mother, who supported and guided me throughout this achievement.

Without her generous support.....The preparation of this thesis would not have been possible.

Imad Juma Mohammed Abunqira

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### ABSTRACT

Dubai is one of seven Emirates that form the United Arab Emirates. The Emirate of Dubai is currently undergoing a fast-paced construction boom that involves huge amounts of concrete mixes. Such mixes are usually delivered to the site in ready form. The major environmental issue with ready-mix concrete production around the world is water pollution. The wash water generated from ready-mix concrete trucks is extremely alkaline and contains significant levels of heavy metals. Removal of heavy metals from the wash water is an environmental problem and economic concern. This demonstrates the urgent need for safe, feasible and economical methods for the elimination of heavy metals from the wash water.

The present study aims at characterizing the heavy metals present in the ready-mix concrete wash water with high levels in addition to investigating the most efficient technologies of removing them.

It is concluded from this study that (1) the possible source of potentially toxic heavy metals in the wash water was the cement sample, (2) high levels of Chromium (Cr) and Strontium (Sr) were found in the wash water with concentrations as high as 2.04 mg/L and 12.21 mg/L, respectively, (3) chemical precipitation was the most efficient technique to remove both the Chromium and Strontium from the wash water, (4) Barium Chloride lowered the Chromium to less than 0.03 mg/L while Disodium Hydrogen Phosphate lowered the Strontium to less than 0.2 mg/L. A conceptual design of a small treatment plant for the ready-mix concrete wash water is proposed.

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# LIST OF ACRONYMS

BaCl <sub>2</sub>	Barium Chloride
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
°C	Degrees Celsius
Na <sub>2</sub> HPO <sub>4</sub>	Disodium Hydrogen Phosphate
EPA	Environmental Protection Agency
FAAS	Flame Atomic Absorption Spectrometer
g	Gram
HCI	Hydrochloric Acid
Kg/m <sup>3</sup>	Kilogram Per Cubic Meter
L	Liter
mg/L	Milligrams Per Liter
min	Minute
mL	Milliliter
mm	Millimeter
ND	Non-Detected
NM	Non-Measured
OPC	Ordinary Portland Cement
TDS	Total Dissolved Solids
TSS	Total Suspended Solids
WHO	World Health Organization

# **CHAPTER I**

# INTRODUCTION AND LITERATURE REVIEW

# **INTRODUCTION AND LITERATURE REVIEW**

In this chapter a brief introduction about heavy metals and their effects are introduced. The ready-mix concrete is also defined along with its function, preparation, and environmental implications. The objectives of the present study and the expected benefits are stated. Also, the methodology and the analytical methods used in the study are listed. In addition, the ready-mix concrete wash water characterization is demonstrated. Finally, current handling and treatment practices in Dubai are presented.

### 1.1 Problem Statement

Dubai is one of the seven Emirates that make up the federation of the United Arab Emirates Figure 1. Construction activity in Dubai is currently at its peak. Construction on a large scale has truly turned Dubai into one of the fastest developing cities in the world. Many areas of Dubai are dominated by the large number of construction cranes. In May 2006, Emmanuelle Landais, said that according to statistics available, about 125,000 tower cranes are operating worldwide. Industry experts cautiously estimate that 15 to 25 % of the world's cranes are currently operating in Dubai, turning it to the city of construction cranes (Emmanuelle, 2006) Figure 2.

Water is the source of life and the most precious commodity for mankind. The water quality is extremely important in our lives because water is essential to all life forms. The availability of fresh water is decreasing with continued rapid industrialization and urbanization in the world. Therefore, the urgent need for the treatment of existing contaminated water and converting it into pure water is evident.

Cement and concrete are key components of both commercial and residential construction in United Arab Emirates. Concrete is a vital component in building construction today. The demand for concrete has risen rapidly over last five years with the need to upgrade urban and community infrastructure such as roads, drainage system, buildings, bridges, hotels, houses, schools, hospitals and shopping centers as part of Dubai economic development. The readymix concrete batch plants in United Arab Emirates are huge. The environmental issue with ready-mix concrete production is water pollution. Mixing concrete requires a great deal of water generating alkaline wash water. Washout water with high pH is the number one environmental issue for the ready-mix concrete industry.

Water pollution associated with heavy metal ions released from industrial wastewater has become a serious problem (Alimarin et al., 1987). The presence of heavy metals in ready-mix concrete wash water at high levels could threaten the structural integrity of roads, buildings and sidewalks. It can also contaminate the nearby waterways, soil, and vegetation (Environment canada's, 1993). This demonstrates the need for control of heavy metals.

### 1.1.1 What are the Heavy Metals?

Heavy metals are those having large atomic numbers. They are widespread in nature. Heavy metals have many natural and/or man-made sources from which they can pass into the environment. Heavy metals such as Cadmium (Cd), Lead (Pb), Nickel (Ni), Vanadium (V), Copper (Cu), Zinc (Zn), and Chromium (Cr) have toxic effect on the ecosystem (Salomons and Forstner, 1984).

Chromium is a toxic metal of widespread use. It is a naturally occurring element found in rocks, animals, plants, soil, and in volcanic dust and gases. Chromium is present in the environment in several different forms. The most common forms are chromium (0), trivalent chromium (111), and hexavalent chromium (VI). Chromium (111) occurs naturally in the environment. Hexavalent chromium (VI) species are known to be much more dangerous than trivalent chromium (111) species (ATSDR, 2000). Strontium is a naturally occurring element as well and found nearly everywhere but in small amounts, so a person can be exposed to low levels of strontium by breathing air, eating food and drinking water. Strontium can exist in two oxidation states: 0 and +2. Natural occurring strontium is not radioactive and exists in four stable isotopes, <sup>84</sup>Sr, <sup>86</sup>Sr, <sup>87</sup>Sr, and <sup>88</sup>Sr. Strontium can also exist as several radioactive isotopes; the most common is <sup>90</sup>Sr. Stable strontium that is dissolved in water comes from strontium in rocks and soil (ATSDR, 2004).

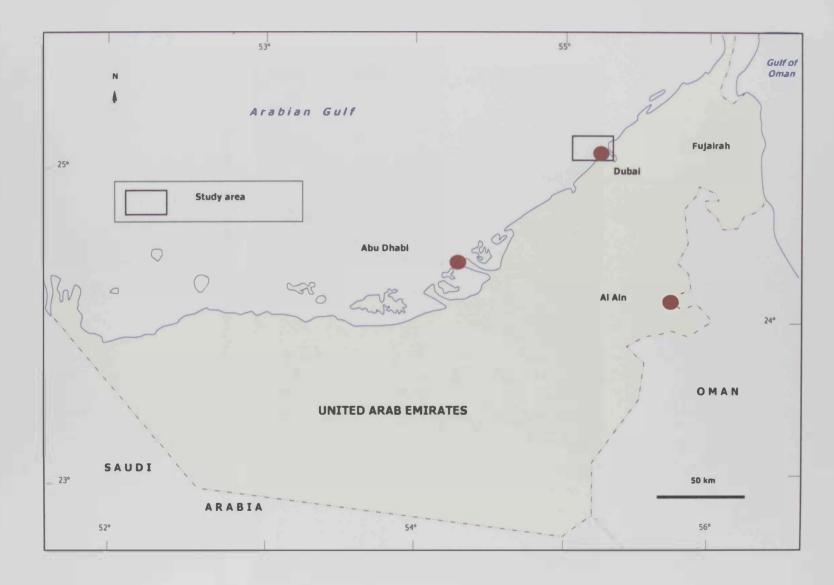


Figure 1: United Arab Emirates map showing Dubai location

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Figure 2: Huge numbers of construction tower cranes in Dubai

#### 1.1.2 What are the Effects of Heavy Metals?

Heavy metals are classified as toxic and dangerous for the human health and environment because they have the potential to cause considerable health and environmental problems. Most of these metals e.g., Zn, Ni, Cu, Cd, Pb, Cr, Fe, Al, and Mn are source of toxicity to the environments (El-sammak and Abdoul-Kassim, 1999). Heavy metals today have a great ecological significance due to their toxicity, bioaccumulation in the food chain and persistence in nature. These elements are not biodegradable and undergo a global ecobiological cycle in which natural waters are the main pathways (Nurnberg, 1984).

Heavy metals are important sources of environmental pollution. Some of them can form compounds which are toxic even in very low concentration. Levels of toxicity can become lethal even before they reach humans. Chromium contamination of the environment has become an important issue due to the potential health threat it poses. The presence of trivalent and hexavalent chromium in the environment is the cause of many well-documented toxic effects such as nausea, skin ulcerations and lung cancer (Ramos et al., 1994; Richard and Bourg, 1991; Visvanathan et al., 1989). Strontium behaves very much like calcium. A large portion of the strontium accumulates in bone. Problems with bone growth may occur in children eating or drinking unusually high levels of Strontium (ATSDR, 2004).

Chromium is included on the US Environmental Protection Agency's (EPA) list of priority pollutants (Cameron, 1992). International Agency for Research on Cancer has classified chromium (VI) in Group 1 (carcinogenic to humans list) and Chromium (III) in group 3. Chromium (VI) is an established human carcinogen (IARC, 1999). Hexavalent chromium is also one of the substances whose use is restricted by the European Restriction of Hazardous Substances Directive.

These heavy metals have harmful effect on human physiology and other biological systems when they exceed the tolerance levels. In fact, these unwanted toxic metals can also be found in the human organs by the means of the food chain involving chronic and acute effects. Heavy metal concentration remains a global problem. There is growing concern worldwide about levels of heavy metals in the environment.

According to the Environmental Protection Agency (EPA), the maximum allowable concentration in drinking water for Chromium is 0.1 mg/L. The World Health Organization (WHO) international standards for drinking water recommended a maximum allowable concentration of 0.05 mg/L for chromium (WHO, 1984). For the strontium (Sr), the Environmental Protection Agency (EPA) recommends that drinking water levels of stable strontium should not be more than 4 milligrams per liter of water (4 mg/L).

Strontium is present in nearly all fresh waters in amounts generally ranging between 0.5 and 1.5 mg/L. Typically, the amount of strontium that has been measured in drinking water in different parts of the United States by the EPA is less than 1 milligram for every liter of water (1 mg/L) (ATSDR, 2004).

#### 1.1.3 What is Ready-Mix Concrete?

Concrete is one of the most common building materials in the world. The basic ingredients for ready-mix concrete are sand, gravel, cement, water and the small amount of various chemicals called admixture that control such properties as workability, setting time, consistency, air content and plasticity Figure 3. Ordinary Portland Cement (OPC) is the most common type of cement in general usage (Klemm, 1994). Chemical admixtures are materials in the form of powder or fluids that are added to the concrete to give it certain characteristics and to improve the quality of concrete during mixing, transporting, placement and curing. A wide range of chemicals are added to cement to act as plasticizers, superplasticizers, accelerators, dispersants, and water-reducing agents (Waddell, 1989).

#### 1.1.4 What is the Function of Ready-Mix Concrete Truck?

Ready-mix concrete plants are the most commonly used plants by the industry. Their function is to combine Ordinary Portland Cement powder with water, sand, gravel and other material to



Figure 3: Cement chemical admixture

form the desired mixture of concrete that can be transported to job sites for pouring. Water is necessary for cleaning out the mixer drum after pouring. Truck drum washout uses a significant volume of water. At the end of the operating day, each ready-mix concrete truck would return from job sites to the concrete plant for cleanout. The mixer truck drum must be washed of concrete; therefore wash water generated from the washout of the interior of a concrete truck mixer drum was one area of concern (Field operations of the concrete, 2006).

In any ready-mix concrete plant, there is always the problem of disposing the wash water resulting from cleaning out the mixer drums. Wash-down water produced during clean-up of equipment must be disposed in a manner that does not and will not contaminate nearby area.

Wash water generated from ready-mix concrete truck are usually very alkaline in nature with a pH ranging between 8 and 12 and sometimes even higher (Dubai Municipality, 2007). The high pH is related to a high content of metal oxides. At these high pH values, most heavy metals in the wash water are considered immobile. Hence, there is a high potential risk of harmful effect on the environment. In several cases, these activities have resulted in negative impacts on the nearby area. Therefore, there is a need to develop technologies that can remove toxic pollutants found in wash water.

## 1.2 Objectives of the Present Study

The overall objectives of this research are firstly, to quantify the heavy metals concentrations in wash water generated from ready-mix concrete trucks. Secondly, to analyze the conventional water quality parameters for the wash water such as pH, color, total dissolved solids (TDS), and total suspended solids (TSS). Thirdly, to propose suitable wastewater treatment method(s) to produce water that can be safely recycled, reused or returned to water bodies without harm. Finally, to design small onsite treatment plant that is consistent with best practices to remove heavy metals from wash water.

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### **1.3** Expected Benefits

After successful completion of this research, we should be able to quantify the heavy metals concentrations in the ready-mix concrete wash water. Also we will be able to design small wastewater treatment plant to minimize the environmental impact of heavy metals pollution. Also, this study can be used to assess possible sources of the heavy metals pollution in the wash water and assess current wastewater treatment practices in Dubai. The ultimate outcome of this research is proposing methods to mitigate, eliminate, and resolve the adverse environmental impact of heavy metals pollution in the wash water. Also this baseline study can be used as reference background for future development in the ready-mix concrete plants.

