STUDY OF BIOPOLYMER-MODIFIED CONCRETE SYSTEM: GEOPOLYMERIZATION OF BIOPOLYMERS

by

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DEDICATION

To my God and my parents…

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

This study depicts the new material modified by biopolymers in a concrete system. New structure was evaluated by instrumental analyses such as XPS, FTIR, and XRD. Leaching procedures (TCLP and SPLP) were also conducted to witness the biopolymers' capacity of binding the wastes in a concrete system. This study will also explain the definition of geopolymer, structure study, formation of geopolymer. And finally, it will confirm that organic containing geopolymer is superior to pure inorganic geopolymer.

Resultant products in practices such as CRT glass showed very high compressive strength and low lead leachability. For selenium waste in a practical case, it supports the opportunity for commercialization of this technology. Only a minute amount of biopolymers is effective in binding metals and giving high strength of workable products.

This organic containing concrete is the first monument discovery in the cement chemistry, and even in the chemistry world. The geopolymerization of biopolymer is also new research that the Maillard reaction product, melanoidin was hired to simulate the process of geopolymerization. More than any other things, geopolymerizaion concept has become enlightened in this study and at the same time is able to project to the future applications that have been under the shade of a biased definition of geopolymer. Herein, new definition can therefore broaden the scope of the geopolymer.

PART I

Concrete Geopolymer

(Waste-Based and Biopolymer-Modified Concrete Geopolymer)

Part I was presented in 2003 AIChE (American Institute of Chemical Engineers) Annual Meeting at San Francisco, awarded as second place for student paper and poster competition in The 96th 2003 Annual Air and Waste Management Association (A&WMA), San Diego.

CHAPTER I

Introduction

Throughout the world, plenty of research has been conducted on the utilization of waste materials, in order either to avert an increasing toxic threat to the environment and humans or to streamline current waste disposal technologies by making them more affordable. In this sense, an economically viable solution to this problem should include the manufacturing of new products, using waste materials for other applications rather than a conventional disposal in a landfill. In this study, type of solidification technology based on concrete material was hired to remediate the toxic metal and hazardous chemicals.

The division of geochemistry in ACS was first initiated to the chemistry regime by Teh Fu (David) Yen back in 1970's (Organic Chemistry Bi-centennial History, 2003 and Kim, Carbohydrate polymers, 2003), later on, Yen immediately proceeded with the concept of "geopolymer" (Young, Atlantic City, New Jersey conference, 1974 and Kim, 2003). Teh Fu Yen, for the first time, introduced the concept of geopolymer in the geochemistry in the history of American Chemistry Society in the early 1970s (Young, et al., 1974), a little later, the term "geopolymers" was again introduced by Davidovits in the mid 1970s (Swanepoel, et al., J.C). During the last decade geopolymeization has emerged as a possible technology for the effective stabilization and immobilization of toxic materials. In spite of the fact that this kind of technology stems from very old history events such as Egyptian construction, little is known about the nature of these reactions or the products. In the last fifteen years, it has been rediscovered and attention has been made to its unique chemical and physical characteristics. This study will attempt to enlighten the structure of geopolymer and to enlarge its useful merits and application options.

Through the literature reviews, it was found difficult to recognize the realm of geopolymer. Some people made an effort to find the geopolymeric structure with help of a variety of instrumental methods. To some extent, those efforts turned out to be a reward. However, many factors governing the formation of geopolymers are still not completely understood. The definition of geopolymer is still controversial. By Davidovits' definition, geopolymers can best viewed as the amorphous equivalent of certain synthetic zeolites, consisting of a polymeric Si-O-Al framework in high alkaline condition. On the other hand, geopolymers are the synthetic analogues of naturally occurring macromolecules, which was proposed by Teh Fu Yen. Geopolymers by Davidovits, so-called, inorganic geopolymers (polysialated aluminosilicate), cannot fully explain the organic containing geopolymers widely existing in the crust of the earth. For this reason, skepticism has arisen in this area. The definition of geopolymers therefore should include both inorganic and organic geopolymers. Typical types of inorganic geopolymers can be categorized as kaolinite (clay) and zeolites and organic geopolymers as the bitumen and kerogen, carbonaceous organic macromolecules, which have been formed in the lithosphere over the geological time scale.

As long as the chapter introduction is concerned, some chapters direct the way how the organic containing concrete or biopolymerized concrete, can be applied into the practical situations such as removal of CRT lead and selenium wastes. For example, Chapter 2 describes the significance of CRT waste and the disposal method in a concrete system, CBC (CRT-Biopolymer-Concrete) technology. Chapter 3 introduces the practice requested by one of environmental consulting firm as a case study. Chapter 4 shows no-waste based biopolymer concrete and demonstrates how the biopolymer affects the concrete structure, supported by XRD analysis and figure of new structure. Chapter 5 leads to instrumental approach to identify the geopolymer, subsequently following up from XRD analysis in previous chapter. Chapter 6 is the comparison between TCLP and SPLP of leaching procedures while Chapter 7 is the comparison between inorganic geopolymer and organic containing geopolymer. Chapter 8 eventually introduces how the biopolymer converts to geopolymer, not in a concrete system. Chapter 9 finally comes to the synthesis of geopolymers with a viewpoint of petroleum.

CHAPTER II

Safe Disposal Technology of Hazardous Cathode Ray Tube Wastes Using Biopolymer-Modified Concrete Systems

2. Safe Disposal Technology of Hazardous Cathode Ray Tube Wastes Using Biopolymer-Modified Concrete Systems

2.1 Introduction

Computer monitors, televisions, some camcorders and other electronic devices contain cathode ray tubes (CRTs), often called "picture tubes," which convert an electronic signal into a visual image. Cathode ray tubes found in computer monitors and television sets contain 20 percent lead oxide by weight, averaging five to eight pounds of lead per unit (American Recycler, 2002) For instance, a typical 17-inch computer monitor contains approximately 2.2 pounds of lead and a 27-inch television contains up to 8 pounds of lead (American Recycler, 2002). When tested, most CRTs exceed the regulatory threshold for lead content and are identified as hazardous materials when discarded. If products containing lead are disposed of in the trash, the lead can potentially contaminate the soil and water supplies. Therefore, disposing of CRTs to the trash or to a municipal landfill is prohibited. People should take their waste CRTs to a collection facility for disposal.

Approximately 2.9 million TVs (74,000 tons) and 3.2 million computer monitors (48,000 tons) are stockpiled, and that is just in California households (American Recycler, 2002). Considering the magnitude of the annual stream of discarded CRTs, it is clear that CRT waste urgently needs to be treated, much more so than other hazardous wastes. In 1996, there were over 300 million CRTs (TVs and monitors) stockpiled in North America. In the same year, 42 million CRTs were sold in the U.S. and 79 million computers were retired (Townsend et al., 1999).

The objective of this study is to address and alleviate the CRT problems by providing a control technology for this hazardous material, also resulting in marketable and recyclable products as well as minimizing hazardous waste. The key point of biotechnology is to use commercially available biopolymers to bind lead from CRT wastes and further obtain building materials such as foundation, bricks, blocks, panels, and insulation. Such building materials, which may be obtained from the recycling of CRT wastes with biopolymers, have potential to show similar or even better mechanical properties than ordinary concrete materials and at the same time a low leachability of Pb.

The idea of using biopolymers to encapsulate the Pb from CRT wastes is the original part of the current work and is based on biopolymer properties. Biopolymers are high-molecular weight compounds with repeated sequences, hence simple functional groups become multiple reactive sites providing ample opportunities for chemical and physical reactions to take place. These reactions cause the crosslinking capacity. Xanthan gum, guar gum, and chitosan were selected for the current study due to their outstanding characteristics of metal uptake, low permeability, and high shear strength as compared to other commercially available biopolymers such as polyhydroxybutyrate (PHB), and polyglutamic acid (Etemadi, O. et al., 2003). Metals can form complexes with the functional groups of organic compounds (Yen, 1999). In case of xanthan gum, because of the presence of particular functional groups such as CH_2OH, OH, O, COOH, and H in its structure, xanthan gum is able to bind metals and sand, as well as cement particles by creating stable interpenetrating cross-linking networks. In addition, crosslinking agent like boric acid producing borate ions was applied to biopolymer reaction. This application shows the crosslink reaction between biopolymer and crosslining agent occurs and eventually helps build up three-dimensional model between target metal, Pb and concrete structure. Biopolymer also functions as the adhesive in a predominantly calcium carbonate matrix (Glass, 1986), explaining that biopolymers utilized can glue lead onto the concrete molecules containing vast amount of calcium carbonate in form of concrete composite.

2.2 Lead in the Environment and Associated Health Effects

2.2.1 Public Health Effects of Lead

Lead is a hazardous substance. Elevated levels above standards, referred to as lead poisoning, may adversely affect mental development and performance, kidney function, and blood chemistry. Young children are particularly at high risk of lead poisoning since their tissues and organs are vulnerable to lead attack occurring in the body. Environmental health concerns and impact on ecosystem regarding various metals' distribution and exposure can be prioritized as Pb > Cd > Cu > Zn or Cd > Pb > Cu > Zn (Siegel, 2002). This means Pb is the most dangerous in the list of health concerning metals to threaten the public health.

Lead is all around us in paint, batteries, drinking water, pottery, hand-glazed ceramics, even crayon and metal-alloy toys for children. Although containment of lead in paint has been banned, potential exposure arises from 20 or more year-old houses, which surpass regulatory policies related to lead since they are not currently retroactive. In most exposure cases, toddlers have been found to administer lead by handling sweet tasting paint flakes. In 1986, the use of lead soldering in plumbing was abruptly halted, thus reducing lead toxicity in drinking water. Before leaded gasoline was banned, vehicular emissions contributed to atmospheric lead. Lead inhalation results in particle deposition in the respiratory system. Particles deposited in the upper parts of lung are usually either removed by coughing or swallowed, whereas dissolution to deeper parts of the lung allows lead to enter the bloodstream.

After lead enters the bloodstream, its' dispersal to vital organs includes the gastrointestinal tract, the hematopoietic system (blood-forming tissues), cardiovascular system, central and peripheral nervous systems, kidneys, immune system, and reproductive system. A prevailing concern is impairment to proper sperm function. Lead exposure may contribute to a reduction in sperm count, according to a new study by fertility researchers (J. of Environmental Science & Tech. April, 2003). The researchers found a significant association between high Pb levels and suboptimal fertilization rates that interfere both the ability for sperm to penetrate the egg and the eggs' subsequent capability to fertilize the egg. Lead levels decrease sperm concentration and change sperm shape, form, and affect its movement, meaning that lead also acts in the testis.

Lead is a cumulative poison; it is systemic until it reaches toxic levels. For adults, about 99% of lead entering the bloodstream leaves the body in form of feces or urine. The rest is stored in bones and teeth. For children, about 70% of the lead in the bloodstream is retained in the bones and teeth of the body. The distinguished lead adsorption rate incurred in young and unborn children, postulates a larger health threat to children than adults because young and unborn children are extremely sensitive to lead. Therefore it is crucial to instill children lead poisoning prevention with maternal women and aid in the prevention of premature births and/or followed by learning retardation and growth deficiency in the children.

Based on epedemiologic animal case studies, the U.S. Environmental Protection Agency (EPA) places lead as a probable human carcinogen. Although studies indicate that lead acetate and lead phosphate cause cancer in laboratory animals, no direct correlation in humans has been confirmed because people are more sensitive to the non-cancer effects of lead than to the cancer effects. Unlike other chemicals, the risk posed by inorganic lead is based on predicted or measured levels of lead in blood rather than on toxicity values, except for tetraethyl lead, an organic form of lead. The EPA has developed mathematical models for estimating lead blood-level concentrations in children and adults caused by exposure to lead bounded soil, air, drinking water, food, and many other sources. For instance, the EPA has estimated that the concentration of lead in blood can exceed 10 μm/dL if the concentration of lead in soil exceeds 400 mg/kg of soil.

2.2.2 Lead in Environments

Lead is a metal found naturally in soil, rocks, water, air, plants, animals, and food. It typically occurs in combination with other elements as lead salts, some of which are soluble in water. The pure metallic form of lead is bluish-gray, but metallic lead rarely occurs naturally. Lead dose not evaporate, however it can be present in air as particles. Since it is an element, it does not degrade nor can it be destroyed. Several radioactive isotopes are also naturally present in the environment, with lead-210 being the isotope of most concern.

Lead is everywhere in the environment. Because of its widespread presence in the environment, lead can enter the body by breathing air, drinking water, soil, and food. Lead concentration in U.S. soil typically ranges from less than 10-30 mg/ kg of soil. However, amounts in the top layers vary widely and can be much higher at areas with heavy human activities. Lead can leach to groundwater over time but is relatively immobile in soil. Lead contamination of the environment was a major problem during the last half of the 20th century, including persistent use of leaded gasoline and industrial demand. In addition, appearance of various electronic appliances such as television sets and computer monitors aggravate the lead problems in nature by producing the E-wastes. Therefore, introducing lead level of environment in this study will be a standard of lead level to be comparable to the products made of lead from CRTs.

2.2.2.1 Lead in water

Lead rarely occurs in drinking water. Lead occurrence is more common at some point in the water delivery system. This occurs as a result of corrosion, the reaction between the water and lead in parts of the distribution system which includes service connection, pipes, solder, and brass fixtures. Water has different characteristics: some water is naturally more corrosive than others. Several factors affect the water corrosivity including acidity, high temperature, low total dissolve solids (TDS), and high amount of dissolved oxygen and carbon dioxide.

Lead in drinking water from plumbing or fixtures, is most commonly happening in either old or new houses. Historically speaking, through the early 1990s, it was quite common for some countries to utilize lead pipes for interior plumbing. Lead piping was also used for the service connections to join residential pipes to public water supply. Lead piping is most likely to be found in homes built before 1930. Copper piping then replaced lead piping, but lead soldering was still used for copper piping. Afterwards, lead-based solder was continuously used for the houses built before 1986, when the enactment of the SDWA (Safe Drinking Water Act) regulated the use of lead soldering (Kawamura, 2000).

Today, brass materials are used for faucets, plumbing fittings, check valves, and well pumps in almost 100 percent of all residential, commercial, private, and municipal water distribution systems. Still, brass contains some level of lead for casting and machining and lead content is restricted to eight percent. Some private well system may have brass or bronze capable of leaching lead. Also, some well screens may contain lead or are installed with a lead packing collar. Potential lead contamination can take place if the well is driven sandpoint well has been shot to clear the screen. Lead shot is sometimes poured into a well to keep out sand. Lead wool can be used for other wells. Additionally, electric current traveling through the ground wire is found to accelerate the corrosion of lead in the pipes. None of these practices are recommendable due to lead leaching. Older water coolers with lead-lined tanks are another lead source in drinking water. The Lead Contamination Control Act of 1988 prohibited the manufacturing and sale of such coolers.

Lead dose not noticeably alter the taste, smell, and color of water and the effects of low levels of lead toxicity in humans may not be obvious, but recent studies have shown it can adversely affect the human health even at lower levels than previously believed. As a result, lead exposure level has been lowered. Particularly, the exposure of infants who drink baby formulas and juices mixing with water is concerned. Infants being fed with formula can get 40 to 60 % of their lead intake from drinking water. On average, approximately 10 to 20 % of children's total lead exposure may come from drinking water.

There are several treatments to handle this lead problem in drinking water, including reverse osmosis, distillation and carbon filters specifically designed to remove lead. These methods are to treat water at only one faucet. Mostly, the heavy metals including lead can be manipulated for raw water through the chemical coagulation and filtration with carbon medium.

EPA has established an enforceable lead concentration action level for public water supplies as well as private water supplies. The lead action level is 15 ppb (0.015 ppm; 0.01 for California). WHO (World Health Organization) has 0.01 ppm and EU has 0.05 ppm (Kawamura, 2000). EPA has also set MCLG (Maximum Contaminant Level Goals), which is desirable, non-enforceable, and health-based goals to assure for a completely safe water supply. In other words, water containing any chemical in certain amount equal or below this level is not expected to cause any health concerns, over a lifetime of drinking this water. The MCLG for lead in drinking water is zero.

To determine the presence of lead in drinking water and its possible source, a specific procedure must be used to collect samples and a certified laboratory used for testing. Now, home test kits are available for first-flush sample, which can be simply carried out in home. If test results indicate the presence of lead and the source is identified, appropriate steps should be taken. If served by a public water system, one can contact the water supplier. If it is a private well, one can check with licensed water well contractor about the well and the pump for potential lead source. Those options include removing the lead source by addressing lead in a domestic water supply, using water treatment equipment, using an alternative water source (bottled water), and managing the water supply.

2.2.2.2 Lead in air

The primary sources of lead in the United States have been emissions from lead smelters and battery plants and from automobiles burning gasoline with lead additives. Transportation sources alone historically contributed approximately 80 % of the annual emissions on a national basis. However, lead concentration in ambient has drastically dropped since the use of unleaded fuel was mandatory (Gasoline with added lead can hardly be available as an automotive fuel in the U.S.) and emission controls on major lead pollution sources were in effect. Lead concentration in air has considerably been decreased due to the enactment of National Ambient Air Quality Standards (NAAQS's). The lead in ambient air quality standards is 1.5 $\mu g/m^3$ as both primary and secondary standard (Institute for Traditional Medicine).

In ambient, the concentrations of lead range from 0.001 to 0.002 $\mu g/m^3$ in remote areas and from 0.2 to 0.4 $\mu g/m^3$ in urban areas. The ambient values can be site-specific depending on the different sites. The highest concentrations are primarily found near lead smelters and along urban freeways, with typical levels of more than 10 $\mu g/m^3$. Apart from those extremely high levels locally concentrated, some cities and adjacent rural areas have shown a 10-fold range of air levels. For instance, Tokyo/Kyoto in Japan had atmospheric lead concentration of 0.075 $\mu g/m^3$, whereas Manila in Philippines had 9 times higher concentration of 0.650 $\mu g/m^3$ (Institute for Traditional Medicine). Speaking of lead content of American ambient during the 1980s, it was reported that it ranged from 0.3-1.1 $\mu g/m^3$ in urban areas, but rural areas ranged one half to one third from 0.15-0.3 $\mu g/m^3$ and the remote areas away from traffic have less than 0.01 $\mu g/m^3$. It is also estimated that natural lead content of air in prehistoric age was even lower than

$0.01\ \mu g/m^3$. Natural ambient lead sources can be volcanic eruptions, soil dust, and sea spray.

2.2.2.3 Lead in soil and plant

The lead contamination in soil is associated with traffic. In a study of soils in the New Orleans area, the lead concentration in high traffic area was 300 ppm with average range of 30-50 ppm in remote sites from traffic. Accordingly, the plant in highly contaminated soil shows high lead content in its tissues since vegetation has high affinity for uptaking the metals. The typical ratio of the concentration of lead in plants to that in the soil on which they grow is estimated at 0.037 (3.7%).

The plant grown in the traffic area had 7.5 ppm of lead content while other plants in the rural areas had less than 0.1 ppm. The fact confirms that high traffic areas have had substantially more lead dusted in the soil than rural areas, which results in that plants in lead contaminated soil are capable of absorbing extra lead. Also, a study of correlation between lead in soil and lead in blood serum showed that when the soil content of lead exceeded about 500 ppm (50 times the average of normal soil; 10 ppm), the human's blood will have some lead level, especially the children's.

Lead concentration in sandy soil is estimated to be 270 times higher than in the pore water between the soil particles. Lead also binds more tightly to clay and loam soils, with very high concentration ranges up to several thousand ppm levels.

2.2.2.4 Lead in food and medications

Most of lead is ingested through food chain. The lead ingested is concentrated as the eutrophic level in the ecosystem is elevated. Reported concentrations of lead in a variety of foods range from 0.002 to 0.65 mg/kg, with higher levels found in vegetables.

These days, there is plenty of herbal consumption like extract, medicines and dietary supplements in forms of tablets, capsule, and pills in the market as the oriental-based medical practices draw attentions as an alternative medical methodology. Chinese herb products have some level of contamination reflecting the lead taken up by plants and animal. Certain products seem to become more contaminated due to following reasons: growing herbs in highly contaminated soils; applying pesticides or fumigants containing lead; manufactured in contaminated facilities; concentrated and remain in the finished products; and intentional addition of lead containing materials in the formulation. More than 90% of the Chinese herbal products meet less than 3 ppm of lead. Some products contain very high lead level. Children's formula (Shang Han Lun and Bao Ying Dan) have 25% lead by weight (Institute for Traditional Medicine). Double Dragon Pills show 80-160 ppm of lead content when concentrated. So, lead content is easily in excess of 100 ppm with intentional addition of mineral compounds containing lead.

The lead limit for pharmaceutical products, according to the U.S. Pharmacopoeia, is 10 ppm. The recommended daily dose of finished lead-related product for ingestion is often less than 6 grams/day. Proposed lead levels should be reduced to 0.8 ppm (total formula) and 2.5 ppm (max. any single ingredient) by the year of 2012 (Institute for Traditional Medicine). The lead content in medication can be further limited by proper monitoring, stringent manufacturing procedures, and avoidance of high lead substances in formulas.

2.2.2.5 Lead in human blood and bone

Blood lead levels in human in the U.S. and Europe during the 1980s and early 1990s generally range from 7-14 μg/dL, while values now are under 4 μg/dL (Institute for Traditional Medicine). In some areas of East and Southeast Asia, lead levels in blood for women were measured at 1.9-6.5 μg/dL. Dietary lead is thought to be attributable to 15-54 % of the blood lead, whereas the rest was due to atmospheric contamination (lead dust) and smoking. For example, Chinese have 4.6 μg/dL of lead in blood, with a dietary intake of 25 μg/day, on the other hand, Japanese living in a cleaner environment have 3.2 μg/dL, with a dietary intake of 15 μg/day. Higher blood lead levels are related with being male, smoking, consumption of lead-contained foods (e.g., milk), contaminated drinking water, and use of herbal products.

Calcium reportedly blocks the absorption of lead from the intestinal tract so that calcium reduces the toxicity of lead. Some foods like tofu (high calcium content) were shown to be closely associated with reduction of lead levels in human blood. Modern human bones often have 20-40 ppm of lead, while bones of Native Americans, about 1,500 year ago, have lead levels of 4 ppm. Bones of ducks have been tested and found to sometimes exceed 20 ppm, attributed to their eating lead shots left by duck hunters. Living organisms including humans are likely to concentrate lead into their calcified structures. For that reason, such structural parts as bone and teeth contain very high level of lead.

2.2.2.6 Lead in industry

Lead-based industries have been increasing environmental health concerns. Lead has been utilized in a variety of applications for years. Lead is introduced into the biosphere through burning of coal in plants and in industrial and household applications of metal products such as steel, brass and bronze, sheet metal, solder, and pipes, lead for batteries, ammunition, medical equipment (radiation shields and surgical equipment), paints, ceramic glazes (tableware and cookware), mirrors, colorant, pigments, light bulbs, foil wrappers, used oil, rubbers, caulking, scientific equipment (circuit boards for electronics), optical equipment, and all kinds of CRTs (cathode ray tubes). In recent years, the quantity of lead used in the manufacture of paints and ceramics has decreased considerably, minimizing the exposable risk of lead to the public. Gasoline additives, tetraethyl lead and tetramethyl lead (volatile organic forms of lead) has been phased out during the 1980s in the U.S.

2.2.2.7 Lead in MSW (Municipal Solid Waste)

Lead is widespread throughout MSW in the United States. This metal accounted for 213,652 tons of waste in 1986 and was projected to over 281,000 tons in 2000, found in both the combustible and non-combustible portions of MSW (Townsend et al., 1999). Lead from batteries took the primary potion of the total lead contribution in MSW.

These batteries are used mainly for automotive products. Approximately, 182,000 tons of lead in batteries was discarded in the year of 2000 (Townsend et al., 1999).

Consumer electronics as television sets, personal computers, radios, and VCRs were the number four source of lead in MSW rankings in 1970. However, they ranked as the second and explain for 28.56 % of lead discards in 1995 as shown in Figure 2.1 (Townsend et al., 1999). They were projected to more than 30% contribution of lead discards in 2000. At this rate, this contribution will be the major portion in MSW as lead in CRTs is aggressively added up every single day. For example, only in California, 10440 tons of lead from CRTs in TVs and 3168 tons from computer monitors are produced and stockpiled in households (estimated from the American Recycler). In Florida, lead from computer monitors and TVs already exceeded 48% of percentage contributions of discarded products containing lead in 1998 (estimated from Townsend et al, 1999).

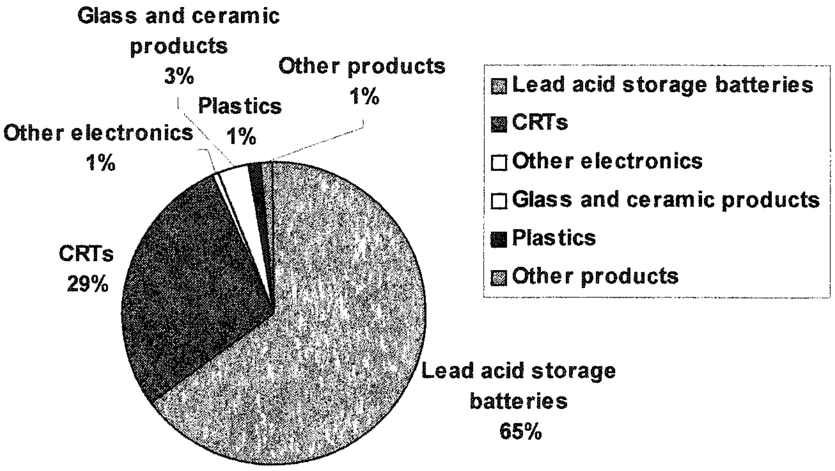


Figure 2.1 Lead in MSW (1995).

2.2.3 Regulatory Fact on Lead

Eleven lead compounds are regulated by the Superfund Amendments addressing emergency planning and community right-to-know requiring that releases of certain chemicals to air, water, or land should be reported annually and listed into a nationwide Toxic Release Inventory. For lead arsenate, a release of over 1 lb (0.454 kg) must be reported immediately, while the quantity for the other lead compounds is 10 lb (4.54 kg).

The EPA demands that lead in air not exceed 1.5 μg/m^3 averaged over three months. For workspace air, the Occupational Safety and Health Administration has established a permissible exposure limit (PEL) of 0.1 mg/m^3 for metallic lead and 0.05 mg/m^3 for lead from soluble compounds. For drinking water, action level for lead is 15 μg/L (0.015 ppm; 0.01 ppm by CA). The EPA announced that identified hazardous concentrations of lead are 40 μg/ft^2 in dust on floors and 250 μg/ft^2 for interior windowsills of house. Also, children's play areas are 400 mg/kg in bare soil and other parts of the yard are 1,200 mg/kg in bare soil. If the concentration of lead in the blood of a worker exceeds 50 μg/dL, the worker is not allowed to remain in the working area. Nonfunctioning CRTs from TVs and monitors are regulated as hazardous wastes. The threshold level of lead toxicity in hazardous materials is 5.0 mg/L (40 CFR Part 261).

2.3 E-wastes and CRT fact

2.3.1 E-wastes

Electronic waste or E-waste is a popular, informal name for electronic products nearing the end of their useful life (California Intergrated Waste Management Board website). Computers, televisions, refrigerators, air conditioners, VCRs, stereos, copiers, fax machines, and cellular phones can join the e-waste stream after their life spans have come to an end. E-waste is generated mainly by three sectors in the U.S.; 1) individuals and small businesses, 2) large businesses, schools, institutions, and governments, 3) original equipment manufacturers (OEMs). Although many obsolete e-wastes can be reused, refurbished, or recycled, the discarding of electronic equipment is spreading. More than 75% of old electronics are in storage because appropriate management is not available. In recent days, emergency regulations, which went into effect on August 3, 2001, facilitate the collection and recycling of CRTs. In the same fashion, CIWMB (California Integrated Waste Management Board) awards contracts to study e-waste in order to promote the attentions from academic and business sectors.

The three Rs, "Reduce, Reuse, Recycle," may help solve this E-waste management. In the realm of solid waste, one can reduce the generation of e-waste through smart procurement and good maintenance, and reuse functioning electronic equipment that can be sold or donated to others who can still use it, and recycle equipment by disassembling it and using some components such as metals, plastics, and glass for manufacturing new products.

Computer monitors, TVs, and other electronic equipments should not be disposed of with regular garbage since e-wastes are rich in hazardous materials. E-waste contains over 1,000 different substances, many of which are toxic and creates serious pollution. Table 2.1 summarizes how much waste is in 500 million computers.

Table 2.1 Waste comparison in 500 million computers

How much waste is in 500 million computers?	
Plastics	6.32 billion pounds
Lead	1.58 billion pounds
Cadmium	3 million pounds
Chromium	1.9 million pounds
Mercury	632,000 pounds

E-waste comprises a witches' brew of toxic materials such as lead and cadmium in circuit boards and batteries; lead oxide and cadmium in monitor CRTs; mercury in switches and flat screen monitors; polychlorinated biphenyls (PCBs) in older capacitors and transformers; brominated flame retardants (BFRs) on printed circuited boards, plastic casings, cables; polyvinyl chloride (PVC) cable insulation that potentially releases toxic dioxins and furans when burned; chromium IV, barium, beryllium, and many more.

These days, it is not difficult to spot dumped TVs and computer monitors in the streets and neighborhoods. Nonfunctioning TVs and monitors should be recycled by organizations equipped and authorized to handle them in a safe manner. The organizations include used or recycled computer dealers, recycling equipment and services, scrap metals, waste disposal facilities, reduction and recycling programs, and environmental and ecological services.

2.3.2 Where Does E-waste Go?

Currently, there are several options available. Storage can be the first option. It is estimated that three-quarters of all computers ever sold in the United States remain stockpiled, awaiting disposal, and the number of these unused, stored computers in the U.S. will soon be as high as 315-680 million units (BAN; The Basel Action Network, SVTC; Silicon Valley Toxics Coalition, 2002). Consumers have an average of two to three obsolete computers and TVs in their garages, closets or storage spaces. Secondly, landfill and incineration have been quite helpful to compensate for the overflowing E-waste stream. According to the EPA, in 1997 more than 3.2 million tons of E-waste ended up in U.S. landfills. However, many waste landfills are starting to leak. In particularly DOE (Dept. of Energy) sites, even the best 'state of the art' technology applied to landfills are not completely secure and a certain amount of chemical and toxic metals leach out. The situation is far worse for the older or less stringently maintained dumpsites. When disposed of in a landfill, E-waste becomes a conglomeration of plastic and steel casings, circuit boards, glass tubes, wires, resistors, capacitors, and other assorted parts and materials (The Basel Action Network; BAN, Silicon Valley Toxics Coalition; SVTC, 2002). Approximately 70% of heavy metals found in landfills, including mercury, lead, and cadmium originate from electronic discards. These toxic metals and chemicals in the form of leachate with very low pH can have very high chance of continuously contaminating groundwater aquifers. Municipal incinerators are some of the largest point sources for air pollution like metal particulates and dioxins even though they contribute to the minimization of the waste stream. For this reason, in 2001, California and Massachusetts banned cathode-ray tube monitors from landfills and incinerators.

The third option is the reuse of E-waste. Reuse constitutes direct second-hand use, or use after slight modifications made to the original functioning equipment (e.g., memory upgrading). Only 3% of discarded computers in 1998 were reused. These computers are later sold in very small numbers at recycling stores or are donated to schools or non-profit organizations like boys and girls clubs. Foreign markets can be another option. Also, a great number of computers are being exported to other countries for reuse. The final option can be domestic recycling. It is estimated in 1998 that only 11% of computers were recycled, including the exportation. The rate of recycling is thought to be increased 18%, which is 12.75 million computers in 2002. However, re-use or recycling computers cannot be the ultimate solution for the current E-waste problem, it can only slow down the speed of waste stream.

2.3.3 Identification and Significance of E-wastes (CRTs)

2.3.3.1 What do CRTs do to us?

A study revealed that approximately 2.9 million TVs (74,000 tons) and 3.2 million computer monitors (48,000 tons) are stockpiled only in California households (American Recycler, 2002). These electronic products (E-waste) contain picture tubes, cathode ray tubes (CRTs), which have potential hazards when broken. They are banned from disposal in state landfills and must be recycled while CRT-containing products are safe which means intact.

Cathode ray tubes found in computer monitors and television sets contain 20 percent lead oxide by weight, averaging five to eight pounds of lead per unit. For instance, a typical 17-inch computer monitor contains approximately 2.2 pounds of lead and a 27-inch television can contain up to 8 pounds of lead (DTSC/CIWMB News Release, 2001). When tested, most CRTs exceed the regulatory threshold for lead content and are liable to be identified as hazardous materials when discarded.

Considering the magnitude of discarded CRT streams annually, CRT wastes should be treated more urgently than any other hazardous wastes. As of 1996, there were over 300 million CRTs (TVs and monitors) stockpiled in North America. In the same year, 42 million CRTs were sold in the U.S. and 79 million computers were retired (Townsend et al., 1999). The ratio of purchase to dumping of computer is expected to be 2:1 by 2005 from 3:2 in 1998 if the annual growth rate for computer sales is regarded as 15 percent (Townsend et al., 1999).

The computer recycling and resale makers tend to expand their business because the number of recycling companies has increased as the life span of computers shortens and the rate of dumped computers increases. A great number of computers are donated to charities and schools from corporations and individuals. Computers may lose 80 % of their initial value within the first year (Townsend et al., 1999). People often find it hard to believe that a machine that cost some thousand dollars when they purchased it is worth only $100 just a couple of years later. This might explain for the big donations from businesses and institutions. Also, many old computers have been exported to other countries where they are considered quite advanced.

However, the recycling of computers is still economically limited in spite of greater tax incentives and a larger supply of computers donated by corporations and individuals. Because the dumped rate of old computers is higher than the rate of new products coming out in the market, which means computer manufacturing technology is so fast.

The disposal option for CRTs is to place CRTs in MSW, which is the least favorable. This can include landfill and incineration. While CRTs in particular represent about 50 % of electronic tonnage, their lead content may be up to as much as 80 % of the toxic metals in discarded proportions of electronics. When disposed in landfills, landfill leachate will typically contain increased concentrations of heavy metals. This is why many landfills no longer accept CRTs, as mentioned earlier. Also, when incinerated on a waste-to-energy basis, heavy metals become highly concentrated in the ash, reasonably limiting the disposal and reuse options.

The tonnage of analog TVs sent for repair and resale will eventually drop as new technology applied to TVs. High definition TVs (HD TVs) will be prevalent between 1998 and 2006. In addition, flat screen monitors without CRTs will replace the old fashioned ones. However, it is obvious that the discarded CRTs will pile up in our backyards as long as the removal technology remains undeveloped and the international exportation and landfill application are banned. Repair, recycling, and disposal businesses that handle CRT-containing products must adhere to state regulations for the handling of these hazardous materials. Inappropriate disposal will end up in a serious soil and groundwater contamination.

In anticipation of continued increases in CRT waste, the U.S. EPA, through the waste board and DTSC, is participating in a national dialog on product stewardship, which includes other states, manufacturers, recyclers, and environmental groups. In addition, the waste board is working to develop environmentally preferable product guidelines for electronic equipment (American Recycler, 2002).

The objective of the study is to address the CRT problems and remediate them by providing control technology of this hazardous material. The developed technology is very effective in terms of methodology and the cost of the process. The key point of the technology is to use biopolymers that are commercially available and allow them to bind lead in E-wastes and further apply to the marketable products.

2.3.4 CRT facts and Lead in CRTs

Cathode-ray tubes are a type of technology utilized in most TVs and computer screens. A CRT employs high voltages to accelerate electrons in the direction of a luminescent material called a "phosphor" deposited on the face of the plate. This luminescent phosphor converts the kinetic energy of the electrons into light. For example, on a color CRT, the phosphors are patterned in dots or stripes of red, green, and blue colors. The electrons are emitted from three cathodes assembled in the electron gun and pass through an apertured metal, shadow mask, during they reach the phosphor. Then picture are created by the focus where the electron beams into tiny spots, which are moved by deflecting the electron beams so that the spots move across the phosphor surface in a left-to-right and top-to-bottom motion (Townsend et al., 1999).

High vacuum is required in the electron gun because in order to achieve long life and bulb, the envelope must have sound mechanical integrity meant to resist the force of atmospheric pressure. Thus electron guns pop up in the disassembling process when a breakable pressure or force is applied. The high voltages that shoot the electrons should be insulated from the external surfaces of the tube and the envelope must also be excellently insulated electrically and insulated from the X-ray because the decelerating electrons produce X-rays.

A CRT display consists of a cathode ray tube (CRT unit), a casing (plastic shell), various metals including precious metals (gold and silver), and non precious metals which can be hazardous. Referring to Table 2.2, Plastics and CRT unit containing lead, aluminum, iron, copper, nickel, and zinc consist of the primary portion in computer monitors in terms of weight. Although there are many issues of environmental concerns in the CRT wastes, the primary ones are the management of end-of-life CRTs and the disposal of lead in the components.

Table 2.2 Composition of a personal desktop computer

(based on total weight: 70 lbs)

	Content (% of total weight)	**Recycling Efficiency (%)**	**Weight of Material (lbs.)**	**Use/Location**
Silica	24.8803	0	15	Glass, solid state devices/ CRT, PWB
Plastics	22.9907	20	13.8	Includes organics, oxides other than silica
Iron	20.4712	80	12.3	Structural, magnetivity/ (steel) housing, CRT, PWB
Aluminum	14.1723	80	8.5	Structural, conductivity/ Housing, CRT, PWB, connectors
Copper	6.9287	90	4.2	Conductivity/CRT,PWB, connectors
Lead	6.2988	5	3.8	Metal joining, radiation shield/ CRT, PWB
Zinc	2.2046	60	1.32	Battery, phosphor emitter/ PWB, CRT
Tin	1.0078	70	0.6	Metal joining/ PWB, CRT
Nickel	0.8503	80	0.51	Structural, magnetivity/ (steel) housing, CRT, PWB
Barium	0.0315	0	< 0.1	Vacuum tube/CRT
Manganese	0.0315	0	< 0.1	Structural, magnetivity/ (steel) housing, CRT, PWB
Silver	0.0189	98	< 0.1	Conductivity/ PWB, connectors
Beryllium	0.0157	0	< 0.1	Thermal conductivity/ PWB, connectors
Tantalum	0.0157	0	< 0.1	Capacitors/ PWB, power supply
Titanium	0.0157	0	< 0.1	Pigment, alloying agent/ (aluminum) housing
Cobalt	0.0157	85	< 0.1	Structural, magnetivity/ (steel) housing, CRT, PWB
Antimony	0.0094	0	< 0.1	Diodes/ housing, PWB, CRT
Cadmium	0.0094	0	< 0.1	Battery, blue-green phosphor emitter/ housing, PWB, CRT
Chromium	0.0063	0	< 0.1	Decorative, hardener/ (steel) housing
Bismuth	0.0063	0	< 0.1	Wetting agent in thick film/ PWB
Mercury	0.0022	0	< 0.1	Batteries, switches/

Table 2.2 continued				housing, PWB
Germanium	0.0016	0	< 0.1	Semiconductor/ PWB
Indium	0.0016	60	< 0.1	Transistor, rectifiers/ PWB
Gold	0.0016	99	< 0.1	Connectivity, conductivity/ PWB, connectors
Ruthenium	0.0016	80	< 0.1	Resistive circuit/ PWB
Selenium	0.0016	70	0.00096	Rectifiers/ PWB
Arsenic	0.0013	0	< 0.1	Doping agents in transistors/ PWB
Gallium	0.0013	0	< 0.1	
Palladium	0.0003	95	< 0.1	Semiconductor/ PWB Connectivity, conductivity/ PWB, connectors
Vanadium	0.0002	0	< 0.1	Red phosphor emitter/ CRT
Europium	0.0002	0	< 0.1	Phosphor activator/ PWB
Niobium	0.0002	0	< 0.1	Welding alloy/ housing
Yttrium	0.0002	0	< 0.1	Red phosphor emitter/ CRT
Terbium	< 0	0	< 0.	Green phosphor activator, dopant/ CRT, PWB
Rhodium	< 0	50	< 0.	Thick film conductor/ PWB
Platinum	< 0	95	< 0.1	Thick film conductor/ PWB

Modified after Handy and Harman Electronic Materials Corp. 2002.

The lead content and chemistry of CRT glass varies by component as well as by different manufacturers. Table 2.3 presents TCLP results of leachable lead content from different manufacturers. Most CRTs manufactured by different companies exceed the regulatory threshold, 5 mg/L, for lead. CRT unit can be separated to three parts: panel (face), funnel (side), and neck. As TCLP lead, monitors show very high concentration of lead, primarily in funnel part of CRT unit for all brands. Hitachi monitor showed 403.6 mg/L of lead, only leached by diluted acid solution (TCLP). Supposedly, it would have high chance for more lead leaching under extreme conditions such as caustic acid. It is noted that lead contents varies from different models and manufacturing years. It is also observed that color CRT glass generally has higher lead content than monochrome (black and white) CRT and that lead content of the CRT is primarily confined to the neck and funnel of the CRT.