The treated water can be beneficial for the production of the new concrete in order to solve their disposal problems in an environmentally sustainable way. In addition, the reuse of the treated drum wash water for drum washout greatly reduces the huge volume of wash water that must be discharged. Also, the wash water generated from ready-mix concrete trucks can be reused locally for agricultural purposes and cars washing stations.

### 1.4 Methodology

Upon investigating 15 ready-mix batching plants in the Emirate of Dubai, the study concluded that Ordinary Portland Cement dominates the concrete mixes utilized in Dubai construction work and is originated from four main sources. This includes Gulf Cement Company (Ras Al Khaimah), National Cement Company (Dubai), Star Cement Company (Ajman), and Sharjah Cement Factory (Sharjah).

In the same manner, the site visits concluded during the study indicated that the oldest and most widespread company manufacturing the cement chemical additives is called AI Gurg Fosroc LLC in Dubai from where four different chemical additives were collected and considered in the study. The chemical additives commercial names are Conplast SP495, Conplast SP430, Conplast P211, and Conplast RP264.

The presence of heavy metals such as Zn, Ni, Cu, Cd, Pb, Cr, and Sr were examined in these different cements and chemical additives samples. According to the analyses results, the potential ready-mix concrete design was prepared from which typical wash water samples were extracted and utilized in further experiments.

The presence of heavy metals such as Zn, Ni, Cu, Cd, Pb, Cr, and Sr were examined in the untreated ready-mix wash water sample using the Flame Atomic Absorption Spectrometer equipment (FAAS). Parameters such as total dissolved solids (TDS), total suspended solids (TSS), color, and pH were measured for the prepared untreated wash water sample.

A number of screening tests were carried out in order to identify an eco-friendly and economically effective treatments of heavy metals-contaminated wash water. Finally, a small onsite wastewater treatment plant was designed to remove heavy metals from the wash water sample.

#### 1.5 Analytical Methods

All chemicals used were of analytical grade quality with a purity greater than 99.9% and were purchased from Merck, (Germany) or Aldrich, (Germany). All glassware and materials used in the experiments were cleaned using distilled water. The analyses results were obtained upon conducting three duplicates in each test and the average was taken and reported in this study with 1% coefficient of variation.

#### **1.5.1 Extraction Procedure**

(1) One gram of the dry cement sample was weighted and placed in a beaker. 25 mL of the concentrated hydrochloric acid (HCl) was added to the beaker. The beaker was gently shaken until all the solids were dissolved. The beaker was then heated to boiling on a hot plate, then the solution was filtered with Whatman grade no 42 filter paper. The filtered liquid was transferred to 250 mL volumetric flask and the volume was made up

to 250 mL with distilled water. A Flame Atomic Absorption Spectrometer was used to determine the concentrations of heavy metals in the solution.

- (2) For the cement chemical admixture samples, 5 mL of the admixture was transferred to 100 mL volumetric flask. Distilled water was added to bring the volume exactly to 100 mL. Then, the 100 mL volumetric flask was gently shaken, after which it was analyzed for heavy metals using Flame Atomic Absorption Spectrometer.
- (3) In case of fine and coarse aggregate samples, a portion of the dry sample was gently crushed in mortar. One gram of the crushed sample was placed in the beaker. 25 mL of the concentrated hydrochloric acid (HCl) was added to the beaker. The beaker was gently shaken until all the solids were dissolved. The beaker was then heated to boiling on a hot plate. The mixtures was then filtered through a Whatman grade no 42 filter paper, and the resulting solution was transferred to 250 mL volumetric flask and brought to a total volume of 250 ml with distilled water. Heavy metals analyses were performed by Flame Atomic Absorption Spectrometer.

#### **1.5.2** Preparation of Tentative Treatment Materials

A number of treatment materials were investigated in this study including fish scale, chlorella pyrenoidosa algae, carpentry sawdust, bentonite, fly ash, and immobilized algae bead. To evaluate the efficiency of removing the heavy metals in wash water by these materials, each material was collected and prepared as explained below.

<u>Fish Scale</u>: Mustafiz and Islam (2002) have proved that the novel technique of using fish scales as adsorbents can eliminate nearly 95% of lead ions in the influent. Experiments have also been conducted with cobalt, zinc, and strontium ions. They also showed a marked decrease of metal concentrations in their respective effluent solutions.

The fish scale is fish waste also known as fish by-products. The fish scale used in this study was collected from Dubai's fish market. These fish scales were placed in a 250 mL conical flask and were carefully washed using the tap water then distilled water to remove all the impurities. Then, the fish scale was activated with sodium hydroxide (NaOH) and gently

washed thoroughly with distilled water until the pH was 7. After the final wash, the washed samples were dried using filter paper and stored in a sealed plastic bag.

<u>Algae</u>: Feng and Aldrich (2004) indicated that biomaterial derived from the South African marine alga Ecklonia maxima can be used as efficient biosorbent material for the treatment of aqueous waste streams contaminated with heavy metals. The rate of adsorption onto the marine algae was high.

In the present study, the chlorella pyrenoidosa algae was provided as powder from Taiwan Chlorella manufacturing company, Ltd.

<u>The Carpentry Sawdust</u>: Shukla and Dubey (2002) indicated that the sawdust material has proven to be a promising material for the removal of contaminants from waste water. Not only is sawdust abundant, but also it is an efficient and economic adsorbent that is effective to many types of pollutants, such as, dyes, oil, salts, heavy metals, etc.

The sawdust is a by-product from the timber industry. It was collected from a carpenter working shop in Dubai. The foreign particles were removed from the sawdust by hand. The carpentry sawdust was used as received.

<u>Bentonite (Saroog)</u>: Vengris and Sveikauskaite (2001) investigated the use of a sorbent produced by the chemical treatment of a locally available clay for the removal of some heavy metals from waste water. The uptake capacity of the modified clay for nickel, copper and zinc ions did significantly increase.

Locally available clay from the United Arab Emirates was used in the investigation. This clay is locally known by name of (Saroog). Bentonite (Saroog) was used in the experiment as received.

<u>Fly Ash</u>: Heechan and Kwanho (2005) evaluated the removal of heavy metals from aqueous solutions by fly ash obtained from an electric power station in the Netherlands. The results of

tests using the fly ash particles as an adsorbent for heavy metal ions showed that zinc, lead, cadmium and copper were adsorbed onto fly ash very rapidly.

Fly ash is a residual waste product from electric power plants. Fly ash is produced as a byproduct substance of the burning of fossil fuels for power generation. The fly ash used in this study was collected from an electric power station (Al-Shouaiby power plant) in the Kingdom of Saudi Arabia (KSA). The fly ash was provided by the electricity generating authorities in the Kingdom of Saudi Arabia. The received fly ash was used in the experiment as received.

<u>The Immobilized Algae Beads</u>: Yean-Chang (2001) founded that the immobilized green microalga Scenedesmus quadricauda can be applied for controlling the water quality in fish cultures. In those cultures with algal beads, the ammonium concentrations decreased noticeably. Abdel Hammed (2007) studied nitrogen and phosphorus uptake by the unicellular green microalga Chlorella vulgaris immobilized in calcium alginate beads. Significant higher nutrients reductions were found in bioreactors containing algal beads. Algal uptake and adsorption on alginate gels were the major processes involved in the removal of nitrogen and phosphate from wastewater.

The chlorella pyrenoidosa alga was immobilized by entrapment in calcium alginate gel beads. Two grams of sodium alginate was poured into a small beaker. 100 mL of distilled water was added to the beaker, then the beaker was heated at 50°C. After cooling, one gram of the chlorella pyrenoidosa alga was added to the beaker. The algae/alginate suspension was drawn into a syringe. A beaker of calcium chloride solution was placed under the syringe. The algae/alginate mixture was allowed to drip slowly from the syringe tip into the liquid below. The calcium chloride solution was swirled gently. The beads of immobilized algae were kept to harden in the calcium chloride solution for 5–10 minutes. The immobilized algae beads were separated from the calcium chloride solution using the tea strainer. Finally, the beads were gently washed with distilled water to remove the unwanted salts such as sodium and calcium from the beads (Debbie, 2008).

#### 1.5.3 Determination of Total Dissolved Solids (TDS)

A well-mixed wash water sample was filtered through a medium slow flow rate filter paper (Whatman, grade No. 42 Ashless, standard grades), and 50 mL of filtered water was placed in a clean graduated cylinder. Before starting the test, the porcelain evaporating dish 250 mL was washed and rinsed with distilled water. Then a clean dish was heated in a drying oven at  $180^{\circ}C \pm 2^{\circ}C$  for one hour before beginning the test. The evaporating dish was removed from the drying oven using metal tongs and placed in a desiccator to cool slowly to room temperature.

The evaporating dish was transferred from the desiccator to a balance and weighed to the nearest 0.1 mg (0.0001 g). This weight was recorded as weigh B. After the initial weigh was taken, the filtered water was poured into the evaporating dish and transferred to a hot plate and left to the dryness. Once again, the evaporating dish was transferred to a drying oven and dried at  $180^{\circ}C \pm 2^{\circ}C$  for one hour, then transferred to a desiccator to cool. Finally, the evaporating dish was weighed to the nearest 0.1 mg (0.0001 g) on an analytical balance and this weight was recorded as weight A. The last two steps were repeated again in the same manner until a constant weight is obtained. The total dissolved solids were calculated using the following equation (Peavy et al., 1985):

mg/L Total Dissolved Solids =  $\frac{(A-B)x|000}{sample volume, mL}$ 

Where:

A = Weight (mg) of residue and dish after drying B = Weight (mg) of the empty dish

### 1.5.4 Determination of pH

The pH was measured using Orion 920A Thermo benchtop meter. Before using the pH meter instrument, it was calibrated at three points using three different standard solutions 4.05, 6.86,

and 9.18. The electrode chamber was rinsed several times with distilled water and once with the solution to be measured. After the reading of the solution was taken, the chamber was rinsed again in the same manner before the next reading was taken. Recalibration of the pH meter was done after every three readings. The pH of the wash water sample was measured by placing the glass electrode in the graduated glass beaker 150 mL and allowing equilibrium for one minute before the reading was taken.

#### 1.5.5 Determination of Metals & Cations by Flame Atomic Absorption Spectrometer

Cement, cement chemical additives, fine aggregate and coarse aggregate samples were prepared for extraction of the available metals. Concentrations of the metals: Zn, Ni, Cu, Cd, Pb, Sr, and Cr in all the prepared extracted solutions were determined using Flame Atomic Absorption Spectrometer. Also, the untreated prepared wash water samples collected from the outlet of the ready-mix truck were analyzed for Cd, Fe, Cr, Cu, Pb, Al, Ni, Zn, and Sr by Flame Atomic Absorption Spectrometer.

The equipment used in heavy metals analysis is Varian Spectr AA880 with double beam spectrometer, spectral response 190–900 nm, fast response deuterium background corrector, rotating 8 – lamp turret and two burners both for air-acetylene and nitrous oxide-acetylene flame. The equipment was available in the department of chemical and petroleum engineering of the United Arab Emirates University Figure 4. The Flame Atomic Absorption Spectrometer was calibrated before each set of measurements using the procedure specified in the manufacturer's manual. Quality control for Flame Atomic Absorption Spectrometer analysis consisted of analysis of check samples and duplicates were preformed to identify the precision and accuracy of the Flame Atomic Absorption Spectrometer results. Analytical results from the Flame Atomic Absorption Spectrometer are given in milligrams per liter (mg/L) of metals in the extracted solutions.



Figure 4: Flame Atomic Absorption Spectrometer instrument

#### 1.5.6 Determination of Anions

lon chromatography is used for water chemistry analysis. It is used to analyze major anions such as chloride, and sulfate in the wash water sample. The equipment used in anions analyses is DIONEX DX500 modular chromatography system with conductivity, electrochemical and absorbance detectors. Common anions are separated using a lonPac AS4A column. The equipment was available in the department of Dubai central laboratory of the Dubai Municipality. The ion chromatography was calibrated using calibration standards before each set of measurements using the procedure specified in the manufacturer's manual. A four point calibration is performed and an independent check quality control sample is analyzed every 5 samples to identify the precision and accuracy of the ion chromatography results.

#### 1.5.7 Statistical Analyses

Microsoft Office EXCEL 2000 software was used to present the data as well as to perform the statistical analyses. These analyses include construction of simple graphs, descriptive statistics and plotting the chart of wash water quality parameters.

### 1.6 Ready-Mix Concrete Wash Water Characterization

While the data available on the levels of heavy metals in the ready-mix concrete wash water sample is limited, no data is published on the removal of heavy metals from ready-mix concrete wash water in Dubai. Valuable information on the concentration of heavy metals in wash water of the ready-mix plant was provided by Dubai Municipality. The analyses results of two old different wash water samples provided from Dubai Municipality are listed in Table I. The wash water samples were analyzed in Food and Environment Laboratory Section at Dubai Municipality.

Parameter	Sample # 1	Sample # 2	Unit
Total Suspended Solids	< 10	64	mg/L
Total Dissolved Solids @ 180°C	4,090	4,045	mg/L
Biochemical Oxygen Demand @ 20°C	25		mg/L
Chemical Oxygen Demand (COD)	166	131	mg/L
Oil and Grease (Emulsified)	< 12	15	mg/L
Copper (Cu)	< 0.05	< 0.05	mg/L
Cadmium (Cd)	< 0.02	< 0.02	mg/L
Lead (Pb)	< 0.4	< 0.4	mg/L
Zinc (Zn)	< 0.02	< 0.02	mg/L
Nickel (Ni)	< 0.2	0.2	mg/L
Chromium (Cr)	3.27	2.94	mg/L
рН	8	10	-
Color	clear	yellowish	-

Table I : Characteristics of ready-mix concrete wash water samples 1&2\*

\* References: Dubai Municipality, date of analyses for samples 1&2 are 14/01/2007 and 27/02/2007, respectively, (Dubai Municipality, 2007).

Based on an overall assessment of the existing data from Dubai Municipality, wash water generated from ready-mix truck can be characterized as highly alkaline with high levels of Chromium (Cr) and total dissolved solids (TDS). No information on the presence of Strontium in the two samples were reported by Dubai Municipality.

## 1.7 Current Handling and Treatment Practices in Dubai

Currently, the ready-mix concrete batching plants in Dubai are generally regulated by Environment Department at Dubai Municipality. This information on the current specific wash water treatment practices at ready-mix concrete batching plants in Dubai were provided by Environment Department at Dubai Municipality. In Dubai, the ready-mix concrete batching plants are treated the wash water by one of these methods:-

- (1) In most plants, Transit mixers are being washed in a wash bay facility wherein wastewater generated is usually collected in a three chambered concrete sedimentation pond connected in series. Cleared wastewater is then pumped to a line wherein it is being blended with sufficient amount of fresh water (usually 1:1 ratio) and then reused again for the same washing purpose. Sludge/Sediments from sedimentation ponds is removed by shovels then collected to a sludge tank or drying bed. Disposal is done in Dubai Municipality designated landfill upon accumulation of sufficient quantity.
- (2) Since Dubai Municipality enforces all batching plants to have Chromium reduction treatment facility, some ready-mix concrete batching plants seek the services of wastewater treatment consultants. The following describes the usual treatment practice recommended by the aforementioned companies: (a) wastewater flows through a three chambered sedimentation tank connected in series. (b) wastewater from the third sedimentation tank is being pumped to a separate tank wherein dosing of Ferrous Sulphate (FeSO<sub>4</sub>) and Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>) is applied. Ferrous Sulphate acts to precipitate Chromium wherein it settles to the tank's bottom. Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>) is being used to lower the pH of the wastewater to 3 since pH of untreated wastewater is usually 11 to 12. (c) wastewater is then pumped to another chamber and Caustic Soda (Sodium Hydroxide) dosing is being done. Caustic Soda is added to bring pH within 7.5 to 8 from a level of 3 in the previous chamber. (d) wastewater is then pumped to a

third chamber wherein a low speed motor is provided to further mix the wastewater. Treated wastewater is then pumped to a separate tank wherein it is used for the same washing purpose. (e) sludge/sediments from sedimentation ponds removal is through shovel and then collected to a sludge tank or drying bed. Disposal is done in Dubai Municipality designated landfill upon accumulation of sufficient quantity.

# **CHAPTER II**

# DESIGN OF READY-MIX CONCRETE WASH WATER SAMPLE

# **DESIGN OF READY-MIX CONCRETE WASH WATER SAMPLE**

In this chapter a brief introduction about the production process of the ready-mix concrete will be introduced. Characterization of dominant composition raw materials will be illustrated. Potential sources of Chromium and Strontium will be stated. Also, critical ready-mix concrete wash water sample will be designed. Finally, characterization of the prepared wash water sample will be discussed.

## 2.1 Survey and Characterization of Current Manufacturing Plants

A survey of the current ready-mix concrete batching plants was conducted by Dubai Municipality in May 2006. The survey results show that there are huge numbers of ready-mix concrete batching plants operating in the Emirates of Dubai. In fact, about 58 ready-mix concrete batching plants were identified according to Dubai Municipality. These batching plants were classified into two groups; permanent Table II and temporary batching plants Table III. The temporary batching plants are primarily limited to big projects in which the plant is dismantled after completing the project.

## 2.1.1 The Production Process of the Ready-Mix Concrete

In general, ready-mix concrete is produced by two methods, batch plant process and central mix process. Ready-mix concrete in Dubai is basically produced by batch plant process. In a batch plant, the dry aggregate and dry cement are weighed and added to a mixer along with appropriate amount of water and chemical admixtures. The measurement of ingredient is conducted by an operator from a central control room. Solid components are accurately metered by weight and added to the truck from overhead silos. Water and chemical admixtures are metered by volume. The concrete is mixed in the truck on the way to the job. For central mixing, the concrete is prepared in a central mixer and then transferred to a mixer truck for delivery to the site of work (Field operations of the concrete, 2006). Ready-mix concrete truck capacities in Dubai are quite variable depending on the capacity of the plant and the expected use of the vehicle. Typically, ready-mix truck capacities range from 5-12 cubic meters of

concrete. The volume of wash water utilized in washing the trucks ranges from 100 to 200 liters for each truck load.

This paragraph summarizes the ready-mix concrete production process. With reference to the numeric labels shown in Figure 5, the main components of the ready-mix batching process are:

- Concrete mixing: Ingredients are added to the drum through a metal chute at the upper rear of the truck.
- (2) Exterior truck wash: After loading, the truck moves to a wash area where wash down the truck exterior is carried out.
- (3) Disposal of returned concrete: Some portion of the concrete load is often left in the truck after unloading. Occasionally, the excess concrete is discharged to the wash water collection system.
- (4) Drum wash: At the end of the operating day, the truck drum must be washed of concrete. While the drum is rotated, the water is added to the drum. Then, the wash water is discharged to the collection tank. In the ready-mix concrete industry, the truck drum washout has the highest water demand where the drum washout uses a significant volume of water (Environment canada's, 1993).

#### 2.2 Characterization of Dominant Composition Raw Materials

The preliminary information about the plants and sources of cement, cement chemical admixtures and aggregates used in the plants were collected from the survey. Representative cement, cement chemical admixtures and aggregate samples were collected and analyzed for heavy metals including Zn, Ni, Cu, Cd, Pb, Cr, and Sr by FAAS.

Table IV lists the concentrations of analyzed metals in different concrete ingredients. The results reveal a varying; yet high, concentration of Chromium (Cr) in all analyzed cement samples. The National Cement Company (Dubai) sample has the highest value with 482.50 mg/L, whereas the lowest value was reported in Star Cement Company (Ajman) sample with 54.00 mg/L.

Name of Establishment	Location		
Al Azzani Ready Mix	Al Qouz Industrial Area		
Al Rawal Ready Mix Concrete	Jebel Ali Industrial Area		
Arabian Mix Co.	Al Qouz Industrial Area		
Austrian Arabian Ready Mix Concrete	Jebel Ali Industrial Area		
Bu Shager Ready Mix Concrete	Jebel Ali Industrial Area		
Conmix Limited Co. LLCDubai Branch	Jebel Ali-Dubai International Airport		
Conmix LTD. Co.	Al Qouz Industrial Area		
Dubai Ready Mix Concrete LLC.	Jebel Ali Industrial Area		
Emirates SAS Ready Mix Co. LLC.(EMIX)	Jebel Ali Industrial Area		
Engineering Contracting Co. LLC	Al Qouz Industrial Area		
Galadari Maxi Mix	Jebel Ali Industrial Area		
Khansaheb Civil Engineering LLC.	Jebel Ali Industrial Area		
Lootah Concrete Products	Jebel Ali Industrial Area		
Mills Bowley Concrete Product (MB Mix)	Jebel Ali-Dubai International Airport		
Modern Concrete Products Factory (Modern Mix)	Al Qouz Industrial Area		
National Ready Mix Concrete , Al Ramool	Al Ramool		
Q-Mix Ready Mix Mfg. LLC.	Al Aweer		
Q-Mix Ready Mix Mfg. LLC.	Jebel Ali Industrial Area		
Quality Ready Mix Industry LLC.	Jebel Ali Industrial Area		

Table II : List of permanent ready-mix concrete batching plants in Dubai

Name of Establishment	Location
Ready Mix Betton	Al Qouz Industrial Area
Ready Mix Gulf LTD.	Al Qouz Industrial Area
RMC Top Mix (CEMEX)	Al Qouz Industrial Area
RMC Topmix LLCJebel Ali	Jebel Ali Industrial Area
Safe Mix Ready Mix Factory LLC.	Jebel Ali Industrial Area
SS Lootah (Br. of Saeed Ahmed Lootah and Sons Group PSC)	Jebel Ali Industrial Area
SS Lootah Contracting Co., Al Qusais-2	Al Qusais-2
SS Lootah Ready Mix	Al Qouz Industrial Area
Technical Ready Mix Concrete Co. LLC, Al Qusais-2	Al Qusais-2
Transgulf Ready Mix Concrete	Jebel Ali Industrial Area
Tremix Ready Mix Concrete Factory	Jebel Ali-Dubai International Airport
Unibeton Ready Mix	Jebel Ali Industrial Area
Universal Concrete Products LTD. Co.	Al Qouz Industrial Area
Universal Concrete Products LTD. Co.(UNIMIX)-JAFZ	Jebel Ali- Jebel Ali Free Zone
Universal Concrete Products LTD. Co.(UNIMIX)-Jebel Ali	Jebel Ali Industrial Area
Wade Adams Contracting LLC.	Jebel Ali Industrial Area

Table II (continued): List of permanent ready-mix concrete batching plants in Dubai\*

\* (Source: Dubai Municipality, 2006)

Table III : List of temporary ready-mix concrete batching plants in Dubai

Name of Establishment	Location
Al Falah Ready Mix Concrete	Al Khail Road/Barsha
Al Naboodah Contracting Co. Dubai Festival City. Nad Al Hamar.	Nad Al Hamar
Al Naboodah Contracting, Al Tawar ( Airport Expansion)	Al Tawar ( Airport Expansion)
Arabian Mix Co Academic City Area, JT Metro Projects	Academic City Area, JT Metro Projects
Arabian Mix CoJebel Ali Industrial Area	Jebel Ali Industrial Area- JT Metro Project
Belhasa Six Construct Co. LLC	Al Jadaf
Belhasa Six Construct Co. LLC, Port Rashid	Port Rashid
Bin Hafeez General Contracting Co International City	Al Aweer - International City
Bin Laden Contracting Co.(Wet Mix) Al Aweer	Academic City
Cemex (Formerly RMC Top Mix), Al Tawar ( Airport Expansion)	Al Tawar ( Airport Expansion)
Dutco Balfour Beatty Group	Al Khail Road
Engineering Contracting Co. Academic City Area	Academic City Area, Zayed
Lootha National Ready Mix. International City-Al Aweer	Al Dahid (Khawaneej)
National Readymix Concrete Co.	Arabian Ranches-Emaar
Ready Mix Beaton, Al Gharhoud	Al Gharhoud
Ready Mix Beaton, Jumeira Residence Project	Jumeira Residence Project
Transgulf Ready Mix Concrete Co. LTD. Al Aweer Plant-2	Al Aweer - Oman Hatta Road
Unec Ready Mix.(Safe Mix Ready Concrete LLC.) Mirdif Plant	Al Aweer – International City

Table III (continued): List of temporary ready-mix concrete batching plants in Dubai \*

Name of Establishment	Location		
Unibeton Ready Mix-Al Barsha 1	Al Barsha		
Unibeton Ready Mix-Jadaf	Al Jadaf		
Universal Concrete Products LTD. Co.	Al Doha St., Burj Dubai		
Universal Concrete Products LTD. CoJumeira Residence Project	Jumeira Residence Project		
Wade Adams Contracting LLC.	Al Khail Road		

\* (Source: Dubai Municipality, 2006)

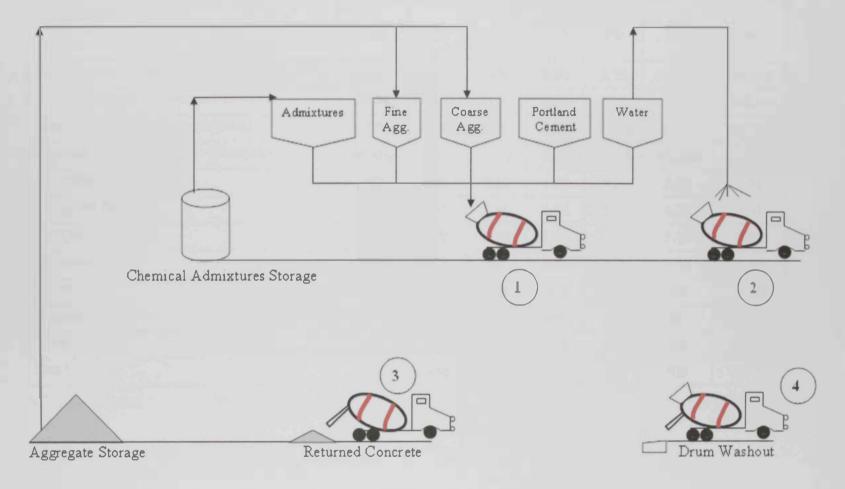


Figure 5: Typical components of batch ready-mix concrete production

Table IV : Concentration of metals in different concrete ingredients

	Metal concentrations (mg/L)						
Sample Description	Zn	Ni	Cu	Cd	Pb	Cr	Sr
Gulf Cement Company (Ras Al Khaimah)	17.00	39.25	20.50	8.50	3.75	188.75	592.50
National Cement Company (Dubai)	64.00	44.50	13.50	8.50	3.25	482.50	968.80
Star Cement Company (Ajman)	69.75	15.50	37.50	9.50	32.50	54.00	957.50
Sharjah Cement Factory (Sharjah)	59.500	ND	25.75	9.00	33.25	121.00	610.00
Conplast SP430	ND	ND	2.36	1.85	ND	2.86	NM
Conplast P211	1.19	ND	1.36	1.02	ND	1.27	NM
Conplast RP264	1.19	ND	1.36	1.02	ND	1.19	NM
Conplast SP495	0.50	ND	3.81	2.15	ND	2.73	9.20
Stone	NM	NM	NM	NM	NM	ND	0.248
Coarse Aggregate	NM	NM	NM	NM	NM	ND	0.500
Mud	NM	NM	NM	NM	NM	ND	6.88
Sand	NM	NM	NM	NM	NM	ND	5.31

ND: Not Detected

NM: Not Measured

According to measurement of trace metals in the cement chemical admixtures samples Table IV, the highest Chromium value was found in Conplast SP430 sample with 2.86 mg/L, whereas Conplast SP495 sample provided the second highest value with 2.73 mg/L. In the case of Strontium, the National Cement Company (Dubai) sample has the highest value with 968.80 mg/L, whereas the lowest value was reported in Gulf Cement Company (Ras Al Khaimah) sample with 592.50 mg/L. The Strontium value was found in Conplast SP495 sample and Conplast SP495 sample were selected to prepare the critical ready-mix concrete wash water sample considered in this study.