Table 2.3

TCLP lead results of different manufacturers of TV and computer monitors

					Leachable lead concentration (mg/L)			
Maker	**TV/ Mon**	**Color/ Mono**	**Model year**	**Tube maker**	**Neck**	**Funnel**	**Panel**	**Weight average**
Acer	Mon	C	93	Panasonic	9.5	347.3	< 1.0	57.2
Digital	Mon	M	90	Clinton	4.2	< 1.0	< 1.0	< 1.0
Elite	Mon	C	92	Chunghwa	9.7	81.2	< 1.0	19.3
Emerson	TV	C	84	Goldstar (LG)	6.5	6.6	< 1.0	1.5
Gateway	Mon	C	93	Toshiba	9.0	9.2	< 1.0	3.2
Gateway	Mon	C	92	Toshiba	12.8	174.5	< 1.0	54.1
HP	Mon	M	84	Matsushita	< 1.0	< 1.0	< 1.0	< 1.0
HP	Mon	M	85	Matsushita	1.7	< 1.0	< 1.0	< 1.0
IBM	Mon	C	87	Matsushita	9.5	38.4	< 1.0	9.4
IBM	Mon	C	89	Panasonic	9.5	142.9	< 1.0	41.5
IBM	Mon	M	92	Phillips	1.1	< 1.0	< 1.0	< 1.0
Imtec	Mon	C	89	Samsung	8.2	200.6	< 1.0	60.8
Imtec	Mon	C	89	Hitachi	13.6	**403.6**	< 1.0	85.6
Memorex	Mon	C	97	Toshiba	10.1	103.0	< 1.0	21.3
Memorex	Mon	C	97	Kch	12.7	49.4	< 1.0	15.4
Memorex	Mon	C	98	Samsung	7.0	25.7	< 1.0	6.1
Memorex	Mon	C	98	Chugnhwa	10.9	7.8	< 1.0	2.3
Memorex	Mon	C	97	Toshiba	8.4	34.9	< 1.0	9.1
Memorex	Mon	C	98	Samsung	7.1	7.1	< 1.0	2.2
Memorex	Mon	C	97	Chunghwa	8.3	35.3	< 1.0	10.6
NEC	Mon	C	87	NEC	11.3	50.3	< 1.0	10.7
Orion	TV	C	96	Orion	9.1	132.5	< 1.0	33.1
Panasonic	TV	C	84	Matsushita	22.4	11.8	< 1.0	3.5
Quasar	TV	C	84	Quasar	13.6	182.4	< 1.0	43.5
Samsung	Mon	M	89	Samsung	< 1.0	< 1.0	< 1.0	< 1.0
Seiko	Mon	C	87	NEC	9.1	100.0	8.0	26.6
Sharp	TV	C	94	Sharp	8.7	16.4	< 1.0	4.4
Sharp	TV	C	84	Sharp	7.9	6.0	< 1.0	1.5
Tandy	Mon	C	85	Sharp	17.6	116.1	< 1.0	35.2
Techmedia	Mon	C	95	Samsung	< 1.0	20.1	< 1.0	6.9
Teknika	TV	M	86	Phillips	1.6	< 1.0	< 1.0	< 1.0
Ttx	Mon	C	91	Chunghwa	7.5	10.0	< 1.0	2.8
Zenith	TV	C	94	Zenith	18.3	198.8	< 1.0	54.5
Zenith	TV	C	94	Zenith	15.8	7.1	< 1.0	1.6
Zenith	TV	C	77	Zenith	< 1.0	97.7	< 1.0	21.9
Zenith	Mon	C	85	Toshiba	7.5	92.1	< 1.0	21.5
Averages					**8.6**	**75.3**	**0.2**	**18.5**

Modified after Townsend et al., 1999.

The industry develops both a no-lead and a 2-3 % of lead content in the CRT with a trend of increasing no-lead composition. This trend is the same for the TVs, which is replaced by HD TV or flat-screen TV with less lead or no lead content. For instance, the thin-film transistor liquid crystal display (TFT-LCD) market may well be on the verge of explosive growth, driven by both monitor and TV demands as the manufacturing cost of high resolution LCD panels must be dropped to the same level of CRT (Samsung electronics, website). Therefore, those new technology-applied screens will replace the CRT currently used in computer monitors and TVs.

2.3.5 Present Market for CRTs and its New Applications

Markets currently exist for both used monitors and TVs and the CRT glass. Of the existing markets for surplus computer monitors and TVs, reuse through resale only creates a positive cash flow for the processor. Markets for the used equipment depend on the working condition of and the demand for the used equipment or parts. There are very few resalable monitors recovered from the sizable surplus streams. Moreover, there are no markets for nonfunctioning VGA monitors or monochrome monitors of any kind. As a result, over 50 percent of all surplus monitors and 80-85 percent of monochrome tubes are useless. Therefore, the number of CRTs remaining after resale requires innovative solutions to improve the sale and reuse of the recycled components. Glass chemistry and innovative research will eventually dictate the potential application for recycled CRT glass. In Table 2.4, present applications for CRT glass are presented.

Table 2.4 Applications for CRT glass

Reuse	Refurbishments and resale	High rate of defective units
Closed-loop glass-to-glass recycling	Remanufacturing CRT glass	Markets for CRT tubes will diminish with new flat-screen technology
Open loop glass-to-glass recycling	Decorative glass tiles	High costs
Lead reutilization	Industrial lead panels	Market is small at this time.
Glass aggregate	Smelting for lead and copper	Few existing smelters, transportation costs are prohibitive.
Exportation	This will vary from reuse to open loop glass-to-glass recycling to "ultimate use" unknown.	Generally recycled using cheap labor Recovering the precious metals is more favored. Exportation will be banned.

While new model computers are valuable on the re-use market, the net value of older models at the point of disposal is very insignificant. For example, in an old computer, the cable (30% copper in PVC sheaths) is worth \$0.09; the hard drive (15% aluminum) is worth \$0.10; 5 pounds of steel can be worth \$0.25; the monitor yoke (60% copper) can be worth \$0.80; central processing unit (CPU) with its gold chips costs \$1.00; the motherboard with its metals (gold, silver, and copper) connectors cost \$2.00 (BAN; The Basel Action Network, SVTC; Silicon Valley Toxics Coalition, 2002). But with this small merit of recyclable components, 50-80% of e-wastes collected for recycling in U.S. are quickly placed on container ships bound for destinations like China, India, and Pakistan. However, this kind of exportation is not allowable as those South East Asian countries realize how hazardous the e-wastes are and measure the devastated impact on their environment, which means the rate of stock piled junky computer and monitors will certainly be increased in the U.S.

Most recyclers, due to the costs of dealing with the disposal of non-recyclable parts and the expense of carefully handling the toxic components, will not take your computer unless you are willing to pay for them to take it. Therefore, building new markets for used CRTs and recycled components is fundamental to developing commercially viable alternatives to the existing computer disposal problems. Accordingly, governmental agencies must establish workable regulatory framework and disposal practices for the management of e-wastes that encourage recycling while protecting public health, worker's safety, and the environment. However, recycling hazardous wastes, even under the best of circumstances, simply moves the hazards into secondary products that eventually have to be disposed of. Basically, the E-waste problem cannot go anywhere without the development of remediation technology.

In this investigation, leaded glass from CRTs creates safe, non-toxic, non-hazardous solutions to the waste streams by making biopolymer-based concrete composite. Some of the promising new applications are as follows: barrier to prevent the leaching of metals and nuclear wastes from landfills, geomaterial by geopolymerization, foundation and building materials for construction, decorative tile, and X-ray shielding products.

2.4 Biopolymer Chemistry

2.4.1 Biotechnology

Biotechnology is an industrial process that uses the scientific research on DNA for practical benefits. Biotechnology is synonymous with genetic engineering because the genes of an organism are changed during the process and the DNA of the organism is recombined. Recombinant DNA and biotechnology can be used to form proteins or enzymes not normally produced in a cell. In addition, bacteria that carry recombinant DNA are released into the environment to increase the fertility of the soil, serve as an insecticide, or relieve pollution.

Today, biotechnology is a state-of-the-art field used to deal with all kinds of science and engineering. There are many examples in our life. Biotechnology is utilized to produce a protein that an organism does not usually produce with the impression of recombinant DNA. For pharmaceutical products, it can help produce proteins like insulin, human growth hormone, and Factor VIII for the protein deficiencies such as diabetes, dwarfism, and impaired blood clotting. This technology also produces therapeutic proteins, tissue plasminogen activator (TPA), and interferon. Vaccines are one of representatives that can be created by biotechnology. For diagnostic testing, DNA probes can detect the target DNA among the mixture of DNA. Using DNA probes and PCR (polymerase chain reaction), scientists are now able to detect the DNA associated with HIV (and AIDS), Lyme disease, and genetic diseases such as cystic fibrosis, muscular dystrophy, Huntington's disease, and fragile X syndrome.

When it comes to gene therapy, biotechnology can correct a deficiency of the enzyme adenosine deaminase (ADA) by using viruses as vectors. Gene therapy has been performed on patients with melanoma (a virulent skin cancer). DNA fingerprinting is a forensic procedure used for identification purposes at a crime scene, where restriction fragment length polymorphisms (RFLPs) act as a molecular fingerprint.

Recombinant DNA and biotechnology have been used to increase the efficiency of plant growth by increasing the plant's ability to fix nitrogen, and increasing the plant's resistance to disease.

Finally, biotechnology has helped achieve a number of significant accomplishments concerning the human genome. Recently, the sequence of human genome has been decoded 100 percent, which is a scientific and historical milestone for human beings. Identification of human genome will aid in solving many puzzles regarding human genetic diseases by devising new diagnostics and treatments.

For our applications, the concept is to allow biopolymers to handle the contaminants in one way or another. Biopolymers that are either produced by bacteria or made commercially are applied into the mixture of concrete and contaminant (CRT waste). Since biopolymers contain a variety of functional groups that give holding capacity and crosslinking property with crosslinking agents, they can provide encapsulation characteristics for a concrete composite. Utilizing biopolymers in biotechnology applications such as this is regarded as promising solution to the problem of metal contamination.

2.4.2 Biopolymers

Biopolymers are high-molecular weight molecules with repeated sequences, which may become multiple reactive sites creating an opportunity for chemical reaction to occur.

Depending on the contained functional groups, biopolymers can bind metals, and can also form interpenetrating cross-linking networks with other polymers or crosslinking agents.

At length, biopolymers produced by microorganisms can be categorized as intracellular and extracellular polymers. Intracellular polymers are polyesters and extracellular polymers are polysaccharides. Bacteria species, Alcaligenes eutrophus, produces large amounts of intracellular polymer, poly-β-hydroxy butyrate (PHB) or valerate. These polymers are found to be ideal binders for enhancing the strength of soil. When it comes to the results for porous media such as sand or clay, the permeability can be reduced to almost one million fold; therefore, the bacteria derived polymers are perfect plugging agents for stopping the plumes of subsurface pollutants. The other type of bacteria species, Xanthomonas campestris, produces an extracellular polymer, xanthan gum. The polysaccharide xanthan gum is most likely to be applicable in a real system, owing to its many merits dealing with environmental problems, so this bacterial gum was investigated for its effects on the stabilization of lead from CRT waste. In addition to xanthan gum, chitosan and guar gum were also utilized to relieve CRT waste problem in this study. Chitosan is a so-called "structural biopolymer" made from crusty outer shell of lobsters and crabs, and guar is a seed gum extracted from plants.

2.4.3 Xanthan Gum

2.4.3.1 Source and Production of Xanthan Gum

Traditionally, industrial gums have been derived from botanical sources; more recently, other valuable polysaccharides have been identified from microbial sources. Included are several gum derivatives, such as propylene glycol alginate, hydroxypropyl guar, and some modified starches.

Xanthan gum is an exocellular heteropolysaccharide produced by Xanthomonas campestris that is a genus of the Pseudomonaceae family. All organisms in this genus are plant pathogens. The gum, often found on green vegetables like cabbage, alfalfa, and beans, 'glues' the bacteria to the leaf surface on which it is secreted while providing protection from the surrounding environment. The bacterium Xanthomonas campestris occurs as single straight rods, 0.4-0.7 μm wide and 0.7-1.8 μm long (Garcia-Ochoa, 2000), shown in Figure 2.2.

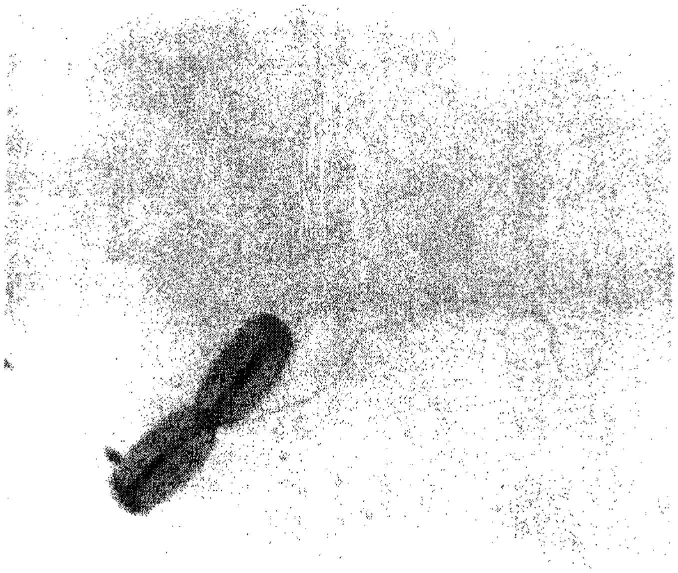


Figure 2.2 Xanthomonas campestris (TEM picture).

The cells are motile, Gram-negative, and they have a single polar flagellum (1.7-3 μm), utilized for locomotion. The colonies are usually yellow, smooth, and viscid, as seen in Figure 2.3. They produce xanthan gum at the cell surface during their normal life cycle through a complex enzymatic process where the gum is elaborated into the surrounding medium.

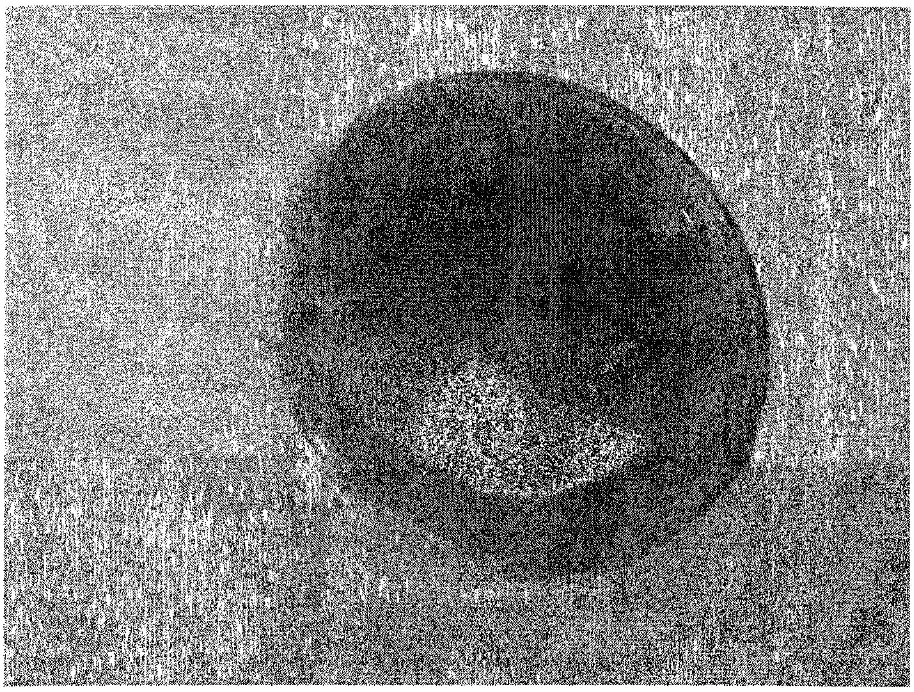


Figure 2.3 Xanthan gum produced by Xanthomonas campestris.

The composition and structure of the xanthan gum produced by commercial fermentation are identical to the polysaccharide formed by Xanthomonas campestris on plants belonging to the cabbage family, where the process occurs naturally. Xanthan gum is produced by aerobic submerged fermentation. The fermentation medium contains a carbohydrate (sugar), nitrogen source, trace elements, and other growth factors.

About 20,000 tons of xanthan gum is produced industrially from Xanthomonas campestris each year. The large-scale production of xanthan gum involves a multi-step inoculum preparation, followed by fermentation in large stainless steel tanks and, finally, product recovery. Fermentation equipment is sterilized before use, and strict aseptic techniques are required to ensure a pure culture. Media compositions as well as fundamental requirements such as aeration, agitation, pH, and temperature are precisely controlled to guarantee optimal results and reproductivity. After fermentation is complete, the broth is pasteurized to kill the organisms before the product is recovered. Typically, xanthan gum is recovered from the fermentation broth by alcohol precipitation. The alcohol is then removed, and the resultant product dried, milled, tested, and packaged (Figure 2.4).

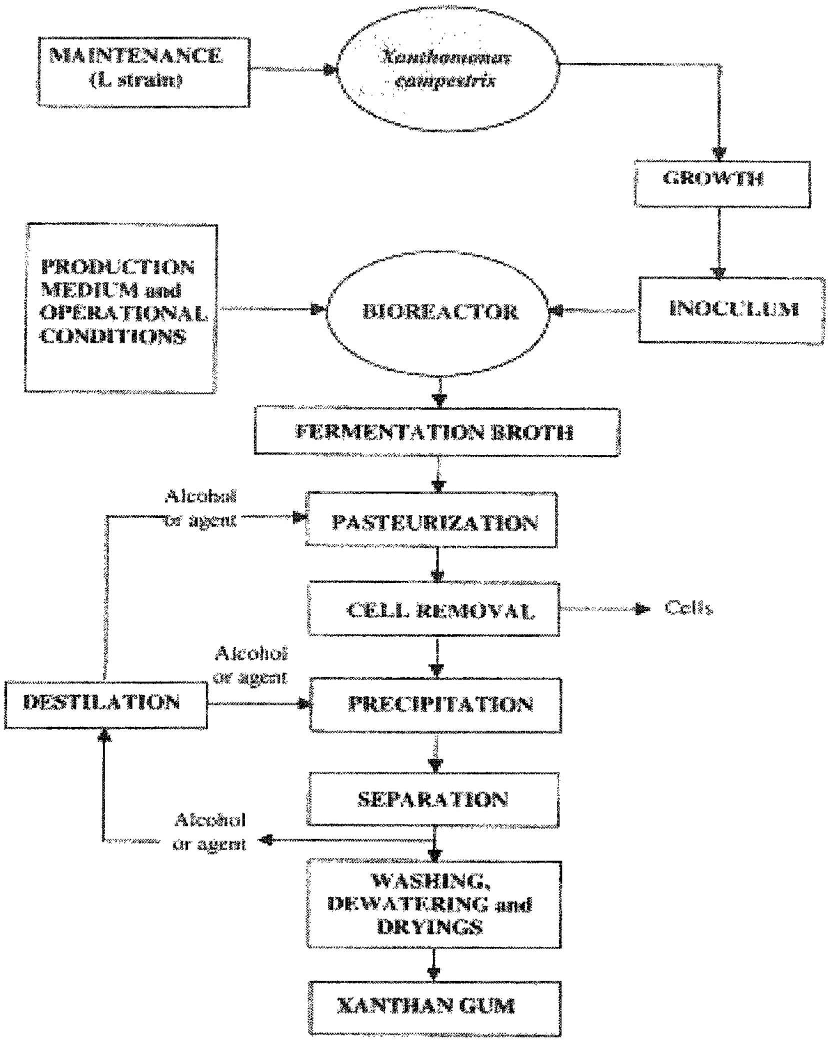


Figure 2.4 Xanthan gum production process (Garcia-Ochoa, 2000).

2.4.3.2 Structure of Xanthan Gum

Each xanthan gum's repeating unit, shown in Figure 2.5, consists of five sugar residues: two glucose, two mannose, and one glucuronic acid, in the molar ratio 2.8:2.0:2.0 (Garcia-Ochoa, 2000). The polymer backbone consists of 1,4 linked β-D-glucose and is therefore identical to cellulose in structure. Trisaccharide side chains on alternating anhydroglucose units distinguish xanthan gum from cellulose. Each side chain is comprised of a glucuronic acid residue between two mannose units. At most of the terminals mannose is a pyruvate moiety; the mannose nearest the main chain carries a single acetyl group at C-6. Numerous studies have indicated a molecular weight for xanthan gum of approximately from 2×10^6 to 20×10^6 Daltons, which corresponds to approximately 2,000 (up to 20,000) repeating units per polymer molecule. Values as high as 50 million have been reported. These differences are thought to be due to the association of polymer chains.

As seen in the structural formula of xanthan gum, there are many functional groups such as CH_2OH, OH, O, COOH, and H, which will play an important role in binding metals and being chemical sites crosslinked with crosslinking agents.

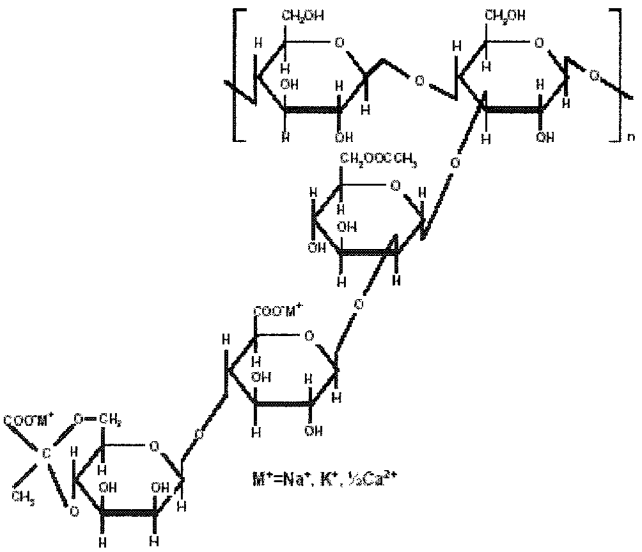


Figure 2.5 Structure of xanthan gum.

X-ray-diffraction studies on oriented xanthan gum fibers identified the molecular conformation as a right-handed, fivefold helix with a rise per backbone disaccharide residue of 0.94 nm, i.e., a fivefold helix with a pitch of 4.7 nm (Fig. 2.6). In this conformation, the trisaccharide side chain is aligned with the backbone and stabilizes the overall conformation by noncovalent interactions, principally hydrogen bonding. Multi-stranded structures in which several xanthan gum polymer chains are aligned or interwined are consistent with x-ray data. Solution studies on the conformation of xanthan gum suggest a rod-like character with some degree of flexibility. Holzwarth and Prestridge (1977) suggested a double or multi-stranded assembly, whereas Norton et al. (1984) argued for a single helical entity in solution (Kelco brochure, 1999). Xanthan gum solutions at low ionic strength undergo a thermal transition that has been detected by a variety of physical methods. Jeanes et al. (1961) first demonstrated this transition by a sigmoidal change in viscosity of 1% salt-free solutions (t_m 55 °C, 131 °F). The subsequent work of Morris et al. (1977) showed that optical rotary and circular dichroic transitions are coincident with the viscosity change, indicating a conformation transition of the molecule (Garcia-Ochoa, 2000). These data are consistent with the unwinding of an ordered structure like a helix into a random coil, with a consequent decrease in effective hydrodynamic volume and, therefore, viscosity.

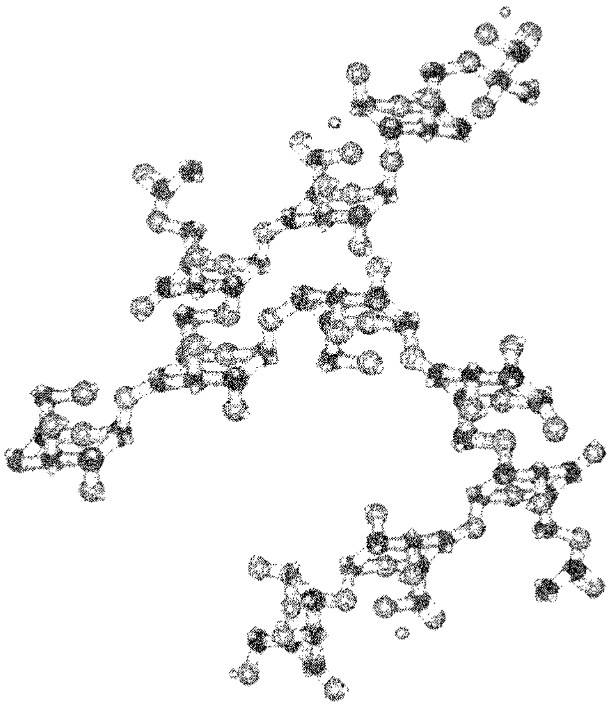


Figure 2.6 Helical conformation of xanthan gum.

Intermolecular and intramolecular association among polymer chains results in the formation of a complex network as a single, double or triple helix. These aggregates are progressively disrupted under the influence of applied shear. Heating a xanthan gum solution above the transition temperature results in the "melting" of the ordered structure. This structure returns to its original state upon cooling, depending on the salt environment

2.4.3.3 Properties of Xanthan Gum

Present knowledge of the structure and conformation of xanthan gum explains many of its unusual solution properties, which are summarized in Table 2.5. Xanthan gum solutions are highly pseudoplastic. When shear stress is increased, viscosity is progressively reduced. Upon the reduction of shear, total viscosity is recovered almost instantaneously. This behavior results from the high-molecular-weight molecule that forms complex molecular aggregates through hydrogen bonds and polymer entanglement. Also, this highly ordered network of entangled, stiff molecules accounts for high viscosity at low shear rates, and in practical terms, for the gum's outstanding suspending properties. Shear thinning results from disaggregation of this network and alignment of individual polymer molecules in the direction of shear force. However, when the shearing ceases, aggregates re-form rapidly.

The ordered conformation is stabilized by hydrogen bonding, but destabilized by the repulsion between the negatively charged groups on the overlapping side chains. A low concentration of electrolyte enhances the ordered conformation of xanthan gum by reducing the electrostatic repulsion between carboxylate anions on the trisaccharide side chains. This stabilized helical structure is even maintained with an increase in temperature, which explains why the viscosity of xanthan gum solutions is insensitive to temperature changes below the transition temperatures. And xanthan gum is highly soluble in both cold and hot water, and this behavior is related to the polyelectrolyte nature of the xanthan molecule. Xanthan solutions are highly viscous even at low polymer concentration (Garcia-Ochoa et al., 2000).

As a result of the rigid helical conformation, xanthan gum viscosity is also insensitive to differences in ionic strength and pH. In contrast, other polysaccharides that are polyelectrolytes normally have a less ordered, or random coil, conformation - a state in which increasing or decreasing electrolyte levels adversely affect solution viscosities. Finally, protection of the backbone by the side chains results in the superior stability of xanthan gum compared to other polysaccharides when exposed to acids, alkalis, and enzymes.

An interesting property of xanthan solutions is the interaction with plant galactomannans, such as locust bean gum and guar gum. So, the addition of any of these galactomannans to a solution of xanthan at room temperature causes a synergistic increase of viscosity.

Table 2.5 Xanthan gum's properties

Rheological properties	**Stability / Compatibility with**
High viscosity at low concentration	Ionic strength variation
High viscosity at low shear rates	Heat
High degree of pseudoplasticity	pH
High elastic modulus	Shear
	Enzymes
	Chemicals (salts, acids, bases etc.)

2.4.3.4 Xanthan Gum's Applications

Currently, the possible number of applications for xanthan gum is enormous. Especially, in the food industry, which has a wide variety of applications for xanthan gum due to its many useful abilities, including emulsion stabilization, temperature stability, compatibility with food ingredients, and its pseudoplastic rheological properties. As a dispersing agent, stabilizer of emulsions, and suspensions, its thickening property enables xanthan gum to be used in pharmaceutical formulations, cosmetics, and agricultural products. The high viscosity and water solubility of the polymer make xanthan gum ideal for drilling fluids in the enhanced oil recovery process used in the petroleum industry. It is also utilized in textile printing pastes, ceramic glazes, slurry explosive formulations, and rust removers.

Table 2.6

Applications of Xanthan Gum

Application	**Category**
Food	Batters, Baked goods, Bakery and pie filings, Bakery flavor emulsions, Beverages, Confectionery, Dairy products, Desserts, Dietetic foods, Dressings, Dry mixes, Frozen foods, Icings and frostings, Relish, Retorted products, Sauces and gravies, Syrups and toppings.
Pharmaceutical	X-ray diagnoses, Coughing preparations, Dentifrice products, Swallowing syrups, Erosion controller.
Personal Care or Cosmetics	Medicated shampoos, Liquid soaps, Toothpaste, Hair gel, Basic foundations, Sun block.
Industrial	Abrasives, Adhesives, Agricultural products, Ceramics, Cleaners, Coatings, Alternative fuels, Paper, Polishes, Textiles, Lubricants.
Oil Field	Drilling fluids, Workover and completion fluids, Gravel packing, Coiled tubing operations, Hydraulic fracturing, Enhanced oil recovery, Profile modifications.

Commercially available biopolymers such as BHP, xanthan gum, or sodium alginate are mixed with porous media. This kind of biopolymer mixture can be applied for landfill liners or covers, where an impermeable soil is required. Initial cost comparisons between use of biopolymers and common use of bentonite as a means of similar reductions in permeability of silts and sandy soils for landfill applications, have been favorable. The potential of using biopolymers for hazardous waste encapsulation, landfill engineering, liquefaction remediation, erosion control bioengineering, etc. is feasible.

2.4.4 Guar Gum

2.4.4.1 Source of Guar Gum

Guar gum (also called guaran) is extracted from the seed of Guar Gum Plant, the leguminous shrub *Cyamopsis tetragonoloba*, where it acts as a food and water reserve.

Figure 2.7 Guar gum plant, *Cyamopsis tetragonoloba*.

Guar is an upright, coarse-growing summer annual legume with trifoliate leaves and rose-colored flowers, known for its drought resistance. Its deep-tap roots allow it to reach moisture deep below the soil surface. Most of the improved varieties of guar have glabrous (smooth, not hairy) leaves, stems and pods. For this reason, improved guar can be grazed for cattle, but original guar cannot be because of its hairy and nettly leaves. Plants have single stems, fine branching or basal branching (depending on the variety) and grow to be 18 to 40 in. tall. Racemes are distributed on the main stem and lateral branches. Pods are generally 1 1/2 to 4 in. long and contain 5 to 12 seeds each. Seeds vary from dull-white to pink to light gray or black and range from 900 to 1,600 seeds/oz. It begins fruiting two months after sowing and can be cut for fodder as soon as the pods begin to develop. It is palatable to stock if cut and wilted and often grown with sorghum. The seeds are used for extraction of gum (mannogalactan). The residue, guar meal, is unpalatable and toxic. Untreated guar meal can constitute up to 25% of cattle rations, and up to 10% of poultry rations. Due to residual gum in the meal the feces will be watery and sticky.

At present, guar gum and locust bean gum are the only two galactomannans utilized on an industrial scale. Interest in guar gum is fairly recent. Its initial development was due to a lack of locust bean gum in the 1940s. Large scale of industrial production in guar gum dates back to the 1950s. World demand for guar has gradually increased, leading to crop introductions in several countries. Guar is native to India and Pakistan, exporting much of their guar crop to the United States and other countries in the form of partially processed endosperm material. It is now grown on more than 100,000 acres in the United States, mainly in West Texas and Oklahoma.

2.4.4.2 Structure of Guar Gum

Guar gum is a galactomannana similar to locust bean gum consisting of a (1→4)-linked β-D-mannopyranose backbone with branchpoints from their 6-positions linked to α-D-galactose (i.e. 1→6-linked-α-D-galactopyranose). Every galactose residue exists between 1.5 - 2 mannose residues.

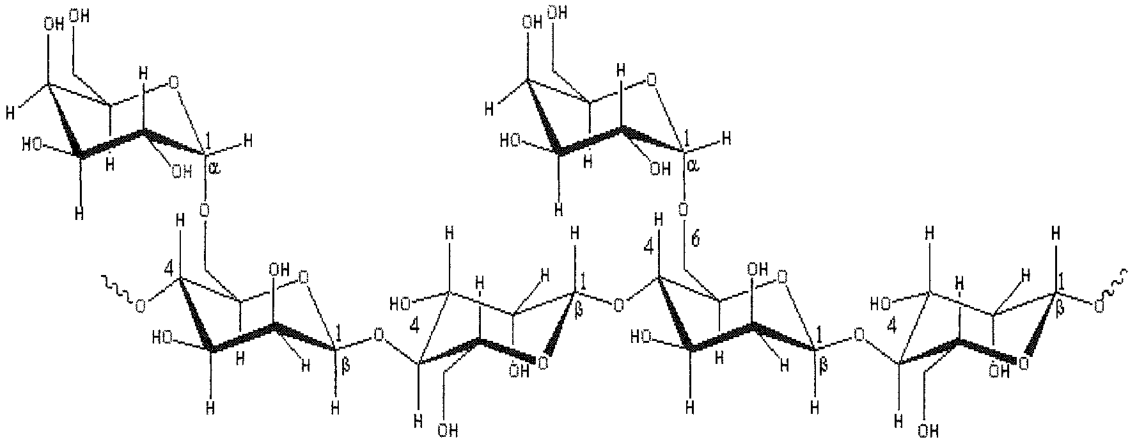


Figure 2.8 Structure of guar gum.

Guar gum is made up of non-ionic polydisperse rod-shaped polymers consisting molecules (longer than found in locust bean gum) made up of about 10,000 residues. The molecular weight of guar is approximately 2×10^6 Da. If the galactose residues were perfectly randomized, it is unlikely that molecules would have more than one such area capable of acting as a junction zone, therefore disallowing gel formation. Higher galactose substitution also increases the stiffness (i.e. decreases the flexibility) but reduces the overall extensibility and radius of gyration of the isolated chains. The galactose residues prevent strong chain interactions by reducing the formation of interor intra-molecular junction zones, where many functional groups are available. They include CH_2OH, O, H, and many OH groups. In this regard, the enzyme is hired to cut the galactose units in guar gum in order to provide more reactions with crosslinkig agents. For instance, Enzymatic hydrolysis of some of the galactose side chains (e.g. using legume α-galactosidase) may allow guar gum to be used to replace a dwindling locust bean gum supply.

2.4.4.3 Properties of Guar Gum

Guar gum is an economical thickener and stabilizer. It hydrates fairly rapidly in cold water to give highly viscous pseudoplastic solutions of generally greater low-shear viscosity when compared with other hydrocolloids and much greater than that of locust bean gum. High concentrations (~ 1%) are very thixotropic but lower concentrations (~ 0.3%) are far less so. Guar gum is more soluble than locust bean gum and a better emulsifier as it has more galactose branch points. Unlike locust bean gum, it does not form gels but does show good stability to freeze-thaw cycles. Guar gum shows high low-shear viscosity but is strongly shear-thinning. Being non-ionic, it is not affected by ionic strength or pH but will degrade at pH extremes at certain temperatures (e.g. pH 3 at 50°C). It shows viscosity synergy with xanthan gum. With casein, it becomes slightly thixotropic forming a biphasic system containing casein micelles. Guar gum retards ice crystal growth non-specifically by slowing mass transfer across solid/liquid interface.

2.4.4.4 Guar Gum's Applications

Unlike the seeds of other legumes, the guar bean has a large endosperm. This spherical-shaped endosperm contains significant amounts of galactomannan gum (19 to 43% of the whole seed), which forms a viscous gel in cold water. Guar gum is the primary marketable product of the plant. It is an excellent soil improvement crop, but is produced mainly for the seeds or "beans" which are enclosed in pods until harvested by combine threshers (Univ. of Purdue). Like other legumes, guar is an excellent soil-building crop with respect to available nitrogen. Root nodules contain nitrogen-fixing bacteria, and crop residues, when plowed under, improve yields of succeeding crops.

In Asia, guar beans are used as a vegetable for human consumption, and the crop is also grown for cattle feed and as a green manure crop. In the United States, highly refined guar gum is used as a stiffener in soft ice cream and sorbets, a stabilizer for cheeses, bakery goods, pastries, instant puddings and whipped cream substitutes, and as a meat binder. In the pharmaceutical and cosmetics industry, it is also used as an effective binder, stabilizer, disintegrator, and thickener. Most of the crop in the United States, however, is grown for a lower grade of guar gum in industrial applications. Industrial applications of guar gum include functions in the textile industry where guar gum's excellent thickening properties are utilized for textile sizing, finishing, and printing. In the paper industry guar is used as an additive where it gives denser surface to the paper used in printing. And in the explosive industry guar is mixed in ammonium nitrate, nitroglycerine, and oil explosives, where it helps maintain the explosive properties of the product even in wet conditions. Guar gum is applicable to oil well drilling mud and ore flotation.

2.4.5 Chitosan

2.4.5.1 Source of Chitosan

Chitosan is the second most abundant natural biopolymer on earth (Lin-Gibson et al., 2003). Technically, chitosan is a derivative of chitin, which can be found in the supporting material of crustaceans, such as crabs, lobsters, and shrimp. It is found even in insects, worms, fungi (fungal mycelia), and mushrooms. It is a complex and natural mucopolysaccharide. Chitin is estimated to be produced annually almost as much as cellulose.

Figure 2.9 Source of chitin and chitosan.

Source: http://www.seabrookstation.com

The percentage of chitin differs depending on the type of creature and the place it is found. As can be seen from Table 2.7, crabs contain the largest percentage of chitin.

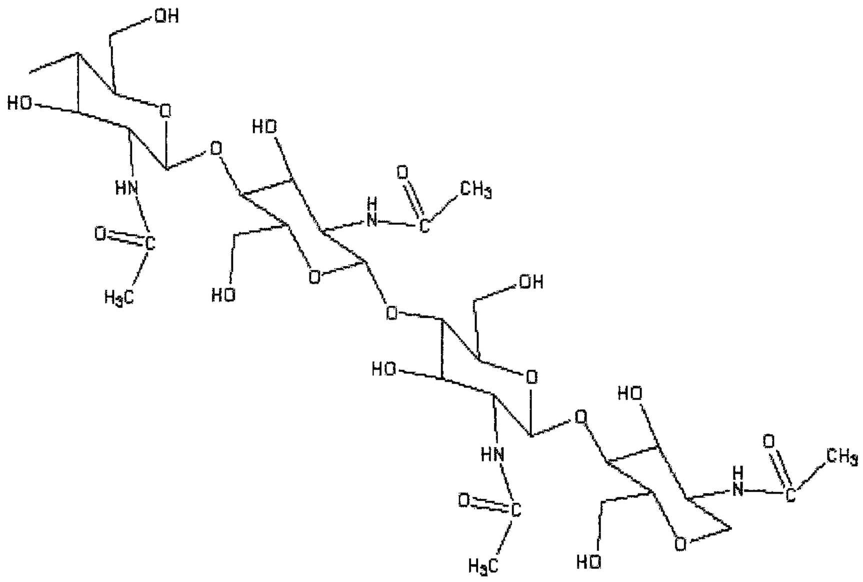
Table 2.7 Proportion of chitin in different creatures

Creature	**Percentage of chitin**
Edible Crab	70%
Hermit Crab	69%
Silk Worm	44%
Spiders	38%
Water Beetle	37%
Cockroaches	35%
Scorpions	30%
Worms	20-38%
Fungi	5-20%
Squid/Octopus	3-20%

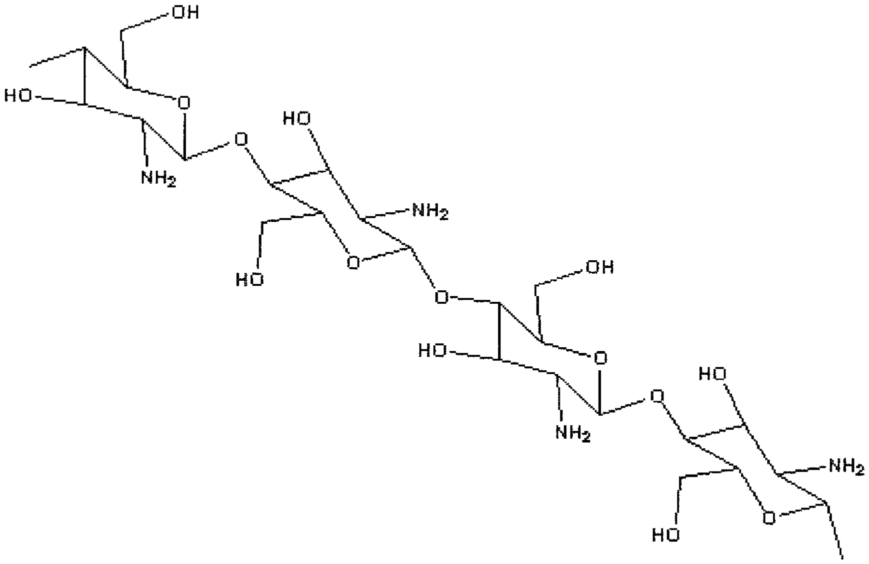
Source: Department of Polymer Science, Univ. of Southern Mississippi, 2000.

2.4.5.2 Structure of Chitosan

The structure of chitin is very similar to cellulose, mostly due to the fact that they are both β (1→4) linked. The difference between the cellulose molecule and the chitin molecule is that chitin has an amide group while cellulose has hydroxyl group (alcohol). Chitosan is a polymer derived from chitin, therefore is very similar to chitin. Chitosan is composed of 2-acetamido-2-deoxy-β-D-glucose (N-acetylglucosamine) through a β(1→4)-linkage (Kumar, 2000), meaning that chitosan is N-deacetylated from chitin, thus chitosan has an amine group instead of an amide group chitin contains. Chitosan does not have any carbons double bonded to oxygen as chitin does. For functional groups in the structure of chitosan, CH_2OH, O, OH, and NH_2 are active.



Chitin



Chitosan

Figure 2.10 Chitin and chitonsan structure.

2.4.5.3 Properties of Chitosan

Chitin is a white, hard, inelastic, basic, nitrogenous polysaccharide with a molecular weight of 1.03×10^6 to 2.5×10^6, and is the major source of surface pollution in coastal areas. Chitin can be degraded by chitinase. Its immunogenicity is exceptionally low, in spite of the presence of nitrogen. It is a highly insoluble material resembling cellulose in its solubility and low chemical reactivity. Like cellulose, it functions naturally as a structural polysaccharide but differs in its properties. Chitin is hydrophobic and soluble in hexafluoroisopropanol, hexafluoroacetone, chloroalcohols, in conjugation with aqueous solutions of mineral acids and dimethylacetamide containing 5% lithium chloride. Chitin has two hydroxyl groups, while chitosan has one amino group and two hydroxyl groups in the repeating hexosamide residue.

Chitosan is a creamy white power with a molecular weight of 1×10^5 to 5×10^5 and is soluble in dilute acids such as acetic acid, formic acid, etc. At room temperature, chitosan forms aldimines and ketimines with aldehydes and ketones, respectively. The process of manufacturing chitosan involves obtaining the resulting chitin from removing protein and calcium carbonate in the crustacean shells, and deacetylating that chin in 40% sodium hydroxide at 120°C for 1-3 h. This process produces 70% deacetylated chitosan.

Chitin and chitosan are of commercial interest due to their high percentage of nitrogen (6.89%) compared to synthetically substituted cellulose (1.25%) (Kumar, 2000), since this makes them a useful chelating agent. In this respect, chitin and chitosan both are recommended as suitable functional materials due to their biocompatibility, biodegrability, non-toxicity, polyoxysalt formation, film-forming ability, optical structural characteristics, adsorption properties, etc.

2.4.5.4 Chitosan's Applications

Chitin and its derivatives are suitable for a number of application in a variety of areas including: medicine (biomedical), pharmaceutics, photography, cosmetics, health care, ophthalmology, paper production, textiles, metal chelation, food additives, antimicrobial agents, adhesives, and other industrial applications. In particular, chitosan can control the release of drug dosage in drug therapy and also shows remarkable effects on treating burn patients because of compatibility with living tissue. Recently, chitosan was reported to reduce serum cholesterol levels. Chitosan can also increase crop yields and clean pools and wastewater in water engineering.