#### 2.2.1 Potential Sources of Chromium

The Chromium forms in the cement industry are Cr (III) and Cr (VI) (Klemm and Waldemar, 1992) which originate from a variety of sources (Lizarraga, 2003). The amount of Cr (VI) in cement can originate from: 1) Oxidation of total Chromium from the raw materials or fuel entering the system based on conditions of the clinker burning process (Chandelle, 2003), 2) Magnesia-chrome kiln refractory brick, if used, 3) Wear metal from crushers and raw mill grinding process, if Chromium alloys are used, and 4) Additions of gypsum, pozzolans, ground granulated blast furnace slag, minerals components, cement kiln dust, and set regulator (Bhatty, 1993).

All quarried raw materials for cement manufacture contain very small or trace quantities of total Chromium, which is a common element in the Earth's crust. The increasing use of many by-product raw materials such as metallurgical slag, spent catalyst fines, flue gas desulfurization gypsum, lime sludge, etc., may contribute additional amounts (Hills and Vagn, 2007).

#### 2.2.2 Potential Sources of Strontium

The manufacture of Ordinary Portland Cement is made from abundant raw materials. Cement raw materials are for the most part dug from the Earth's crust and contain most of the elements

in the periodic table. Strontium occurs naturally in the minerals celestite ( $SrSO_4$ ) and strontianite ( $SrCO_3$ ). Celestite is mostly found in sedimentary rocks, often associated with the minerals gypsum, anhydrite, and halite (Wikipedia, 2008). Therefore, addition of gypsum in the cement manufacturing process may contribute to additional amount of Strontium.

#### 2.3 Design of Critical Ready-Mix Concrete Wash Water Sample

The ratio of the amount of water to the amount of cement in concrete is called the water/cement ratio. Such ratio has great influence on the quality of concrete produced as it is the key factor that determines the strength of concrete.

The strength, durability and other desirable properties of concrete are inversely proportional to the water/cement ratio. Since the compressive strength of the concrete decreases as the water/cement ratio goes up, a lower water/cement ratio leads to higher strength and durability. The proposed concrete mix design has low water/cement ratio, to increase the cement and the additives as well as to increase the strength and durability of concrete. The expected concrete slump is 0-10 mm and the expected concrete strength is 60-70 MPa. (Waddell, 1989).

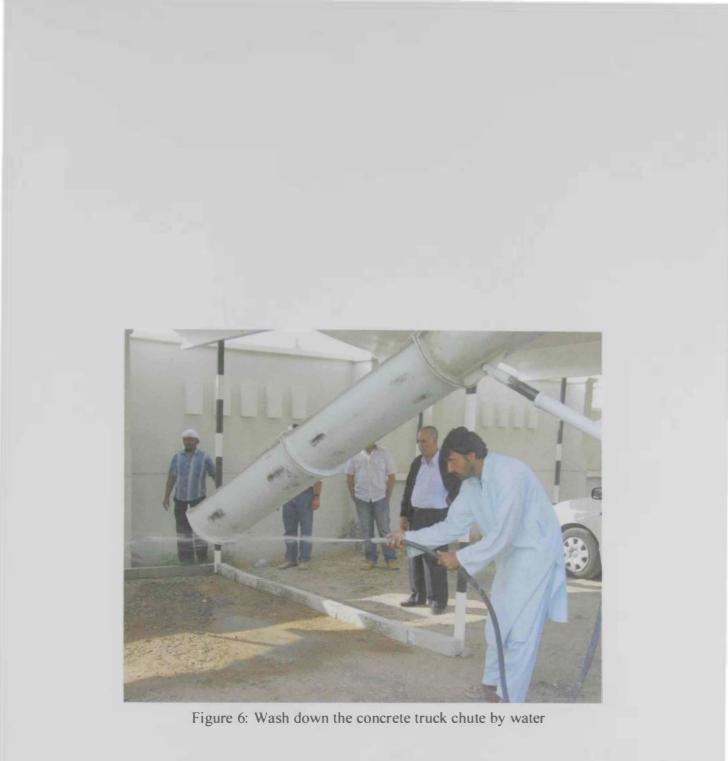
A critical ready-mix concrete mix was designed to reflect the highest potential levels of pollutants found in the analyzed concrete ingredients; mainly Chromium and Strontium. This implied considering the lowest possible water/cement ratio needed for workability purposes. The composition of that mix is given in Table V.

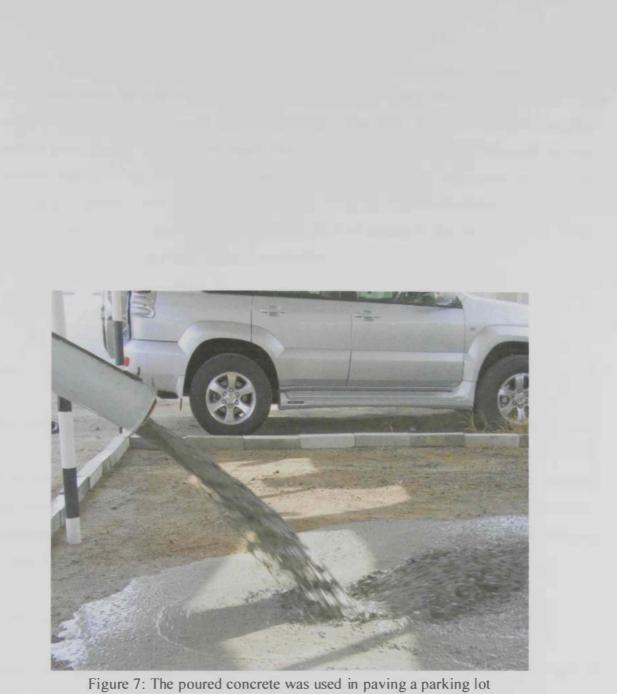
#### 2.4 **Preparation of Designed Sample**

All the proposed materials were delivered to the ready-mix concrete batch plant where the components were blended in the rotating truck's mixer drum until delivery to the university laboratory site. Before the unloading, the driver wash down the concrete truck chute by water Figure 6. The poured concrete was used in paving a parking lot near the laboratory Figure 7.

Ingredients	Typical Composition
Ordinary Portland Cement	370 (Kg/m <sup>3</sup> )
Fine Aggregate (sand & Dune Sand)	718 (Kg/m <sup>3</sup> )
Coarse Aggregate (20mm)	968 (Kg/m <sup>3</sup> )
Coarse Aggregate (10mm)	408 (Kg/m <sup>3</sup> )
Water	151 (L)
Cement Chemical Admixtures	11.1 (Kg/m <sup>3</sup> )
Water/Cement ratio	0.41

Table V: Composition of the critical ready-mix concrete (1.0 m<sup>3</sup>)





Since the truck concrete load was 2.30 m<sup>3</sup>, a maximum possible volume of wash water (45 liters of tab water) was poured into the truck drum after unloading Figure 8. The truck drum was agitated for 20 min to ensure complete mixing of the added fresh water with the residue concrete into truck drum. The wash water from the truck drum was then discharged into big top open container Figure 9. Prior to lab analyses, the ready-mix concrete wash water sample was kept and stored in two big plastic containers (25 L capacity) with sealed lids to prevent sample contamination Figure 10. The concentrations of metals in the prepared wash water sample were estimated by FAAS as explained earlier.

#### 2.5 Characterization of the Prepared Wash Water Sample

#### 2.5.1 Heavy Metals in the Prepared Wash Water Sample

The metals of interest Zn, Ni, Cu, Cd, Pb, Cr, and Sr were identified in the wash water sample by FAAS and the results are given in Table VI. The concentration of Chromium in the wash water samples of the study was very high (2.591 mg/L). As mentioned before, the presence of Chromium in high concentration in cement was directly associated with the production method of cement. The results obtained show that the Strontium was found in the analyzed sample with high concentration as well (10.345 mg/L).

#### 2.5.2 Cations and Anions Concentrations in the Prepared Wash Water Sample

Table VII shows the data obtained from determination of the cations and anions concentrations in the wash water sample. The most abundant cations present in the wash water are calcium (Ca), magnesium (Mg), sodium (Na), and potassium (K). Their concentrations were 772.58 mg/L, 0.004 mg/L, 488.07 mg/L and 473.65 mg/L, respectively. Also, Table VII shows the anions concentrations in the wash water sample. The most abundant anions in wash water are bicarbonate (HCO<sub>3</sub>), chloride (Cl), and sulfate (SO<sub>4</sub>). Their concentrations were 0 mg/L, 88 mg/L and 685 mg/L, respectively. The carbonate ions concentration in the wash water was 90 mg/L and the hydroxide ion concentration was 650 mg/L. This produces a total alkalinity of 1896 mg/L as CaCO<sub>3</sub> for which the pH was found 13.05.



Figure 8: Wash water was added into the truck drum after unloading



Figure 9: Wash water generated from concrete truck drum



Figure 10: Wash water sample was stored in big plastic containers

#### 2.5.3 Solids and Hardness of the Prepared Wash Water Sample

Table VIII presents the levels of solids and hardness of the wash water sample. Since the investigated sample was left to settle down its particles before the analysis, the suspended solids were very low (3 mg/L). The total dissolved solids and total hardness were found; 5890 mg/L and 1150 mg/L, respectively. It is worth mentioning that the raw wash water sample before settling is highly turbid. After settlement, the color of the mixtures was yellowish.

Metal concentrations (mg/L)								
Zn	Ni	Cu	Cd	Pb	Cr	Sr		
0.026	0.0464	0.0235	0.041	0.604	2.591	10.345		

Table VI : Heavy metals in the prepared wash water sample

Table VII : Cations and Anions concentrations in the prepared wash water sample

Cations (mg/L)	Al	Ba	Ca	Fe	К	Na	Mg
(	0.2900	0.2229	772.58	0.009	473.65	488.07	0.004
Anions (mg/L)	SO4	CI.	HCO <sub>3</sub> -	CO <sub>3</sub> <sup>-</sup>	11117	OH -	
(	685	88	0	90	1-3/14	650	

Table VIII : Solids and Hardness of the prepared wash water sample

Parameter	Concentration Level
Total Suspended Solids (mg/L)	3
Total Dissolved Solids (mg/L)	5890
Total Hardness (mg/L)	1150

## **CHAPTER III**

# REMOVAL OF IDENTIFIED POLLUTANTS IN READY-MIX WASH WATER

### REMOVAL OF IDENTIFIED POLLUTANTS IN READY-MIX WASH WATER

In this chapter the common removal practices of identified pollutants; Chromium and Strontium will be introduced. Results of initial screening of treatment methods will be illustrated. Finally, alternative treatment techniques and materials will be evaluated.

#### 3.1 Common Removal Practices of Identified Pollutants

Several researchers provided significant information on the concentration of heavy metals in the industrial wastewater around the world. Removal of heavy metals from industrial wastewater is of primary importance because they are not only causing contamination of water bodies but are also extremely toxic to many life forms (Aslam and Malik, 2004). A limited number of studies were carried out on the removal of heavy metals from the wash water generated from the ready-mix concrete truck in the UAE as well as other countries.

Several methods have been developed for removal of toxic heavy metals from wastewater when they are present in high concentrations. The methods currently in practice include chemical precipitation, electrodialysis, biosorption processes, solvent extraction (Patterson, 1985), electrochemical treatment (Eilbeck, 1987), ion exchange, reverse osmosis (Zhang et al.,1999; Lienonen and Lehto, 2000), coagulation, evaporation, membrane filtration and adsorption (Bartosch et al., 2000).