For example, the use of chitosan to bind metal ions for wastewater treatment has been long known and its ability to adsorb metallic ions from aqueous solutions has been extensively studied (Jha et al., 1988; Deans and Dixon, 1992; Findon et al., 1993; Wan Ngah and Liang, 1999; and Schmuhl et al., 2001). As for a case study, chitosan was utilized to reduce the turbidity in ponds caused by construction runoff. Also, it can remove phosphorous, heavy metals, and oils from the water. It is commonly used by aquariums to clean water and is safe for fish. There are a number of investigations regarding the use of chitosan, for nuclear waste treatment.

Chitin and chitosan have a wide scope of applications. They may be employed to relieve a good number of environmental problems we may encounter in the modern world.

2.5 Cement Chemistry

2.5.1 Portland Cement

Chemically defined hydraulic cement not only hardens by reacting with water but also forms a water-resistant product. Cements set and harden as a result of chemical reactions with water in appropriate proportions and continue to harden even if stored under water after hydration is finished. Portland cement is the most typical cement. Portland cement is manufactured by heating a mixture of finely ground limestone or shales and clay, ultimately to a temperature of approximately 1450°C and then the gypsum (white mineral) is added to the mixture or clinker (incombustible residue), controlling the rate of setting time. The clinker in nodules typically has a composition of 67% CaO (alite), 22% SiO_2 (belite), 5% Al_2O_3 (aluminate), 3% FeO_3 (ferrite), and 3% of other components. The composition rate is varied for different cements (Taylor, 1990).

Alite is the most important constituent of all normal Portland cement clinkers, ranging 50-70% of clinker composition. Chemically speaking, it is tricalcium silicate (Ca_3SiO_5 or $3CaOSiO_2$ or C_3S) that is modified in composition and becomes a crystal structure with the incorporation of foreign ions, especially Mg^{2+}, Al^{3+}, and Fe^{3+}. It reacts quickly with water, which is related to heat evolution and contributes to further strength development, particularly at ages up to 28 days.

Belite constitutes 15-30% of normal Portland cement clinkers. It is dicalcium silicate (Ca_2SiO_4 or C_2S) incorporated by foreign ions and normally presents as the β polymorph. It reacts slowly with water, unlike alite, thus contributing little to the strength for the first 28 days, but substantially to the further increase in strength at later ages. For example, after one year, the strength developed from pure alite comes close to that from pure belite under comparable conditions.

Aluminate makes up 5-10% of normal cement. It is tricalcium aluminate ($Ca_3Al_2O_6$ or C_3A), modified in composition and incorporated by foreign ions, particularly, Si^{4+}, Fe^{3+}, Na^+, and K^+. Aluminate reacts rapidly with water and relates with heat evolution like alite. It can also cause undesirably fast setting unless a set-controlling agent, gypsum, is added.

Ferrite makes up a proportion of 5-15% of normal cement, expressed as tetracalcium aluminoferrite (Ca_2AlFeO_5 or C_4AF). It is substantially modified in composition by the ratio of Al/Fe and incorporated by foreign ions similar to all other phases like alite, belite, and aluminate. The reaction rates vary according to its proportions.

The content of these components (C_3S, C_2S, C_3A, and C_4AF) primarily affects the behavior of each type of cement. In simplest terms, early hydration of cement is principally controlled by the amount and activity of C3A, and therefore hydrates very fast and will influence early bonding characteristics (U.S. Dept of Transportation).

Different types of Portland cement are manufactured to meet a variety of physical and chemical requirements for specific purposes. The American Society for Testing and Materials (ASTM) Designation C 150 provides for eight types of Portland cement. Eight types of Portland cements and their uses are summarized in Table 2.8 (modified after U.S. Dept of Transportation).

Table 2.8 Portland cement types and their usage

Cement type	**Usage**
I	General purpose cement, when there are no extenuating conditions More than 90% of cement production in U.S. Cements that simultaneously meet requirements of Type I and II are widely available.
II	Aids in proving moderate resistance to sulfate attack More than 90% of cement production in U.S. Type II with low alkali (total alkali as Na_2O < 0.6%) is often specified in regions where aggregates susceptible to alkali-silica reactivity are employed.
III	When high-early strength is required 2.5% of cement production in U.S.
IV	When a low heat of hydration is desired (in massive structures) Only available for specific request
V*	When high sulfate resistance is required < 2.5% production in U.S.
IA*	A type I cement containing an integral air-entraining agent
IIA*	A type II cement containing an integral air-entraining agent
IIIA*	A type III cement containing an integral air-entraining agent

*These cements are in limited production and not widely available.

Type I is normal, general-purpose cement suitable for all uses where the special properties of other types are not required. It is used where cement or concrete is not subject to particular exposures, such as sulfate attack from soil or water (acid rain), or an objectionable temperature rise caused by hydration heat. Its applications include general construction projects such as reinforced concrete buildings, floors, pavements general construction projects such as reinforced concrete buildings, floors, pavements and sidewalks, railway structures, bridges, tanks, reservoirs, culverts, sewer and water pipes, some masonry units, other precast products, and more (Rinker Materials Co.). Type II is utilized where precaution against moderate sulfate attack is important, as in drainage structures for groundwater with moderate levels of sulfate concentrations. Type II cement generates less heat than Type I, because it reacts more slowly with water. It will reduce rises in temperature, which is particularly important when the concrete is used in warm weather. Its applications include large pipers, heavy retaining walls, and abutments. Type III is a high-early strength cement that causes concrete to set and gain high strengths rapidly. It is chemically and physically similar to Type I, except for finer particle size, which will increase water demand and thus lower long-term strength. It is used when the structure must be put into service quickly. Type IV is cement with a low heat of hydration for use where the rate and amount of heat generation should be minimized. Thus the development of strength is achieved at a slower rate than other cement types. It is used for massive concrete structures like large gravity dams, where the temperature rise during curing is critical. Type V is severe sulfate-resisting cement, primarily for soils or groundwater with high sulfate content.

An "A" (e.g., Type IA, IIA, IIIA) indicates that the cement has an air-entraining agent, which means that it corresponds in composition to ASTM Type I, II, III, respectively, except for small quantities of air-entraining materials interground with the clinker to produce minute, well-distributed, and completely separated air bubbles. These types of cements are resistible to freeze-thaw action.

In addition of the eight types of Portland cements, blended and composite cements are available and more popular for particular applications. They are hydraulic cements manufactured by a blend of Portland cement with recycled or inorganic materials such as pulverized-fuel ash (fly ash; pfa), microsilica (condensed silica fume), grounded granulated blast-furnace slag (ggbfs), and natural pozzolanas. Some of their characteristics can include lower heat, lower permeability, slower strength gain, higher ultimate strength, better durability, and more convenience. ASTM C 595 specifications list the following types in the U.S.A. (Portland Cement Association):

Type IS: Portland blast-furnace slag cement
Type IP and Type P: Portland-pozzolan cement
Type I (PM): Pozzolan-modified Portland cement
Type S: Slag cement
Type I (SM): Slag-modified Portland cement

Expansive cement as modified Portland cement is also available containing hydraulic calcium silicates, upon being mixed with water and forms a paste that increases in volume significantly more than Portland cement. The advantages of using expansive cements are to induce tensile stress large enough to compensate for drying shrinkage and cracking stress. Three kinds of expansive cements are defined in ASTM C 845 (U.S. Dept. of Transportation):

Type K: contains anhydrous calcium aluminate, significant amount in the U.S.

Type M: contains calcium alumimate and calcium sulfate

Type S: contains tricalcium aluminate and calcium sulfate

2.5.2 Cement Property and Factors Affecting Cement and Concrete Property

The properties of cement depend on the quantities and qualities of its components. For physical properties of Portland cements, ASTM C 150 and AASHTO M 85 have specified certain physical requirements for each type of cement. They include 1) fineness, 2) soundness, 3) consistency, 4) setting time, 5) compressive strength, 6) heat of hydration, 7) specific gravity, and 8) loss of ignition (U.S. Dept. of Transportation). Each of these properties has an impact on the performance of cement or in concrete. To take a couple of examples, the fineness of the cement affects the rate of hydration. Greater fineness provides more surface areas for hydration, causing greater early strength and more rapid heat generation. So, Type III in finer particles gives early strength with fast heat generation, compared to Type I in coarser particles. Soundness of the concrete can be defined as the ability of hardened cement paste to retain its volume after setting and can be characterized by measuring the expansion of mortar bars in an autoclave. However, coarse cement gives a higher ultimate strength and a lower early-strength.

Cement composition and fineness play a significant role in controlling concrete properties. Fineness of cement affects the placeability, workability, and water content of a concrete mixture. Cement composition also affects the permeability of concrete by controlling the rate of hydration. The coarse cement is likely to produce higher porosity paste than finer cement. However, the ultimate porosity and permeability are unaffected (U.S. Dept. of Transportation). The C3S and C2S will have the primary influence on a long-term development of structure. Cements with high content of C3S will hydrate more rapidly and lead to higher early strength. Cements with high content of C2S will hydrate much more slowly, leading to a denser ultimate structure with higher long-term strength, as described earlier. The relative ratio of C3S to C2S, and the overall fineness of cements, has been steadily increasing over the past few decades (U.S. Dept. of Transportation). Corrosion of embedded steel is occurred by C3A content, since the higher C3A will corrode the steel with more chlorides being tied as chloroaluminate complexes. But, cement composition has only a minor effect on freeze-thaw resistance. Table 2.9 summarizes the effects of cements on concrete properties (U.S. Dept. of Transportation).

Table 2.9 Effects of cements on concrete properties

Cement Properties	**Cement Effects**
Placeability	Cement amount, fineness, setting characteristics
Strength	Cement composition (C3S, C2S and C3A), loss on ignition, fineness, water ratio
Drying shrinkage	Sulfur content, cement composition
Permeability	Cement composition, fineness
Resistance to sulfate	C3A content
Alkali silica reactivity	Alkali content
Corrosion of embedded steel	Cement composition (C3A content)

Rheology of concrete is an important factor in describing the workability of the cement, which indicates the ease with which a concrete can be mixed, transported, placed, and compacted to give uniform material. The rheological behavior is affected by the method of mixing, w/c ratio, particle size distribution, porosity of the hardened paste, age, presence of admixtures, air entrapped, relative humidity (RH), and cement composition. Among these, w/c ratio and particle (pore) size distributions are significant in controlling the concrete mix.

It was noted that early strengths achievable today in concrete could not have been achieved in the past except at low w/c (water/cement) ratio, which would have rendered concretes unworkable (Taylor, 1990). The cement with high w/c may have durability problems because the higher w/c invariably leads to higher permeability in the concrete. Most investigators appear to have agreed with the observation that complete hydration cannot occur if w/c is below a value in the region of 0.38. So, the w/c ratio was manipulated as 0.397 as it is typically 0.3-0.6 (Taylor, 1990).

For Portland cement paste 5 min after mixing, flocs of small particles and of large particles with adhering small ones are observed. The average distance between flocs is about 3 μm. At 2h, C-S-H and ettringite is observed on the grain surfaces and the flocs got more definite. At 6h, the layers of hydration products has become much thicker and a three-dimensional structure is formed through the linking of the larger grains and small grains of concrete ingredients, so-called pore size distribution occurs.

2.5.3 Composite Cements and CRT Composite

A composite cement is a hydraulic cement composed of Portland cement and one or more inorganic materials that take part in the hydration reactions and there by make a substantial contribution to the hydration product (Taylor, 1990). The inorganic materials can be mineral additions. The most important are pulverized-fuel ash (fly ash; pfa), ground granulated blast furnace slag (ggbfs), natural pozzolanas and microsilica (condensed silica fume). These waste materials can be added and grounded together with the cement clinker and gypsum, or mixed with Portland cement, which is called intergrinding and blending, respectively. For the cement manufacturer, intergrinding provides a degree of flexibility in changing the volume of cement production to meeting demand. The necessity for utilizing waste materials and decreasing overall energy consumption are major reasons to manufacturing composite cements. Also, composite should have properties that are desirable for particular purposes, such as slower and decreased total evolution in massive structure, improved durability or, with microsilica, strengths above the normal range. In this notion, CRT composite recycling CRT waste should show the higher durability and strength than ordinary concrete.

For CRT composite, crushed CRT glass was sieved into two kinds of sizes like fine (powered) and coarse CRT glass, determined by the US standard mesh size. Fine CRTs are less than #140 mesh (0.105 mm) and coarse CRTs between #100-40 mesh (0.149-0.42 mm). With this CRT glass sample, CRT composite was made in different proportions of biopolymer or crosslinked solution, sand, and cement. The presence of a small proportion of crystalline material finely dispersed in the glass improves gridability or reactivity of composite. Reactivity obviously depends on bulk composition, glass content, and fineness of grinding, though these are probably not the only factors, and the relations with composition of concrete and glass content are complex. The beneficial effect of small crystalline phases provides the mechanical strength in the glass of composite and nucleation sites for hydration products. With respect to this idea, the suitability of use of CRT glass in the concrete composite can be reasoned.

2.5.4 Mechanism of Adsorption of Lead onto Ordinary Concrete Microstructure

Internal structure of hydrated cement refers to microstructure. Development of the microstructure of hydrated cement occurs after the concrete has set and continues for months or even for years. The microstructure of cement hydrates will determine the mechanical behavior and durability of the concrete.

For a Portland cement paste without admixtures, two or three layers of C-S-H (calcium silicate hydrate) can roll into fibers. This C-S-H gel is viewed as a three-dimensional mass, which tends to form subparallel groups a few layers thick and which enclosed pores of dimensions ranging from interlayer spaces. Basically, the gel of cement paste has an internal structure with a variety of pores such as micropores (< 2 nm), mesopores (2-50 nm), and macropores (>50 nm), which makes size distribution of pore in concrete internal microstructure shown in Figure 2.11 of the structure of the C-S-H gel of Portland cement paste (modified after Taylor, 1990). These micro pores tend to have narrow entrances which are tight and compact enough to trap lead particles in relatively micros-size. After hours, the layers of hydration products are much thicker and a three-dimensional structure is formed through the linking of the larger grains to smaller ones.

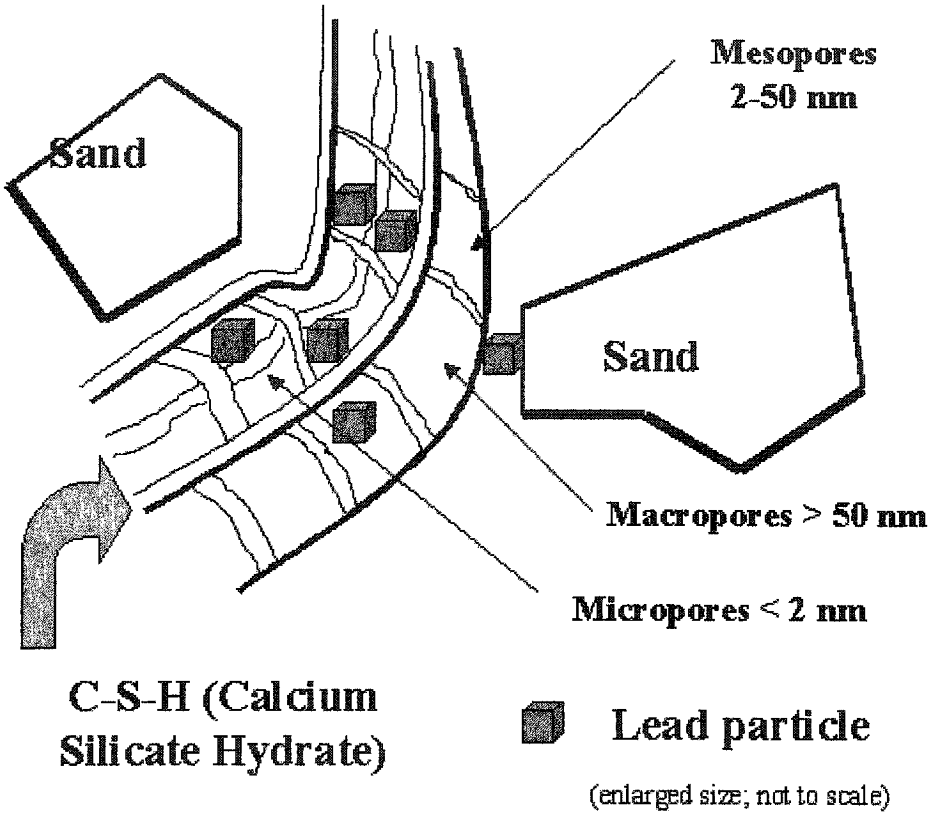


Figure 2.11 The structure of the C-S-H gel of Portland cement paste.

Strength of concrete cannot be explained by relating it empirically to porosity or pore size distribution: it is necessary to know what holds the material together. Therefore, specific binding capacities occurring in the concrete mix must be considered. Physical and chemical bonds are so important in building up concrete structure among particles such as cement and sand. Concrete mass involves the interplay of van der Waals bonds, electrostatic bonds, and hydrogen bonds. Many types of interatomic force (van der Waals) exist in cement paste. Between particles, cohesion has often been attributed to the interlocking of fibrous or acicular particles. The attractive forces could be direct or indirect, through interposed H_2O molecules forming ion-dipole attraction, ionic covalent bonds, and hydrogen bonds which occur in C-S-H layers and within particles (Taylor, 1990). Particularly, many oxygen bonds provided by sand (Si-) and cement (Ca-) are widely occurring in the concrete during the curing time. In this sense, the method of mixing is important to build up the dimensional structure and rheological behavior of concrete. Manual mixing is intended to increase the adsorption of lead to the microstructure of cement, depending upon the size distribution and chemical bridging of particles involved in the hydration product. In this regard, C-S-H layers may perform as a fish net to entrap lead particles. However, this dimensional structure can be deteriorated by the introduction of acidic liquid such as acid rain. For this reason, the complete structural enforcement of the composite by application of gum is necessarily required.

2.6 Crosslink Chemistry

2.6.1 Crosslink Phenomena

Cross-link can be described in both intra- and inter-molecular connections between target structure and crosslinker (crosslinking agent). This phenomenon takes place in two and three dimensions. In terms of binding, crosslinking can be either chemical (eg., covalent bonds) or physical (eg., ionic, hydrogen, van der Waals bonds) (Alupei et al, 2002). Also, many functional groups make a major contribution to building the crosslinking structure.

Figure 2.12 shows that a crosslinking network may be prepared either by using bifuctional monomers and multifunctional crosslinking agents or by using the reactive side (functional group) or end groups of linear polymers.

At length, crosslink phenomena can occur in intramolecular and intermolecular network by interactions between biopolymers themselves due to their reactive sites, and by interactions between biopolymer (structure) and crosslinker (crosslink agent) in Figure 2.13.

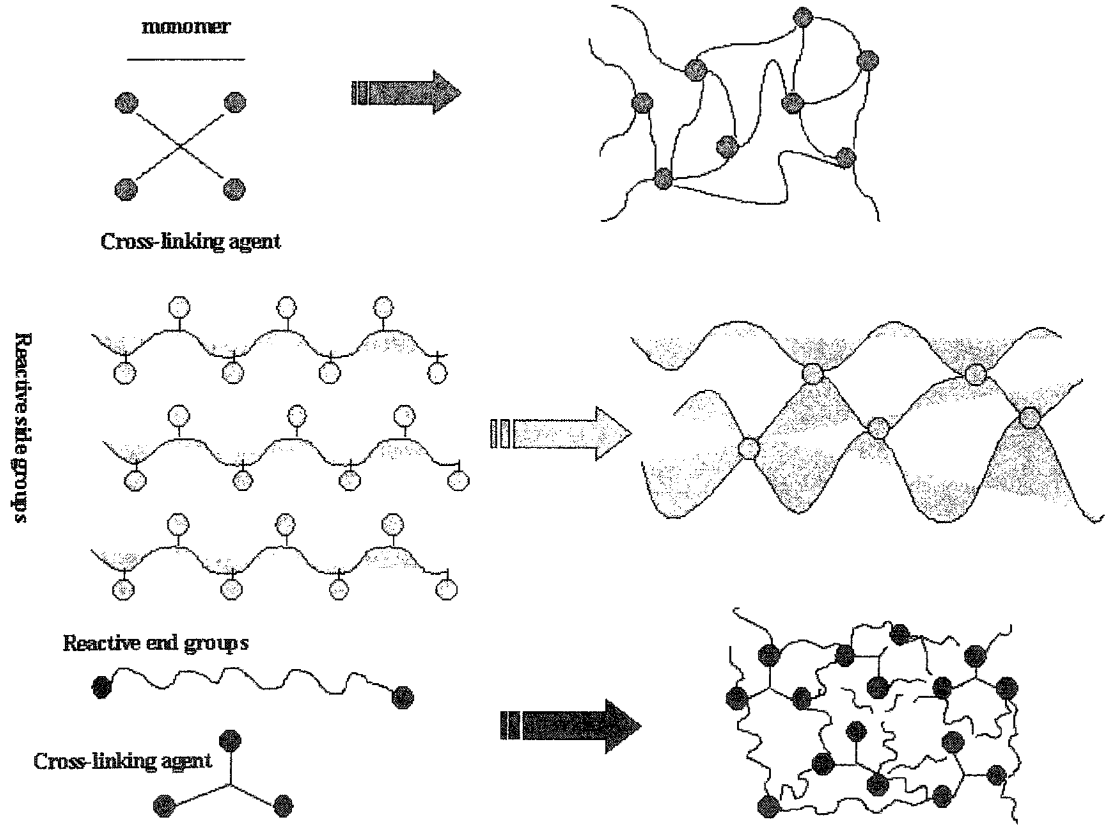


Figure 2.12 Cross-linking copolymerization (modified after Glass, 1989).

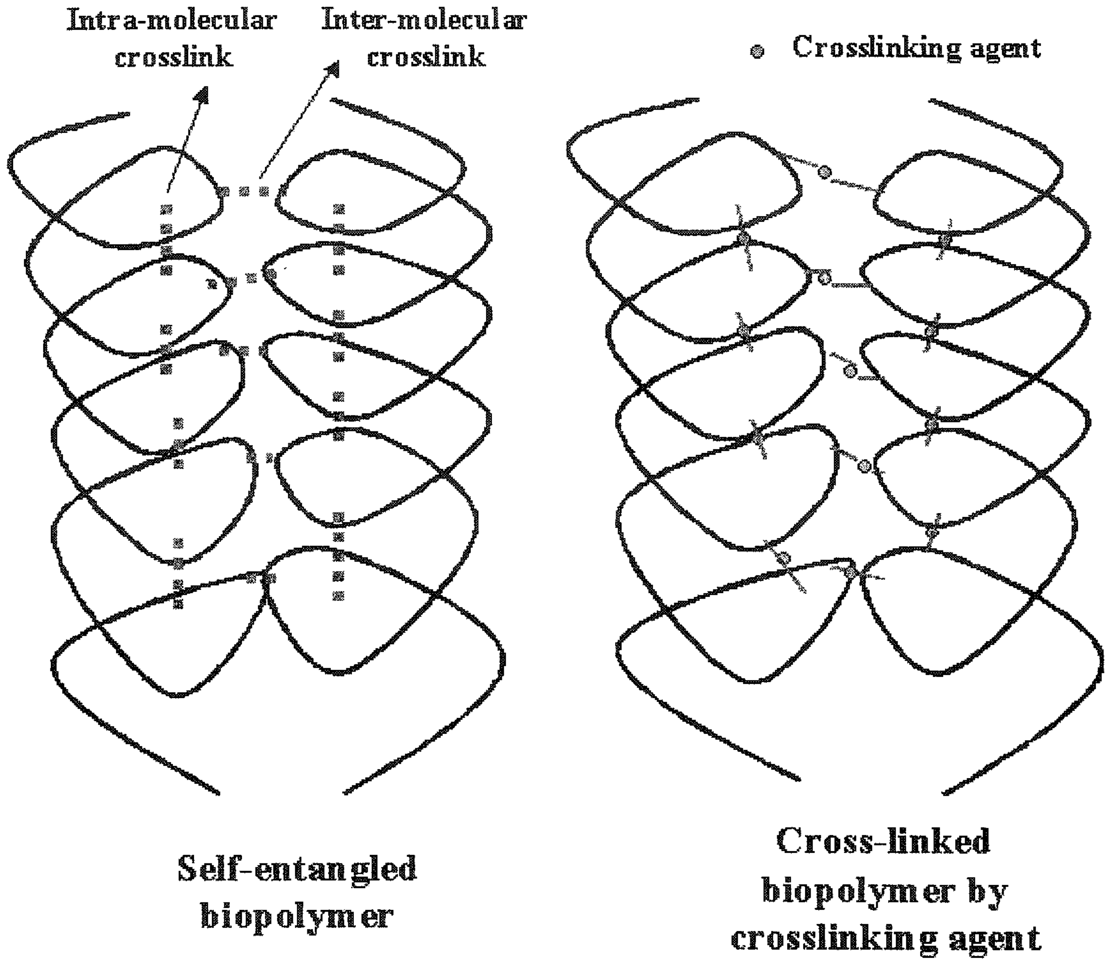


Figure 2.13 Typical crosslink phenomena.

2.6.2 Guar Gum and Boric Acid

Guar gum consists of long branching polymers of mannose and galactose in a 2(or 1.5):1 ratio. The galactose substituents are regularly distributed along the mannose chain. These galactose units are normally attached in no specific pattern.

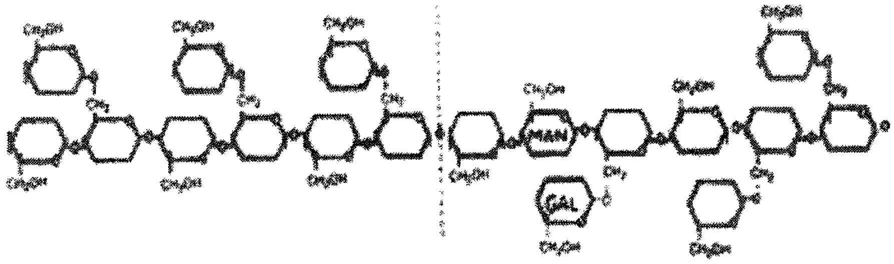


Figure 2.14 Mannose and galactose in guar gum.

Crosslink reaction between guar gum and boric acid occurs. Boric acid, $B(OH)_3$, dissociates to borate ion, $B(OH)_4^-$ that is the effective species in crosslinking, and its concentration is a function of the pH, temperature, and concentration of boric acid in the solution (Kesavan et al, 1992). An acid-base equilibrium is established between boric acid and monoborate ions, as seen in equation 2.1.

$$B(OH)_3 + H_2O \overset{K_A}{\leftrightarrow} B(OH)_4^- + H^+ \qquad pK_A = 9.0\text{-}9.2 \qquad [2.1]$$

The monoborate ions react with the *cis*-hydroxyl groups in guar to form crossliked structure. Since galactose unit and mannose unit are the repeating units in guar, similar reactions are expected to occur between the borate ion and the hydroxyl groups on guar. The reactions of the borate ions with polyols (cis-hydroxyls) are described as follows:

$$A + B^- \overset{K_1}{\leftrightarrow} AB^- \qquad [2.2]$$

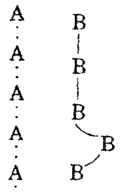
$$2A + B^- \overset{K_2}{\leftrightarrow} A_2B^- \qquad [2.3]$$

where A refers to the polyol, B^- refers to $B(OH)_4^-$, and AB^- and A_2B^- are the 1:1 and 2:1 complex structures occurred by the reaction of one polyol with one borate ion and two polyols with one borate ion, respectively. The rheological properties of the borate-cross linked gels depend strongly on the number of effective cross-links (eg., the concentration of A_2B^-). They exhibit fluid-like behavior at low pH (about pH 7.0) and solid-like behavior at high pH (about pH 9-9.5), showing blue in color change. The solid-like gel forms as soon as pH increases around pH 9. Similar transition from fluid-like to solid-like behavior is observed as the temperature is decreased from 65 to 15 °C. At high temperature, the number of cross-links decreases because reactions equations 2.1-3 have positive activation energies. Therefore, the loss in intermolecular association, and the resulting loss in viscosity, has been the major limitation in the use of borate gels in high-temperature applications. Also, the number of cross-links decreases exponentially with decreasing of pH due to equations 8.1-3. The reduction of number of cross-links can be expected e^{-3}-which for this system would produce less than one borate cross-link per chain. However, the exact equilibrium constants and activation energies for this guar gum crosslinked by borate ions are not known.

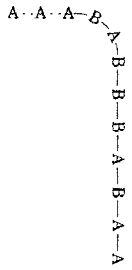
2.6.3 Xanthan Gum and Guar Gum

Polymers can be classified as homopolymers with one type of repeating unit in their structure. If there are more than one type of repeating units (two, for example), they are called copolymers; three, terpolymers; and so on until the repeating units reach *n*, for which the word is multipolymer or *n*-polymer (Yen, T.F. 1999).

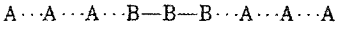
Figure 2.15 illustrates the interpenetrating polymer network, an essential step in copolymerization. An interpenetrating polymer network is the entangling and twisting of two polymers that have the same cross-link or a covalent bond between nonconsecutive parts of each polymer. This is similar to the interaction of a polymer complex that creates polycation and polyanion, and is more tightly bound due to the covalent bonding.



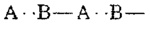
a) polymer blend



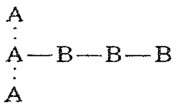
b) random copolymer



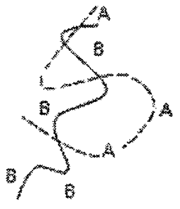
c) block copolymer



d) alternating copolymer



e) graft copolymer



f) interpenetrating polymer network

Figure 2.15 Interactions of two different types of polymers (A and B are repeating sequences. A is linked by dots; B is linked by lines).

In this sense, interaction between xanthan and guar gum can occur, which can belong to alternating copolymer or graft copolymer. Guar gum and locust bean are the galactomannans most commonly employed in the industry (Maier et al., 1993), since low cost and abundance are major factors contributing to the popularity of galactomannans (Pai, et al, 2002). They are formed by a backbone chain of mannose units linked to a monomolecular unit of galactose. The relation between mannose and galactose and hair-like distribution of galactose in the backbone is typical of every galactomannan (Hui et al, 1964). Galactose residues are not uniformly distributed; there are regions with many galactose residues (hairy regions) and others without galactose (smooth regions) where the polymer interaction between xanthan and guar can possibly take place, because smooth regions provide attaching sites for xanthan molecules. Figure 2.16 illustrates the synergic interaction between xanthan and guar.

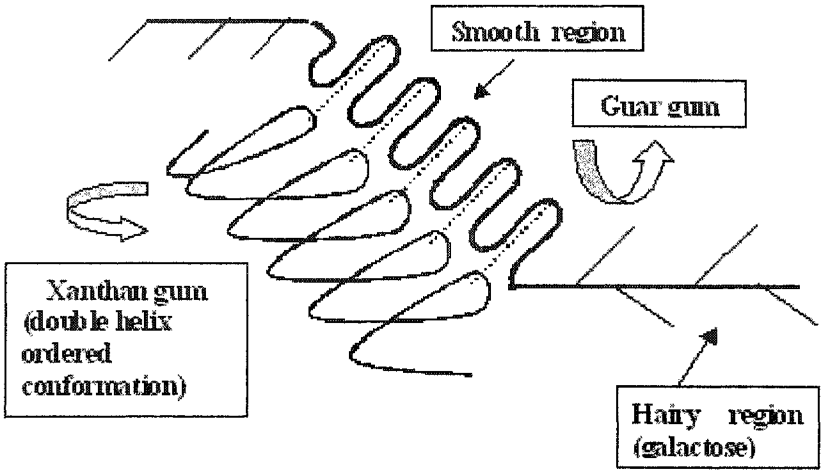


Figure 2.16 Synergic interactions between xanthan gum and guar gum.

2.7 Experimental Procedures

2.7.1 Materials and Methodologies

2.7.1.1 CRT Samples and Lead in CRT for CBC Composite

A CRT display consists of a cathode ray tube, a casing (plastic shell), metals, various connecting wiring, integrated circuit (IC), shielding, rubber, and a deflection yoke, as seen in Table 9.1. A glass tube ranges in weight from 8 to 70 pounds depending on its size and manufacturer. Referring to Table 2.10, the CRT unit is a major component (48.23%) of computer monitor by weight.

Table 2.10

Composition of 14-in. color monitor

	Material	**Weight (kg)**	**Percent (%)**
Shell	plastic	2.032	17.38
CRT explosion protection unit	steel	0.213	1.82

Table 2.10 continued

CRT unit		5.638	**48.23**
Shadow mask	steel	0.455	3.89
Panel glass	glass	3.356	28.71
Funnel glass	glass	1.731	14.81
Gun	steel, glass, copper, plastic	0.096	0.82
Yoke	copper, plastic, steel	0.598	5.04
Metal parts	steel	0.542	4.64
IC board	IC, resin, copper, steel	1.676	14.34
Wire	copper, plastic	0.661	5.65
Rubber parts	rubber	0.048	0.41
Plastic parts	plastic	0.291	2.49
Total		11.690	100.00

Modified after Lee, C-H, 2002.

Color computer monitors (different manufacturing models and years) were manually dismantled into plastic shell, inner electric parts, and CRT glass that was separated into panel, funnel, and neck glass. These were crushed, grounded, and mixed altogether for homogenous lead concentration, even though lead is mostly confined to the funnel and neck parts of CRT glass. In this manner, the total concentration of lead could be averaged in the mixture of neck, funnel and panel glass. The total concentration of lead of well-mixed sample (coarse CRT glass) was approximately 5883 mg/kg measured by ICP-MS, shown in Table 2.11, indicating that the concentration of lead in funnel and neck part of glass would be more than 5883 mg/kg. The lead concentration of funnel and panel glass showed 143,000 mg/kg and 11,300 mg/kg, respectively (Lee, 2002).

Table 2.11

ICP-MS elemental analysis of CRT glass (coarse size)

Element	**Concentration (mg/kg)**	**Element**	**Concentration (mg/kg)**
Be	< 0.00005	Cu	3.926
Na	437.6	Zn	568.5
Mg	6.667	As	0.2546
Al	91.93	Se	1.368
K	440.3	Sr	100.1
Ca	194.4	Mo	< 0.00028
Ti	1.79	Ag	< 0.00018
V	< 0.00016	Cd	< 0.00015
Cr	1.23	Sn	0.4959
Fe	21.16	Sb	8.602
Mn	5.282	Ba	270.8
Fe	19.38	Tl	0.1325
Co	< 0.00017	**Pb**	**5883**
Ni	< 0.00023		

< below detection limit

Crushed CRT glass was sieved into two different sized fractions, fine and coarse CRT glasses. Fine CRT samples are less than #140 mesh (< 0.105 mm) and coarse CRT samples between #100-40 mesh (0.149-0.42 mm). Fine sized CRT glass is expected to have a much higher content of lead, considering the surface area of fine glass particles. As shown in TCLP results of Table 2.12, neck and funnel parts contain enormous amount of lead. Data of samples 25, 26, and 35 were obtained from other researchers' work to compare with data we found in our laboratory. Our samples show the same pattern, that the funnel part has the highest lead concentration, and that fine glass samples contain higher lead content than coarse samples. For general samples, lead concentration is averaged in mixture of panel, funnel, and neck parts. Sample 1 is expected to have very high lead content for its neck and funnel part. CRT samples are manufactured by NEC, IBM, Apple Computer (Apple Multiple Scan 17-inch, 1995), and other manufacturers.

Table 2.12

TCLP results of fine and coarse samples in different parts of CRT unit

	Sample #	**Coarse sample (mg/L)**	**Fine sample (mg/L)**
Mixed sample	1	307.3	782
	4	78.95	132.9
	5	43.70	64.92
Panel	3	6.86	6.55
Funnel	3	77.67	162.92
Neck	3	12.44	53.59
Funnel	25*	149.2	198.2
Funnel	26*	209.8	439.7
Funnel	35*	44.7	171.5

* Samples are from Handy and Harman Electronic Materials Corp. 2002.

2.7.1.2 Biopolymers (xanthan gum, guar gum, and chitosan) and Crosslinking Agent (boric acid)

Xanthan gum solution was prepared in deionized water at concentrations of 0.1% (1000 mg/L) and 0.5% (5000 mg/l), using xanthan gum power manufactured by CPKelco (Kelzant). Guar gum was purchased from Gum Technology (Coyote Brand Guar: High Viscosity), prepared in DI water at concentration of 0.1% and 0.5%. Chitosan was obtained from MegaCare Inc., S. Elmonte, CA and prepared in the same concentrations as xanthan and guar gum. Chitosan is insoluble in water so that it was dissolved in 1% acetic acid. Boric acid was used as crosslinking agent and prepared in DI water at concentrations of 0.1% and 0.5%. For the preparation of guar and boric crosslinked solutions and guar and xanthan gum crosslinked solutions, 0.1% guar gum was mixed with boric 0.1% at volume ratio of 4 to 1, and 0.1% xanthan gum with guar gum 0.1% at the same volume ratio. For concrete materials, we used industrial sand manufactured by Accosand Inc. (Ottawa sand) and cement I-II type.

2.7.1.3 CBC (CRT-Biopolymer-Concrete) Composite

The experiment is designed to meet the qualifications of commercial products that cause no hazard to humans or the environment. The first stage will focus on the best combination of composites to give the most strength and least leaching of lead. Each sample is tested in terms of strength and leachability of lead, which are compressive and tensile (split) strength, and the TCLP (Toxicity Characteristic Leaching Procedure: USEPA method 1311) approved by EPA. Toxicity is identified through a laboratory procedure and the TCLP was developed for use in the assessment of waste disposal facilities, rather than mining operations. The TCLP (USEPA Method 1311) evaluates metal mobility in a sanitary landfill. The extraction fluid for the TCLP is a buffered organic acid (acetic acid).

ICP/MS by Perkin Elmer (ICP Optima 3300 Dr) and AAE by Perkin Elmer (AAnalyst 300) were utilized to measure the total metals and the lead concentration. Some samples were analyzed by Calscience in California. In particular, mechanical testing method follows the guidance provided by CE 334 class information and lab manager in the Department of Civil Engineering at USC.

CRT-Biopolymer-Concrete (CBC) composites were built at different compositions of each ingredient, which will be shown in each biopolymer section. All CBC specimens were made and cured for seven days. CRT and sand portions in CBC composite were variable with other portions remaining. The purpose of this lies in that CRT glass may replace sand in concrete composite, increasing the strength of composite or at least showing similar strength to that of ordinary mixing concrete with very low leaching of lead from CRT glass.

Mixing is performed in the sequence of C(cement)-S(sand)-W(water)-C(cement)-S(sand)-CRT-W(water)-Biopolymer solution. For example, CBC 1 has the order of mixing, C(550g)-S(1000g)-W(147g) were pasted and another paste, C(500g)-S(900g)-CRT(350g)-W(200g)-X.G.(70g) was added on to the paste previously made. The thorough mixing of CRT and ingredients of concrete composite is intended assure that the CRT lead particles are distributed onto microstructure of concrete system with encapsulation of xanthan gum solution.

A uniform gel of biopolymer is produced by heating (to "melt") the gel to more than 65 °C for several minutes and subsequently cooling down. This process is repeated several times to produce the homogeneous gel. Similarly, homogenous paste with biopolymers or crosslinking agent is affected by the temperature change that occurs in the chemical reaction of cement. The temperature in cement increases up to 100 °C and then cools down to room temperature. This reaction may help the formation of homogenous paste for the CRT composite.

Another set of experiments included the increase of the concentration of biopolymers, to 5000 mg/L (0.5%), and application of a crosslinking agent like boric acid among numerous agents providing crosslinking properties. Similar to that of the initial set, mixing was conducted. For instance, CBC 6 or 11 has the order of mixing, C(550g)-S(1000g)-Water(147g) were pasted and another paste, C(500g)-S(900g)-CRT(350g)-Water(200g)-Guar gum solution(70g) or Crosslinked solution (70g ; guar gum and boric acid), was added on to the paste previously made and then well mixed. When changing the amount of biopolymer and crosslinked solution without water, C(550g)-S(1000g)-Guar gum solution(147g), for examples of CBC 7 and CBC 12, was pasted and another paste was added, C(500g)-S(900g)-CRT(350g)-Guar gum solution(270g) or Crosslinked solution (270g ; guar gum and boric). These samples are placed in a plastic cylinder casing with 4 in. diameter and 8 in. height for curing with a sealed top. After 7-day of curing, samples are tested for compressive and tensile strength.

2.7.2 Results and Discussion

Xanthan Gum

2.7.2.1 Results of Xanthan Gum and Discussion

Table 2.13

CBC compositions and results of xanthan gum

	CBC 1 X.G. 0.1% (70g) Weight (g) / (%)	**CBC 2** X.G. 0.5% (70g) Weight (g) / (%)	**CBC 3** X.G. 0.1% (417g) Weight (g) / (%)	**CBC 4** X.G. 0.5% (417g) Weight (g) / (%)
Water	347 / 9.34	347 / 9.34	---	---
Cement (Type I & II)	1050 / 28.25	1050 / 28.25	1050 / 28.25	1050 / 28.25
Sand	1900 / 51.12	1900 / 51.12	1900 / 51.12	1900 / 51.12
CRT glass	350 / 9.42	350 / 9.42	350 / 9.42	350 / 9.42
Xanthan gum solution	70 / 1.88	70 / 1.88	417 / 11.22	417 / 11.22
TCLP (mg/L)	0.0972	0.003	0.1435	0.0475
Compressive strength (psi)	4938	4673	4133	3242
Tensile strength (psi)	576	491	454	364

Trapped air was less than 0.1% by weight.

As shown in Table 2.13, various compositional ratios of composite mix were tested for CBC made from xanthan gum. All specimens were cured for 7 days. CBC 1, 2, 3, and 4 are recommended in terms of lead leaching since they are below 5 mg/L as current lead standard. However, CBC 3 (417 g of 0.1% xanthan gum solution), and CBC 4 (417 g of 0.5% xanthan gum solution) have weaker strengths of compression and tensile than those of ordinary concrete with 4135 psi of compressive strength and 447 psi of tensile strength, as seen in Table 2.14. However, CBC 1 (70 g of 0.1% xanthan gum solution) and CBC 2 (70 g of 0.5% xanthan gum solution) showed approximately 20% and 13% higher compressive strength, respectively. The same trend is true for tensile strength, actually, 30% higher strength for CBC 1 and 10% for CBC 2. This is because certain amount of water is required to build the concrete structure, which is related to water/cement (w/c) ratio. Water/cement ratio for this concrete composite was programmed as 0.397. It was observed that appropriate concrete curing is not likely to occur significantly below or above 0.397 in this composite. Most investigators appear to have agreed with the observation that complete hydration cannot occur if w/c is below a value in the region of 0.38, although Rossler and Odler reported that hydration was complete in a paste with w/c = 0.22 (Taylor, 1990).

Table 2.14

Ordinary concrete compositions and results of mechanical tests

Total weight: 3717g **w/c: 0.397**	**Ordinary cement** **Weight (g) / (%)**
Water	417 / 11.22
Cement (Type I & II)	1050 / 28.25
Sand	2250 / 60.53
Compressive strength (psi)	4135
Tensile strength (psi)	447

Too much water or too little water does not add to the strength of a concrete structure. If a paste having w/c < 0.38 is cured under sealed conditions, there will be insufficient water fill the gel pores completely, and the capillary pores will be empty. The effective RH (relative humidity) will be low, and hydration will become very slow or stop, even though free space remains. This phenomenon is called self-desiccation. Even at higher w/c ratios under sealed conditions, partial emptiness of pores and bleeding effect will interrupt the hydration and produce irreversible changes in pore structure, which will reduce the final strength. It is therefore important to provide an adequate amount of water for complete curing.

Compressive strength is correlated to tensile strength. Interestingly, CBC composite shows relatively high tensile strength in CBCs, considering the equation below.

$$f_t = \alpha\sqrt{f_c} \quad (\alpha \approx 4) \qquad [2.4]$$

Where, f_t (psi) : tensile strength

f_c (psi) : compressive strength

Based on the equation 2.4, the tensile strength of CBC 1 would be 281 psi. In fact, tests show that CBC 1 can have more than double its strength to 576 psi. So, the CBC composite mix gives higher tensile strength in composite, indicating the mixing ratio is plausible in providing reasonable strengths.

2.7.2.2

Encapsulation of Lead by Xanthan Gum

As a result of the rigid helical conformation, viscosity of xanthan gum is relatively insensitive to differences in ionic strength and pH, which explains for the low leaching of lead in CCX composite. In other words, protection of backbone by the side chains results in the superior stability of xanthan gum compared to other polysaccharides when exposed to acids, alkalis, and enzymes. Also, xanthan gum showed outstanding characteristics of metal uptake, low permeability, and high shear strength among such biopolymers as xanthan, chitosan, polyhydroxybutyrate, guar gum, and polyglutamic acid (Etimadi, O., et al., 2002).

Xanthan gum is giant, high-molecular weight compounds ($2 \times 10^6 - 20 \times 10^6$ Da) in repeated sequences, hence simple functional groups become multiple reactive sites providing ample opportunities for chemical and physical reactions to take place. These reactions cause the crosslinking capacity. Depending on specific functional groups such as CH_2OH, OH, O, COOH, and H in the structure of monomer, xanthan gum is able to bind metals by structuring a coordination model which can wrap Pb in all binding connections from functional groups surrounded, shown in Figure 2.17. Eventually, this coordination model attaches onto sand and cement particles by creating stable interpenetrating cross-linking networks. Since metals can form complexes with the functional groups of organic compounds, if there is more than one functional group, functional groups can chelate with metals (Yen, 1999). For instance, lead has a high affinity for oxygen, sulfur, and nitrogen in chelating process so that it can easily click with lone pair in oxygen in biopolymer. It appears that biopolymer, xanthan gum, containing lead is quite resistant to microbial attack because it was observed that xanthan gum was hardly deteriorated by microorganisms after xanthan gum (0.1%) in column pack with sand was run through with 5,000 mg/L lead, meaning that complex between lead and biopolymer becomes stabilized. In addition, polymer functions as the adhesive in a predominantly calcium carbonate matrix (Glass, 1986), showing that xanthan gum can also glue lead onto the cement molecules in CCB composite. In the illustration of Figure 2.17, biopolymer is introduced to bind metal (Pb) on one side of itself in coordination structure, and have sand or cement particles attached on the other side of itself, creating a crosslinked composite.

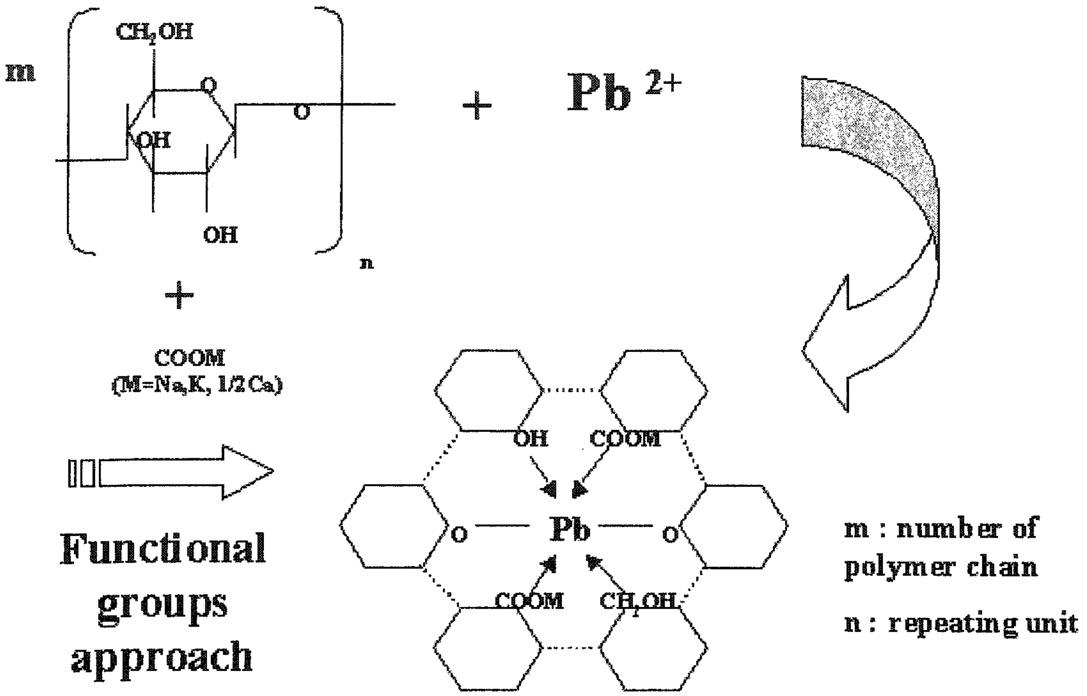


Figure 2.17 Coordination model of lead stabilization in xanthan gum.

Guar Gum

2.7.2.3 Results of Guar Gum and Discussion

Table 2.15

CBC compositions and results of guar gum

	CBC 5 G.G. 0.1% (70g) Weight (g) / (%)	**CBC 6** G.G. 0.5% (70g) Weight (g) / (%)	**CBC 7** G.G. 0.1% (417g) Weight (g) / (%)
Water	347 / 9.34	347 / 9.34	---
Cement	1050 / 28.25	1050 / 28.25	1050 / 28.25
Sand	1900 / 51.12	1900 / 51.12	1900 / 51.12

Table 2.15 continued

CRT glass	350 / 9.42	350 / 9.42	350 / 9.42
Guar gum solution	70 / 1.88	70 / 1.88	417 / 11.22
TCLP (mg/L)	0.283	0.247	N/D
Compressive strength (psi)	5452	4772	3470

N/D: Non-detectable

Table 2.15 shows composite mix of guar gum, also tested for TCLP and compressive strength. All specimens were cured for seven days, as well. Specimens blended with guar gum were very dark in color unlike ordinary concrete which is normally in whiter color, meaning that some reaction was observably initiated for biopolymer composite. CBC 5 and 6 showed enough strength for construction material, when comparing with ordinary concrete. Amazingly, CBC 5 showed the most compressive strength among all CBC samples, 32 % higher strength than ordinary concrete. For the TCLP, they are all below 5 mg/L of lead leachability. CBC 7 has no value of lead leaching, mixed with 417 g of 0.1 % guar gum solution. However, CBC 7 presented weak compressive strength, attributable to low w/c ratio, which may interfere with the occurrence of chemical reaction in concrete. This result is in accordance to that of xanthan gum, mixed in 417 g of 0.1 % or 0.5 % xanthan gum solution.

2.7.2.4

Encapsulation of Lead by Guar Gum

Guar is a naturally occurring polysaccharide composed of a linear backbone of (1-4)-β-linked D-mannose units with (1-5)-α-linked D-galactose units randomly attached as side chains. These side chains are hairy and backbone chains are smooth. They include functional groups: CH_2OH, O, H, and many OH groups both from *trans*-hydroxyls (mannose) and *cis*-hydroxyls (galactose). Especially, many OH groups can be available for crosslink reaction with borate ion from boric acid. They form a strong chain interaction through the inter- and intra-molecular junction zones. Seen in Figure 2.18, different functional groups approach the Pb to connect each other in coordination structure. Ultimately, this coordination model attaches to concrete and creates a three-dimensional interpenetrating cross-link network, similar to xanthan gum.

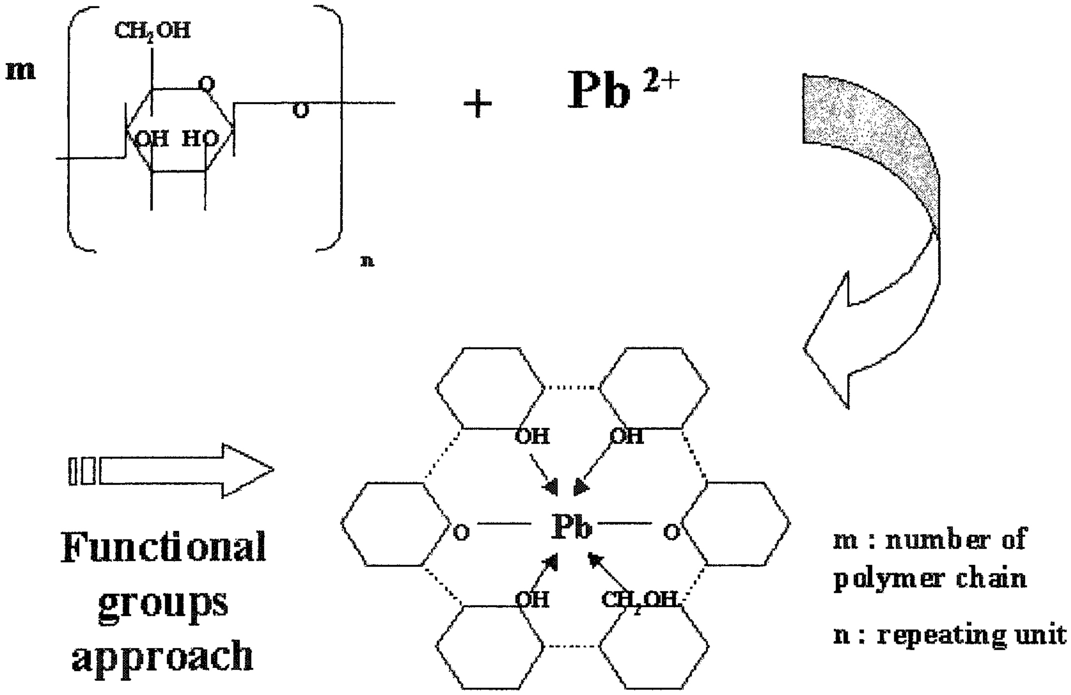


Figure 2.18 Coordination model of lead stabilization in guar gum.

Chitosan

2.7.2.5 Results of Chitosan and Discussion

Table 2.16

CBC compositions and results of chitosan

	CBC 8 Chitosan 0.1% (70g) Weight (g) / (%)	**CBC 9** Chitosan 0.5% (70g) Weight (g) / (%)	**CBC 10** Chitosan 0.1% (417g) Weight (g) / (%)
Water	347 / 9.34	347 / 9.34	---
Cement	1050 / 28.25	1050 / 28.25	1050 / 28.25
Sand	1900 / 51.12	1900 / 51.12	1900 / 51.12
CRT glass	350 / 9.42	350 / 9.42	350 / 9.42
Chitosan solution	70 / 1.88	70 / 1.88	417 / 11.22
TCLP (mg/L)	0.152	0.097	N/D
Compressive strength (psi)	5213	5339	3688

N/D: Non-detectable

Composite with chitosan was made the same way that other biopolymers such xanthan and guar gum were. Table 2.16 shows composite mix of chitosan and results of TCLP and compressive strength. CBC 8 and 9 showed high compressive strengths while CBC 10 showed relatively low strength because of water shortage for strong cement. Interestingly, CBC 9 showed high compressive strength, compared with CBC 2 (4673 psi) and CBC 6 (4772 psi), showing 32 % higher strength than ordinary concrete. Xanthan and guar gum both showed the decrease of strength with increasing concentration of biopolymer from 0.1% to 0.5%. This is explained by that xanthan and guar gum are viscous materials that need a certain amount of water to keep their structure, hydrogel. On the contrary, chitosan dose not show viscosity even at high concentration, 0.5%. Therefore, it cannot be concluded that viscosity of biopolymer is related to strength of concrete composite, as postulated. Instead, water ratio is very significant factor in building strong concrete composites in this study. For the TCLP, they are all recommendable, under 5 mg/L of lead leachability. CBC 10 has no lead leaching, mixed with 417 g of 0.1 % chitosan solution.

2.7.2.6

Encapsulation of Lead by Chitosan

Metal capture by chitosan has been widely known in industry because chitosan has a natural selectivity for heavy metal ions. In particular, chitosan is useful for biosorption process and the treatment of wastewater containing heavy metals. Mckay et al. (1989) used chitosan for the removal of Cu^{2+}, Hg^{2+}, Ni^{2+}, and Zn^{2+}. Nair and Madhavan (1984) used chitosan for the removal of mercury from solutions. Jha et al. (1988) studied the adsorption of Cd^{2+} on chitosan powder using various particle sizes. Maruca et al. (1982) made use of chitosan flakes of 0.4-4 mm for the removal of Cr(III) from wastewater. From a number of literatures it is clear that chitosan is plausible material to remove numerous metals (Cu (II), Pb(II), U(VI), Cr(III), Cr(VI), Ni(II), Cd(II), Zn(II), Co(II), Fe(II), Mn(II), Pt(IV), Ir(III), Pd(II), V(V), and V(IV) from heavy metal sources (Schmuhl, 2001). These kinds of metal uptake results from the functional groups like many hydrogen bonds, hydroxyl and amino groups, which function actively in the inter- and intra-molecular structure between adsorbent, adsorbate, and biopolymer.

According to the mechanism of metal uptake by Findon et al. (1993) and Chui et al. (1996), Pb is chelated with the NH_2 and NH groups in the chitosan chain and chitosan, amino sugar, is the major effective binding sites for metal ions, forming stable complexes in coordination. In other words, nitrogen electrons present in the amino and N-acetylamino groups can establish dative bonds with transition metal ions, as well as other functional bonds like oxygen, alcohol, and some hydroxyl groups in this biopolymer may function as donors. Hence, all binding groups in chitosan can build up coordination model, which can stabilize Pb in the strong form of wrapping structure, shown in Figure 2.19.

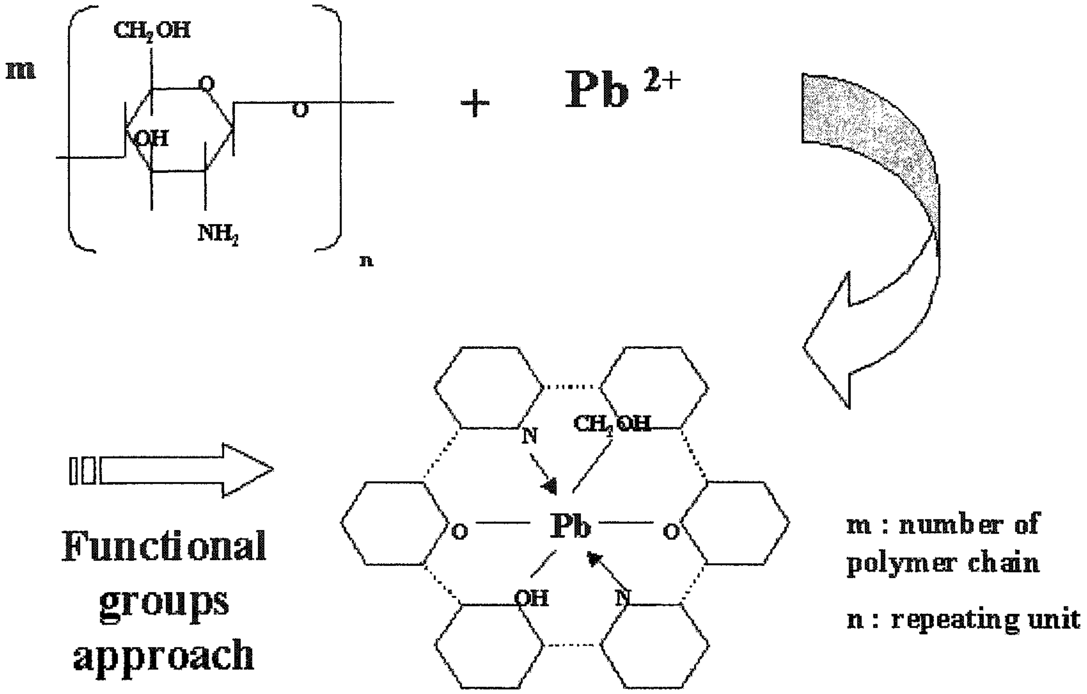


Figure 2.19 Coordination model of lead stabilization in chitosan.

The processing of crustacean shells mainly involves the removal of proteins and the dissociation of calcium carbonate which is present in crab shells in high concentrations. Structurally, chitosan is very strongly crosslinked with calcium carbonate encasing the crustacean shells, which can be supported by Glass (1986) that in many life forms, polymer works as the adhesive in a calcium carbonate matrix. Likewise, chitosan can make coordination structures with cement that is rich in calcium carbonate. For this reason, as well as other reasons like the functional groups found in chitosan, the phenomena of lead stabilization in CBC composite with chitosan can occur.

Guar Gum and Boric Acid

2.7.2.7 Results of Guar Gum and Boric Acid and Discussion

Table 2.17

CBC compositions and results of crosslinked solution (guar gum and boric acid)

	CBC 11 G.G & boric solution 0.1% (70g) Weight (g) / (%)	**CBC 12** G.G & boric solution 0.1 % (417g) Weight (g) / (%)
Water	347 / 9.34	---
Cement	1050 / 28.25	1050 / 28.25
Sand	1900 / 51.12	1900 / 51.12
CRT glass	350 / 9.42	350 / 9.42
Crosslinked solution	70 / 1.88	417 / 11.22
TCLP (mg/L)	N/D	0.1480
Compressive strength (psi)	5047	5018

N/D: Non-detectable

Composite was mixed with crosslinked solution made of guar gum and boric acid at volume ratio of 4 to 1. Table 2.17 presents the proportion of mix and results of TCLP and compressive strength. Both of CBC 11 and 12 showed high compressive strengths.

For CBC 12 mixed in 417 g of polymer solution, it shows higher compressive strength, compared to CBC 3 (4133 psi), CBC 7 (3470 psi), and CBC 10 (3688 psi). This can be explained by that the property of guar gum has changed to that of crosslinked gel where water needed for guar gum may be transferred to water for C-S-H in cement. In this sense, strong concrete can occur without adequate water for composite with guar and boric. Regarding the TCLP, CBC 11 and 12 are permissible, under 5 mg/L of lead leachability. CBC 11 has no lead leachability.

2.7.2.8

Encapsulation of Lead by Guar Gum and Boric Acid

The reaction between guar and boric acid is dependent on pH and temperature. The reaction favors a weak base (pH=9) and avoids high temperature. As seen in Figure 2.20, viscosity of crosslinked solution drastically increased over pH 9, although small increase of viscosity was also observed when increasing concentration of crosslinking agent 0.1% to 0.5%. It is obvious that crosslinking reaction in guar and boric was caused by pH manipulation. The pH value of composite automatically pops up when mixing with cement paste, containing plenty of alkaline materials, which can be advantageous of putting CRT glass into concrete, mixed with crosslinked biopolymer solution. Concerning temperature, composite is built at room temperature, meaning that temperature outside of the composite dose not affect the crosslinking phenomena, except for cement mixing temperature occurring inside of composite. As mentioned, this temperature may be beneficial to the formation of homogenous mix of composite.

Thus, this kind of favorable environment to crosslink reaction is able to secure a good number of crosslinks between guar gum (hydroxyl groups) and boric acid (borate ions) in CBC composite.

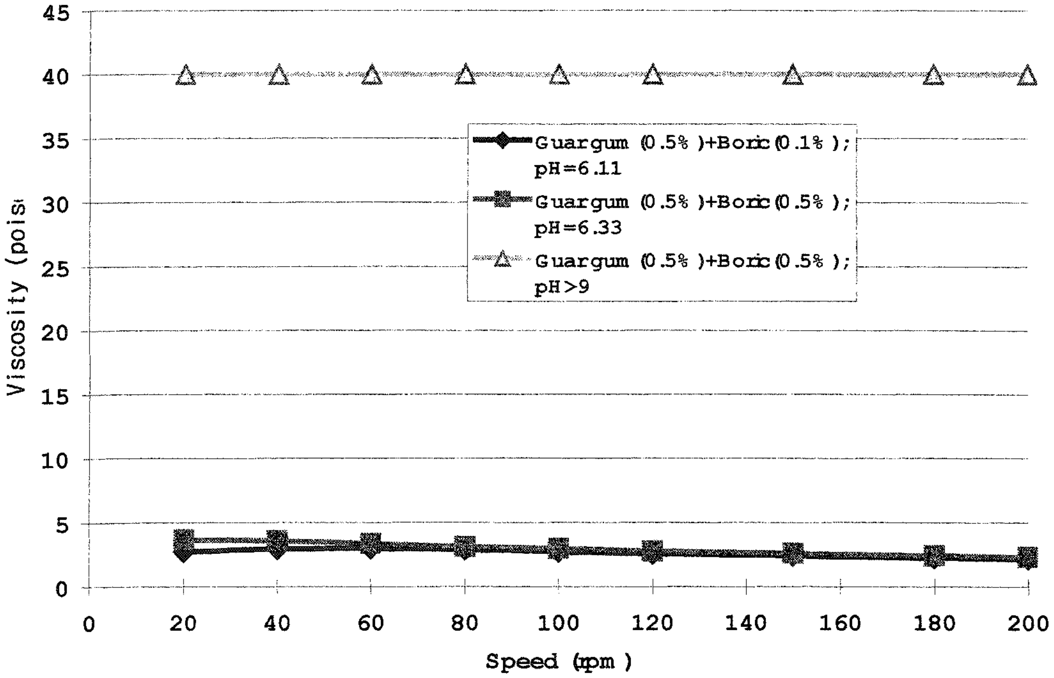


Figure 2.20 Viscosity change of crosslinked solution of guar and boric.

Xanthan and Guar Gum

2.7.2.9 Results of Xanthan and Guar gum and Discussion

Table 2.18

CBC compositions and results of crosslinked solution (xanthan and guar gum)

	CBC 13 X.G & G.G solution 0.1% (70g) Weight (g) / (%)	**CBC 14** X.G & G.G solution 0.1 % (417g) Weight (g) / (%)
Water	347 / 9.34	---

Table 2.18 continued

Cement	1050 / 28.25	1050 / 28.25
Sand	1900 / 51.12	1900 / 51.12
CRT glass	350 / 9.42	350 / 9.42
Crosslinked solution	70 / 1.88	417 / 11.22
TCLP (mg/L)	N/D	0.2529
Compressive strength (psi)	5446	3068

N/D: Non-detectable

Crosslinked solution of xanthan and guar gum was utilized for composites CBC 13 and 14 in Table 2.18. In terms of compressive strength, CBC 13 showed the second strongest strength, whereas CBC 14 showed the least strength among all CBC composites. The volume ratio of xanthan and guar gum was 4:1. Crosslink reaction occurred due to crosslinking property of blending two different polymers. In fact, xanthan or guar gum is not crosslinking agent but it can play the role of crosslinking agent. Crosslinking property is remarkably reduced in CBC composite when amount of crosslinked solution is increased. CBC made a very weak composite with 26 % reduced strength of compression. When comparing CBC 14 in crosslink with polymer and CBC 12 in crosslink with agent, CBC 12 showed very high strength although it was made in high volume of solution (417 g). Mostly, CBCs mixed in 417 g of solution showed weak strength, regardless of type and concentration of polymer. Borate ions do not need certain amount of water to keep it in shape unlike xanthan and guar gum. For this reason, blending two polymers showed same weakness as high volumes of polymer solution used in other polymers like CBC 4, 7, and 10. As for TCLP, CBC 13 and 14 are benign to humans and the environment, below 5 mg/L of lead. CBC 13 has no lead leachability.

2.7.2.10

Encapsulation of Lead by Xanthan Gum and Guar Gum

The trisaccharide branches of xanthan gum appear to be closely aligned with the polymer backbone, so that the resulting stiff chain may exist as a single, double, or triple helix, which can interact with other polymer molecules to form a complex. As a result, xanthan and guar gum mix can give synergic effect of connecting xanthan gum to unsubstituted mannose regions (smooth part) of guar gum, and bind metal ions onto concrete microstructure.

Combination of xanthan and guar gum takes advantage of their functional groups available, provided by both polymers, meaning that the effect of combination is more than that of a single polymer used. The crosslinked structure occurred by these polymers is likely to contain a larger number of functional bridges to reach the target metal. So, the crosslinking effect is lucid.

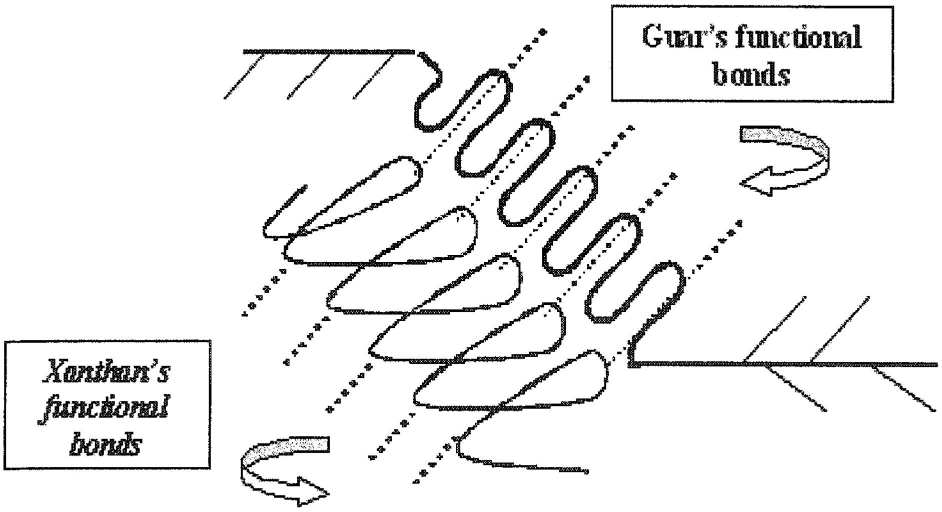


Figure 2.21 Crosslinked copolymer containing functional groups from both biopolymers.

2.7.3 Overall Results and Discussion

2.7.3.1 Overall Results and Discussion

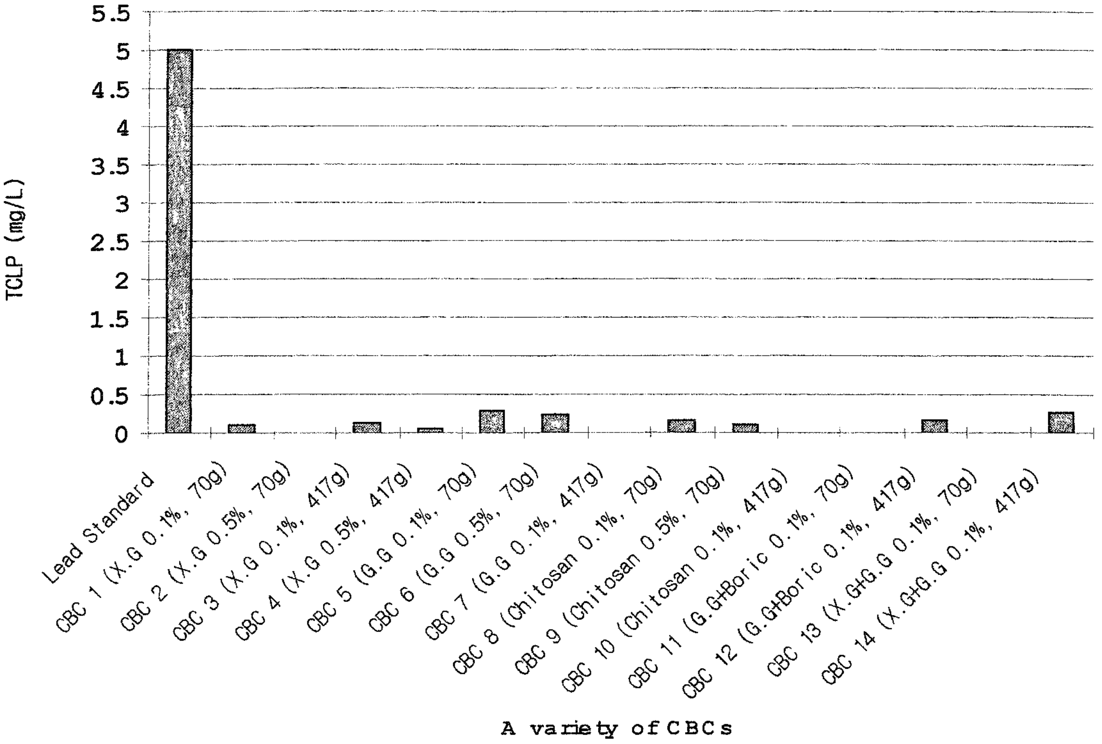


Figure 2.22 TCLP Results of CBCs.

In terms of TCLP results, all products of CBC composites are harmless to humans and the environment because all are under the standard of lead, 5 mg/L. Some composites showed no lead leaching at all. They are CBC 7 (guar gum 0.1%, 417g), CBC 10 (chitosan 0.1%, 417g), CBC 11 (guar gum 0.1% and boric 0.1%, 70g), and CBC 13 (xanthan 0.1% and guar gum 0.1%, 70g). CBC 11 and 13 showed very high compressive strength while CBC 7 and CBC 10 did not present enough strength, rather weaker than ordinary concrete strength. With respect to this result, TCLP results are more related to chemical reaction and mechanical result, like compressive strength is related to physical reaction. Biopolymer reaction is mainly associated with leaching result, TCLP, so long as biopolymer may bind metal, Pb. Addition of biopolymer regardless of specific amount in this study certainly resulted in a sharp decrease of lead, considering initial concentration of lead content (several thousand ppm and initial TCLP) in CRT glass.

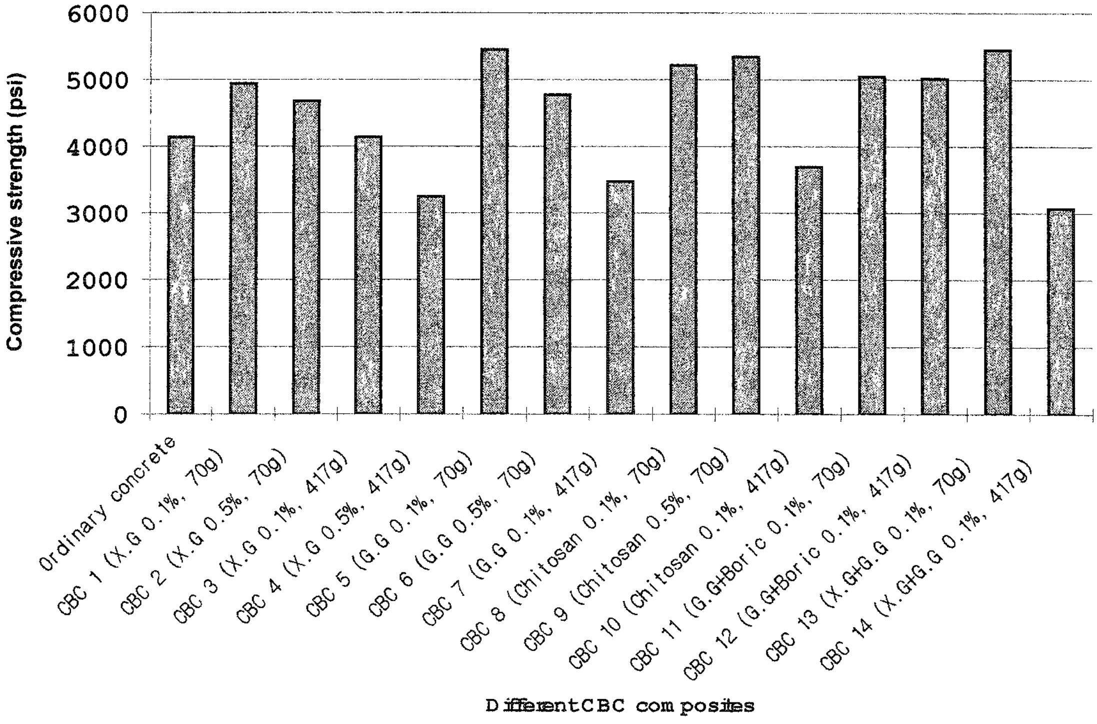


Figure 2.23 Comparison of compressive strength of CBCs.

Adding biopolymer and crosslinked solution in concrete composite helped increase the strength of composite, referring to CBC 1 (xanthan 0.1%, 70g; 4938 psi), CBC 2 (xanthan 0.5%, 70g; 4673 psi), CBC 5 (guar 0.1%, 70g; 5452 psi), CBC 6 (guar 0.5%, 70g; 4772), CBC 8 (chitosan 0.1%, 70g; 5213 psi), CBC 9 (chitosan 0.5%, 70g; 5339 psi), CBC 11 (guar 0.1% and boric 0.1%, 70g; 5047 psi), CBC 12 (guar 0.1% and boric 0.1%, 417g; 5018 psi), and CBC 13 (xanthan 0.1% and guar 0.1%, 70g; 5446 psi). Especially, crosslink causes very high strength for both CBC 11 and 12, regardless of volume of biopolymer solution. However, weak strength of compression was observed in excessive amount (417g) of polymer and crosslinked solution in cases of CBC 4 (xanthan 0.5%, 417g; 3242 psi), CBC 7 (guar 0.1%, 417g; 3470 psi), CBC 10 (chitosan 0.1%, 417g; 3688 psi), and CBC 14 (xanthan 0.1% and guar 0.1%, 417g; 3068 psi).

Water ratio in cement is a key parameter in determining the strength of CBC composites. Adequate strength could not be obtained until water was supplied to build fundamental concrete structure, regardless of an increase in biopolymer concentration. The capacity of the hydrogels, biopolymer solution, to absorb water is enormous and can be as much as 1000 times the weight of the polymer (Glass, 1989). One liter of water (0.1%; 1g in 1 L of water) may barely be adequate to have complete solublized polymer solution. This is especially true for viscous polymers, like xanthan and guar gum, which cannot acquire high strength even though their polymer concentration becomes five times higher (0.1% to 0.5%), in CBC 1, 2, and CBC 3, 4, and CBC 5, 6 except for CBC 8 (chitosan 0.1%, 70g) and CBC 9 (chitosan 0.5%, 70g), containing low viscosity of polymer solution. Therefore, one type of characteristics of biopolymer solution, viscosity, is not favorable to increase composite strength. The viscosity of polymers is shown in Figure 2.24.

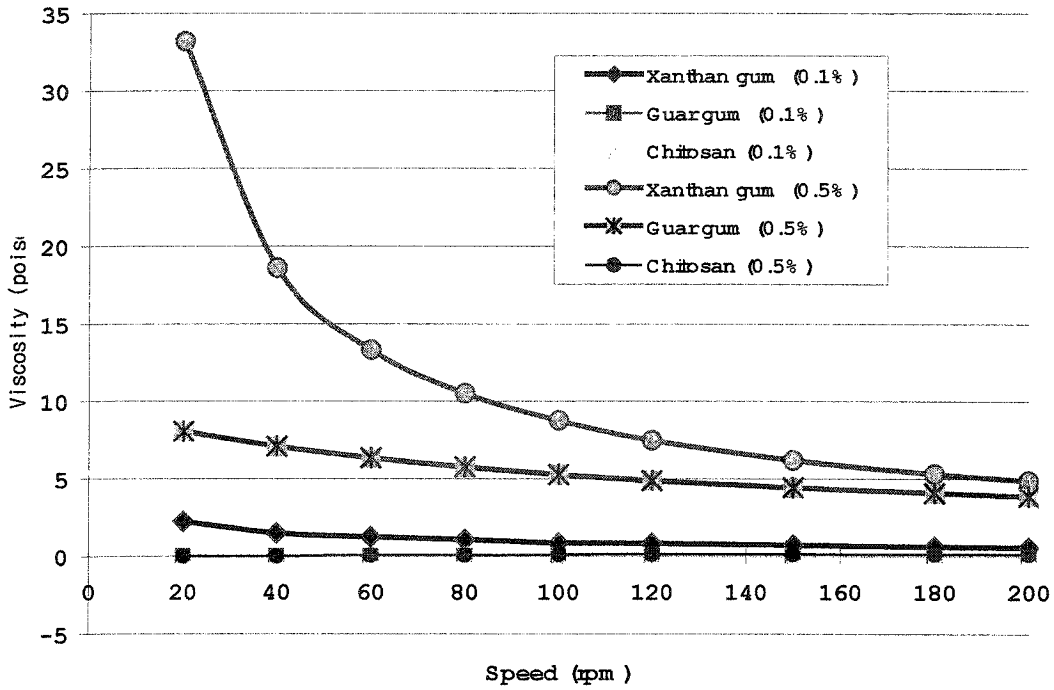


Figure 2.24 Viscosity of different biopolymers at concentrations 0.1 and 0.5%.

Difference of strength in CBC composites may be explained by comparison of compressive stress curve. Guar gum (Figure 2.25) and xanthan gum (Figure 2.28) at a concentration of 0.1% with volumes of 70 g and 417 g showed identical curves, meaning that those composites conform to the regular concrete curve. Figure 2.26 showed no difference in curve shape between low and high volume of biopolymer solutions used for biopolymer crosslinked composites. In Figure 2.27, three curves overlapped each other in a typical form of well-cured concrete. Three curves represent pure biopolymer composite (CBC 5), agent-crosslinked composite (CBC 11), and biopolymer-crosslinked composite (CBC 13). Good curing composites showed very similar trend of stress curve.

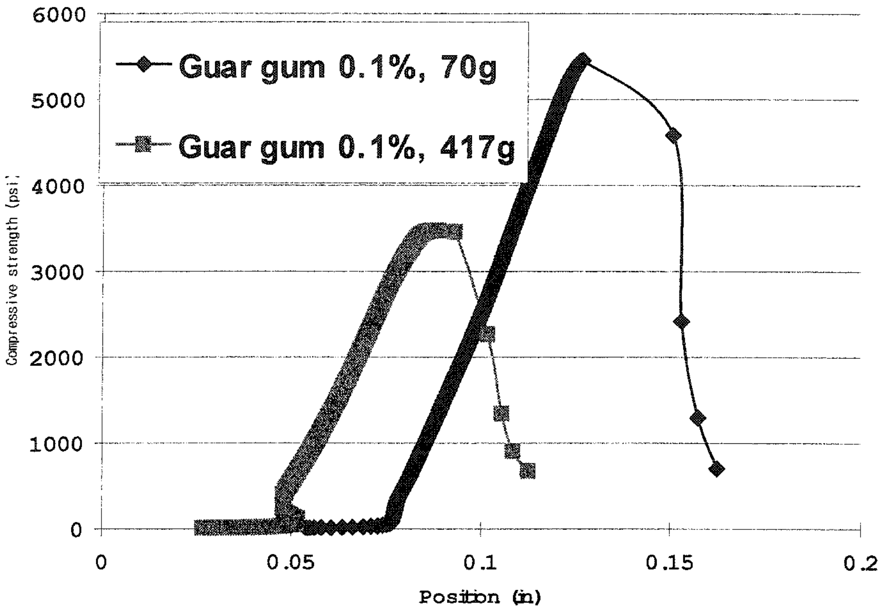


Figure 2.25 Compressive stress curve for guar gum CBC 5 and 7.

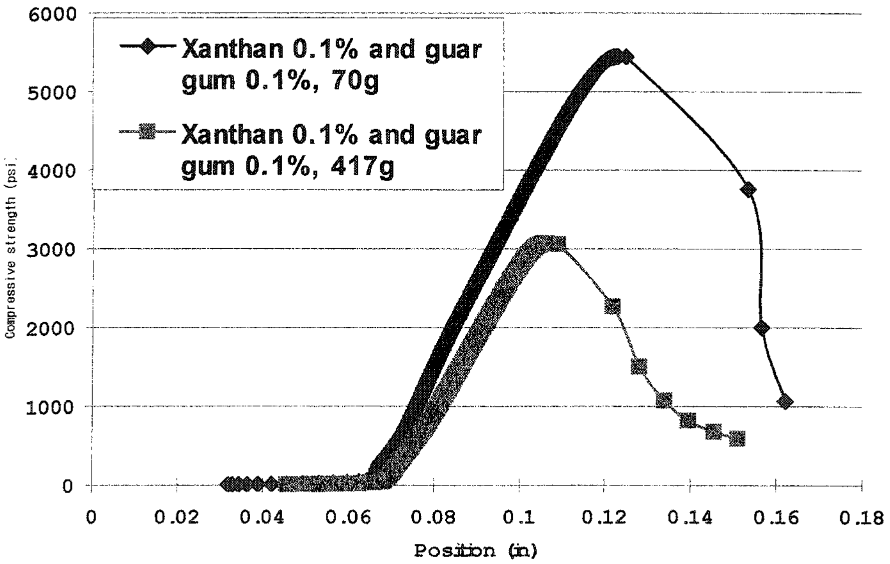


Figure 2.26 Compressive stress curve for xanthan and guar CBC 13 and 14.