#### 3.1.1 Removal of Chromium

A wide range of physical and chemical processes is available for the removal of Chromium (Cr) from industrial wastewater. In one study, electrochemical techniques have been used in removing heavy metals from municipal wastewater sludge. Their techniques allowed the removal of Nickel, Chromium, Zinc, and Copper from the sludge samples at removal levels reaching 41%, 8%, 6.7%, and 4.7%, respectively (Mohamed and Saleh, 2000). Lopez-Delgado

et al. (1997) concluded that the blast furnace sludge was found to be an effective sorbent for Pb, Zn, Cd, Cu and Cr ions. Patoczka et al. (1998) has proved that the ferric chloride is an effective method to be used to remove Chromium (Cr) from industrial wastewater. Li (2001) found that by using a proper combination of chromium reduction and precipitation methods, the treated wastewater sample can meet the discharge limits. Hosseini and Mirbagheri (2003) demonstrated that lime is a cheap and excellent chemical for efficient coagulation and precipitation of copper and chromium ions from wastewater. XU et al. (2005) concluded that anaerobic bio-filter bed showed high efficiency in removing hexavalent chromium. Acosta et al. (2004) found that the biomass of C. neoformans, natural sediment, Helmintosporium sp and chitosan was efficient to remove chromium (VI) from aqueous solutions. Mohanty et al. (2005) indicated that the biomass of E. Crassipes is suitable for development of efficient biosorbent for the removal of chromium from wastewater of chemical and allied process industries. Kanamadi and Ramachandra (2005) indicated that the Bengal gram husk (Cicer arientinum) is an excellent material for biosorption of Cr (VI) to treat wastewaters containing low concentration of the metal. Suwannee and Suttawadee (2006) showed that the scrap iron filings appear to be a very good metallic system, a non-toxic substance and a low cost material for the rapid removal of Cr (VI) contained in chromium plating wastewater.

In addition to the above removal methods, micro-organisms and biosorption techniques are techniques for removal of heavy metals from industrial water. In one example study, Saifuddin and Raziah (2007) have utilized yeast Saccharomyces cerevisiae immobilized in chitosan in column reactor to remove chromium metal ion in aqueous solutions. Suleman and Anwar (2007) concluded that adsorbent prepared from ficus religiosa leaves can be utilized for the treatment of heavy metals such as Cr (VI) and Pb in wastewater. Priya et al. (2007) reported that the Pithophora alga is efficient biosorbent for the removal of chromium (VI), nickel (II) and copper (II) ions from aqueous solutions. Mahvi et al. (2007) showed platanus orientalis leaves ash was more favorable than living ones in removing chromium from the aqueous solution. Moreover, Arivoli et al. (2007) showed that the activated carbon (BC) could be used for the removal of chromium ion from aqueous solution.

#### 3.1.2 Removal of Strontium

Hobbs and Fleischman (1993) performed a study on Strontium and Actinide removal from alkaline high-level waste solutions. Based on the measured removal rates, Monosodium titanate (MST) exhibits rapid removal kinetics for strontium and the actinides from alkaline high-level waste solutions. Chaalal and Islam (2001) has proved that a combination of biomass treatment, fluidized bed/membrane reactor, and a minimum-suspension fluidized bed reactor is an acceptable solution to removing strontium while minimizing the generation of secondary waste. Cristopher et al. (2006) reported that high removals (>90 percent) of strontium were attained via intermediate chemical demineralization (ICD). Hobbs et al. (2006) proved that the new Sodium Titanate material exhibits increased removal kinetics and capacity of Sr-90 and Sodium Titanate appears to be an excellent candidate for replacing the baseline Monosodium Titanate (MST) for nuclear waste processing at the Savannah River Site. Hobbs et al. (2007) concluded that the modified Monosodium Titanate represents a much improved sorbent for the separation of strontium and actinides from alkaline waste solutions and recommend continued development of the material as a replacement for the baseline Monosodium Titanate for waste treatment facilities at the Savannah River Site.

#### 3.2 Initial Screening of Treatment Tests

The treatment of ready-mix concrete wash water and the production of high quality water is a broad field for research. A comprehensive investigation of separation materials that could be utilized in ready-mix concrete plant treatment facility for removal of Chromium and Strontium was conducted and described below.

#### 3.2.1 Considered Treatment Technologies

A number of materials have been studied for their capacity to remove toxic heavy metals, including cationic resin, commercial granular activated carbon, bentonite (saroog), fly ash, chlorella pyrenoidosa alga, immobilized algae beads, carpentry sawdust and fish scale. A number of screening experiments were done. The aim of conducting a series of screening tests

is to investigate the efficiency of stated materials with regard to Chromium and Strontium removal from the ready-mix concrete wash water sample.

In one experiment, a sample of the ready-mix concrete wash water was divided into eight portions of equal volumes (100 mL) in eight glass bottles (250 mL with screw cap). Then, 0.1 gram of all materials stated above was weighed before being added to the samples in the glass bottles Figure 11. The bottles were shaken slowly by a shaker Figure 12 for 48 hours at room temperature ( $25 \pm 1^{\circ}$ C). The solutions were then filtered through Whatman grade no 42 filter paper to separate the solid from the liquid phase. After filtration, concentrations of the metals Cr and Sr in the filtered solution were determined using Flame Atomic Absorption Spectrometer.

In the same manner, the second experiment on the sample was done by adding one gram of all materials stated above and then the same procedure was followed as that for 0.1 gram.

The third experiment was designed to investigate the removal of Chromium and Strontium from the wash water using different weights from the immobilized algae bead samples 2g, 10g, 20g, 30g and 40g. Then, all the procedures mentioned above were followed.

The fourth experiment on the sample was done using the chemical precipitation process. Three chemicals; sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), ferrous sulfate (FeSO<sub>4</sub>) and sodium hydroxide (NaOH) were used for the removal of heavy metals from the wash water sample. 100 mL of the fresh wash water sample was transferred into clean glass bottle (250 mL with screw cap). 0.1 gram of ferrous sulfate (FeSO<sub>4</sub>) and about three drops of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) were added to the bottle. The solution was mixed vigorously, then 0.3 gram of the sodium hydroxide (NaOH) was added. The liquid was kept on the shaker at (25 ± 1°C) for 2 hours. The solution was filtered through Whatman grade no 42 filter paper. Finally, the metals (Cr and Sr) concentrations were measured by FAAS.

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Figure 11: Wash water sample after adding the removal materials



Figure 12: The bottles were shaken by a shaker

#### 3.2.2 Results of Screening Tests

Table IX demonstrates the effect of 0.1 gram of different materials on Chromium and Strontium removal. The present investigation evaluates the use of cationic resin, commercial granular activated carbon, bentonite (saroog), fly ash, chlorella pyrenoidosa algae, carpentry sawdust and fish scale for the elimination of heavy metals from the wash water sample. The concentrations of Strontium and Chromium in the untreated wash water sample (feed) were 12.255 mg/L and 2.094 mg/L respectively. After treatment with these materials, the concentration of Strontium varied between (10.521 mg/L tol1.823 mg/L). Also, the removal percentage varied for the materials used. The minimum removal percentage was for the fish scale (3.53% removal), whereas the maximum value was found for Chlorella Pyrenoidosa Alga (about 14.15%). For the Chromium, it was observed that minimum removal occurred with cationic resin, for which Cr reduced from 2.094 mg/L to 2.063 mg/L about (1.48% removal). The maximum removal of Cr occurred with Chlorella Pyrenoidosa (14.04% removal).

Table X shows the results of the influence of 1.0 gram dose of the same materials on treating the wash water sample. This resulted in a maximum reduction of Sr from 12.208 mg/L to 7.725 mg/L (36.72% removal) using 1.0 gram Chlorella Pyrenoidosa Algae, while Cr was reduced from 2.042 to 1.557 mg/L (23.75% removal) using fly ash.

Table XI illustrates the effect of using different dosages of Immobilized Algae Bead on Cr and Sr removal. It was observed that maximum removal for Sr occurred at 40 gram dose of Immobilized Algae Bead where Sr dropped from 12.208 mg/L to 2.600 mg/L (78.70% removal) and Cr dropped from 2.042 mg/L to 1.333 mg/L (34.72% removal) using the same amount of Immobilized Algae Bead.

Table XII reports the analysis results of using a mixture of  $H_2SO_4$ , FeSO<sub>4</sub> and NaOH on treating the ready-mix concrete wash water sample. The results show a complete removal of Cr (100.00% removal) while the Sr removal was much less (21.04% removal).

Sample identification	Sr (mg/L)	Sr Removal %	Cr (mg/L)	Cr Removal %
Untreated Wash Water (feed)	12.255	-	2.094	1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1
Cationic Resin	11.307	7.74	2.063	1.48
Granular Activated Carbon	11.583	5.48	2.031	3.01
Bentonite (Saroog)	11.535	5.88	2.052	2.01
Fly Ash	11.333	7.52	2.026	3.25
Chlorella Pyrenoidosa Alga	10.521	14.15	1.800	14.04
Carpentry Sawdust	11.391	7.05	1.880	10.22
Fish Scale	11.823	3.53	2.026	3.25

Table IX : Effect of 0.1 gram weights of several materials on Cr and Sr removal

Table X : Effect of 1.0 gram weights of several materials on Cr and Sr removal

Sample identification	Sr (mg/L)	Sr Removal %	Cr (mg/L)	Cr Removal %
Untreated Wash Water (feed)	12.208	-	2.042	-
Cationic Resin	11.307	7.38	1.995	2.30
Granular Activated Carbon	10.635	12.88	2.005	1.81
Bentonite (Saroog)	10.443	14.46	1.984	2.84
Fly Ash	11.271	7.68	1.557	23.75
Chlorella Pyrenoidosa Alga	7.725	36.72	2.000	2.06
Carpentry Sawdust	11.281	7.59	1.698	16.85
Fish Scale	10.151	16.85	1.896	7.15

Sample identification	Sr (mg/L)	Sr Removal %	Cr (mg/L)	Cr Removal %
Untreated wash water (feed)	12.208		2.042	
(2 g) Immobilized Algae Bead	11.083	9.56	1.964	6.21
(10 g) Immobilized Algae Bead	8.396	31.23	1.802	11.75
(20 g) Immobilized Algae Bead	5.979	51.02	1.660	18.71
(30 g) Immobilized Algae Bead	4.240	65.27	1.474	27.82
(40 g) Immobilized Algae Bead	2.600	78.70	1.333	34.72

Table XI : Effect of immobilized algae bead dosages on Cr and Sr removal

Table XII : Effect of mixture of chemicals ( $H_2SO_4$ , FeSO<sub>4</sub> and NaOH) on Cr and Sr removal

Sample identification	Sr (mg/L)	Sr Removal %	Cr (mg/L)	Cr Removal %
Untreated wash water (feed)	12.255	-	2.094	-
Mixture of chemicals (3 drops of H <sub>2</sub> SO <sub>4</sub> , 0.1g of FeSO <sub>4</sub> and 0.3g of NaOH)	9.677	21.04	0.00	100.00

Based on the above results, the following conclusions can be made from the initial screening of treatment methods:

- (1) By comparing the analytical results in Tables IX and X, it was observed that the extent of percent removal increased with increasing dosage of materials almost for all the tests except that for Sr with cationic resin and for Cr with Chlorella Pyrenoidosa Alga and granular activated carbon. Since the percent removal of Sr did not exceed the level of (36.72% removal) and for Cr at best did not exceed the level of (23.75% removal) in both experiments, it is concluded that the removal efficiency of Cr and Sr by these materials is poor.
- (2) It is evident from the results obtained in Table X that the 1.0 gram of the above stated materials was insufficient dose to complete full removal of Chromium.
- (3) From the results shows in Table XI, it is obvious that the concentration of Chromium in the treated wash water sample was still above the allowable limits.
- (4) The results listed in Table XII showed an excellent reduction of Chromium using a mixture of several chemicals, but it was not effective for Strontium removal.

#### **3.3** Alternative Treatment Techniques and Materials

Chemical precipitation operation is known to remove heavy metals from water (Hosseini and Mirbagheri, 2003). In this study applicability of chemical compounds such as Calcium Carbonate (CaCO<sub>3</sub>), Calcium Hydroxide Ca(OH)<sub>2</sub>, Calcium Chloride (CaCl<sub>2</sub>), Calcium Sulfate (CaSO<sub>4</sub>), Barium Chloride (BaCl<sub>2</sub>), Sodium Carbonate (Na<sub>2</sub>CO<sub>3</sub>), Disodium Hydrogen Phosphate (Na<sub>2</sub>HPO<sub>4</sub>) and Tetrasodium Diphosphate Na<sub>4</sub>(PO<sub>4</sub>)<sub>2</sub> in removing Chromium and Strontium from ready-mix concrete wash water were evaluated.

Wash water sample containing Chromium and Strontium were treated with the above cited chemical compounds by the following procedure: A sample of the ready-mix concrete wash water was divided into eight portions of equal volumes (100 mL) in eight glass bottles (250 mL with screw cap). Then, 0.5 gram of all above-mentioned chemical compounds was added to the polluted samples. The sample was then mixed slowly using a shaker for 2 hours to create good sample-chemical contact. After this, they were filtered individually using

Whatman grade no 42 filter paper. Finally, the concentrations of Chromium and Strontium in the clarified solution were detected by Flame Atomic Absorption Spectrometer and the results are illustrated in Table XIII.

A different set of chemicals were tested for treating the wash water sample containing Chromium and Strontium by precipitation. After Chromium removal with barium chloride, the Chromium concentration in treated wash water sample was reduced to the 0.00 mg/L. Maximum precipitation occurred with 0.5 gram of barium chloride showing 100% efficiency in Chromium precipitation. The data recorded indicate that the barium chloride is more efficient in removal of all Chromium metal in substantial amounts from the wash water. None of the other chemical compounds that were used in the treatment were not effective for Chromium removal.