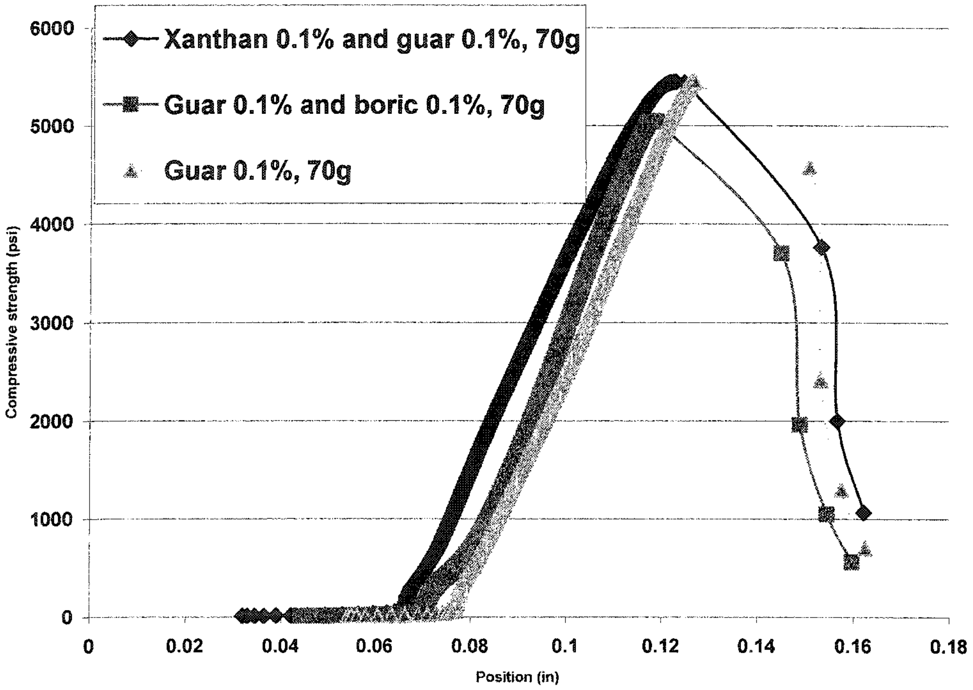


Figure 2.27 Compressive stress curve for CBC 5, 11, and 13.

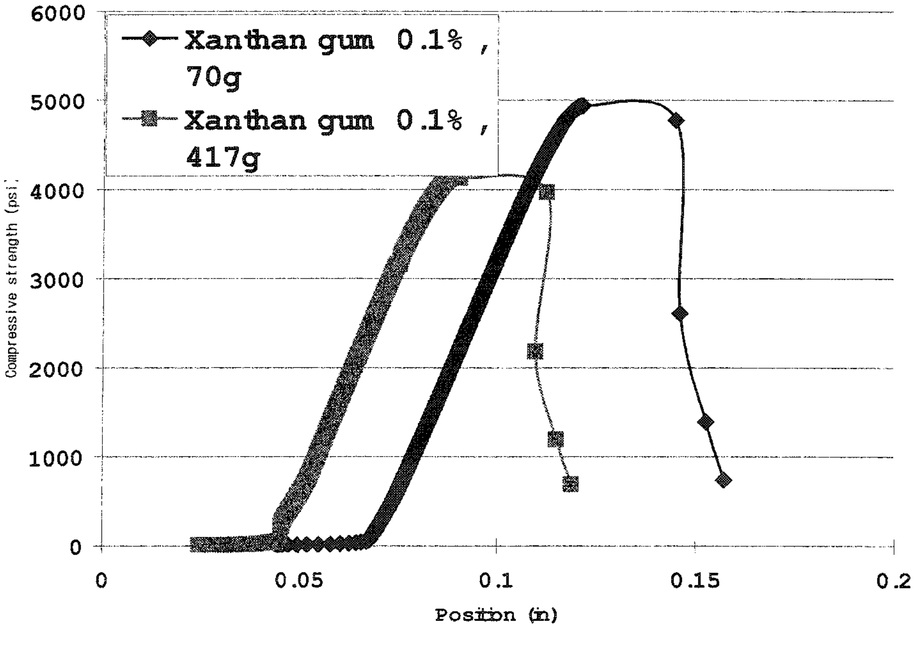


Figure 2.28 Compressive stress curve for CBC 1 and 3.

2.7.3.2

Encapsulation of Lead in Crosslinked Structure by Biopolymers and Crosslinking Agent

The removal of Cu and Al by humic complexes onto tobermorite was studied by Japanese researchers (Kaneco et al., 2003). They investigated the promotion of a surface-metal-humic substance caused by bridging process so that metal/humic acid complexes were effectively removed by adsorption onto tobermorite. They made use of humic material as function of biopolymers, similar to our study, giving the encapsulation-effect between tobermorite (type of silica rock) and target metals. Because humic materials with relatively large molecular weight contain a large number of reactive groups such as carboxylic and phenolic groups, they can induce the chelation with metal as well as the attachment of metal/humic complexes on the silica rock.

Similarly, it may be understood that biopolymers can attach the metal onto the concrete, as mentioned earlier. Figure 2.29 summarizes how lead from CRT waste can be bound inside of concrete structure. Composite is crosslinked by biopolymer. The involvement of functional groups is essential for this crosslink reaction to take place. Gigantic molecular polymers provide ample chemical sites for lead to bind onto concrete structure. As seen, a biopolymer is placed between lead and concrete, helping the bridging reaction. Many different functional groups and bindings owned by xanthan gum, guar gum, and chitosan spread themselves along the backbone of polymers in intra- and intermolecular three- dimensional coordination. This crosslinked composite will potentially become a geopolymer over the years. In such a manner, bounded metal becomes chemically and physically trapped and stabilized in a geopolymerized step and will not be leached out.

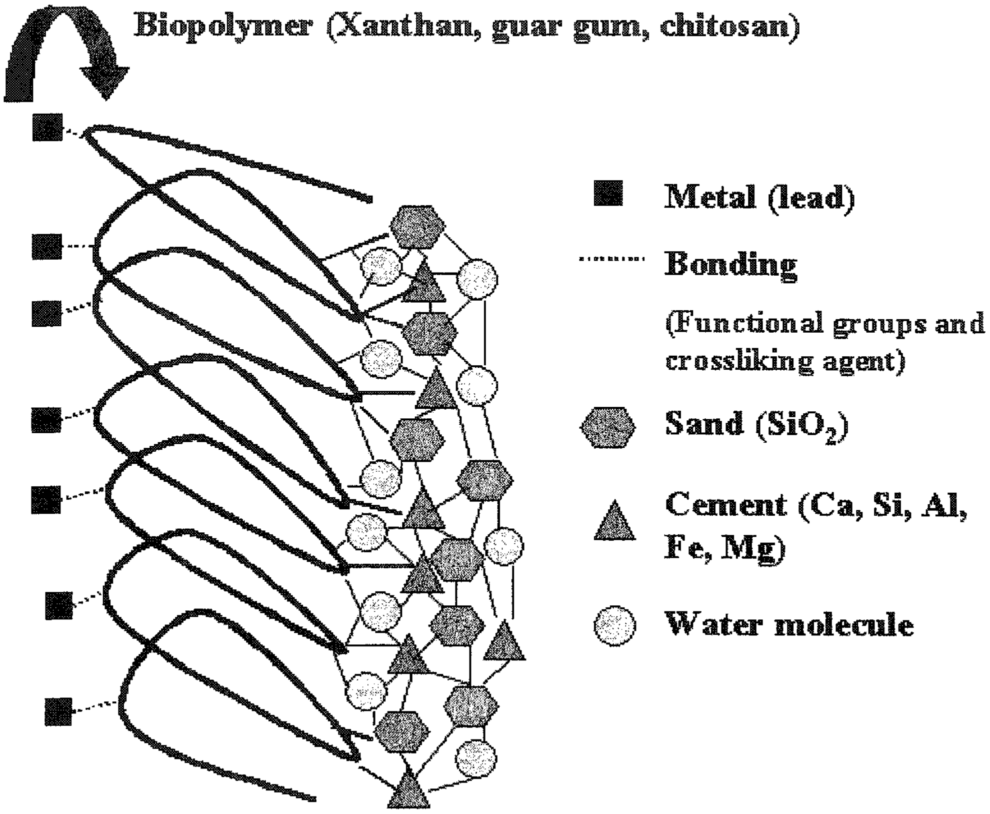


Figure 2.29 Simplified diagram of crosslinking structure in CRT-Biopolymer-Concrete (CBC) composite.

The formation of geopolymer from biopolymer (or biomass) is complex and involves many steps. Over time, biopolymers interacting with metal will eventually form geopolymers, which in this case, form kerogen. Geopolymers thus formed are useful in this study because they are thermally and mechanically stable under many conditions. They do not pyrolyze below 400°C, they are protective and waterproof (under conditions of $K \ll 10^{-12}$ cm/s). They can be used as reactor coolants (in the case of oligophenylenes) and are stable in concentrated acids, such as HF, HCl, and H_2SO_4. Most importantly, metals trapped in geopolymers cannot be leached in the presence of an aggressive liquid in the geosphere. The concept of the accelerated formation of geopolymers used to treat the contaminated sites or toxic metals will assist in stabilizing the metals and preventing the metals from being leached out under extreme conditions in nature.

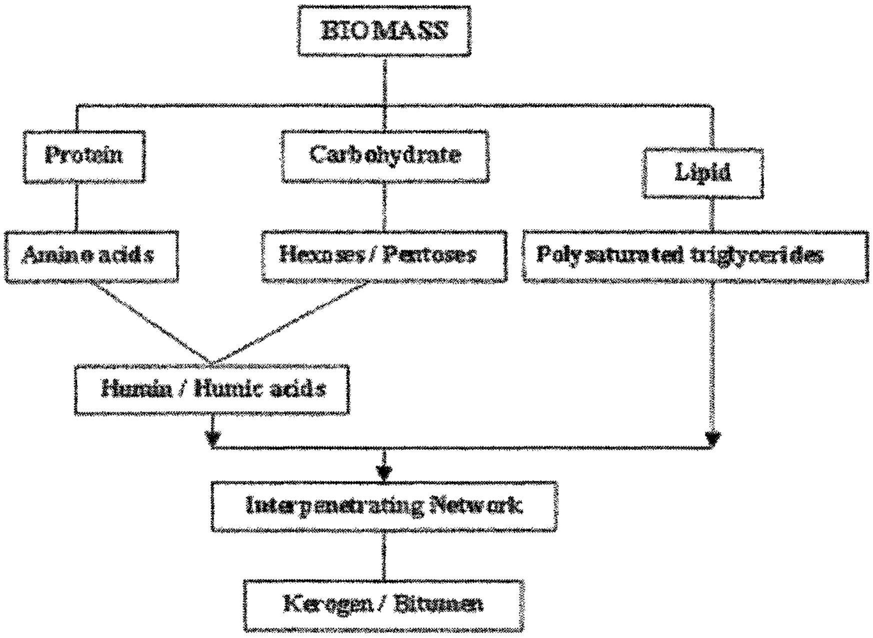


Figure 2.30 Formation of geopolymer (kerogen) from biomass.

2.8 Conclusions

In this study, the leaded glass from CRTs, using the intra- and inter-crosslinking power of xanthan gum, guar gum, and chitosan was transformed into safe, non-toxic, non-hazardous products with possible applications such as foundation and building materials for construction, environmental barriers as an encapsulation matrix to prevent the leaching of metals and nuclear wastes from landfills, decorative tiles, and X-ray shielding products.

In general, CBC (CRT-Biopolymer-Concrete) composites showed competitive compressive and tensile strengths, compared to those of ordinary concrete mixtures. Some crosslinked composites showed more than 30% higher strength in the best workable performance. CBC composites proved very consistent in the results of compression test. CRT glass can replace sand in the CBC composite, knowing that addition of CRT glass has become part of phase of cement simply containing 67% CaO (alite), 22% SiO_2 (belite), 5% Al_2O_3 (aluminate), and 3% FeO_3 (ferrite). Apart from this, CRT glass is very close to sand material in terms of chemical structure. CRT glass and concrete materials are compatible one another.

The results of leaching tests showed a considerable decrease in Pb leachability, less than 5 mg/L or below 0.75 mg/L. Some composites showed the leachable lead below the drinking water or groundwater standard of 0.005 mg/L of lead. Such low leaching will be expected to remain the same or decrease throughout geopolymerization steps for many years. It is not necessary to add large amounts of biopolymer solution in order to obtain high strengths of composite and low leachability of lead. In this study, for example, a very minute amount of 70 mg or 417 mg of biopolymer in 3717 g of concrete can be translated into a pure biopolymer in the range of 18-107 ppm by weight in terms of composite. Yet, this minute amount of biopolymer is effective in binding Pb and giving high strength of workable composite.

CHAPTER III

Selenium Biopolymer Concrete

Encapsulation of Selenium Wastes in a Biopolymer-modified Concrete System

3. Selenium Biopolymer Concrete

3.1 Introduction

An innovative solidification/stabilization technology so-called biopolymer modified concrete was recently developed and proved efficient in the treatment of cathode ray tube glass containing Pb (Kim et al, 2003). The technology uses the ability of biopolymers to bind to cement and to metals acting as an adhesive and improving the general mechanic characteristics of concrete. Cement usually contains oxides of Ca, Si, Al and Fe which can form hydrogen bonds with biopolymer's amino, hydroxyl, carbonyl, and carboxylic repetitive groups during hydration. Based on this principle, hazardous waste material can be entrapped in the biopolymer-modified concrete system that prevents the leaching of contaminants. Moreover, the obtained concrete may prove similar or even better in mechanic characteristics as compared to ordinary concrete and could be used for buildings, road pavements, etc. The improvement of the mechanical strength of concrete by the addition of small amounts of biopolymer is justified by the creation of physical and chemical binding between the biopolymer repetitive functional groups and the cement particles. Based on the described principle, a series of tests were conducted to check the feasibility for encapsulation of the Guardian Industry's waste into such biopolymer-modified concrete with little or no leaching of Se.

The choice of certain biopolymers which were added in small percentage (0.1% concentration) to the concrete composites was based on their commercial availability, low cost and proven performance from our previous experiments related to encapsulation of Pb from CRT waste. Thus, chitosan showed the best results of lead immobilization for CRT waste disposal. Also, blending of two different biopolymers such as xanthan and guar gum may present the advantage of the synergic effect of crosslink reaction with increase ability to improve the mechanical characteristics of the mixture (composite concrete). The purpose of experiments is to cope out environmental problems with selenium containing glass waste in a biopolymer-modified concrete and to find the best combination of waste and concrete materials with biopolymer solution.

3.2 Procedure of Experiment

In Table 1, the ingredient of concrete composite has three different options. Waste portion was tried at 1, 3, 5% of total weight of composite. Concrete composites were prepared at different ratios of sand and waste (selenium glass waste), and cured for 7 d in standard plastic cylinder case (4 in × 8 in). These cylinder concretes are to test in terms of compressive strength after 7 d curing. For most of waste based concretes, cement and water amount (or water and cement ratio) is appropriately fixed and other ingredients are variable. Water and cement ratio is 0.397 but letting waste to absorb water fully, considering the previous results that selenium waste inherently absorbs many folds of water added, as 417g including water and biopolymer solution water is not adequate.

Table 3.1 Composition of concrete composite (in gram)

	1% waste concrete	**3% waste concrete**	**5% waste concrete**
Waste (selenium glass powder)	37.17	111.51	185.85
Water	347	347	347
Cement (type I & II)	1050	1050	1050
Sand	2212. 83	2139	2064.15
Chitosan solution (0.1% conc.) or Xanthan gum + guar gum :(0.1% conc.)	70	70	70

3.3 Results and Discussion

3.3.1 Compressive Strength

As shown in Table 2, two different biopolymerized concrete composites showed different compressive strength, according to varied waste containments. Considering the strength of ordinary concrete, 4135 psi, 1% waste contained concretes are showing the plausible strength for both of chitosan and xanthan + guar concretes. In the case of selenium waste concrete, xanthan gum with guar gum showed higher strength than chitosan concrete for all different waste ratios. Particularly, 5% containing concretes are very weak and fragile. Therefore, it may not be reasonable to add more than 5% waste content by weight onto concrete mix. Optimum percentage of selenium waste content for making concrete composite would be around 1-2% by weight.

Table 3.2

Compressive strength of biopolymer-modified concrete containing different selenium waste proportions

Tests	**Biopolymer solution**	**Different waste content**		
		1% waste concrete	**3% waste concrete**	**5% waste concrete**
Compressive strength (psi)	Chitosan solution (0.1% conc.)	4787	2896	1615
	Xanthan gum + guar gum: (0.1% conc.)	5050	3481	1940
TCLP (mg/L)	Chitosan solution (0.1% conc.)	<0.15	2.62	8.48
	Xanthan gum + guar gum: (0.1% conc.)	<0.15	2.56	8.16

All specimen are in duplicate tests.

At the time being, 1% seems to be the best amount of waste to be added to the concrete mixture in order to obtain a final product with superior mechanical strength than ordinary concrete with potential marketable value.

3.3.2 Leaching of Selenium (TCLP)

From all the experimental concrete mixtures, only those with 1% waste addition passed the TCLP test for Se (1 mg/L EPA limit for hazardous waste) with non-detectable values of extracted Se (while the experimental limit was 0.15 mg/L). All other samples have higher concentration of selenium when being leached with acetic acid. It is pretty plausible if the consideration of initial concentration of selenium, 45900-46600 mg/kg, while the Se by TCLP test is between 65-68.8 mg/L was made. The leachability of Se was, as logically expected, increasing with the increasing in waste amount added to the mixture. The type of biopolymer added seems to have little or even no influence on Se leachability with only small differences recorded between composites with same waste percentage but different biopolymers added (xanthan + guar vs. chitosan). However, the addition of small amount of biopolymer products are considered crucial to obtain a concrete composite with superior mechanical strength as well as to prevent the leaching of Se. This is due to the creation of cross-linking between the biopolymer functional groups and the cement particles, creating thus networks that entrap the Se species inside.

3.4 Conclusions

A logical conclusion from these preliminary experiments is that the addition of a large percentage of Guardian waste to concrete is not viable for this type of waste with a high water demand that inhibits the cement reaction. For this reason, both the 20% and 30% waste composites have a number of pores inside of concrete (data not shown), unlike the property of CRT glass, which means the extra water amount was still not adequate. At this point, optimum water ratio and appropriate composition is the key to find the best results. A decrease in the percentage of Guardian waste to the concrete increased the mechanical strength of the resulted concrete composites, too. The optimum percentage of selenium waste content for making concrete composite is around 1-2% by weight. Such a composite has no se leachability and improved mechanical strength compared to ordinary concrete with subsequent marketable value.

CHAPTER IV

Biopolymer-Modified Concrete

New Concrete Composite Modified with Biopolymers

4. Biopolymer-Modified Concrete

4.1 Introduction

Biomaterials have been widely used in many applications. Among a list of biomaterials, biopolymers have drawn the most attention due to their versatile merits, being beneficial to a number of areas such as food, pharmaceutical, cosmetics, petroleum, agricultural, paper, textiles and so many industries. Biopolymers own different functional groups according to their types and characteristics. Biopolymers, xanthan gum and chitosan, used in this study, are very famous and useful in the food and pharmaceutical industry, since xanthan gum has many functional groups such as CH_2OH, OH, O, COOH, and H, while chitosan has such groups as CH_2OH, OH, O, NH_2 active. Those properties make biopolymers good binder and emulsifier. It was ascertained that this kind of biopolymers play an important role in binding metals and being chemical sites crosslinked, showing excellent removal of Pb from cathode ray tubes of computer monitors (Kim et al., AIChE 2003 conference).

A great deal of attempts was made to create new material based on cement and concrete. Utilizing biopolymer in concrete system is very new attempt. Efforts to increase the strength of concrete, in particular, have been made through years. In many ways, the waste based or synthetic polymer concrete composite have been prevalent, indeed, made an improvement of concrete materials. However, those materials may be in the category of hazardous materials after use to be required for disposal or special treatment with extra expense. Biopolymers used are in food grade and very safe to human and environment, so that biopolymerized concrete dose not need any costly method to dispose of.

Simple compressive tests support that addition of biopolymer solution result in the increase of concrete strength, as waste based concrete composite modified with biopolymer showed very high strength (Kim et al., 2003). With the help of XRD analysis, biopolymerized concrete turned out to be a new class of mineral that was depicted in the concept of geopolymer (ACS Long Beach 2003). This new type of material can belong to new definition of geopolymer that contains both organic and inorganic, which will last long and come to the permanent stabilization in the nature.

The objective of this study is to affirm that the small amount of biopolymer solution is able to increase the strength of concrete, using the benign material instead of possible toxic waste or modified concrete with synthetic materials, and to characterize the new class of geopolymer.

4.2 Experimental Procedure

4.2.1 Materials and Methods

The experiment was designed to focus on the best combination of composites to give the most compressive strength. Cube and cylinder tests were performed. The samples were cast in cube mold with the size of 2 in. × 2 in. made of metal alloy, allowed to set for 24 h at room temperature before being removed from the metal molds, and kept for another 6 days in water chamber at room temperature. Cylinder cast is 4 in. × 8 in. plastic mold. All specimens for cylinder concrete were made and cured for seven days. Each sample of composite was tested in triplicate and for compressive strength using Instron 5592, Satec. X-ray powder diffractograms were obtained using a Rigaku Geigerflex X-ray diffractometer with Cu Kα radiation generated at 30 mA and 40 kV. Specimens were step-scanned as random powder mounts from 5 to 70° 2θ at 0.02° 2θ steps integrated at the rate of 0.3 s per step.

Biopolymer-modified concrete composites (BCC) were built at different portions of biopolymer solution and water content, with other portions remaining constant. Biopolymer solution, 0.1% for both biopolymers, was added by weight as 2, 5, 8, and 11% of total weight (Table 4.1). 11% of biopolymer content by weight means that only biopolymer solution was added in the mixing. Mixing is performed in the sequence of C(cement)-S(sand)-W(water)-C(cement)-S(sand)-W(water)-Biopolymer solution. For example, cylinder BCC 1 has the order of mixing, C(500g)-S(1000g)-W(147g) were pasted and another paste, C(550g)-S(1250g)-W(200g)-X.G. solution(70g) was added on to the paste previously made. As for cube BCC, certain amount of ingredients of materials was prepared to make the cube BCC according to the same ratio of cylinder BCC. The thorough mixing of CRT and ingredients of concrete composite is intended to assure that the biopolymers are distributed onto microstructure of concrete system, building up the crosslinked structure with the power of biopolymer.

Table 4.1 Composition of biopolymerized concrete (cylinder)

	Ordinary concrete (g)	**2% Biopolymer concrete (g)**	**5% Biopolymer concrete (g)**	**8% Biopolymer concrete (g)**	**11% Biopolymer concrete (g)**
Water	417	347	231	120	N/A
Cement	1050	1050	1050	1050	1050
Sand	2250	2250	2250	2250	2250
Biopolymer solution	N/A	70	186	297	417

N/A: Non Applicable

Xanthan gum solution was prepared in deionized water at concentrations of 0.1% (1000 mg/L), using xanthan gum power manufactured by CPKelco (Kelzant). Chitosan was obtained from MegaCare Inc. in S. El Monte, California and prepared in the same concentration as xanthan. Chitosan is insoluble in water so that it had to be dissolved in 1% acetic acid. For concrete materials, we used industrial sand manufactured by Accosand Inc. (Ottawa sand) and cement I-II type manufactured by California Portland cement company, COLTON.

4.3. Results and Discussion

4.3.1 Compressive Strength

Table 4.2

Compressive strength of xanthan gum and chitosan biopolymer concrete

	Biopolymer solution content by weight base (%)				
	0 ordinary concrete	**2**	**5**	**8**	**11**
Cube XG	4218	7073	5730	5550	4180
Cube chitosan	4218	8996	7527	6273	5841
Cylinder XG	4135	5131	4687	4614	4601
Cylinder chitosan	4135	6079	5896	5930	5975

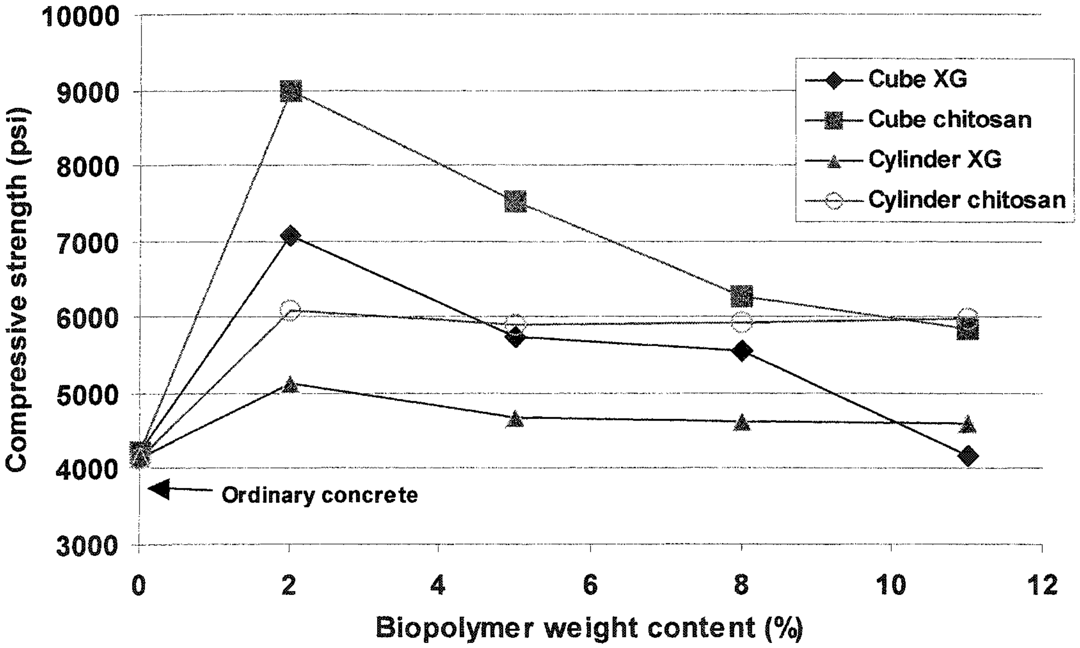


Figure 4.1 Comparison of compressive strength for xanthan gum and chitosan concrete at different weight contents.

In Table 4.2 and Figure 4.1, compressive strength was compared according to different biopolymer solution containments. As expected, the addition of biopolymer solution in the concrete mix results in the increase of compressive strength of concrete. Overall, cube concrete showed much higher strength than cylinder concrete samples, due to the difference of surface area. It appears that cube tests have a tendency to present the distinct results of strength difference. Both of cases are all for 2% weight content of biopolymer solution. In particular, cube chitosan concrete showed extraordinarily high compressive strength than ordinary concrete's, which was more than double strength. All specimen were stronger than ordinary concrete, other than cube concrete containing 11% xanthan gum solution by weight, which is in accordance with the results of CBC 3, made with 0.1% xanthan solution in 11% weight. The extreme addition of biopolymer solution may cause the decrease of compressive strength (Kim et al, AIChE Annual Meeting, A&WMA Annual conference, 2003). It is observed that involvement of biopolymer solution in the concrete mix evidently increases the strength but the strength starts to decrease as the weight content rate of biopolymer increases. Cylinder concrete shows the smoother decrease rate of strength. The strength of both biopolymer concrete has become very similar since 5% content of biopolymer. These results are related with water / cement ratio (w/c), which was believed that high viscous biopolymer is acting as a hindrance when it comes to the increase of strength of concrete. Because viscous biopolymer like xanthan gum shows the weaker strength, lowering the w/c ratio, than less viscous biopolymer like chitosan. Also, it was discovered that the extreme amount of biopolymer addition may change the structure of cement concrete other than the change of w/c ratio, which results in the decrease of strength, regardless of viscosity extent of biopolymer.

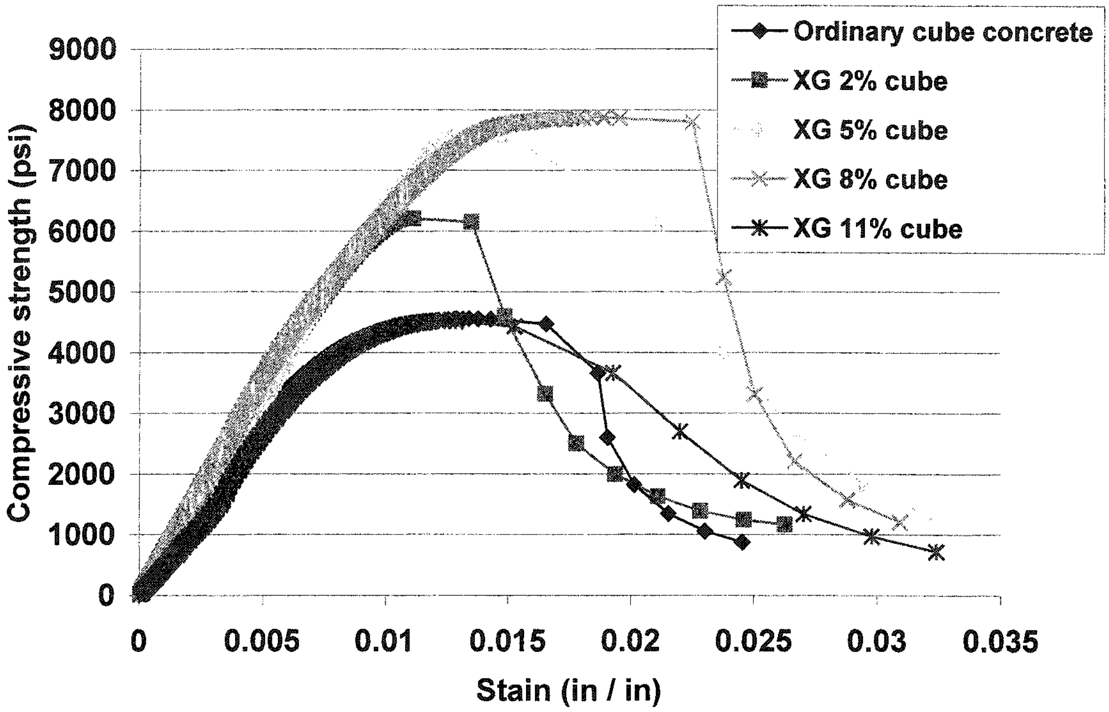


Figure 4.2 Comparison of compressive strength curve between ordinary cube and xanthan gum cube concrete.

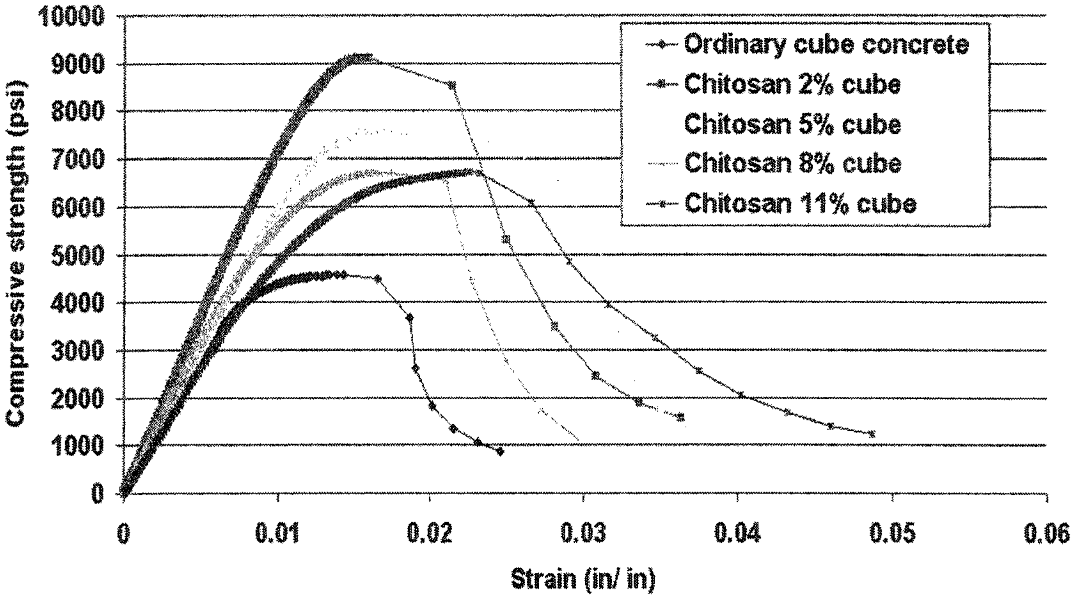


Figure 4.3 Comparison of compressive strength curve between ordinary cube and chitosan cube concrete.

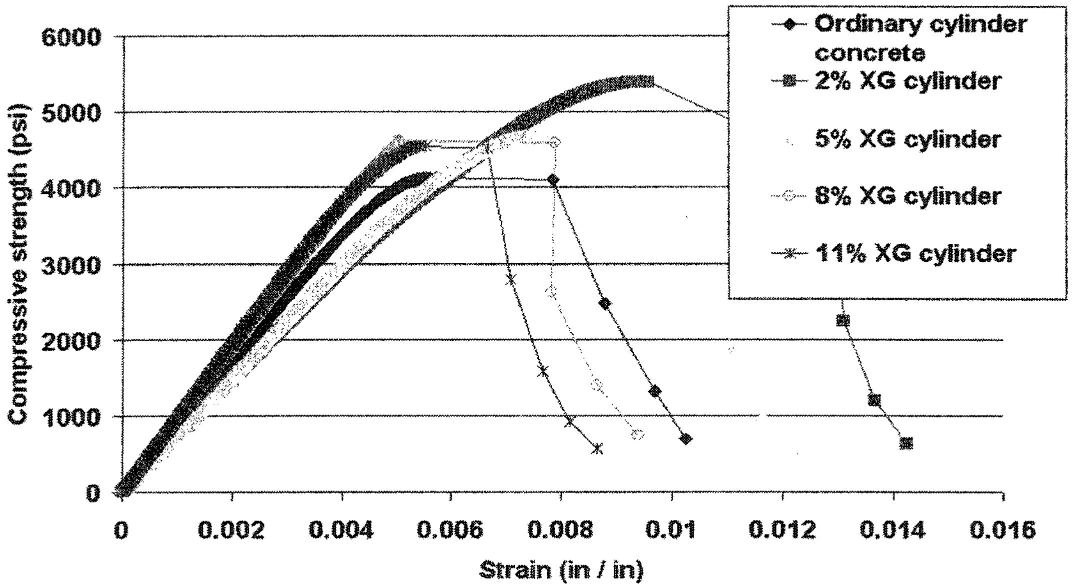


Figure 4.4 Comparison of compressive strength curve between ordinary and xanthan gum cylinder concrete.

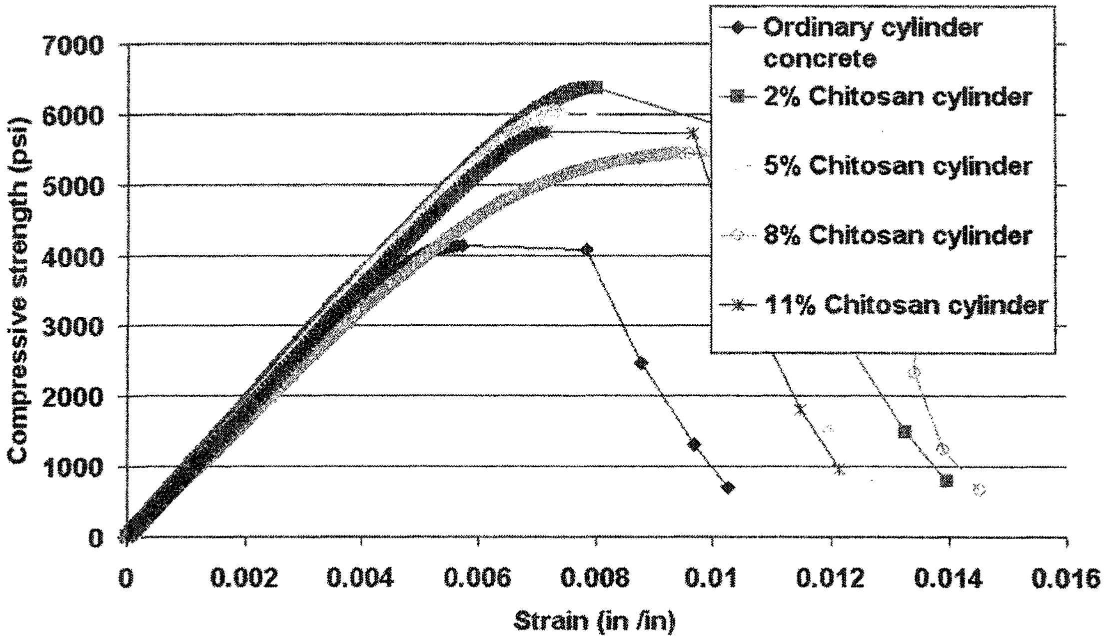


Figure 4.5 Comparison of compressive strength curve between ordinary and chitosan cylinder concrete.

In Figure 4.2-5, the compressive strengths of cube and cylinder samples were plotted in terms of strain and stress. All samples are well fitted with ordinary concrete curve. In particular, chitosan cylinder concrete straights up along with the ordinary cylinder concrete. It indicates that biopolymerized concrete complies to ordinary concrete curve, without the noticeable change of strain. It is amazing that concrete composite with biopolymer, following the pattern of ordinary concrete shows the high compressive strength, which means this biopolymerized concrete may become a new class of cementitious materials that will be confirmed by XRD results.

4.3.2 XRD (X-ray Diffraction)

X-ray diffractograms were obtained for all biopolymer concretes in order to grasp a better understanding of the structural implications caused by the involvement of biopolymers. Figure 1 represents the ordinary pattern of concrete. The X-ray diffractograms of selected samples are presented in Figure 4.7-8 and 4.10-11. Ordinary concrete, primarily made of sand material (61%), is close to quartz with characteristic peaks at 21 and 27° 2θ (Phair, et al., 2002).

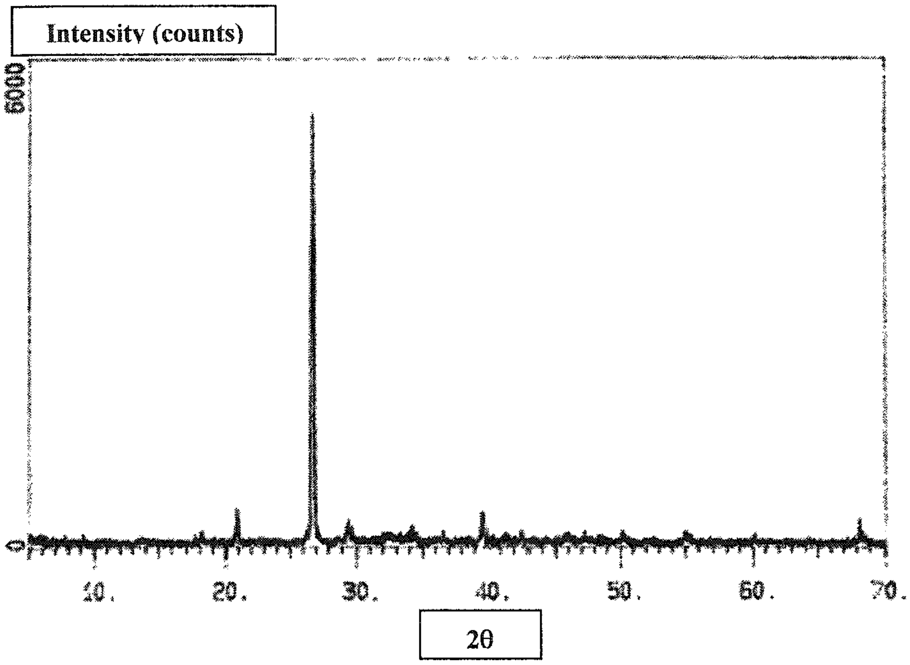


Figure 4.6 X-ray diffraction patterns of ordinary concrete.

Figure 4.7 and 4.8 represent the X-ray diffraction of 5% and 11% xanthan gum concrete by weight percent. It is evident that addition of biopolymer changed the structure of concrete, since the unobservable peaks in ordinary concrete were identified in the xanthan gum concretes. Figure 4 is xanthan gum peak only, with characteristic peaks around 19 and 32° 2θ whose peaks are the fingerprint of xanthan gum and equally owned by the pattern of 5% xanthan gum concrete. 11% xanthan gum concrete also contains those peaks which became bigger, but they are a little shifted. The quartz peaks outstandingly remain in xanthan gum concretes, indicating that biopolymerized concrete confine to the structural pattern of ordinary concrete.

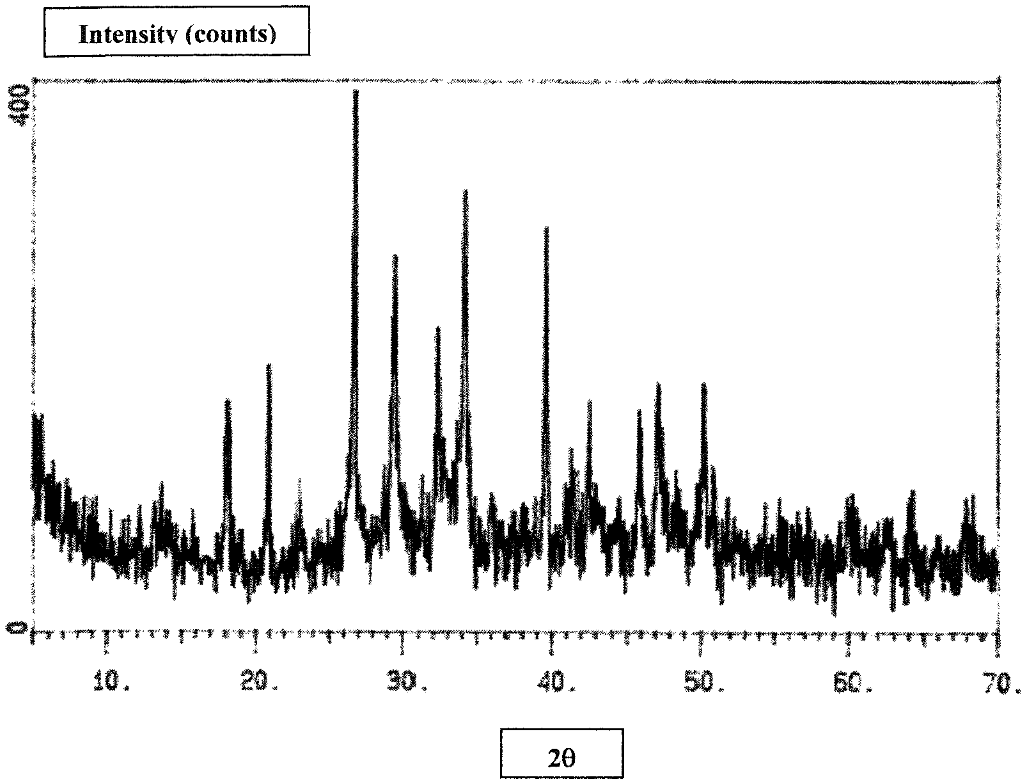


Figure 4.7 X-ray diffraction patterns of 5% xanthan gum concrete.

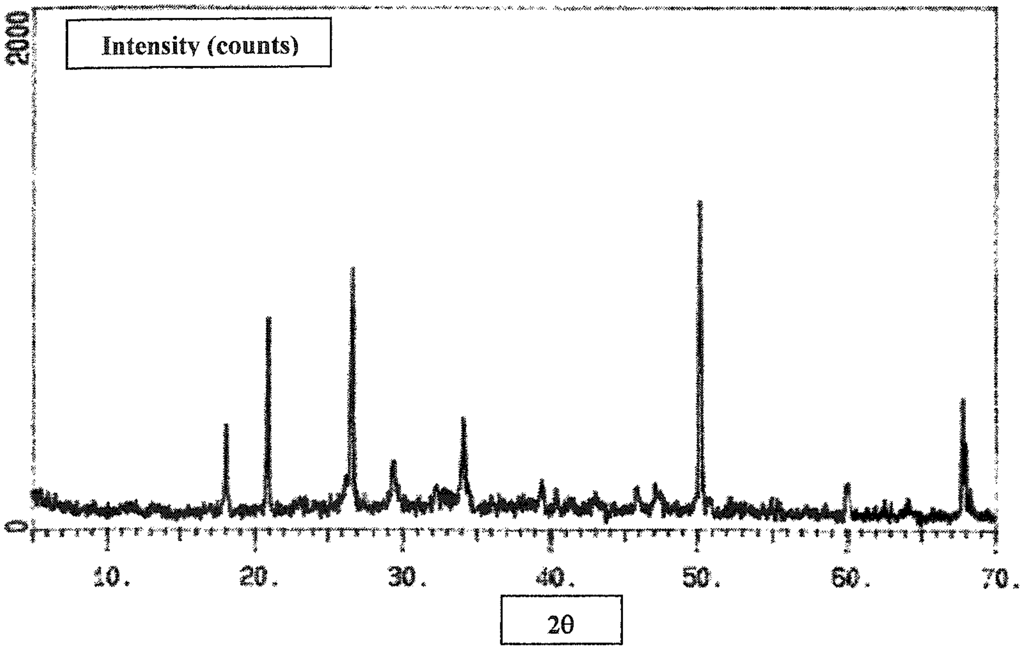


Figure 4.8 X-ray diffraction patterns of 11% xanthan gum concrete.

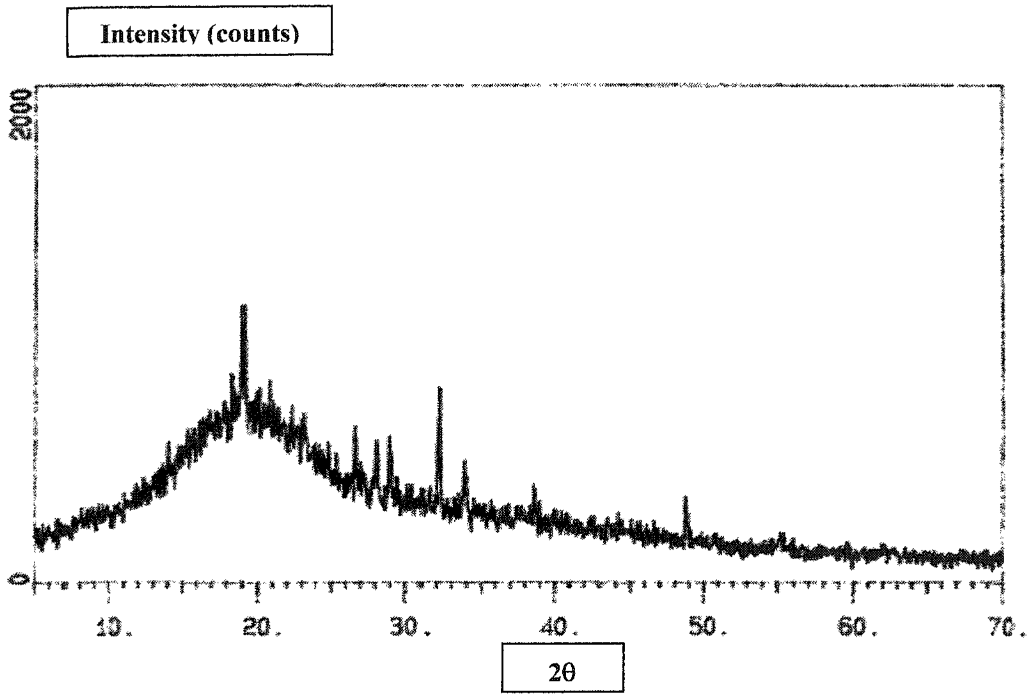


Figure 4.9 X-ray diffraction patterns of xanthan gum powder.

Figures 4.10 and 4.11 are 5% and 11% chitosan concrete by weight percent. The addition of biopolymer obviously resulted in the change of the structure of concrete, because some new peaks not shown in the ordinary concrete were recognized in the chitosan concretes. Figure 4.12 is chitosan peak only, with characteristic peaks around 19 and 28-29° 2θ whose peaks also belong to the both patterns of 5% and 11% chitosan concretes. Those peaks in 11% chitosan concrete became bigger. The quartz peaks remain in chitosan concretes. Xanthan gum and chitosan concretes also showed the major peaks with *d*-spacing values of 3.03, 2.61 A of standard cementitious matrix and 1.77 and 1.54 A of calcium silicate (Phair et al., 2002).

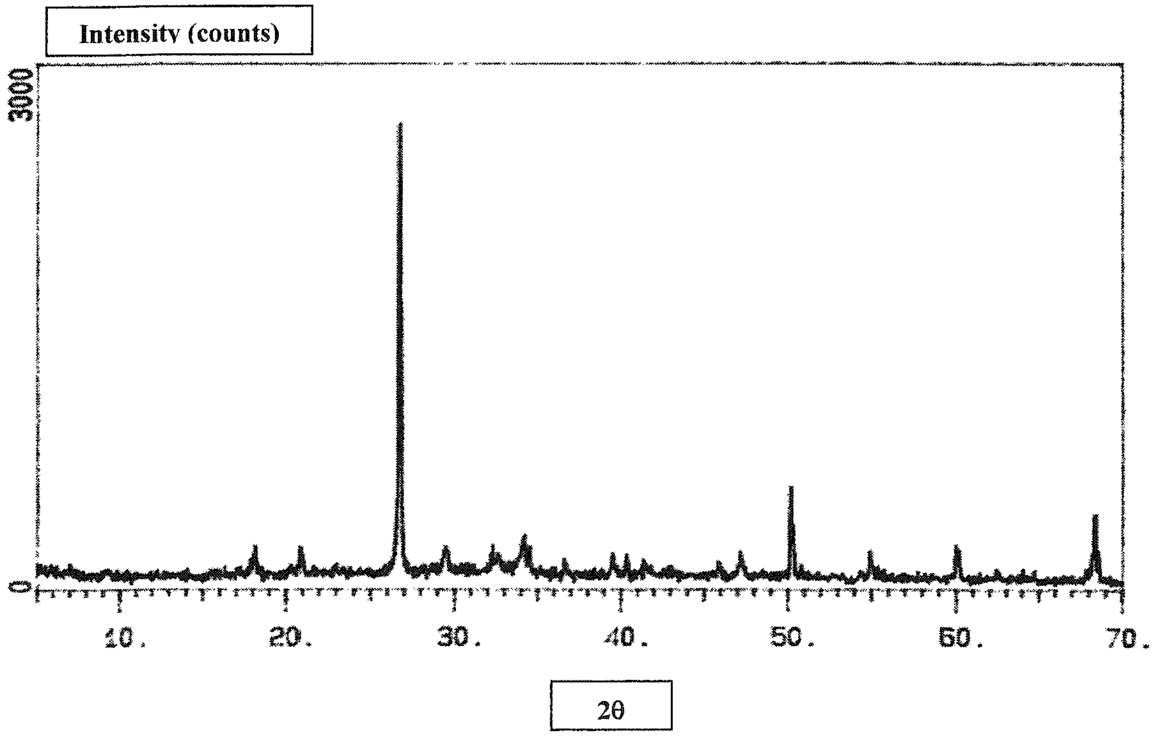


Figure 4.10 X-ray diffraction patterns of 5% chitosan concrete.

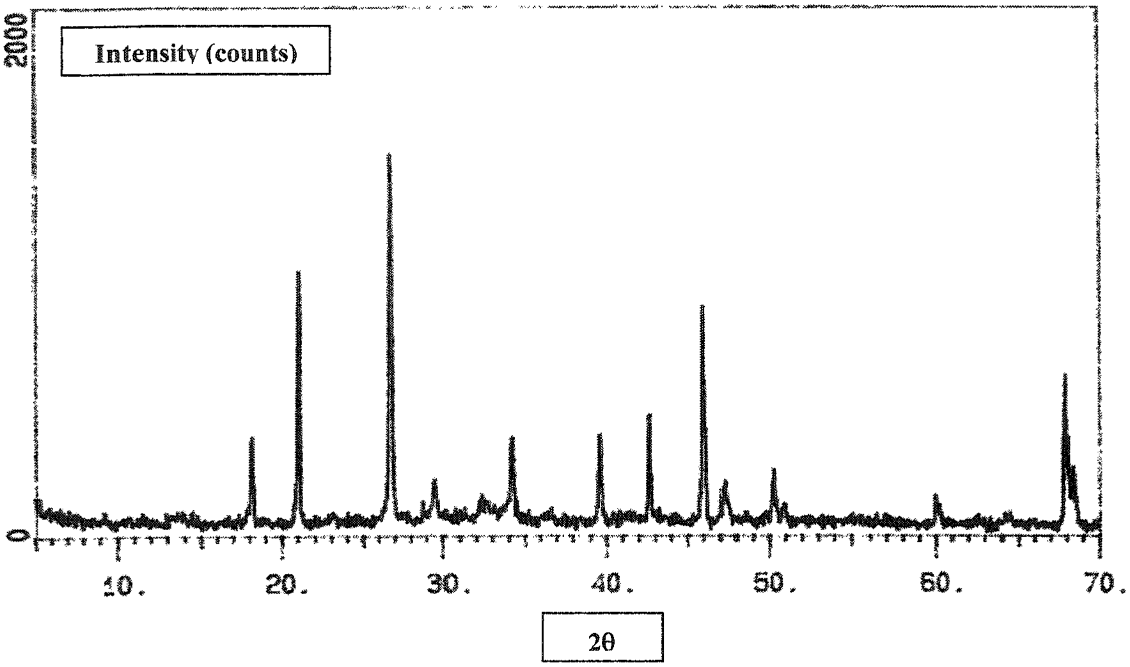


Figure 4.11 X-ray diffraction patterns of 11% chitosan concrete.

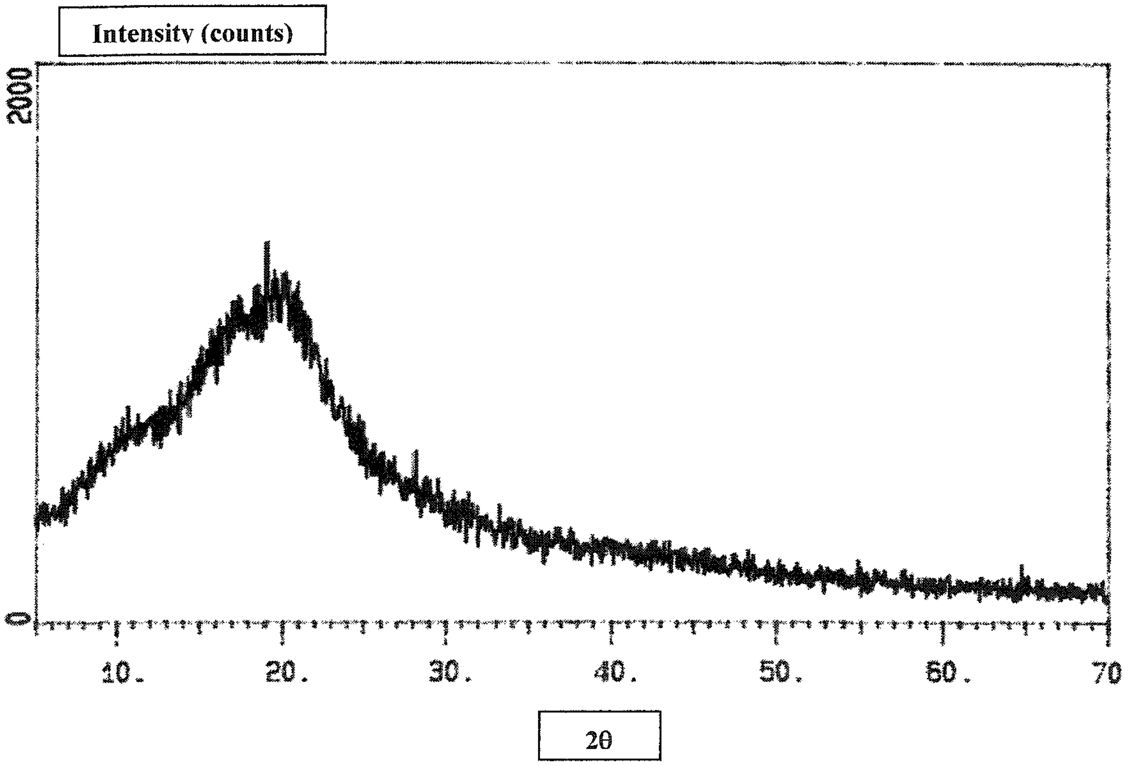


Figure 4.12 X-ray diffraction patterns of chitosan powder.

4.3.3. Model Structure of Biopolymerized Concrete

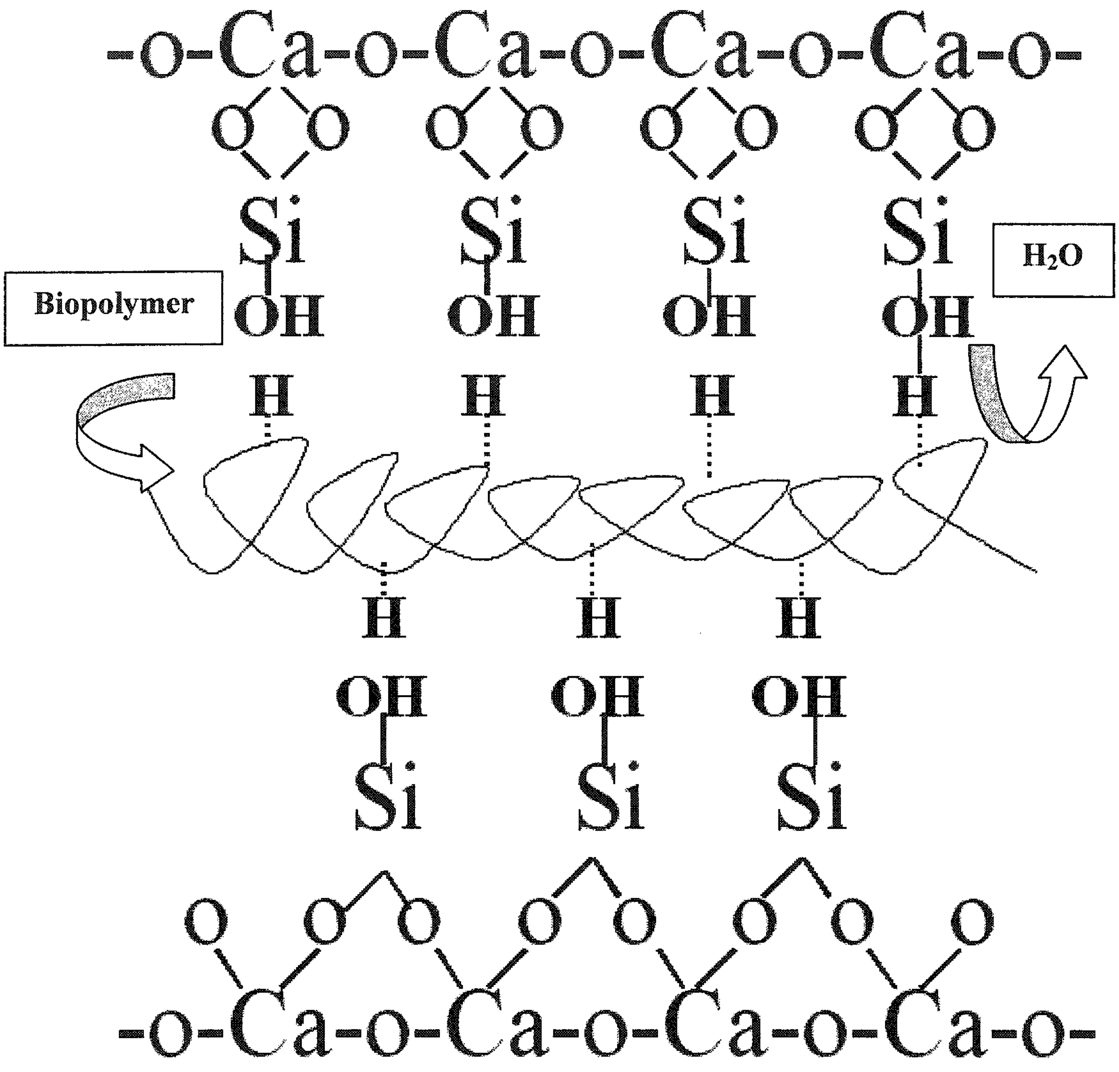


Figure 4.13 Biopolymerized concrete structure.

As shown in Chapter 5, XPS results can support the biopolymerized concrete structure, containing a variety of oxides. Many oxygen bonds are likely to push up the structural foundation in a biopolymer concrete. Particularly, Ca and Si play a primary role of backbone chain. In this pattern, biopolymers with a great number of hydrogen bonds and functional groups are able to condense with hydroxyl groups in concrete molecules by constructing the three-dimensional crosslink structure, when letting the reaction of concrete and biopolymer occur (Kim, D. et al., 2003). This kind of new structure can increase the strength of concrete. Shear strength of sand is proven to be increased due to interpenetrating polymer network (IPN) caused by biopolymer crosslink capacity (Etemadi, et al., 2003). Other than this fact affecting the strength, calcium and silicate involvement seems to increase the concrete structure. More content of Si than Al showed higher strength of geopolymers (Phair, et al., 2002). It seems that Si is a strength controlling factor. In other literature, geopolymers containing a higher weight percentage of calcium and silicate showed the higher strength of structure (Xu, et al., 2002). In other words, the presence of calcium and silicate acting as a backbone along with biopolymer, is related to the interwoveness of crystalline formation, which will affect the final mechanical strength of concrete matrix.

4.4 Conclusions

Ordinary concrete products seem amorphous to X-rays, this dose not guarantee the absence of small disordered crystals and therefore some or total cristallinity could well be present to a certain extent (Van Jaarsveld, J.G.S. et al., 1997). However, the biopolymerized concrete may add up much of the physical strength because of increased crystallization contacts between more amorphous regions and biopolymer, which results from the crosslink capacity of biopolymer. This is in accordance with the previous observation reporting that a higher strength geopolymer matrix is associated with a more desirable internal microstructure (Xu, et al., 2002). Based on this concept, biopolymerized concrete is likely to become a new phase internal microstructure by affecting the chemistry and morphology of structure formation. This type of new mineral composite with food-grade biopolymers can be used for building materials and immobilization systems of toxic metals that was proven by CBC (CRT concrete), and causes no disposal problem after concrete destruction and may meet the needs of strong concrete. In addition to the strength of concrete, the smell and dust of concrete was noticeably reduced when testing compressive strength. This can be also further study when it comes to making an environmentally improved green material.

CHAPTER V

Characterization of Biopolymer-Modified Concrete Geopolymer

Instrumental Analysis on Concrete Geopolymers

5. Characterization of Biopolymer-Modified Concrete Geopolymer

5.1 Introduction

Through a number of literatures on cement or concrete chemistry, it is found that not little efforts were made to discover the structure and chemical or physical background of concrete materials. In this study, instrumental analysis on concrete geopolymers was experimented. The frequently used methods were applied as a surface chemistry, XPS, FTIR, and XRD. Each analysis has characteristic viewpoints to provide the information on the concrete geopolymers. It may help characterize the concrete geopolymer by collecting the data supplied by different instruments.

5.2 Instrumental Analysis

5.2.1 XPS (X-ray Photoelectron Spectroscopy)

5.2.1.1 Experimental Procedure

The XPS experiments were conducted with a VG Scientific LTD ESCA Lab II spectrometer, under 1 eV / step, 50 min / sec, 100 sweeps, 100 eV of pass energy. Mg Kα radiation was used as an X-ray source. All concrete samples were dried in the vacuum chamber for 24 h to eliminate the vapor interaction. Sample 1 is ordinary concrete mix and sample 2 contains CRT glass, treated with xanthan gum 0.1 % concentration in 2% of weight portion. Sample 3, 4, 5, and 6 are all biopolymerized concrete without waste. Sample 3 and 4 contain 5% and 11% of 0.1 % xanthan gum solution by weight, respectively. The same is for sample 5 and 6 with 0.1% chitosan solution.

5.2.1.2 Results and Discussion

The concrete contains plenty of different oxides such as Fe_2O_3, MnO, TiO_2, CaO, K_2O, SO_3, P_2O_5, SiO_2, Al_2O_3, MgO, and Na_2O, supported by XRF (X-ray Fluorescence Spectrometry) fusion analysis (Van Jaarsveld et al., 1999). In Figures 5.1-6 for XPS, all spectra show very high oxygen bonds energy, associated with major concrete components, CaO, SiO_2, Al_2O_3, MgO, although some detection limit compounds not shown. Oxygen bonds are important even for the increase of strength of materials by adding fly ash with high content of extra oxides (Van Jaarsveld, et al., 2002).

Comparing the spectrum of Figure 5.1 (ordinary concrete) and Figure 5.2 (xanthan gum treated CRT concrete), they look the same but sample 2 contains the Pb peaks. Two mounds of Pb peak are present on the surface of sample. The partially resolved Pb 4f 7/2 and 5/2 doublelet was observed at 140 and 145 eV respectively, consistent with an oxidized form of lead. Normally, survey scans are run at low resolutions and high sensitivity. The data were collected at 1.0 eV intervals, so the uncertainty in the peak position is very nearly ± 1.0 eV. The Pb 4f 7/2 photoelectron peak shifts from 136.9 eV for metallic lead to a range of 137-139 for the oxides. The survey scan is sufficient to distinguish metallic lead from the oxidized forms but insufficient to distinguish PbO from PbO_2 or Pb_3O_4 or even from $PbSO_4$. Pb presence is very small, if considering initial value of Pb content in CRT glass such as 5883 mg/kg. It may explain that XPS method is able to cover the very shallow surface, 20 aungstrom. Most of lead particles may be bound inside of concrete microstructure containing a variety of pores that efficiently entrap the Pb particles (ref. cement chemistry in Chapter 2). Indeed, the leaching tests can confirm the fact that lead can be leached out by acid introduction, even though lead does not show on the surface. Lead oxide on the surface may be involved in the different oxidation state. Technically speaking, lead is less liable to show on the surface than other competitive elements showing the great amount in the peak. The state of lead in concrete may be further studied.

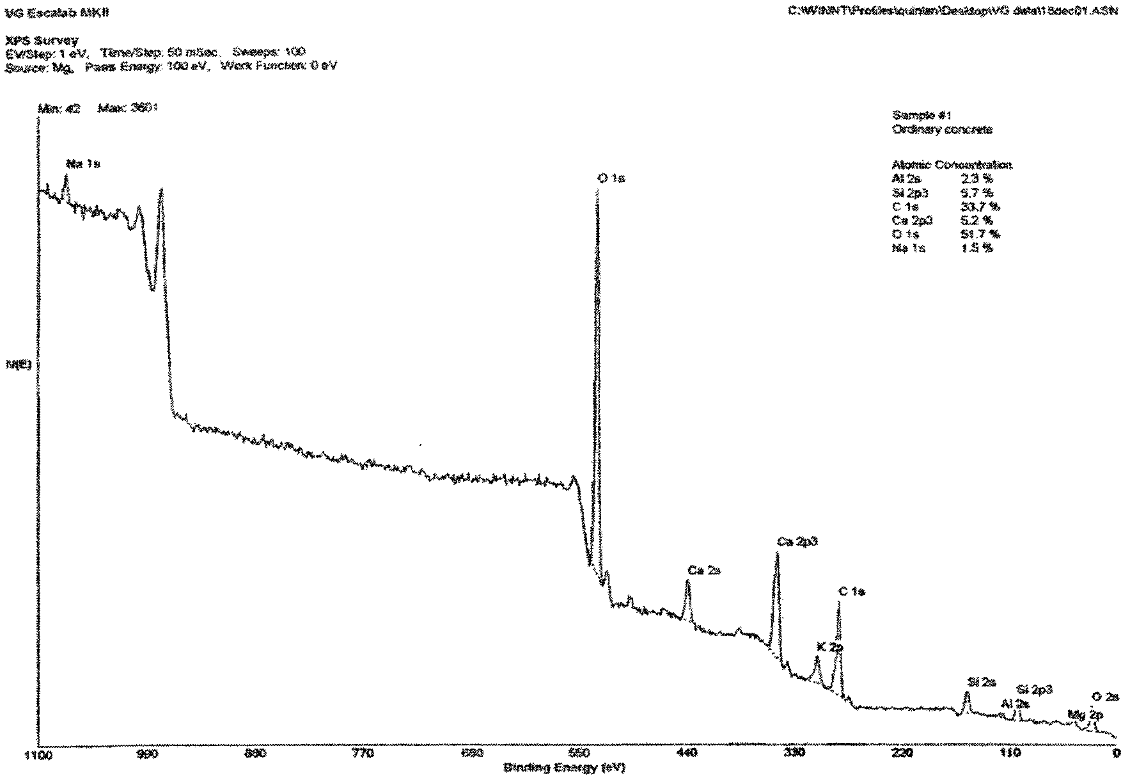


Figure 5.1. XPS of ordinary concrete.

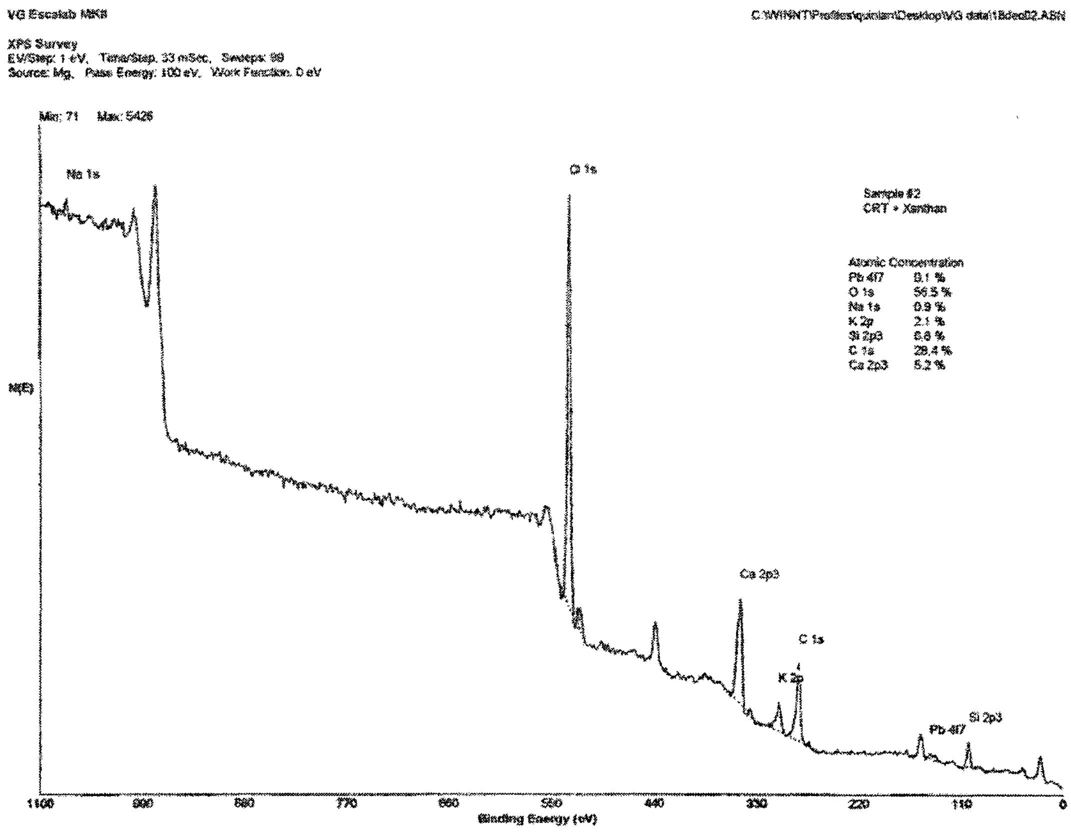


Figure 5.2 XPS of CRT concrete treated with xanthan gum.

(0.1% conc. and 70g of xanthan gum solution)

Biopolymer concretes (5% and 11% by weight-base xanthan gum and chitosan concretes), samples 5.3-6, have no bumps around Pb peak. Carbon peak may relate to biopolymer involvement due to its long chain of carbon backbone, but in the peaks, regardless of biopolymer containment, carbon peaks look all the same in all samples. This may be attributable to the bulky size of concrete materials and the big interference of CO_2 in ambient.

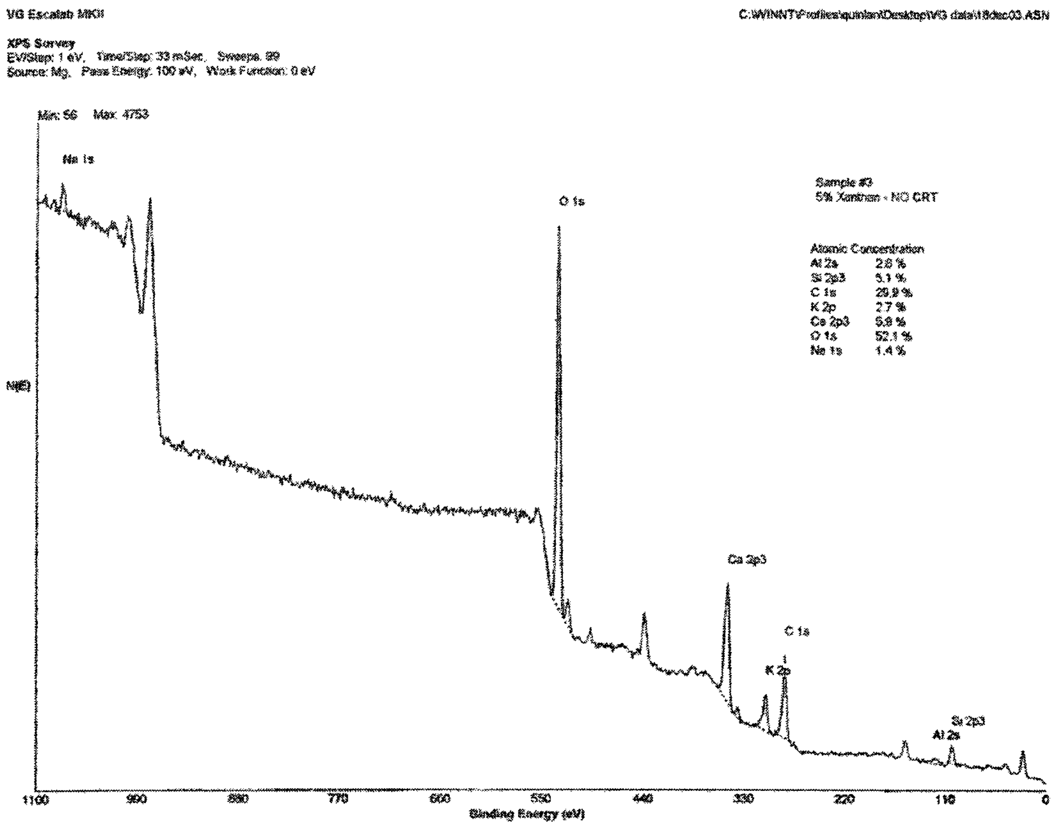


Figure 5.3 XPS of xanthan gum concrete by 5% weight and 0.1% concentration.

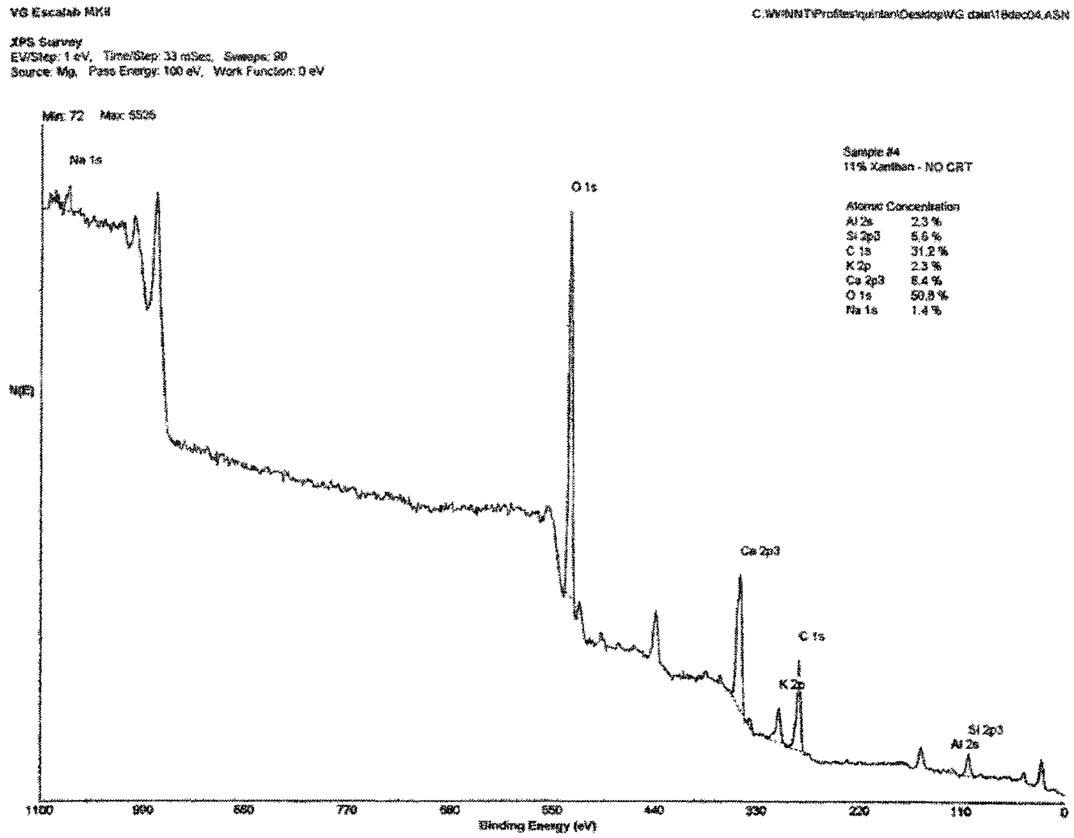


Figure 5.4 XPS of xanthan gum concrete by 11% weight and 0.1% concentration.

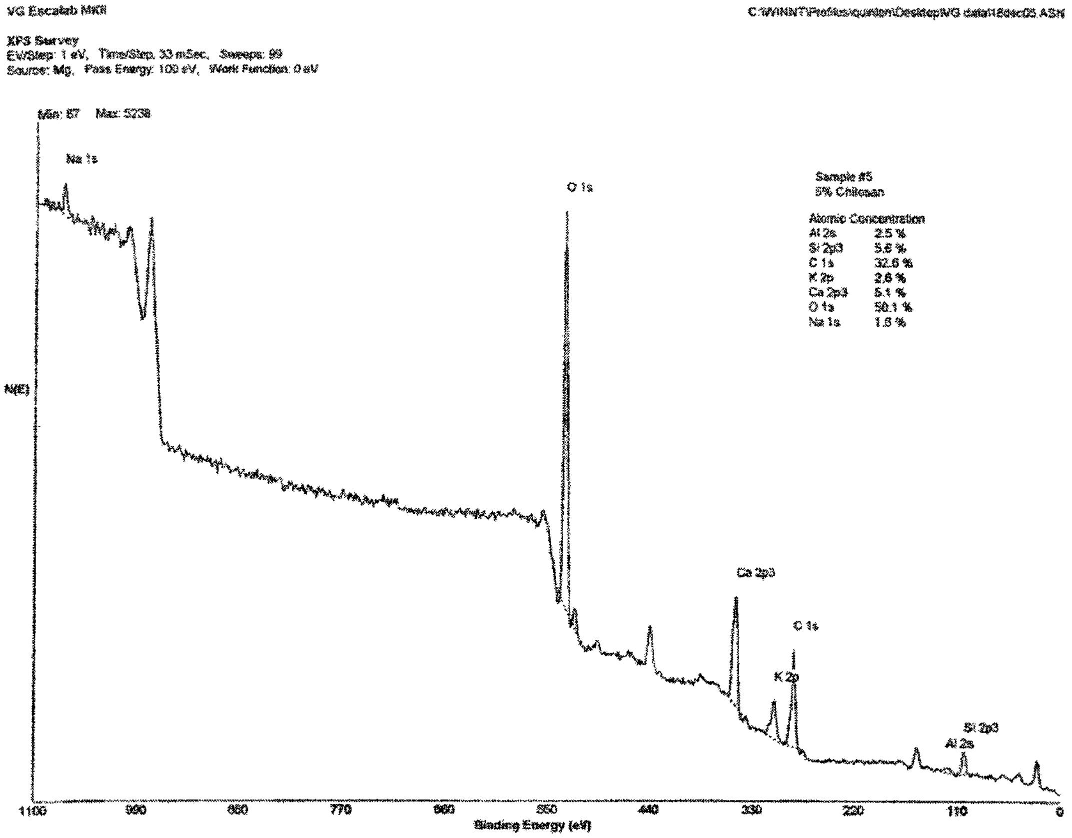


Figure 5.5 XPS of chitosan concrete by 5% weight and 0.1% concentration.

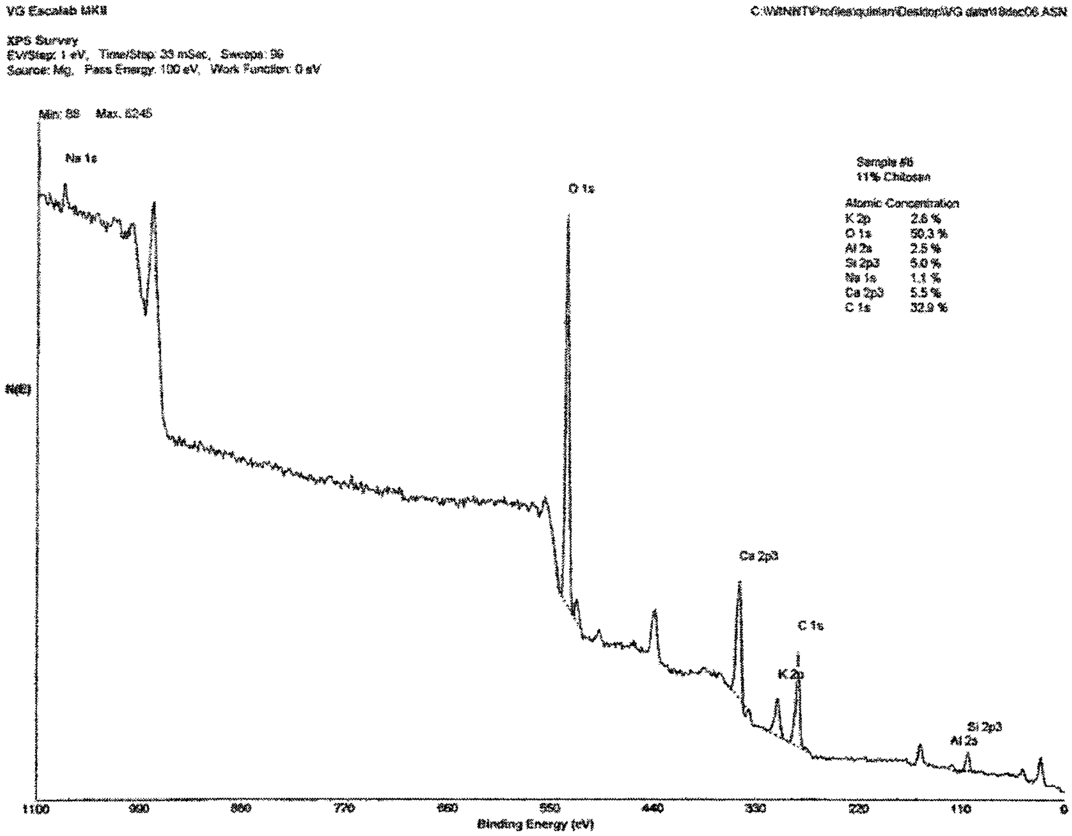


Figure 5.6 XPS of chitosan concrete by 11% weight and 0.1% concentration.

As seen in Chapter 4, biopolymerized concrete, the model structure of biopolymerized concrete was constructed. It can be still significant that XPS may support the model structure newly built. XPS data may explain the biopolymerized structure, being primarily constructed with oxygen bonds.

5.2.2 FTIR (Fourier Transform Infrared)

5.2.2.1 Experimental Procedure

Infrared spectra of the ground samples were recorded using the KBr pellet technique of sample and KBr ratio (1:60) on a MIDAC M-series FTIR spectrometer. Selected concrete samples and the process of making pellet were prepared in a dry box and KBr was in an oven for 24h at 100 °C to avoid moisture in the ambient due to KBr's moisture sensitivity.