The last three chemical compounds Sodium Carbonate  $(Na_2CO_3)$ , Disodium Hydrogen Phosphate  $(Na_2HPO_4)$  and Tetrasodium Diphosphate  $Na_4(PO_4)_2$  were all effective for Strontium removal. However, the other chemicals were not effective. The maximum removal efficiencies in these experiments were obtained with Disodium Hydrogen Phosphate  $(Na_2HPO_4)$  showing 99.48% efficiency in Strontium precipitation. These three chemicals were selected for their high removal capacity of Strontium.

A survey on the cost and the availability of these three chemicals in Dubai market was conducted. It is concluded that these chemicals are inexpensive and readily available. The precipitation process with Disodium Hydrogen Phosphate can greatly reduce the Strontium level in the wash water. So, Disodium Hydrogen Phosphate (Na<sub>2</sub>HPO<sub>4</sub>) was selected for further Strontium treatment and Barium Chloride (BaCl<sub>2</sub>) was selected for Chromium treatment.

Sample identification	Sr (mg/L)	Sr Removal %	Cr (mg/L)	Cr Removal %
Untreated wash water (feed)	12.208	-	2.042	-
Calcium Carbonate (CaCO <sub>3</sub> )	12.200	0.07	1.957	4.16
Calcium Hydroxide Ca(OH) <sub>2</sub>	12.029	1.47	1.936	5.19
Calcium Chloride (CaCl <sub>2</sub> )	11.878	2.70	1.900	6.95
Calcium Sulfate (CaSO <sub>4</sub> )	12.044	1.34	1.921	5.93
Barium Chloride (BaCl <sub>2</sub> )	7.787	36.21	0.00	100.00
Sodium Carbonate (Na <sub>2</sub> CO <sub>3</sub> )	0.146	98.80	1.942	4.90
Disodium Hydrogen Phosphate (Na <sub>2</sub> HPO <sub>4</sub> )	0.063	99.48	1.884	7.74
Tetrasodium Diphosphate Na <sub>4</sub> (PO <sub>4</sub> ) <sub>2</sub>	0.973	92.03	1.858	9.01

 Table XIII : % removal of Cr and Sr by using lists of chemicals

## **CHAPTER IV**

### **DESIGN OF TREATMENT METHOD**

### **DESIGN OF TREATMENT METHOD**

In this chapter, the selected treatment technique will be evaluated and optimized. The effects of dosage and mixing time on removal efficiency of Chromium and Strontium will be studied. Also, stoichiometric analysis and pH stabilization will be discussed. Finally, a conceptual design of a small treatment plant for the ready-mix concrete wash water is proposed.

#### 4.1 Dosage Identification

Chemical precipitation is a promising method for removing heavy metals from ready-mix concrete wash water. Disodium Hydrogen Phosphate (Na<sub>2</sub>HPO<sub>4</sub>) was selected as a candidate treatment material for Strontium removal while Barium Chloride (BaCl<sub>2</sub>) was selected for Chromium removal.

The removal of Chromium (Cr) and Strontium (Sr) from ready-mix concrete wash water using Barium Chloride and Disodium Hydrogen Phosphate was investigated under different experimental conditions such as the effects of the pH and the weights of Barium Chloride Table XIV and Disodium Hydrogen Phosphate Table XV. A new set of experiments were conducted in order to optimize the treatment conditions. Weights of 0.05g, 0.10g, 0.20g, 0.30g, 0.40g, and 0.50 g from each chemical compound were tested with a sample volume of 100 mL. The mixing time for all tests was set at 120 minutes. The same procedures were followed as with that of lists of chemicals. To calculate the weight of precipitates, this procedure was followed. The precipitates were transferred to glass dish then kept overnight in drying oven at 70°C. The final weights were calculated by electronic balance.

According to the analysis results listed in Table XIV, the pre-treatment analysis gave the following values: Sr 12.208 mg/L and Cr 2.042 mg/L. Removal of Cr was optimized with 5.0 g/L of Barium Chloride, reducing the amount of Cr and Sr by 100.00% and 36.21%, respectively.

Sample Identification	Sr (mg/L)	Removal%	Cr (mg/L)	Removal%	Weight of Precipitate, g	рН
Untreated wash water (Feed)	12.208		2.0417	-		-
Treated with 0.05 g BaCl <sub>2</sub>	8.151	33.23	1.2232	40.09	0.0512	12.68
Treated with 0.10 g BaCl <sub>2</sub>	5.632	53.87	0.7079	65.33	0.1128	12.68
Treated with 0.20 g BaCl <sub>2</sub>	4.325	64.57	0.0833	95.92	0.2094	12.62
Treated with 0.30 g BaCl <sub>2</sub>	9.952	18.48	0.0208	98.98	0.2340	12.60
Treated with 0.40 g BaCl <sub>2</sub>	11.305	7.40	0.0104	99.49	0.2386	12.59
Treated with 0.50 g BaCl <sub>2</sub>	7.787	36.21	0.000	100.00	0.2386	12.59

Table XIV : Removal of Sr and Cr from 100 mL wash water sample using Barium Chloride

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Table XV : Removal of Sr and Cr from 100 mL wash water sample using Disodium Hydrogen Phosphate

Sample Identification	Sr (mg/L)	Removal%	Cr (mg/L)	Removal%	Weight of Precipitate, g	рН
Untreated wash water (Feed)	12.208	-	2.0417	-	-	-
Treated with 0.05 g Na <sub>2</sub> HPO <sub>4</sub>	12.200	0.07	1.7412	14.72	0.0512	12.73
Treated with 0.10 g Na <sub>2</sub> HPO <sub>4</sub>	12.180	0.23	1.7489	14.34	0.1050	12.76
Treated with 0.20 g Na <sub>2</sub> HPO <sub>4</sub>	7.808	36.04	1.7489	14.34	0.1959	12.79
Treated with 0.30 g Na <sub>2</sub> HPO <sub>4</sub>	0.593	95.14	1.7489	14.34	0.2402	12.79
Treated with 0.40 g Na <sub>2</sub> HPO <sub>4</sub>	0.073	99.40	1.7905	12.30	0.2496	12.80
Treated with 0.50 g Na <sub>2</sub> HPO <sub>4</sub>	0.063	99.48	1.8842	7.71	0.2496	12.80

Table XV shows that it was sufficient to reduce the Strontium concentrations in the wash water sample to 0.063 mg/L using as low dosage as 5.0 g/L of Disodium Hydrogen Phosphate. The removal percentage of Sr and Cr varied widely among treatments. The maximum Sr removal efficiency obtained in the experiment was 99.48% associated with 7.71% Cr removal efficiency.

Figure 13 shows the effect of Barium Chloride on the removal of Strontium and Chromium. Precipitation gradually increases from 40.09% to 100.00% with increase in Barium Chloride dose from 0.5 to 2.0 g/L in the case of Chromium and then became almost constant since all Chromium was removed. In order to lower the Chromium below the prescribed 0.05 mg/L standards, full removal is considered and corresponded to optimal dosage of Barium Chloride of 5.0 g/L.

Strontium precipitation was found to increase from 33.23 to 64.57% with increase in Barium Chloride dose from 0.5 g/L to 2.0 g/L. Then, the precipitation decreased from 64.57% to 7.40% with increase of Barium Chloride dose from 2.0 g/L to 4.0 g/L then again the Sr removal increased from 7.40% to 36.21% with an increase of dosage of Barium Chloride to 5 g/L. These plots showed that the Strontium precipitated increased sharply at the beginning then strongly decreased and then again increased with higher Barium Chloride amounts.

Figure 14 reports the percentage removal of Strontium and Chromium for different dosages of Disodium Hydrogen Phosphate 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0 g/L. Analysis of the results shows that the precipitation of Strontium increased with increasing the initial Disodium Hydrogen Phosphate dose. The percentage removal of Strontium increased with increasing dosages of Disodium Hydrogen Phosphate. The maximum precipitation of Sr occurred with 5.0 g/L of Disodium Hydrogen Phosphate (99.48% removal). To lower the concentration of Strontium to below 4.0 mg/L as per EPA regulations, the optimal dosage of Disodium Hydrogen Phosphate is 3.0 g/L.

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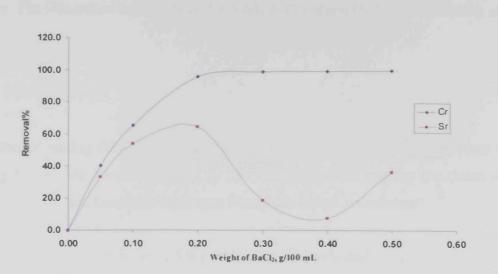
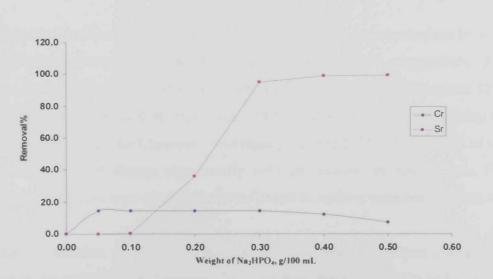
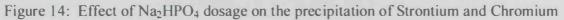


Figure 13: Effect of BaCl<sub>2</sub> dosage on the precipitation of Strontium and Chromium





Chromium at the beginning precipitated with 0.5 g/L of Disodium Hydrogen Phosphate then the Chromium did not change significantly with an increase in Disodium Hydrogen Phosphate dosages. The Chromium concentration for 5 g/L of Disodium Hydrogen Phosphate was 1.8842 mg/L.

#### 4.2 Mixing Time

The effect of mixing time on removal efficiency of Chromium and Strontium was studied by varying the mixing period from 15 to 120 minutes, while keeping the doses of Barium Chloride 5.0 g/L and Disodium Hydrogen Phosphate 3.0 g/L as constant.

The procedures were as follows; 5.0 g of Barium Chloride and 3.0 g of Disodium Hydrogen Phosphate were mixed together before being added to 100 mL of polluted wash water. Then, the samples were shaken for different intervals of times (15, 30, 45, 60, 75, 90 and 120 minutes), after which, they were filtered using Whatman grade no 42 filter paper. The concentrations of Chromium and Strontium were measured using FAAS. The results of the analyses are shown in Table XVI.

After conducting a series of tests, the Chromium and Strontium concentrations in the untreated wash water sample were found to be 2.0417 mg/L and 12.208 mg/L, respectively. Quantitative removals of most of the Cr and Sr were obtained within a very short time (about 15 minutes). The percentage removal of Chromium was 100% within 15 minutes of mixing time. The precipitation equilibrium for Chromium was rapidly achieved. The precipitation of Chromium and Strontium did not change significantly with an increase in mixing time. The results indicate that 15 minutes time of mixing was sufficient to achieve complete removal of Cr.

The order of addition of Barium Chloride and Disodium Hydrogen Phosphate is very important to the treatment applications. To investigate the effect of the order of addition of these two chemicals on the Chromium and Strontium removal, the following two sequences were tested. For sequence 1; 0.5 gram of Barium Chloride was added to the 100 mL of the sample. The samples were shaken for 5 minutes. After this, 0.3 gram of Disodium Hydrogen

Mixing Time, (min)	Sr (mg/L)	Sr Removal %	Cr (mg/L)	Cr Removal %
15	4.34	64.45	0.00	100.00
30	4.44	63.63	0.00	100.00
45	4.38	64.12	0.00	100.00
60	5.03	58.80	0.00	100.00
75	4.59	62.40	0.00	100.00
90	4.92	59.70	0.00	100.00
120	5.47	55.19	0.00	100.00

Table XVI : Effect of mixing time on quality of wash water

Phosphate was added to the sample and was shaken for two hours. In case of sequence 2; 0.3 gram of Disodium Hydrogen Phosphate was added to the 100 mL of the sample. Then, the samples were shaken for 5 minutes. After this, 0.5 gram of Barium Chloride was added to the sample and was shaken for two hours. Finally, the samples were filtered and the Chromium and Strontium were measured by Flame Atomic Absorption Spectrometer. The results are presented in Table XVII.

Results indicate that the Chromium was fully removed in both experiments indicating that the order of addition is not important for the removal of Chromium. But for Strontium removal, sequence 1 gives slightly more removal percent (58.55%) than sequence 2 (57.08%). As can be seen, the Strontium concentration still remains high in both cases. To decrease the Strontium concentration, it was suggested to treat the wash water sample with 4.0 g/L of Barium Chloride and Disodium Hydrogen Phosphate.

Two steps of treatments were conducted. In step one, 0.4 gram of Disodium Hydrogen Phosphate was added to the 100 mL of the sample. The sample was shaken for 10 minutes then filtered and the concentrations of Chromium and Strontium were finally measured using Flame Atomic Absorption Spectrometer. In step two of the treatments, 0.4 gram of Barium Chloride was added to the filtrate obtained from step one. The sample was shaken for another 10 minutes and then filtered. Finally, the concentrations of Chromium and Strontium were measured using Flame Atomic Absorption Spectrometer Table XVIII.

Table XVIII shows the results obtained from two steps of treatments. The original concentrations of the Strontium and Chromium in the untreated wash water sample were 12.208 mg/L and 2.0417 mg/L, respectively. After treating the wash water with 4.0 g/L of the Disodium Hydrogen Phosphate, the concentrations were decreased to 0.0510 mg/L and 1.6580 mg/L, respectively. Also, Table XVIII presents the quality of the wash water sample after completion of the treatment process. The percentage removal of the Strontium and Chromium were 98.68% and 98.73% respectively. The slight increase of Strontium in the water after treatment with Barium Chloride may be attributed to its light release from the developed sludge associated with slight change of pH.