5.2.2.2 Results and Discussion

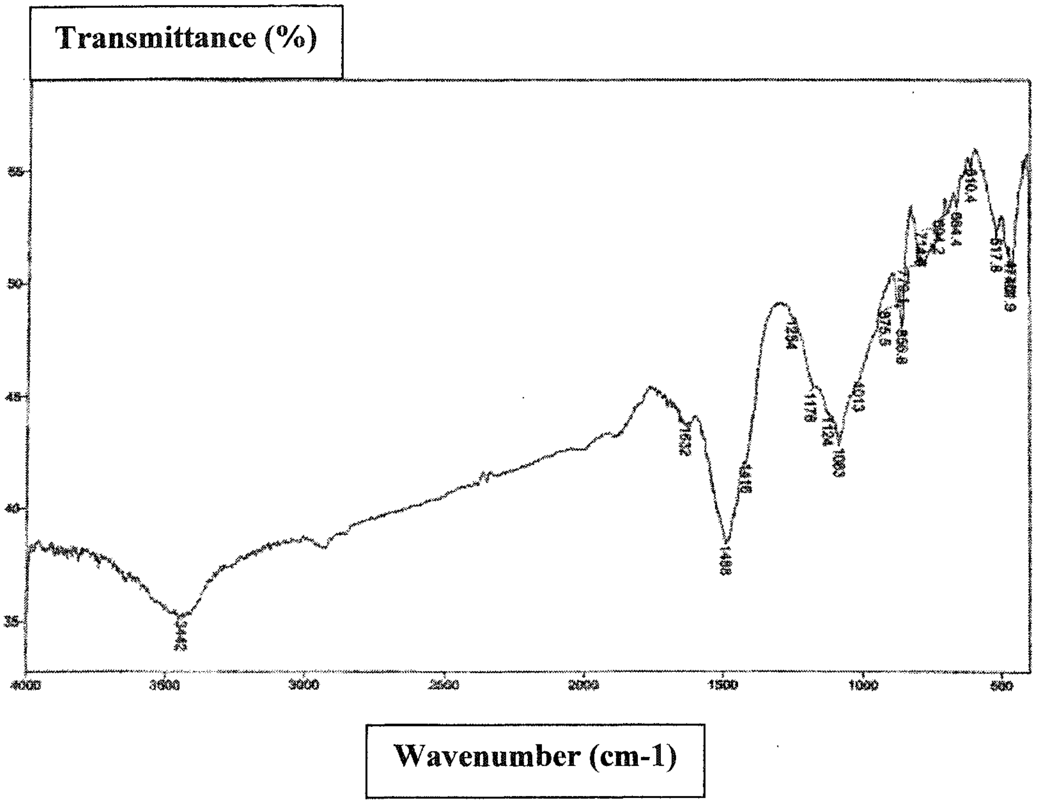


Figure 5.7 FTIR spectrum of ordinary concrete.

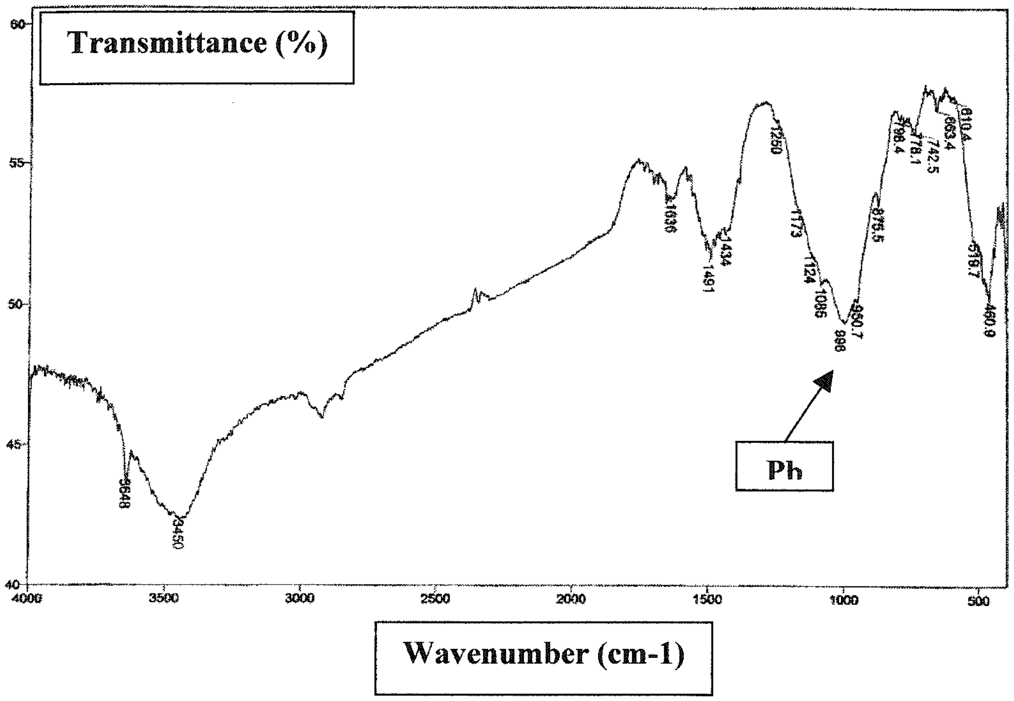


Figure 5.8 FTIR spectrum of CRT concrete.

In Figure 5.7, ordinary concrete was recorded to provide the basic background for other modified concrete samples. Water molecule peaks at the bands of 3442 cm^{-1} and 1632 cm^{-1} were found in ordinary concrete. The band around 1013 cm^{-1} explains for asymmetric Si-O stretching and the band around 517.8 cm^{-1} is due to out-of-plane Si-O bending, while the band at 461.9 cm^{-1} is caused by in-plane Si-O bending. In Figure 5.8, new peak, 998 cm^{-1} has emerged and may be the Pb as well as 1491 cm^{-1} due to carbonation shrinks. Large peaks remain around 3450 cm^{-1} and 1636 cm^{-1} due to vibrations of H_2O.

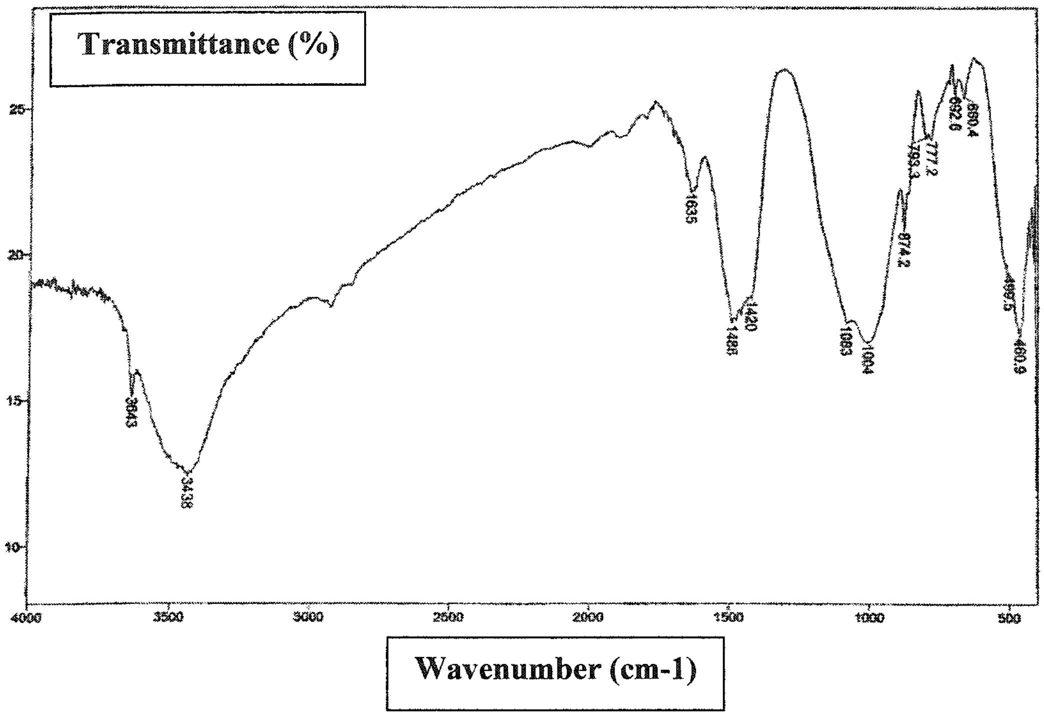


Figure 5.9 FTIR spectrum of 5% xanthan gum concrete.

In Figures 5.9 and 5.10, xanthan gum concretes with 5% and 11% weight, were recorded in order to fingerprint the chemical change of more inclusion of biopolymers. There is little difference between 5% and 11% xanthan gum concretes except for the presence of ordinary concrete patterns in 5% xanthan gum concrete, indicating that 11% xanthan gum concrete has changed its binding energy, with more involvement of biopolymer solutions. Also, in Figure 5.11, the addition of nitrogen containing compounds was evaluated to see how green tea may affect the biopolymer binding onto the concrete molecules. The C-N stretch, in so far as it can be identified with any single absorption, is usually assigned near 1400 cm^{-1} that is compensated with 1414 cm^{-1} in this study. The band around 2800 cm^{-1} can be the free NH, related to the polymer absorption.

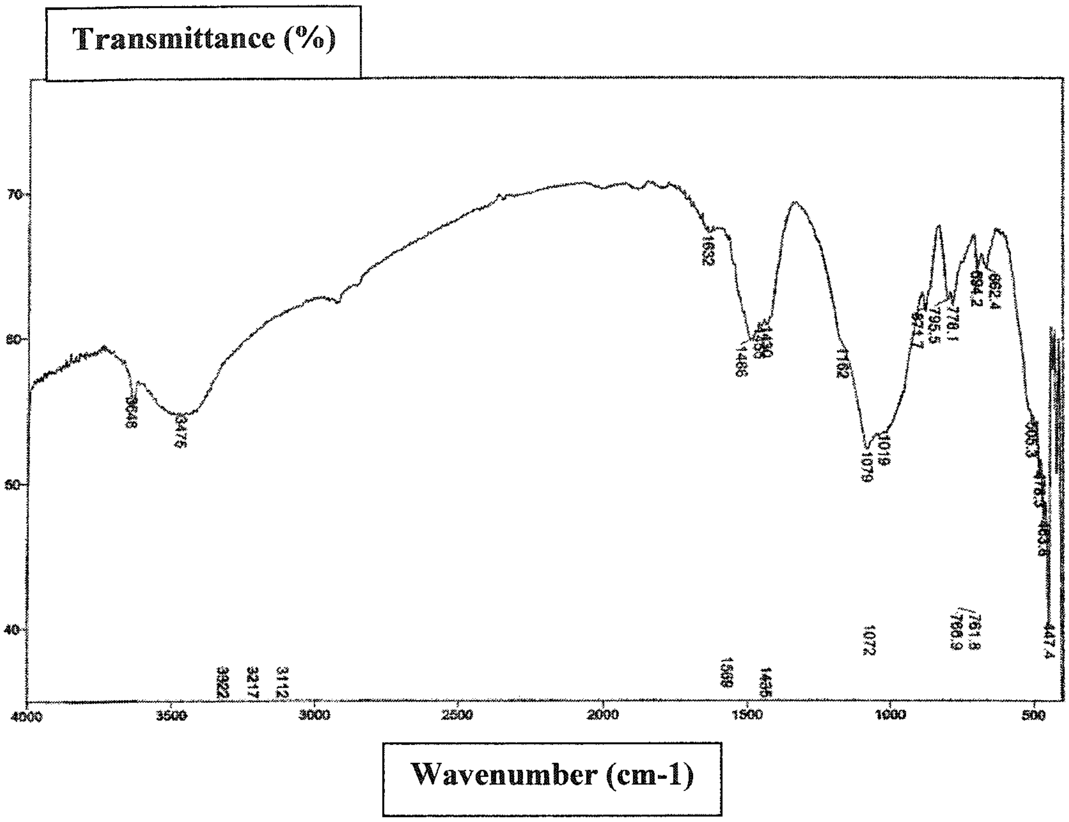


Figure 5.10 FTIR spectrum of 11% xanthan gum concrete.

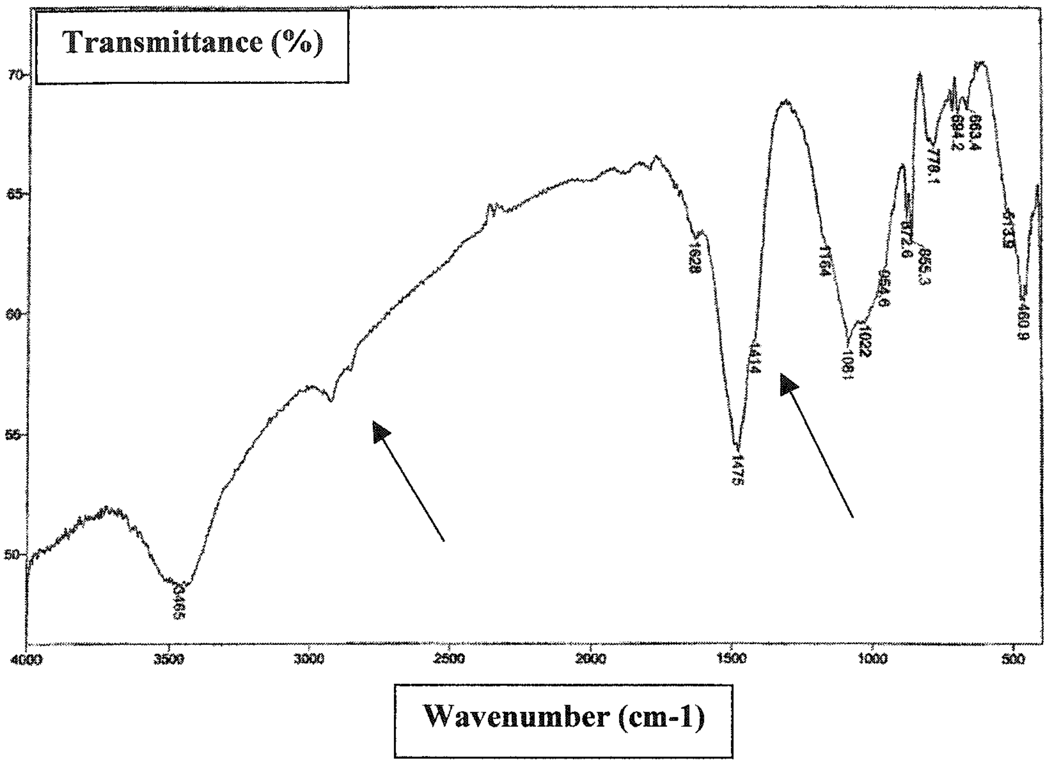


Figure 5.11 FTIR spectrum of 11% xanthan gum + green tea concrete.

5.2.3 XRD

5.2.3.1 Experimental Procedure

X-ray powder diffractograms were obtained using a Rigaku Geigerflex X-ray diffractometer with Cu Kα radiation generated at 30 mA and 40 kV. Specimens were step-scanned as random powder mounts from 5 to 70° 2θ at 0.02° 2θ steps integrated at the rate of 0.3 s per step. Xanthan gum (5% and 11% by weight) solution, 0.1%, was experimented with green tea solution, prepared in deionized water for 20 min dipping of a tea bag. 1 mL of green tea was dripping onto 2 g of ground concrete samples that were cooked in a vial for 4h at 65 °C and 90 °C. CRT concrete treated with xanthan gum

(70g of solution) was X-ray scanned. Also, Guar gum plus boric (CBC 12) and xanthan gum plus guar (CBC 14) concretes were scanned.

5.2.3.2 Results and Discussion

The electron diffraction study was conducted by concentrating on newly formed phases and ensure that they resemble a new structure.

In Chapter 4, xanthan gum and chitosan concrete showed the different pattern of X-ray diffractogram ordinary concrete do not have. Similarly, the biopolymer (xanthan gum) concrete reacting with green tea is different from ordinary concrete (Figure 5.12-15).

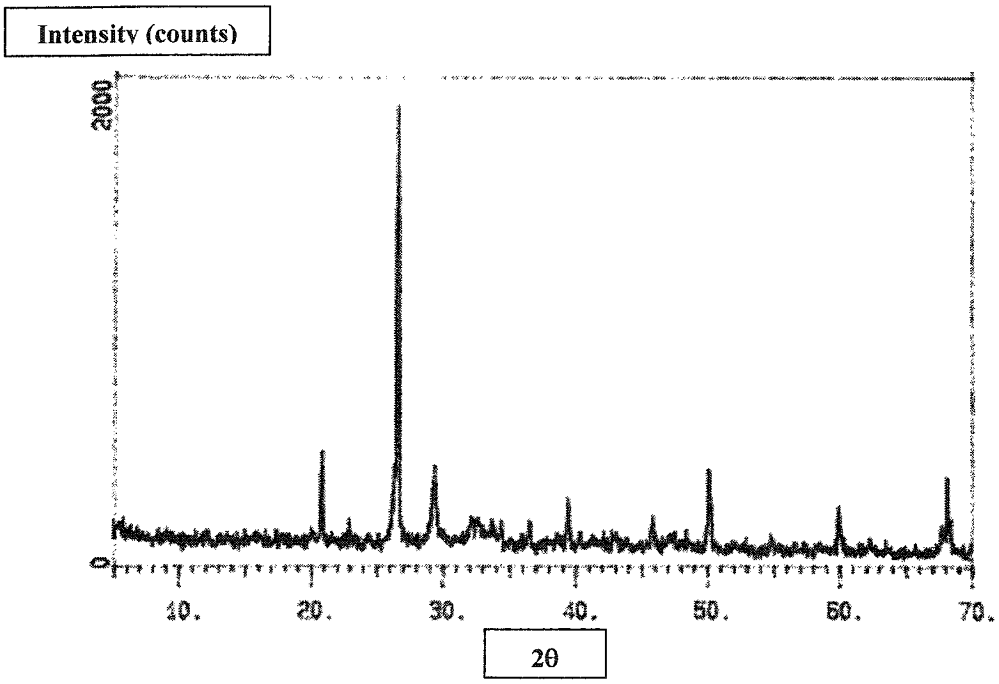


Figure 5.12 XRD spectrum of 5% xanthan gum + green tea concrete at 65°C.

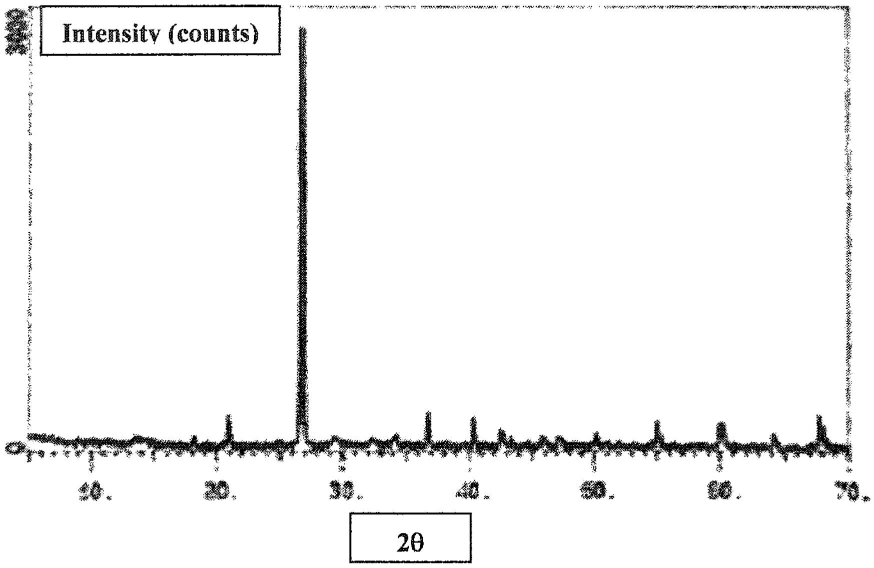


Figure 5.13 XRD spectrum of 11% xanthan gum + green tea concrete at 65°C.

Xanthan gum concretes both in 5% and 11% weight, plus green tea, cooked at 65 °C have the xanthan gum fingerprints peaks around 19 and 32° 2θ. As for concrete of 11% xanthan gum + green tea, it is in similar pattern to 11% xanthan gum concrete, which indicates that green tea has less effect on a structure difference. However, the characteristic peaks of concrete and xanthan gum are more prominent as temperature in geo-chamber goes up (Figure 12 and 14 or Figure 13 and 15).

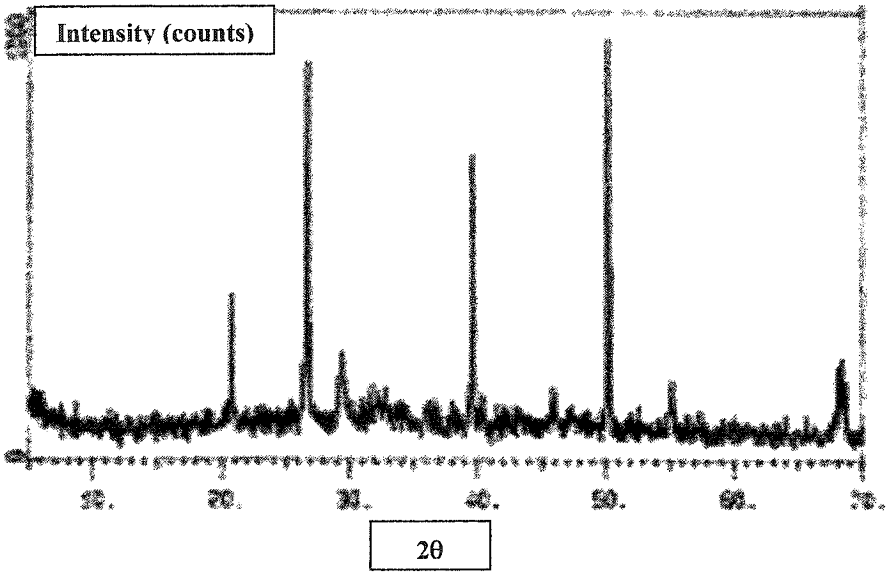


Figure 5.14 XRD spectrum of 5% xanthan gum + green tea concrete at 90°C.

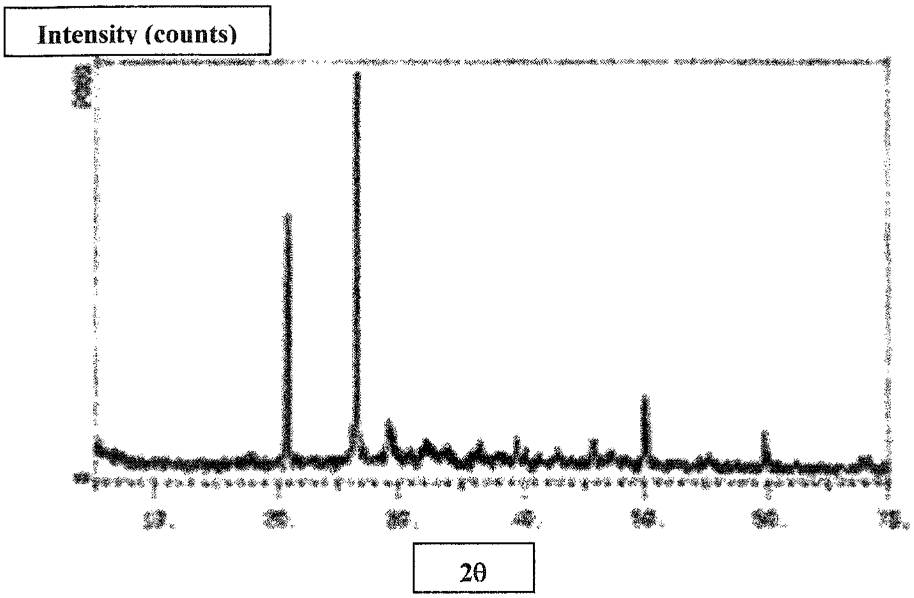


Figure 5.15 XRD spectrum of 11% xanthan gum + green tea concrete at 90°C.

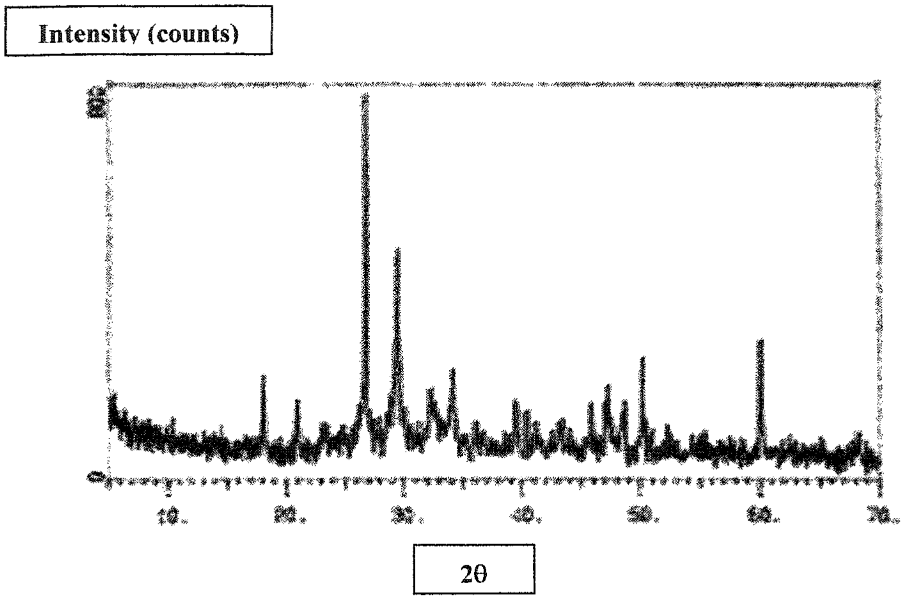


Figure 5.16 XRD spectrum of CRT concrete treated with xanthan gum.

Xanthan gum (2% weight) treated CRT concrete was recorded in Figure 5.16, where xanthan gum's characteristic peaks were found and quartz have become more noticeable since it contains CRT glass, quartz. It was not found that lead particles in concrete may affect the XRD spectrum.

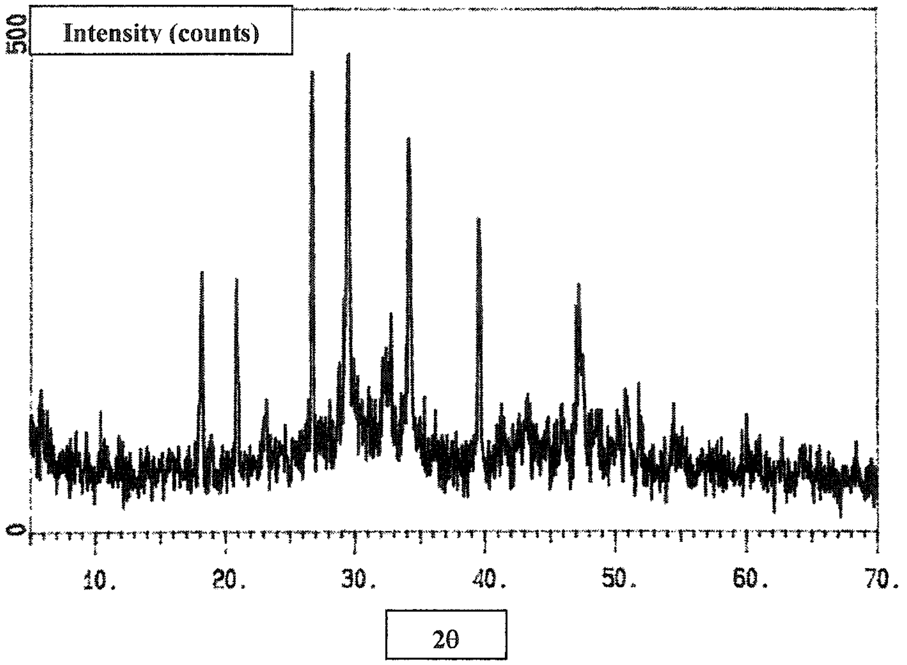


Figure 5.17 XRD spectrum of xanthan gum plus guar gum concrete.

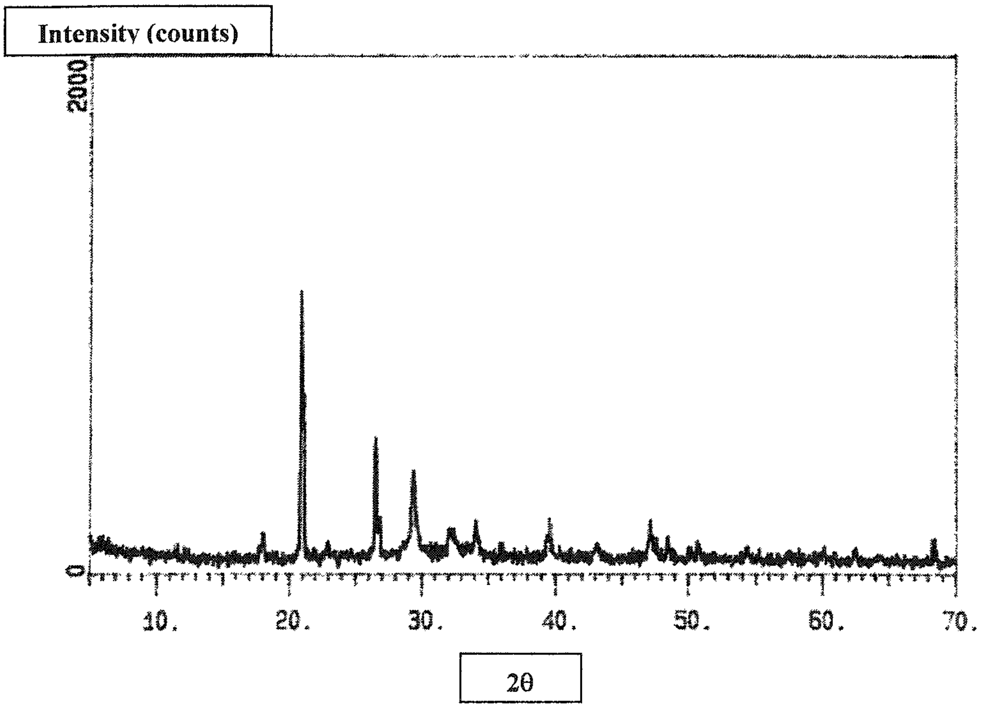


Figure 5.18 XRD spectrum of guar gum plus boric concrete.

Xanthan gum mixed with guar gum (11% weight) in Figure 5.17, can be comparable with 5% xanthan gum concrete in Chapter 4, since they are identically similar. It is interesting that especially, peak 29° 2θ in xanthan gum plus guar gum is bigger than that of 5% xanthan gum only. In Figure 5.18, guar gum peak around 29° 2θ was equally found in guar gum plus boric concrete. It can be assumed that 32° 2θ is unique to xanthan gum while 29° 2θ is to guar gum. It is the first work never done before so that this kind of interpretation may be significant reference for biopolymer containing concrete. It can be very important that the new type of mineral was discovered. The addition of biopolymer affects a new phase formation.

5.3 Conclusions of Instrumental Analysis

It is complex to identify and characterize the concrete-based geopolymer, making use of three methods such as XPS, FTIR, and XRD. They may provide the fragmented information of the concrete geopolymer. Most of the instrumental analysis is subject to the surface region of samples. What is clear from XPS, FTIR, and XRD analyses is that there is a strong chemical reason for the observed differences in the physical properties of the concrete geopolymers, mostly due to the increasing extent of polycondensation, confirmed by the crosslink power of biopolymers. In other words, the nature of biopolymer either physically or chemically influences the structure of concrete without changing the basic Ca and Si building blocks of concrete matrix.

CHAPTER VI

TCLP vs. SPLP

TCLP (Toxicity Characteristic Leaching Procedure) versus SPLP (Synthetic Precipitation Leaching Procedure)

6. TCLP vs. SPLP

6.1 Introduction

Toxicity is identified through a laboratory procedure called the Toxicity Characteristic Leaching Procedure (TCLP) and Synthetic Precipitation Leaching Procedure (SPLP), which are approved by EPA. The SPLP and TCLP were developed for use in the assessment of waste disposal facilities, rather than mining operations. The TCLP (USEPA Method 1311) evaluates metal mobility in a sanitary landfill, while the SPLP (USEPA Method 1312) was developed to evaluate the fate and transport of metals in an engineered land disposal facility from which municipal solid waste is excluded. The extraction fluid for the TCLP is a buffered organic acid (acetic acid), while that for the SPLP is an aqueous solution (of sulfuric and nitric acids) intended to simulate the acid rain.

The TCLP was designed to determine which solid wastes posed sufficient risk to human health and the environment when mismanaged that they should be managed as hazardous wastes (with additional regulations). It simply means that the waste can be disposed in a non-hazardous, but lined (often double- lined) sanitary landfill. In fact, before a hazardous waste can be disposed in a hazardous waste landfill, the TCLP lead leaching levels would have to be reduced to less than 0.75 mg/L of lead (see the RCRA land disposal restrictions outlined in 40CFR268). Thus would be a more real benchmark to compare to, and being lower than this value simply indicates that it is treated enough to be placed in a hazardous waste landfill. Under typical practices of most states, reuse of a waste like this in the environment would require comparison to groundwater or drinking water standards (0.015 mg/L). And normally the synthetic leaching precipitation leaching procedure (SPLP) would be required. Based on this notion, SPLP tests were performed as well as TCLP tests after geopolymerization process, simulating the aging process.

6.2 Experimental Procedure

SPLP test strictly complies to the EPA method 1312 and when it comes to TCLP test (refer to Chapter 2, CRT concrete). Samples showing best results of leaching tests in Table 6.1 were selected. Selected CRT concretes were size-reduced into less than 0.95 cm. Those samples were leached with acetic acid for TCLP and sulfuric/nitric acid (6:4) for SPLP and shaken for 18±2 h in the shaking chamber at 30-35 rpm. Concrete samples were analyzed with ICP.

6.2.1 Results and Discussion

Table 6.1 presents the results of TCLP and SPLP. As far as the TCLP for CRT concrete treated with different biopolymer options are concerned (refer to Chapter 2 CRT concrete), all products of CBC composites are below the standard of lead leachability, 5 mg/L, and further, they are below 0.75 mg/L, which is a benchmark to be placed in landfill. The goal of the CBC for lead is targeted towards the safe disposal value, e.g., the drinking water or groundwater standard of 0.015 mg/L of lead. Considering this is the preliminary investigation, only a small amount of biopolymer, about 18 or 107 ppm in the total composite weight, is admixed. Some composites even showed much lower lead value than detection limit (0.001 mg/L), such as CBC 7 (guar gum 0.1%, 417 g) and CBC 10 (chitosan 0.1%, 417 g).

Table 6.1 TCLP and SPLP of selected CBCs

	TCLP	**SPLP**
CBC 2 (Xanthan gum 0.5% conc. 2% addition by weight)	0.003	< 0.05
CBC 7 (Guar gum 0.1% conc. 11% addition by weight)	<<	< 0.05
CBC 10 (Chitosan 0.1% conc. 11% addition by weight)	<<	< 0.05
CBC 11 (Guar+boric 0.1% conc. 2% addition by weight)	<<	< 0.05
CBC 13 (Xanthan+guar gum 0.1% conc. 2% addition by weight)	<<	< 0.05

<< below detection limit for ICP, 0.001 mg/L.

As for the SPLP of selected CBCs, they are over the drinking water standard, 0.015 mg/L. However, those samples meet the sanitary landfill standard, 0.75 mg/L. TCLP is more reliable when SPLP value is higher than TCLP value. In the case of CBCs, TCLP is acceptable for the leaching procedure.

One of reasons that Pb particles may be entrapped in the concrete, due to the ionic size, ionic radii, 1.20 A, which was explained by two of the main factors influencing the incorporation of an ion into a geopolymer structure were thought to be the ionic size and valence of a specific ion (Van Jaarsveld, J.G.S. et al., 1999) and a reasonable correlation between ionic size and leaching efficiency (Davidovits et al., 1990). Even, Pb inclusion instead of Cu serves to strengthen the structure in terms of the compressive strength. Doubling of the mass amount of Pb ions in matrix resulted in an even stronger product. (Van Jaarsveld, J.G.S. et al., 1999). The reason for contribution to a stronger structure is of a physical nature, such as through more efficient packing or its larger radius.

6.3 Conclusions

The SPLP was originally designed as an alternative to the TCLP. Like the TCLP, the SPLP is designed to determine the mobility of both organic and inorganic contaminants contained in wastes. In contrast to the TCLP, however, the SPLP is not based on a mismanagement scenario that assumes that waste is co-disposed with MSW in a landfill. Rather, the SPLP is intended to simulate the effect of acid rain on land-disposal wastes. While the TCLP relies on extraction fluids that simulate the organic acids that would form from decomposing wastes in a landfill, the SPLP requires the use of extraction fluids that simulate acid rain, which is the only difference between two methods. While significant differences between the SPLP and TCLP results were found, in some cases, SPLP concentrations were higher than TCLP concentrations for the same sample material. Given the inconsistency of results in these two evaluations, the Agency dose not feel justified in proposing to allow use of the SPLP as an alternative to the TCLP at this time (U.S. EPA, 1995).

There appears to be little evidence to support industry's suggestion that the Agency substitute use of the SPLP for the TCLP. As a consequence, the Agency continues to support the use of the TCLP for determining whether waste streams are hazardous by nature of toxicity characteristic. In addition, industry has submitted no data to conclusively demonstrate that the SPLP would more accurately identify mineral processing wastes as hazardous by toxicity characteristic. This provides further evidence still that EPA is justified in applying the TCLP to mineral processing wastes (U.S. EPA, 1995).

Leaching studies are a very powerful tool to determine the immobilization efficiencies of metal and quantify the binding capacity of biopolymer in concrete geopolymer systems. It may tell a limit to the amount of metals geopolymer can tolerate. The metal is physically and chemically bonded to the structure. The immobilization of metals occurs through the formation of metal silicate chelates that serve to stabilize the polymeric silicate chains through active metal oxide and hydroxide bonds (Trezek et al., 1992), which is in an agreement with new structure of biopolymerized concrete geopolymer that efficiently entrap the metals.

CHAPTER VII

Comparison of Organic Containing Geopolymer and Inorganic Geopolymer

7. Comparison of Organic Containing Geopolymer and Inorganic Geopolymer

7.1 Comparison between inorganic geopolymer and geopolymer containing geopolymer

Inorganic geopolymer and geopolymer containing geopolymer was compared in terms of compressive strength, permeability, structure, and so on. Table 7.1 shows the comparable differences.

Table 7.1

Comparison of inorganic geopolymer and organic containing geopolymer

	Inorganic geopolymer*	**Organic geopolymer (Portland cement based)**
Compressive strength	1450-4351 psi (very varied values depending on alkali solution): after 14d curing	4600-6100 psi : after 7d curing
Pressure for manufacturing	Need for reduction of pore sizes	No need
Permeability	10^{-9}	10^{-10}
Structure building block	Silica and alumina	Calcium and silica

Table 7.1 continued

Heavy metal removal (Pb)	60 %	99.99 % for best results
pH for manufacturing	>12 (14 is best)	mild basic
Shrinkage for 7d	0.2 %	1.0 %
Curing time	1 d	7-30 d

*based on Van Jaarsveld et al., 1999.

In terms of compressive strength, organic geopolymer is superior to inorganic geopolymer. Inorganic geopolymer shows the fluctuated value of strength according to the alkaline solutions such as KOH or NaOH. These values were obtained from 14d curing. The value will be lowered provided it is 7d curing. On the other hand, organic geopolymer's value after 7d curing is very trustworthy since its minimum and maximum values are strong enough for construction materials, comparing the strength of ordinary concrete, 4135 psi in this study.

For the pressure of manufacturing, inorganic geopolymer requires for pressure while making it, while organic geopolymer dose not need it. As for the permeability, both geopolymers show similar values that are very low permeability, comparing with sand ($10^{-1} - 10^{-3}$) and clay (10^{-7}). When it comes to the structure, inorganic geopolymer contains the majority of silica and alumina, so-called, aluminosilicate while organic geopolymer does calcium and silica as a backbone polymer. As mentioned earlier in previous chapters, the inclusion of calcium is important back-up of building blocks for the strong structure, which was already agreed by Xu and Van Deventer, 2002). Heavy metal immobilization occurs in both geopolymers. Removal efficiency of Pb is very high for organic geopolymers, due to the characteristic property of Pb in organic geopolymers. Inorganic geopolymers requires very high alkaline condition in manufacturing it. On the contrary, organic geopolymers need the mild basic condition. Only merits for inorganic geopolymers are short curing time and low shrinkage of which properties do not affect the commercial availability for organic geopolymers. The most important merit for organic geopolymer is no need to avoid the current Portland cement commercial situation where world cement market has been for centuries.

The price comparison between ordinary concrete and biopolymerized concrete with CRT is that biopolymer-modified concrete can be made. For example, only the difference between ordinary concrete and CRT concrete is the involvement of CRT portion and biopolymer solution. Like it was mentioned, CRT glass was intended to replace the sand portion, which results in the reduction of the price of materials. The biopolymer solution may add up on the price of total price of materials.

Table 7.2

Cost comparison of xanthan gum and chitosan

	Xanthan gum	**Chitosan**
Biopolymer solution used to make 2%-11% by wt. in composite	70-417 g	70-417g
ppm value in total weight of composite	18-107 mg/kg	18-107 mg/kg
Unit price of biopolymer	$5 / 1kg	$20 / 1kg
ppm value price used to make 3717 g of composite	0.009-0.0535 cents <<< less than $1	0.036-0.214 cents

However, the biopolymer is very minute amount to be added in the composite, as of ppm level range (18-107 mg/kg). In Figure 7.2, this value of pure xanthan gum is in the range of price (0.009-0.0535 cents), considering the price of xanthan gum as $5 /

1 kg, while the value of pure chitosan has the range of price (0.036-0.214 cents) for $20 / 1 kg. The price of biopolymer consumption for the composite is less than a dollar. It is concluded that bioplymer involvement dose not affect the price increase, which means, this technology is very economical.

PART II

Geopolymerization

(Geopolymerization of Biopolymers and Synthesis of Geopolymer)

Part II was presented in 2003 ACS (American Chemistry Society) West Regional Meeting at Long Beach, and published in Journal of Carbohydrate Polymers in 2004 (Kim et al., 2004).

CHAPTER VIII

Geopolymerization of Biopolymers

8. Geopolymerization of Biopolymers

8.1 Introduction

Melanoidins are materials formed primarily by the interactions between carbohydrates (carbonyl groups) and amino acids or proteins (free amino groups). The complex network of interactions, resulting in melanoidins as the final reaction products, is commonly referred as the Maillard reaction. It occurs in most foods upon heating or during storage and also in the human body. The Maillard reaction is responsible for flavor, aromas, nutritional value, textural properties, and color development in food.

The significance of this type of the Maillard reaction is implicit in the formation of melanoidin in a wide variety of natural processes. Organic sediments found in our ecosystem are abound in possible raw materials for the melanoidin reaction, for example, nucleic acids, proteins, polysaccharides, and mucopolysaccharides (Young et al., 1974). Therefore, it may also play an important role in the formation of humic acids under natural environments. On the basis of the similarities of the physical and chemical properties of the melanoidins and humic acids (Stevenson, 1982), melanoidins could be precursors of nitrogen-containing humic acids. Humic acids form interpenetrating polymer networks (IPN) with polysaturated triglycerides, which may be a marker for geopolymers.

The concept of geopolymerization has emerged as a possible technological solution for the effective stabilization and immobilization of toxic materials during the last decade (Van Jaarsveld et al., 1997). It is evident from the literature written by a few scientists that the formation and structure of geopolymers are still poorly understood. Van Jaarsveld and Van Deventer introduced the geopolymers with matrices well suited for the immobilization of toxic materials some years ago. This type of geopolymers, so-called, inorganic geopolymers, cannot fully explain the organic containing geopolymers widely existing in the crust of the earth. In this sense, the definition of geopolymers should include both inorganic and organic geopolymers; inorganic geopolymers are the synthetic analogues of natural aluminosilicate materials (Van Jaarsveld et al, 2002) and organic geopolymers are the synthetic analogues of naturally occurring macromolecules. Typical types of inorganic geopolymers can be categorized as kaolinite (clay) and zeolites and organic geopolymers as the bitumen and kerogen, carbonaceous organic macromolecules, which have been formed in the lithosphere over the geological time scale.

In a sense, the connection between biopolymer-modified concrete and geopolymerization should have to be elucidated before the geopolymerization of pure biopolymers. Biopolymer containing concrete materials are apt to have a mechanical strength and durability since their structural characteristics are similar to those of Egyptian building materials showing the unique design of inorganic and organic compounds (e.g., humic materials in clay and straw) involvement. This organic part in concrete composite will have a high chance to transform to humic materials, pre-form of geopolymer, in nature, which is main concept of geopolymerization. This type of concrete is still in chance to be exposed to the reactions with organic materials widely existing in environment, even though the concrete dose not contain the organics. Both cases of organic-modified concrete and Egyptian construction materials ascertain that small amounts of organic materials involved in bulky size of inorganics tend to amply control the property of composite materials, due to the cross-linked reaction between organic and inorganic compounds.

Part II will introduce how biopolymers simply transform to geopolymers and help enlighten the concept of geopolymerization. Characterization of geopolymers in nature can be identified through simulative geo-chamber (pressure cooker) with model compounds and biopolymers. Therefore, simulations should address that biopolymers may covert to geopolymers, although some biopolymers do not contain the nitrogen functional groups. Still, biopolymers can react with soil amino groups, forming geopolymers.

8.2 Experimental Procedure

All reactants were dissolved in deionized water and cooked at 105 °C or 135 °C in an aging chamber, pressure cooker (6 quart) with 15 psi, manufactured by Presto. The conversion time of geopolymers can be shortened by appropriate temperature treatment, as a trade off can be made between time (geological age) and temperature.

For this reason, a pressure cooker can be utilized as an aging chamber. Reaction time was applied at 2 h or 4 h interval. Glucosamine, glucose, and glycine were prepared for different combinations of experiments, in the concentrations of 0.01 M, and 0.01 M, 0.25 M and 0.5, 1, 2 M, respectively. Glucose was manufactured by Mallinckrodt and glucosamine and glycine were manufactured by Aldrich. Green tea was used as nitrogen containing organic matter. A tea bag, made by YAMAmotoYAMA, was dipped in the DI water of 250 mL beaker for 20 min. It should be cool down for the precipitates to settle down. Human urine was also used. 10 mL of each solution of different concentrations, prepared at a ratio of one to one, was poured into 30 mL vials that would be placed in the chamber with glass wool clogged on top of vials in order to prevent a severe evaporation of solutions. The Maillard reaction in this study was evaluated by UV / visible Spectrometer, Vectra 286/12, Hewlett Packard. Xanthan (0.1 % and 0.2 %) and chitosan solution (0.1 %) were prepared for the Browning effect of the Maillard reaction.

8.3 Results and Discussion

Melanoidin has a strong absorption band between 280 and 300 nm in UV spectra (Young et al., 1974). Measuring the rate of melanoidin formation in model systems will allow early detection of the Maillard reaction. Figure 8.1 shows the peaks of melanoidin formed in the Maillard reaction of model system (glucose: 0.25 M and glycine: 0.5 M). Melanoidin formation is equivalent to the color change distinctly observed by naked eyes. This yellow-brown pigment is referred to as a melanoidin chromophore that is simply shown in the crosslinked reaction caused by covalent bonds between glucose and glycine.

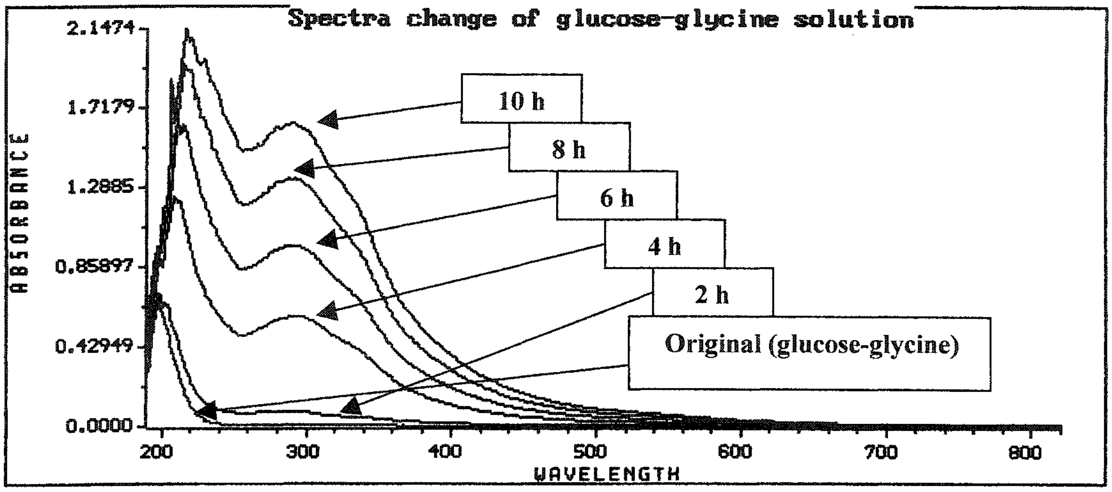


Figure 8.1 Melanoidin peaks occurring in the Maillard reaction of model compounds.

Glucosamine (0.01 M) was cooked at 105°C for 10 h at a two-hour interval. The peaks at 280 nm distinctly grew as the geo-chamber reaction proceeded, shown in Figure 8.2. Glucosamine contains the amino group in its structure. No melanoidin peak was shown in the original spectrum of glucosamine. The Maillard reaction occurs under heat when the amino group in glucosamine forms the melanoidins by crosslinking with carbohydrates in the glucosamine. The color became more yellowish as time progressed.

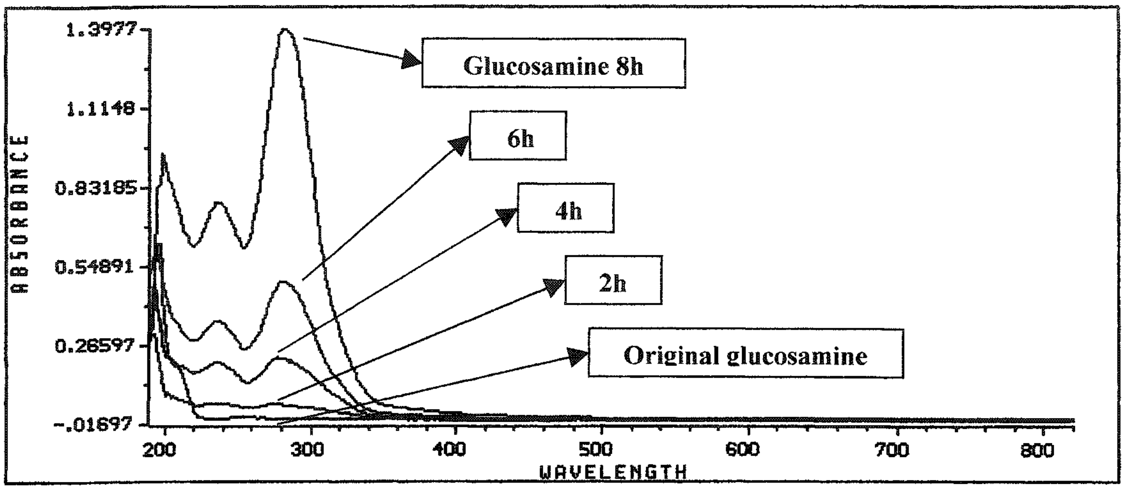


Figure 8.2 The Maillard Browning of glucosamine at a different time frame.

The rate of Maillard reaction is known to be affected by chemical, physical, and physico-chemical factors (Manzocco et al., 1999). Parameters affecting the kinetic behavior of normal Maillard reaction are also true for those of the Maillard reaction occurring in biopolymers, which includes an increase in temperature and time of heating, water activity, pH, carbon-to-nitrogen ratio, the degree of unsaturation, and the chemical aromaticity.

The production of melanoidin varies especially with the temperature and time of heating. Water is produced during the Maillard reaction, thus the reaction occurs less readily with a high water activity, a_w. The concentration of melanoidin produced is very mild. Hence, the product from the Maillard reaction in this study can be a low molecular weight water-soluble Mailllard reaction product (LMW).

The Maillard reaction in chitosan solution is totally dependent on aging time and temperature as original chitosan does not have any peak around 280 nm as shown in

Figure 8.6. In Figure 8.3, the production of melanoidin compound increases with temperature and aging time increasing, although many intermediates are involved. It shows the reaction time and temperature dependence in the Maillard reaction of chitosan. The Maillard reaction is also influenced by the participating reactants.

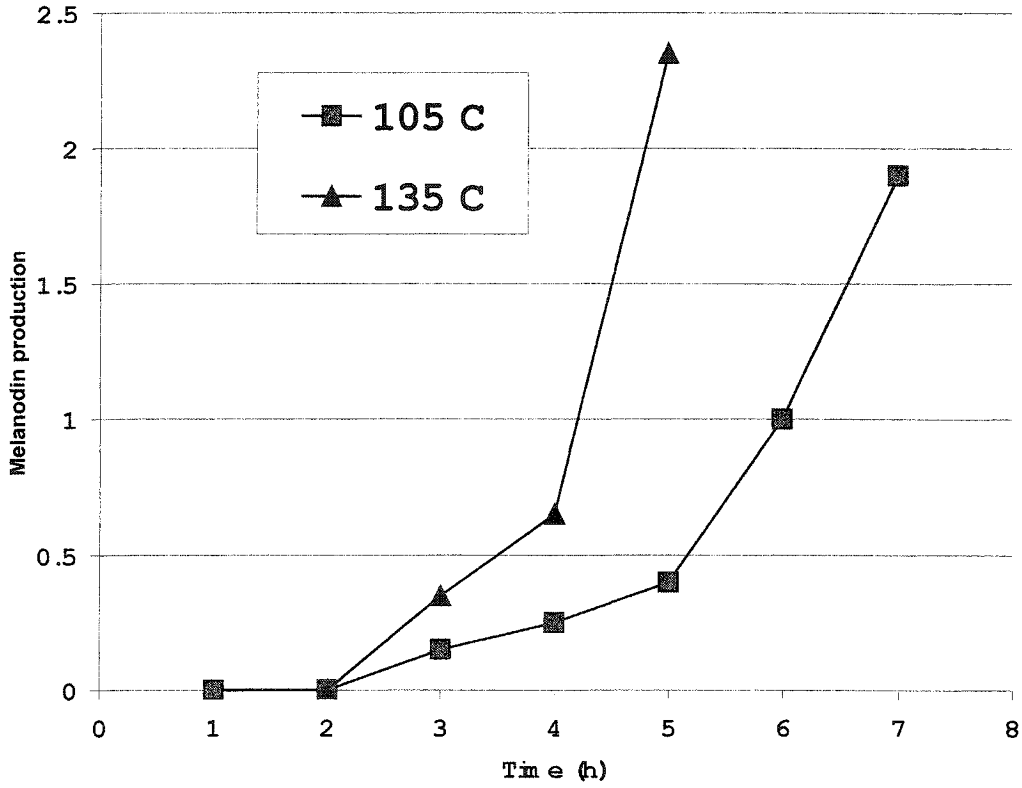


Figure 8.3 Melanoidin production at different aging time and temperature.

Chitosan + Glucose (0.01 M) was compared with glucosamine (0.01 M) at the same reaction time of 8 h. Original chitosan dose not have middle peaks around 220-260 nm. Both peaks are in the same shape in Figure 8.4, which means chitosan + glucose forms glucosamine under heat. Chitosan plays a role in providing nitrogen functional group, thus producing the melanoidin with glucose, carbohydrate. Both peaks have the distinct melanoidin peak.

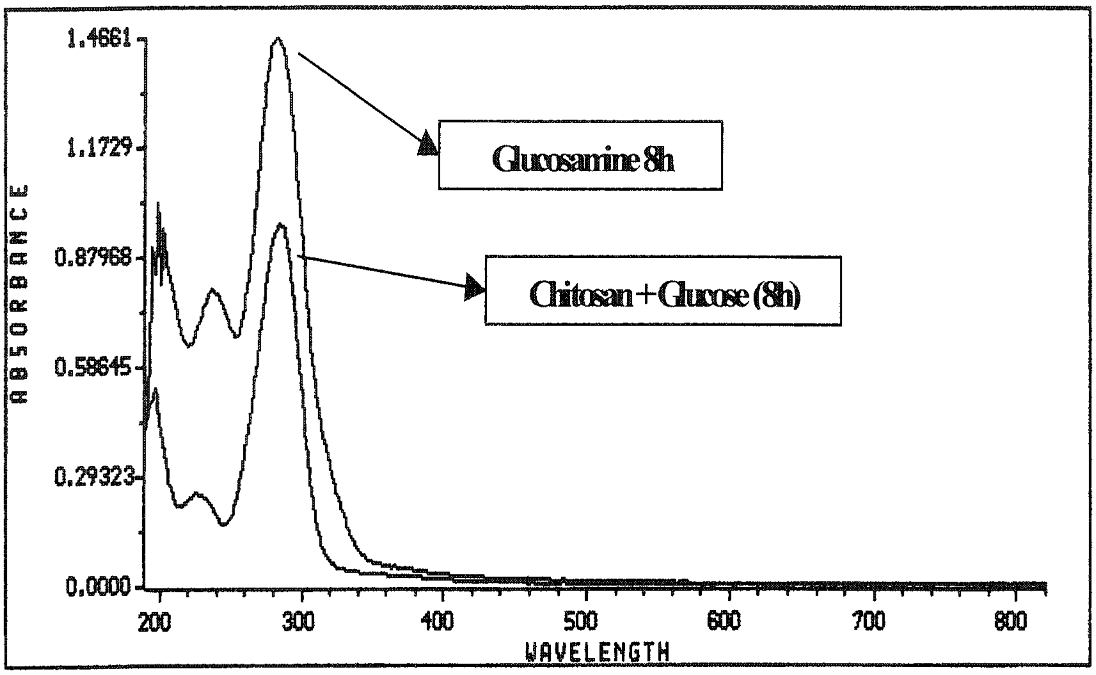


Figure 8.4 Spectra comparison of glucosamine and chitosan + glucose in the Maillard Browning.

Chitosan + Glucosamine (0.01 M) was also cooked for 8 h, and compared with glucosamine (0.01 M) and chitosan + glucose (0.01 M). Chitosan + Glucosamine showed the same melanoidin peak in Figure 8.5, although it had different shapes of peaks, comparing with those of glucosamine and chitosan + glucose around 200-260 nm. Taking into consideration the original spectra of chitosan + glucose and chitosan + glucosamine, heat obviously changed the chemical structure of samples. Chitosan + Glucose has higher concentration of melanoidin formation than Chitosan + Glucosamine that was expected to have more melanoidin production due to its more nitrogen groups. The Maillard reaction depends on the availability of carbohydrate reacting with amine groups, meaning that extra amine group is not necessary for the Maillard reaction to take place. Also, extra carbohydrate is not required for the occurrence of the Maillard reaction, observing that melanoidin peaks are overlapped in the solution of 0.1 % and 0.2 % xanthan gum reacting with green tea (Figure 8.8).

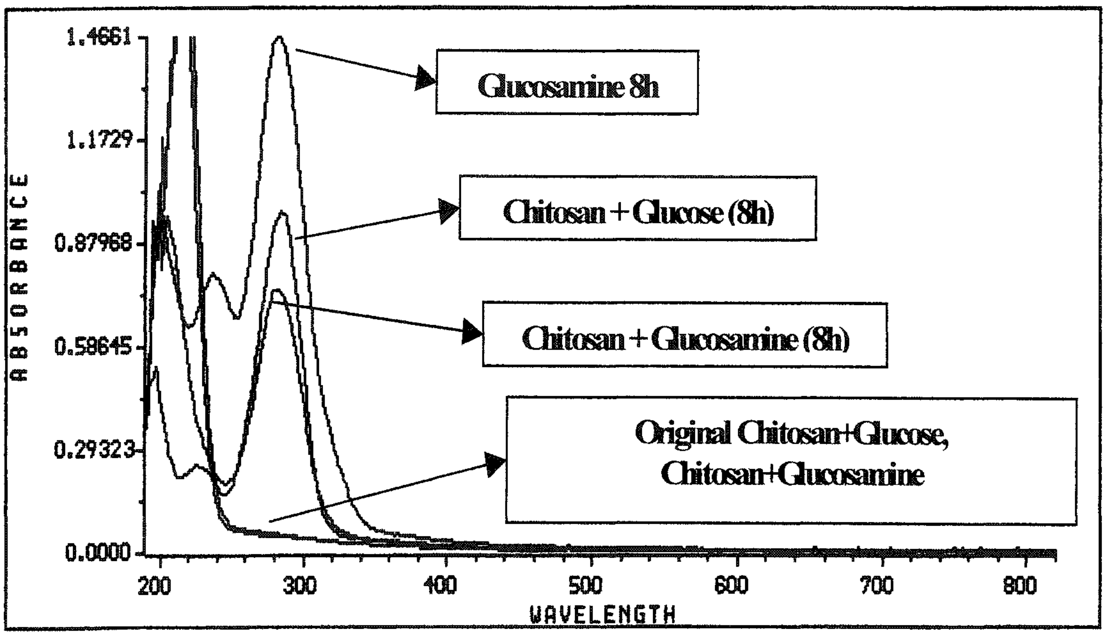


Figure 8.5 The Maillard Browning of chitosan + glucose and chitosan + glucosamine.

The color change hardly happened in xanthan gum system while the color apparently changed in chitosan system, although the color change in chitosan was not obvious for 10 h. An observable color change was made after 16 h. The Maillard Browning actually occurred according to the spectra in Figure 8.6.

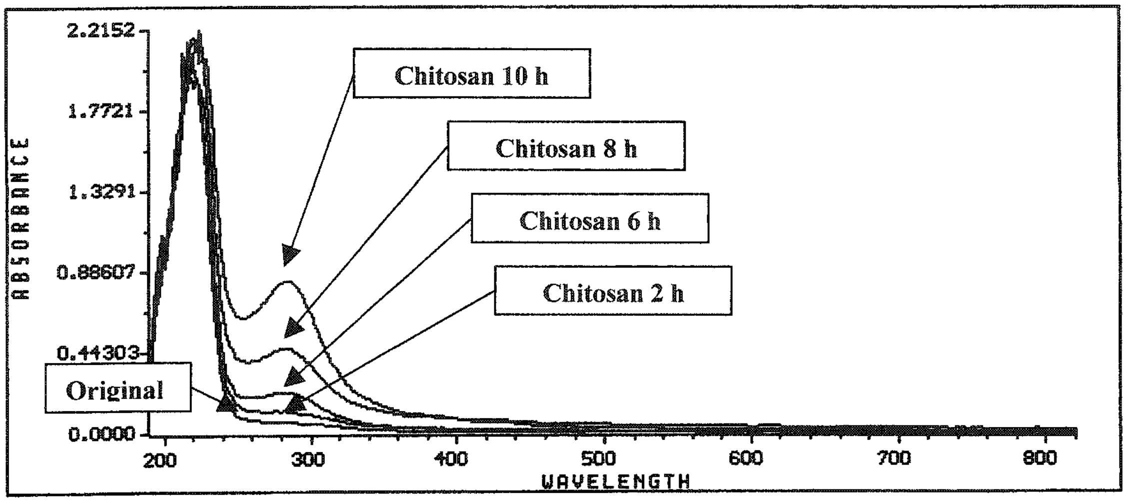


Figure 8.6 Spectra of melanoidin in the Maillard Browning of chitosan.

Chitosan shows the same melanoidin's peak around 280 nm as shown in model system of glucose and glycine solution as reaction time progresses in an aging chamber, since it structurally contains a nitrogen compound working as an amino group. However, xanthan gum does not show the melanoidin's peak as shown in chitosan and model system (Figure 8.7), due to the reason that it does not contain such a nitrogen function as an amino group, which is necessarily required to make the Maillard reaction happen.

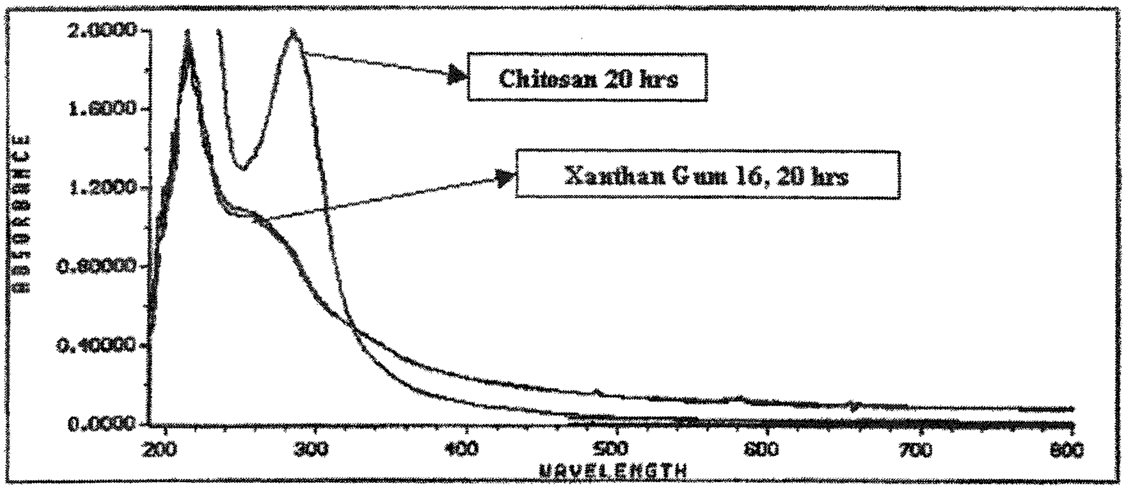


Figure 8.7 Comparison of xanthan gum and chitosan spectra in terms of melanoidin.

Biopolymers like xanthan gum, not having nitrogen groups in their structures still have a chance to react with nitrogen containing organic matters occurring in nature, e.g., urine, tea, caffeine, etc. As a result, xanthan gum showed the same melanoidin peak when reacting with such nitrogen containing organic matters, shown in Figures 8.8 and 8.9. Theoretically, biopolymers can convert to geopolymers in a natural environment where nitrogen-containing organic compounds are in wide occurrence.

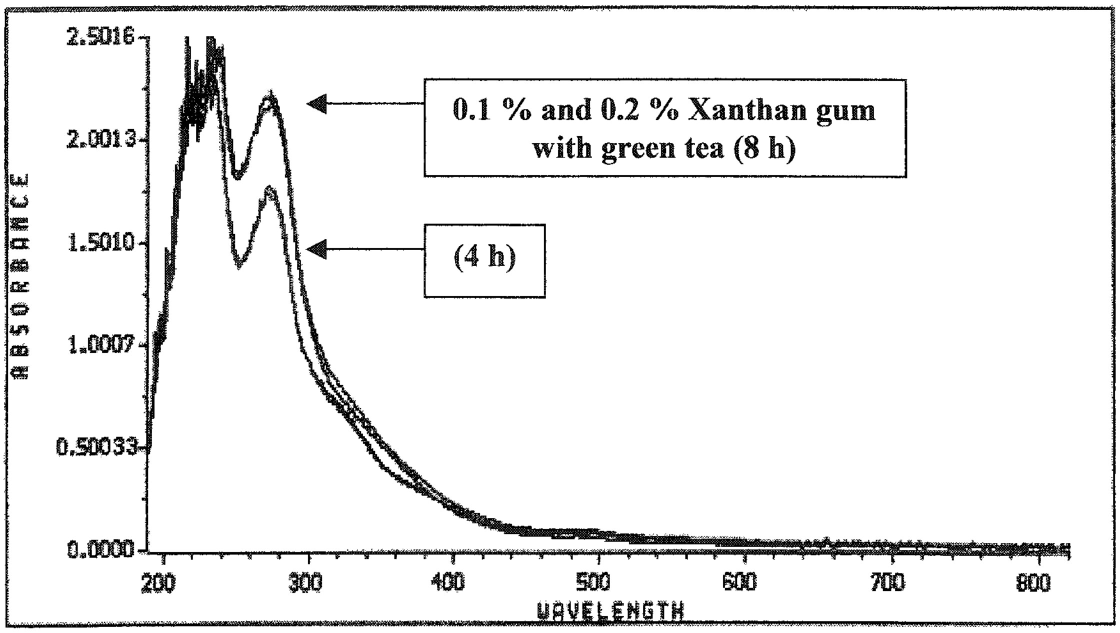


Figure 8.8 Occurrence of melanoidin from the Maillard reaction of xanthan gum reacting with green tea.

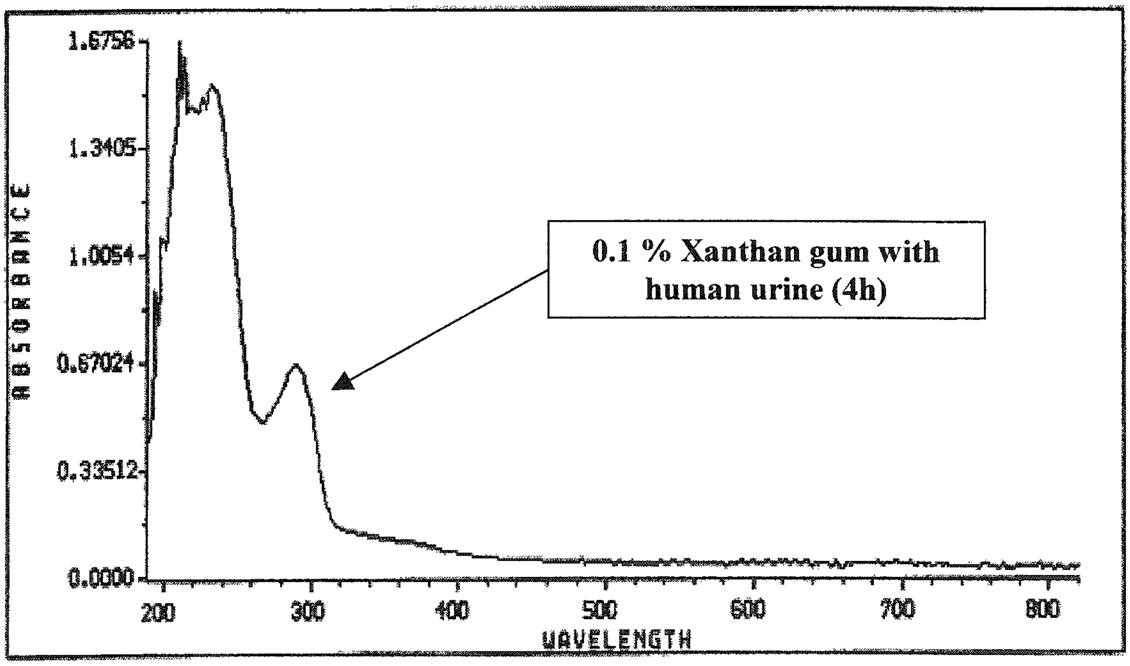


Figure 8.9 Occurrence of melanoidin from the Maillard reaction of xanthan gum reacting with human urine.

8.4 Conclusions

The Maillard reaction can simulate a possible pathway for the formation of geopolymers in nature, a characteristic property of which is the content of high concentration of humic materials, containing melanoidin, a precursor of humic material.

1) The Maillard reactions occurring in these experiments of glucosamine, chitosan + glucose, and chitosan + glucosamine are strongly dependent upon temperature and aging time. Considering that the original peaks do not have malanoidins, the reactions never take place without temperature.
2) The Maillard reaction also depends on the carbohydrate molecules as well as on the nitrogen functional groups, which means the appropriate ratio of carbohydrate and nitrogen groups would cause the Maillard reaction to start.
3) Chitosan can be a source of nitrogen containing organic to make the Maillard reaction happen. It can form melanoidin or humic acid when reacting with a carbohydrate.
4) Xanthan gum does not show the melanoidin peaks upon being heated unlike chitosan. However, it shows the melanoidin peaks when reacting with nitrogen containing organic materials such as urine, glycine, and green tea, which can take place in natural soil.

CHAPTER IX

Synthesis of Geopolymer and its Unique Property

9. Synthesis of Geopolymer and its Unique Property

Geopolymer is the most stable form in the earth. Some construction materials can exist and last for long due to this concept of geopolymers. For example, most of Egyptian building structures are in shape by today, since they are under the theory of geopolymer, where organic involvement is necessarily required for the formation of geopolymer. Again, the geopolymer proposed by Davidovits contains no organic part, which is a big misinterpretation that may have been a limitation for themselves. One example can explain for the bias, even Egyptian builders used the plants (eg., straw) for giving more strength of ancient concretes and mortars. They mixed inorganic materials and organic source that can be very small amount comparing to bulky size of inorganics. Nevertheless, organics are a key parameter governing the strength and durability of structure. In this chapter out of scope of concrete-based geopolymer, synthesis of geopolymer based on petroleum was conducted according to the Formation of geopolymer (kerogen) from biomass.

Bitumen and kerogen are carbonaceous organic macromolecules, which can be classified as geo-polymers since they have been formed in the lithosphere over the geological time scale. They can produce oil, gas and carbon, which are the precursors for petroleum. A modern analogy of geopolymers is the humus materials, which are resistant to biodegradation since they are crosslinked. A sample geopolymer formation can be visualized through the transformation scheme as shown in Figure 9.1.

The conversion time of geopolymers can be shortened by appropriate temperature treatment as a trade off can be made between time (geological age) and temperature. The advantages of geopolymers are as follows:

- Metals cannot be leached out in aqueous solution of various pH levels.
- Metals are coordinated through gaps or holes of the carbonized condensed aromatic rings or in association in the π-system.
- Radiation stable- asphaltene is a free-radical acceptor and has extremely low G-yield.
- Chemically stable- kerogen can be stable in concentrated acids, e.g., HF, HCl, and H_2SO_4.
- Thermally and mechanically stable- not pyrolyzed below 400°C.
- Content of high concentration of humic materials.
- Resistance to microbial degradation.

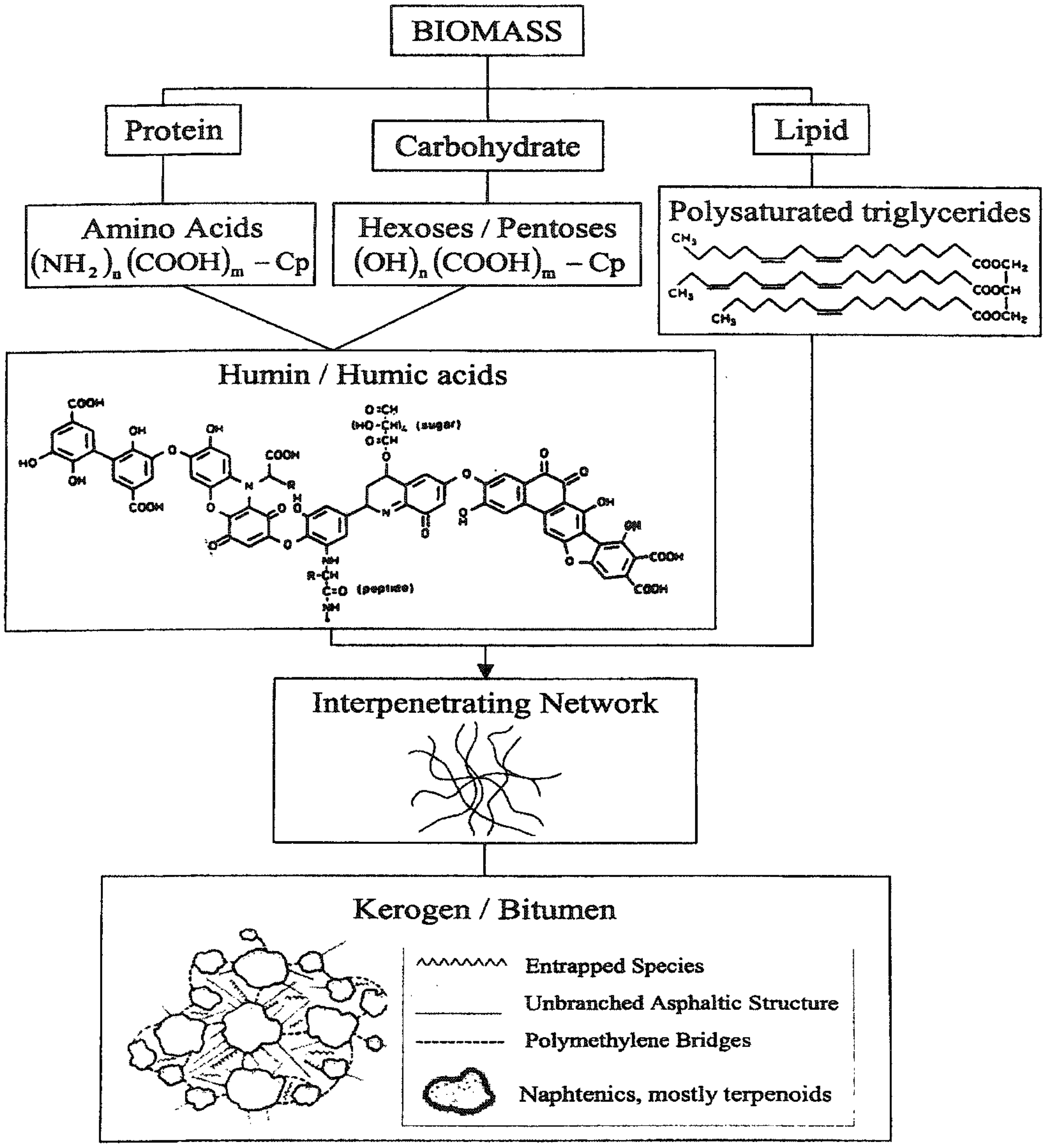


Figure 9.1 The Formation of geopolymer (kerogen) from biomass.

CHAPTER X

Summary, Conclusions, and Recommnedations

In general, CBC composites showed competitive strength of compression when compared with that of ordinary concrete mixtures. Some cross-linked composites showed more than 30% higher strength in the best workable performance. CBC composites proved very consistent in the results of the compression test. CRT glass can replace sand in the CBC composite, knowing that addition of CRT glass has become part of phases of cement, simply containing 67% CaO (alite), 22% SiO_2 (belite), 5% Al_2O_3 (aluminate), and 3% FeO_3 (ferrite). Apart from this, CRT glass is very close to sand material in terms of chemical structure. Thus, CRT glass and concrete materials are compatible with one another. Also, lead from CRT and biopolymers have a high affinity for carbonate systems. Chelation between them enables the cross-link reaction to occur within a concrete microstructure.

As the first case study, selenium wastes were experimented on in order to remove the selenium concentration in its byproduct from glass manufacturing company. A logical conclusion from the preliminary experiments is that the addition of a large percentage of selenium waste to concrete is not viable for this type of waste because of a high water demand that inhibits the cement reaction. High content of waste containment was tried at more than 30% of weight as waste. Cement reaction hardly occurs in terms of strength. Thus, a decrease in the percentage of selenium waste to the concrete was the only solution, and finally increased the mechanical strength of the resulted concrete composites. The optimum percentage of selenium waste content for making concrete composite is around 1-2% by weight. Such a composite has no selenium leachability and improved mechanical strength compared to ordinary concrete with subsequent marketable value.

Biopolymerized concrete with no waste showed very high compressive strength for both biopolymer solutions such as xanthan gum and chitosan. Tests show a pronounced trend in the increased amount of strength of cube concrete over cylinder concrete. Excessive amount of biopolymer involvement is not appropriate to increase the strength of structure. A new structure was built, based on XPS and FTIR analyses. XRD data support the fact that biopolymer containment leads to a new phase of material by maximizing the crystallinity of the amorphous region in concrete molecules to be crosslinked by biopolymer chain system. Based on this concept, biopolymerized concrete is more likely to become a new phase internal microstructure by affecting the chemistry and morphology of current concrete structure. This type of new mineral composite using food-grade biopolymers can be used for building materials and immobilization systems of toxic metals, proven by CBC (CRT concrete), and causes no disposal problem after concrete was used and may meet the needs of environmental products with less concrete smell and dust as well as strong structure in the future.

The results of leaching tests of CRT composite showed a considerable decrease in Pb leachability, less than 5 mg/L or below 0.75 mg/L. Some composites showed the leachable lead below the drinking water or groundwater standard of 0.005 mg/L of lead. Such low leaching is expected to remain the same or decrease throughout geopolymerization steps for many years. It is not necessary to add large amounts of biopolymer solution in order to obtain high strengths of composite and low leachability of lead. In this study, for example, a very minute amount of 70 mg or 417 mg of biopolymer in 3717 g of concrete can be translated into a pure biopolymer within the range of 18-107 ppm by weight in terms of composite. Yet, this minute amount of biopolymer is effective in binding Pb and giving high strength of workable composite. This efficient and cost-effective CBC (CRT-Biopolymer-Concrete) composite is a new class of biopolymer-modified material that can potentially perform an important role in relieving the current CRT waste problem. In this sense, the leaded glass from CRTs, using the cross-linking capacity of xanthan gum, guar gum, and chitosan, was transformed into safer, less toxic, and less hazardous products with possible applications such as foundation and building materials for construction, environmental barriers as an encapsulation matrix to prevent the leaching of metals and low-level nuclear waste encapsulation, nuclear power plant reactors, decorative tiles, and X-ray shielding products.

Leaching studies are a very powerful tool to determine the immobilization efficiencies of metal and quantify the binding capacity of biopolymer in concrete geopolymer systems, which can compensate for the limitation of surface analysis of instrumental methods. TCLP and SPLP tests were conducted. Both results are very recommendable under EPA standard, 5 mg/L for Pb and CRT concrete is slightly over the drinking water standard, 0.015 mg/L. According to EPA recommendations, TCLP data are more reliable to choose than SPLP when SPLP values are higher than TCLP. In this case, SPLP data are not an appropriate analysis for CRT concrete.

It is complicated to identify and characterize the concrete-based geopolymers, since they are partially in amorphous phase. Making use of three methods such as XPS, FTIR, and XRD were helpful and informative although they may provide the fragmented information of the concrete geopolymer. Most of the instrumental analysis is subject to the surface region of samples. Nonetheless, what is clear from XPS, FTIR, and XRD analyses is that there is a strong chemical reason for the observed differences in the physical properties of the concrete geopolymers, mostly due to the increasing extent of polycondensation, confirmed by the crosslink power of biopolymers. In other words, the nature of biopolymer either physically or chemically influences the structure of concrete without changing the basic Ca and Si building blocks of concrete matrix. In this sense, this instrumental approach is worth researching since no one tried to enlighten the biopolymer containing concrete and can put up a milestone on the geopolymer chemistry.

The comparison was made between inorganic geopolymer and organic containing geopolymer, in terms of compressive strength, pressure need while manufacturing, permeability, structure, efficiency of heavy metal removal, pH, shrinkage, and curing time. In most of the categories compared, organic containing geopolymer in Portland cement base is incomparably excellent to the pure inorganic geopolymer made with Al and Si in hydroxyl solution.

As long as it is concerned about the connection between biopolymer-modified concrete and geopolymerization of biopolymers, its initial results confirm that biopolymer-containing concrete materials are likely to have a strength and durability of materials, which is strongly supported by the historical fact that Egyptian building materials last until modern age due to the characteristic design of mixture of organic (e.g., humic materials in river clay and straw) and inorganic compounds, similar to that of biopolymerized concrete composites that are in this study. Organic containing materials, analogues of biopolymer, may transfer to a form of geopolymer containing high humic materials through the geopolymerization reaction for the geological time period.

The Maillard reaction occurring in biopolymers was investigated to prove that biopolymers could convert to geopolymers over the years. Melanoidin chromophore was used as a marker for the Maillard reaction to take place. A characteristic property of geopolymers is the high content of humic materials, particularly humic and fulvic acids containing melanoidin. Chitosan can play the role of nitrogen functional groups, forming the precursor of the melanoidin compound. We observed the absorption peak that is identified by UV-Vis Spectrometry, in the chitosan as easy as in the glucose-glycine or glucosamine, respectively. This peak represents the formation of melanoidin, the Maillard product. However, xanthan gum, not containing nitrogenous functions, did not yield the melanoidin peak that would be shown when xanthan gum also reacts with nitrogen containing organic molecules such as caffeine (eg., coffee), glycine, green tea, and urine. The Maillard reactions are dependent upon temperature, and reaction time and occurred in the following experiments: glucosamine, chitosan plus glucose, chitosan plus glucosamine, xanthan gum plus tea, and xanthan gum plus urine. These reactions also depend on the carbohydrate molecules as well as on the existence of nitrogen functional groups. Simple Maillard reaction in biopolymers can help simulate a possible pathway for the geopolymerization phenomena in natural environment.

In the synthesis of geopolymer based on petroleum, analysis of products is very multi-tasking because geopolymer is in various forms, similar to that of humic acid whose standard model should have to be elucidated in the first place. Considering the complexity of model of amorphous humic materials and the communication between humic material as precursor for pre-form of geopolymer and geopolymer, the study of humic materials along with geopolymer should proceed with high technological background (e.g., computer-assisted method). Concrete containing biopolymer for the first time was researched and analyzed by instrumental methods. Indeed, it seems small but great that it may lay out the foundation for the geopolymer and its related chemistry based on this study, if it is projected in the future.

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