Table XVII : Effect of the order of addition of Barium Chloride and DisodiumHydrogen Phosphate on the removal of Chromium and Strontium

Sample Description	Sr (mg/L)	Sr Removal %	Cr (mg/L)	Cr Removal %
Sequence1 (first Barium Chloride then Disodium Hydrogen Phosphate)	5.06	58.55	0.00	100.00
Sequence 2 (first Disodium Hydrogen Phosphate then Barium Chloride)	5.24	57.08	0.00	100.00

Table XVIII : Strontium and Chromium residuals for 10 minutes mixing time

4.0 g/L Disodium Hydrogen	Sr (mg/L)	Sr Removal %	Cr (mg/L)	Cr Removal %
Phosphate addition	0.0510	99.58	1.6580	18.79
4.0 g/L Barium Chloride	Sr (mg/L)	Sr Removal %	Cr (mg/L)	Cr Removal %
addition	0.1615	98.68	0.0260	98.73

The final concentrations of Strontium and Chromium in the treated wash water sample were 0.1615 mg/L and 0.0260 mg/L respectively, which are below the allowable limits of the environmental standards for water.

This work clearly indicates the potential of using Barium Chloride and Disodium Hydrogen Phosphate for the removal of Chromium and Strontium from wash water sample. 0.4 gram of both Chemical compounds for each 100 mL of wash water was found adequate to remove 98.73% of the Chromium and 98.68% of the Strontium. These results indicate that 4.0 g/L of Barium Chloride and Disodium Hydrogen Phosphate could be an effective option to reduce Chromium concentration to environmentally acceptable levels. In this study, it was also found that a time of 10 minutes was sufficient for precipitation to reach equilibrium.

#### 4.3 Stoichiometric Analysis and pH Stabilization

In this section, the variation of total dissolved solids, heavy metals, anions and cations due to the applied treatment is evaluated. Table XIX presents the influence of the addition of Barium Chloride and Disodium Hydrogen Phosphate on the total dissolved solids. It is evident that the total dissolved solids increased after addition of Barium Chloride (4794 mg/L).

Comparison of heavy metals concentrations before the treatment and after each process of the treatment is shown in Table XX. The concentrations of heavy metals such as Zn, Ni, Cu, Cd, and Pb decreased after addition of Disodium Hydrogen Phosphate and Barium Chloride. The initial concentration of the Lead was 0.604 mg/L and after completion of the treatment it decreased to 0.0040 mg/L.

Table XXI shows comparison of cations concentrations before the treatment and after each process of the treatment. The Barium concentration gradually increased after additions of Barium Chloride with 163.13 mg/L, because of the addition of Barium Chloride. The Sodium concentration in the fresh wash water sample was 488.07 mg/L. After addition of the Disodium Hydrogen Phosphate, it increased to 1110.79 mg/L. It is concluded that the addition of the Disodium Hydrogen Phosphate increased the sodium concentration in the wash water sample.

Table XXII presents comparison of anions concentrations before the treatment and after each process of the treatment. The concentration of Chloride ions after treatment with Barium Chloride increased to 1420 mg/L due to the addition of Barium Chloride. No specifications on the presence of the cations and anions in the wash water were available in the Dubai Municipality records.

The Total Hardness (TH) for the untreated wash sample was 1150 mg/L. The Total Hardness (TH) for the sample after treatment with Barium Chloride was found to be 75 mg/L. The pH condition of the wash water is an extremely important factor in the quality of the water obtained from the treatment. The wash water from ready-mix concrete truck drum contains high pH levels. Highly alkaline wash water is caustic and considered to be corrosive. The ready-mix concrete wash water sample with high pH may be classified as special waste and require special handling. The pH for the original wash water sample was 12.28. The present investigation evaluates the use of CO<sub>2</sub> bubbling for lowering the pH readings. To lower the pH, the following procedures were followed; one gram of Disodium Hydrogen Phosphate was added to 250 mL of the fresh wash water sample and was shaken for 10 minutes. Then, 0.8 gram of Barium Chloride was mixed with 200 mL of the filtrate and was also shaken for 10 minutes at a flow rate of 4 L/min.

Table XXIII shows the effect of  $CO_2$  bubbling on the pH value. The high pH in the treated wash water decreased readily once in contact with  $CO_2$  bubbling and the pH decreased from 12.28 to 5.87. Lowering the pH of the wash water by addition of acids (i.e. sulfuric acid) were not considered because they may contribute to the amounts of ions in the wash water sample.

Table XIX : Comparison of total dissolved solids before the treatment and after each process of the treatments

Sample Description	Concentrations (mg/L)
TDS - Before the treatment	4106
TDS - After treatment with (Na <sub>2</sub> HPO <sub>4</sub> )	4180
TDS - After treatment with (BaCl <sub>2</sub> )	4794
After bubbling with CO <sub>2</sub>	2740

Table XX : Comparison of heavy metals concentrations before the treatment and after each process of the treatment

			Metal co	ncentratio	ons (mg/L)		
Sample Description	Zn (mg/L)	Ni (mg/L)	Cu (mg/L)	Cd (mg/L)	Pb (mg/L)	Cr (mg/L)	Sr (mg/L)
Wash water before the treatment	0.026	0.0464	0.0235	0.041	0.604	2.591	10.345
After treatment with (Na <sub>2</sub> HPO <sub>4</sub> )	0.0050	0.0029	0.0023	0.0001	0.0055	1.9038	0.0409
After treatment with (BaCl <sub>2</sub> )	0.0007	0.0028	0.0009	0.0000	0.0051	0.0025	0.0098
After bubbling with CO <sub>2</sub>	0.0004	0.0019	0.0003	0.0000	0.0040	0.0022	0.0093

Table XXI : Comparison of cations concentrations before the treatment and after each process of the treatment

		Cations concentrations (mg/L)				
Sample Description	Al (mg/L)	Ba (mg/L)	Ca (mg/L)	Fe (mg/L)	K (mg/L)	Na (mg/L)
Wash water before the treatment	0.2900	0.2229	772.58	0.009	473.65	488.07
After treatment with (Na <sub>2</sub> HPO <sub>4</sub> )	0.2925	0.2677	2.0832	0.012	474.56	1110.79
After treatment with (BaCl <sub>2</sub> )	0.1800	163.13	0.0247	0.006	473.10	1088.44
After bubbling with CO <sub>2</sub>	0.1790	153.00	0.0210	0.005	472.00	1065.10

Table XXII : Comparison of anions concentrations before the treatment and after each process of the treatment

	- 1	Anions	ons (mg/L)	;/L)		
Sample Description	SO <sub>4</sub> (mg/L)	Cl <sup>·</sup> (mg/L)	HCO <sub>3</sub> · (mg/L)	CO <sub>3</sub> (mg/L)	OH (mg/L)	
Wash water before the treatment	685	88	0	90	650	
After treatment with (Na <sub>2</sub> HPO <sub>4</sub> )	640	355	0	510	20	
After treatment with (BaCl <sub>2</sub> )	5	1420	0	50	425	
After bubbling with CO2	5	1410	0	46	419	

Table XXIII : Comparison of pH values before the treatment, after each process of the

treatment and after bubbling with carbon dioxide gas

pH - Before the treatment	12.28
pH - After treatment with (Na <sub>2</sub> HPO <sub>4</sub> )	12.05
pH - After treatment with (BaCl <sub>2</sub> )	11.86
pH - After bubbling with CO <sub>2</sub>	5.87

### 4.4 Settling Conditions and Need of Settling Tank

Settling can be defined as a physical separation process of different phases in a mixture. Settling time is the allowed time for different particle sizes to settle out of suspension. This study examines the settling characteristics of the treated wash water sample under controlled laboratory conditions. The effect of time on settling and the settling velocity were studied. The settling behavior of treated wash water sample was observed through settling tests. The following procedures were used. In one experiment, 100 mL of the untreated wash water sample was placed in conical flask (100 mL). 0.4 gram of Disodium Hydrogen Phosphate was added to the conical flask. Then, the mixture was shaken for 10 minutes and then the mixture was left to settle down in graduated cylinder. Same procedures were repeated with 0.4 gram of the Barium Chloride. Finally, the height of the turbid solution with time was recorded.

Figures 15 & 16 depict the evaluation of settled sludges with time. This includes the heights of settled sludges of Disodium Hydrogen Phosphate and Barium Chloride mixtures after 30 and 1200 minutes. The graduated cylinder with symbol A represents the heights of settled sludges of Barium Chloride mixtures, whereas the graduated cylinder with symbol B represents the heights of settled sludges of Disodium Hydrogen Phosphate mixtures. Table XXIV reports the heights of the turbid solution at these time instants 30, 60, 90, 120, 150, 180, 210, 240, and 1200 minutes. After 150 minutes of elapsed time, the height of settled sludges of Disodium Hydrogen Phosphate was not clear and has some turbidity and become clear after 24 hours. After 1200 minutes of elapsed time, the height of settled sludges of the experiments the mixtures were extremely turbid. These results show that the settling velocity was very small and the particles need long time to settle. Therefore, the results reveal the need of having settling tanks following the mixing process.

#### 4.5 Generated Sludge

The sludge quantities generated by these processes are small. The mass of sludge for 100 mL of wash water sample after mixing and precipitation was about 1 gram in the Disodium

Hydrogen Phosphate as well as in the Barium Chloride case. Furthermore, sedimentation in Disodium Hydrogen Phosphate process was faster than that in the Barium Chloride operation.

After completion of the settling process, the sludge was separated from the graduated cylinder by filtration with Whatman grade no 42 filter paper and then dried at 70°C overnight in drying oven. To regenerate the heavy metals from the generated sludge, concentrated nitric acid and hydrochloric acid were added to the sludge to dissolve and extract the heavy metals. The sludge generated from the Barium Chloride operation did not dissolve in concentrated nitric and hydrochloric acids.

Table XXV shows the heavy metals concentrations in the sludge after addition of Disodium Hydrogen Phosphate. The concentrations of Zn, Ni, Cu, Cd, Pb, Cr, and Sr were found to be 0.0193 mg/L, 0.0040 mg/L, 0.0010 mg/L, 0.0002 mg/L, 0.0009 mg/L, 0.0268 mg/L, and 4.2429 mg/L, respectively. Table XXVI presents cations concentrations in the same separated sludge. The cations concentrations of the Al, Ba, Ca, Fe, K, and Na in the extracted liquid from the sludge were 0.0304 mg/L, 0.8478 mg/L, 11.2525 mg/L, 0.0200 mg/L, 9.6421 mg/L and 17.6857 mg/L, respectively.

### 4.6 Conceptual Design of Treatment Plant

The optimum experimental conditions, derived from the aforementioned results, are presented briefly in this section. The optimum dosage of the Disodium Hydrogen Phosphate and Barium Chloride were found to be 0.4 gram and the mixing time was 10 minutes. After optimizing the process operating conditions of the wastewater treatment unit, the treated wastewater can meet the discharge regulated limits.

A typical ready-mix concrete wash water treatment plant process is proposed in Figure 17. The four primary components of a conceptual treatment plant are the collecting tank, the two mixing tanks and the settling tank. The collecting tank is the interface between the engineered system and the ready-mix truck wash water sample.

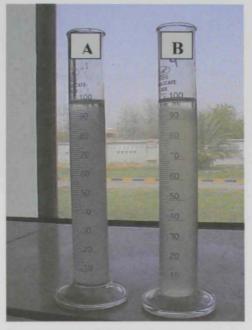


Figure 15: Heights of (A) BaCl<sub>2</sub> & (B) Na<sub>2</sub>HPO<sub>4</sub> mixtures after 30 minutes of elapsed time

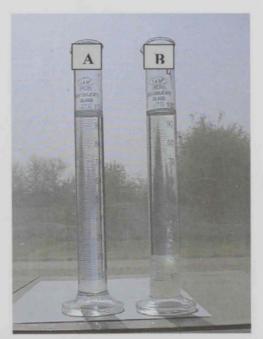


Figure 16: Heights of (A) BaCl<sub>2</sub> & (B) Na<sub>2</sub>HPO<sub>4</sub> mixtures after 1200 minutes of elapsed time

Time (minutes)	Sludge for Chromium Precipitation (mL)	Sludge in Strontium Precipitation (mL)
30	98 mL	97 mL
60	95 mL	93 mL
90	90 mL	73 mL
120	90 mL	59 mL
150	The solution still has	50 mL
180	some turbidity and	45 mL
210	become clear after 24 h	40 mL
240		38 mL
1200		20 mL

## Table XXIV : Variation of sludge height with time

			Metal con	centration	is (mg/L)		
Sample Description	Zn (mg/L)	Ni (mg/L)	Cu (mg/L)	Cd (mg/L)	Pb (mg/L)	Cr (mg/L)	Sr (mg/L)
After treatment with (Na <sub>2</sub> HPO <sub>4</sub> )	0.0193	0.0040	0.0010	0.0002	0.0009	0.0268	4.2429

Table XXV : Heavy metals concentrations in the sludge generated with Sr precipitation

Table XXVI : Cations concentrations in the sludge generated with Sr precipitation

		Cat	ions concen	itrations (r	ng/L)	
Sample Description	Al (mg/L)	Ba (mg/L)	Ca (mg/L)	Fe (mg/L)	K (mg/L)	Na (mg/L)
After treatment with (Na <sub>2</sub> HPO <sub>4</sub> )	0.0304	0.8478	11.2525	0.0200	9.6421	17.6857

The collecting tank is used to settle and concentrate most of the particular material to the bottom of the tank as primary sludge. The first mixing tank is for the addition and mixing of Disodium Hydrogen Phosphate and the second mixing tank is for the addition and mixing of Barium Chloride. The Carbon Dioxide gas cylinder is connected to the effluent of the second mixing tank to inject the CO<sub>2</sub> gas in order to lower the pH. In the settling tank the fluid velocity is very low and the particles have enough time to settle down to the bottom of the settling tank as secondary sludge. After settling, the supernatant clean water can be reused. The settling tank must be cleaned out periodically and the collected waste should be hauled to the dump. The proposed treatment scheme offers an acceptable solution to removing Chromium and Strontium from the wash water generated by the ready-mix concrete truck.

Onsite wastewater treatment system designs vary according to the site and the requirements. About 58 ready-mix concrete batching plants were identified operating in Emirate of Dubai with an average of 35 truck mixers. Assuming the maximum amount of water used per day for washing would be 150 L per truck. The maximum wash water generated from each company per day 150 L\* 1 Company \* 35 trucks = 5250 L, when the plant is operating at maximum capacity. The wash water treatment plant is with a total capacity of a maximum of 5.250 cubic meter of wash water per day.

To calculate a rough estimate of the operating cost, the masses of Disodium Hydrogen Phosphate and Barium Chloride are calculated for the estimated plant capacity. This produces 21 Kilograms of Disodium Hydrogen Phosphate and 21 Kilograms of Barium Chloride.

According to the chemicals cost survey, the cost of one kilograms of Barium Chloride is 105 Arab Emirates Dirhams, while the cost of one kilograms of Disodium Hydrogen Phosphate is 84 Arab Emirates Dirhams. Then, if we need 21 kilograms of Barium Chloride daily, the cost will be 2205 Arab Emirates Dirhams. In case of Disodium Hydrogen Phosphate the cost will be 1764 Arab Emirates Dirhams daily bases. The total operating cost approximately will be 3969 Arab Emirates Dirhams per day.

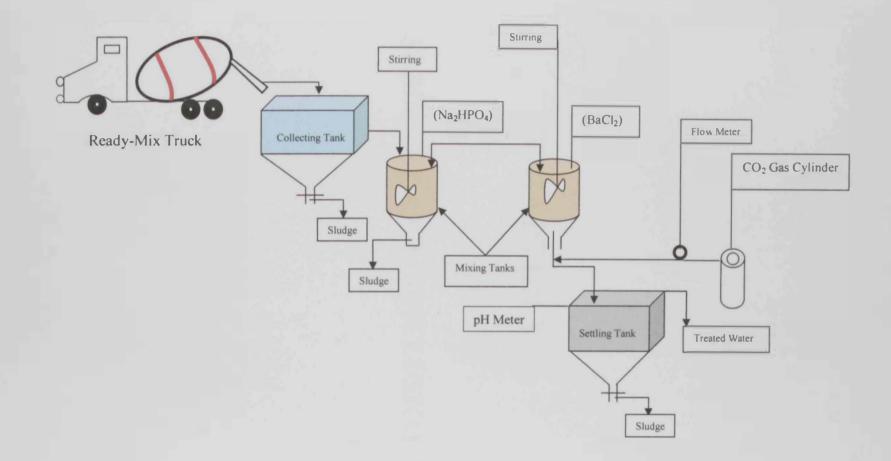


Figure 17: Conceptual design of treatment plant

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# **CHAPTER V**

**SUMMARY AND CONCLUSION** 

### SUMMARY AND CONCLUSION

The major environmental issue with ready-mix concrete production around the world is water pollution. The wash water generated from ready-mix concrete trucks is extremely alkaline and contains significant quantities of heavy metals.

The objective of the present study was to quantify the heavy metal concentrations in wash water generated from ready-mix concrete truck. The present work also analyzes the conventional water quality parameters for the wash water such as pH, color, total dissolved solids (TDS), and total suspended solids (TSS). The study aims to design small onsite treatment plant that is consistent with best practices to remove heavy metals from wash water. The results can be used as reference background for future development in the ready-mix concrete plants and in solving some water quality-related problems.

The cement sample was collected from National Cement Company in Dubai while the cement chemical additives were collected from Al Gurg Fosroc LLC in Dubai. All the selected materials were delivered to the ready-mix concrete batch plant, after which all of the components were discharged into the truck drum. Prior to lab analyses, the ready-mix concrete wash water sample from the truck drum was kept and stored in two big plastic gallons. The concentrations of heavy metals, cations and anions in the prepared wash water sample were estimated by Flame Atomic Absorption Spectrometer.

The concentration of Chromium in the wash water samples was very high (2.591 mg/L). The presence of Chromium in higher concentration was directly associated with the production of cement. The Strontium was found in the analyzed sample with high concentration as well (12.255 mg/L).

The concentrations of calcium, sodium and potassium in the wash water were 772.58 mg/L, 488.07 mg/L and 473.65 mg/L respectively. The concentrations of chloride, and sulfate ions in the wash water were 88 mg/L and 685 mg/L respectively. Also, the hydroxide ion concentration was found to be 650 mg/L.

The wash water is frequently strongly alkaline with pH values generally over 13. The analyzed wash water sample contains a high level of total dissolved solids (TDS) equals to 5890 mg/L. The wash water Sample is highly turbid. After settling, the color of the mixtures was yellowish. The ready-mix concrete wash water sample was characterized by high levels of total hardness (TH) equal to 1150 mg/L. Therefore the wash water sample generated from ready-mix concrete truck drum is considered as very hard water.

The methods currently used for removal of heavy metals from industrial wastewater include chemical precipitation, ion exchange, reverse osmosis, electrochemical treatment, coagulation, biosorption processes, evaporation, membrane filtration, electrodialysis, solvent extraction and adsorption. A number of materials have been studied for their capacity to remove toxic heavy metals, including cationic resin, commercial granular activated carbon, bentonite (saroog), fly ash, chlorella pyrenoidosa alga, immobilized algae beads, carpentry sawdust, fish scale, Barium Chloride, Calcium Carbonate, Calcium Hydroxide, Calcium Chloride, Calcium Sulfate, Sodium Carbonate, Disodium Hydrogen Phosphate and Tetrasodium Diphosphate. From that long list of materials and compounds, Disodium Hydrogen Phosphate (Na<sub>2</sub>HPO<sub>4</sub>) was selected for Strontium treatment and Barium Chloride (BaCl<sub>2</sub>) was selected for Chromium treatment.

After Chromium removal with Barium Chloride, the Chromium concentration in treated wash water sample was reduced to the 0.0260 mg/L showing more than 98.73% efficiency in Chromium precipitation. The maximum removal efficiencies of Sr with Disodium Hydrogen Phosphate (Na<sub>2</sub>HPO<sub>4</sub>) was 99.68%.

Dosages of 4.0 g/L for both chemical compounds were found adequate to remove 98.73% of the Chromium and 98.68% of the Strontium in the wash water. Optimum mixing time for both chemical compounds was found to be 10 minutes.

The pH of the treated wash water was adjusted using  $CO_2$  bubbling. The high pH in the treated wash water decreased readily once in contact with  $CO_2$  and the pH reading decreased from 12.28 to 5.87.

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The settling behavior of treated wash water sample including the effect of time on settling and the settling velocities were studied by the settling experiments. The results showed that the settling velocity for the sludge generated with Barium Chloride is very slow and requires about 24 hours to settle down. Such velocity limits the design of the settling tank required in the process.

The sludge quantities generated by these processes are small. The mass of sludge for 100 mL of wash water sample after mixing and precipitation was about 1 gram in the case of Disodium Hydrogen Phosphate as well as Barium Chloride.

An onsite wash water conceptual treatment plant design may consist of four primary components. This includes a collecting tank, two mixing tanks for mixing the Barium Chloride and the Disodium Hydrogen Phosphate, and a settling tank. Carbon Dioxide should be ingested at the effluent of the second mixing tank.

Based on the above-mentioned results, the following conclusions were reached:

- The level of Chromium and Strontium in the wash water were 2.094 mg/L and 12.255 mg/L respectively, which are above the permissible limits.
- 2. The high concentration of Chromium in the wash water samples of the study is mainly due to cement production process.
- The Barium Chloride holds great potential to remove the Chromium from the wash water generated from ready-mix concrete truck where the Chromium was reduced to less than 0.05 mg/L.
- 4. The Disodium Hydrogen Phosphate was considerably effective in removing Strontium (Sr) from wash water where the Strontium (Sr) dropped to less than 0.5 mg/L.
- An optimum dosage of 4.0 g/L was found for both Disodium Hydrogen Phosphate and Barium Chloride for Sr and Cr precipitation; respectively. The optimum mixing time in both cases was 10 minutes.
- 6. Carbon Dioxide gas bubbling was found considerably effective in lowering the pH to less than 6.0.

- 7. The mass of sludge in both precipitation processes was identical (1 g/100 mL).
- 8. The settling velocity in case of Strontium precipitation was much faster than that with Chromium precipitation.
- 9. Comparing the existing handling and treatment practices in Dubai and the proposed wash water treatment plant, it is concluded that the proposed system used two chemical compounds to lower the concentrations of Chromium and Strontium in the wash water sample in stead of using three chemical compounds to lower only the Chromium concentration. Moreover, the proposed system minimizes the operating cost since it consists of four primary components instead of having six chambered tanks.

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المجموعات الخاصة SPECIAL COLLECTIONS

الملخص باللغة العربية

دبي احدى الإمارات المسبع، وهي تمر الآن بوتيرة مريعة من النهضة العمرانية التي تتضمن على كميات كبيرة من الخرسانة الجاهزة. تلوث المياه هو المشكلة البيئية الرئيسة مع ابتاج الخرسانة الجاهزة حول العالم، حيث أن المياه الناتجة عن غسيل خزانات شاحنات نقل الخرسانة الجاهزة هي فلوية للغاية وتحتوي على مستويات كبيرة من المعادن الثقيلة. وازالة المعادن الثقيلة من مياه الغسيل هي مشكلة بينية وفلق اقتصادي. وهذا يدل على الحاجة الملحة لطرق معالجة آمنة، متوفرة، واقتصادية لإزالة المعادن الثقيلة من المياه الذاتجة عن غسيل خزانات شاحنات نقل الخرسانة الجاهزة.

تهدف الدراسة الحالية إلى تحديد خصائص المعادن الثقيلة الموجودة في المياه الناتجة من غسيل خزانات شاحنات نقل الخرسانة الجاهزة بمستويات مرتفعة، بالإضافة إلى تحرّى التقنيات الأكثر كفاءة لإزالتهم.

وقد أظهرت الدراسة أن مصدر المعلان الثقيلة المعلمة في مياه الغسيل هو عينات الإسمنت. كما أوضحت الدراسة وجود نسب مرتفعة للعنصرين الكرميوم والستروونشيوم في مياه الغسيل تصل إلى ٢.٠٤ ملغ / لتر و ١٢.٢١ ملغ / لتر، على التوالي. وأظهرت نتائج التجارب أن الترسيب الكيمياني هو أكثر التقنيات كفاءة لإزالة كل من الكرميوم والستروونشيوم في مياه الغسيل تصل إلى ٢.٠٤ ملغ / لتر و ١٢.٢١ ملغ / لتر، على التوالي. وأظهرت نتائج التجارب أن الترسيب الكيمياني هو أكثر التقنيات كفاءة لإزالة كل من الكرميوم والستروونشيوم من مياه الغسيل تصل إلى ٤.٠٤ ملغ / لتر و ١٢.٢١ ملغ / لتر، على التوالي. وأظهرت نتائج التجارب أن الترسيب الكيمياني هو أكثر التقنيات كفاءة لإزالة كل من الكرميوم والستروونشيوم من مياه الغسيل. كما أوضحت الدراسة فعالية استخدام المركب الكيميائي باريوم كلورايد في إزالة نسبة عنصر الكرميوم المرتفعة في المياه إلى أقل من ٢٠٠ ملغ / لتر، في حين تم استخدام المركب الكيميائي داي صوديوم هيدروجين فوسفيت في إزالة نسبة عنصر الستروونشيوم المرتفعة في المياه إلى أقل من ٢٠٠ ملغ / لتر، في حين تم استخدام المركب الكيميائي داي صوديوم هيدروجين فوسفيت في المياه إلى أقل من ٢٠٠ ملغ / لتر، في حين تم استخدام المركب الكيميائي داي موديوم هيدروجين فوسفيت في إزالة نسبة عنصر الستروونشيوم المرتفعة في المياه والوصول بها إلى أقل من ٢٠٠ ملغ / لتر، في حين تم المياه والوصول بها إلى أقل من ٢٠ ماني موديوم المرتفية في إزالة نسبة عنصر الستروونشيوم المرتفعة في المياه والوصول بها إلى أقل من ٢٠

جامعة الإمارات العربية المتحدة عمادة الدراسات الطيا برنامج ماجستير علوم البينة

إزالة معادن ثقيلة مختارة من المياه الناتجة من غسيل خزانات شاحنات نقل الخرسانة الجاهزة في دبي بدولة الإمارات العربية المتحدة

رسالة مقدمة من الطالب

عماد جمعه محمد أبو نقيره

إلى

جامعة الإمارات العربية المتحدة استكمالا لمتطلبات الحصول على درجة الماجستير في علوم البينة

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