ผลกระทบของโครเมียมต่อกำลังของวัสดุจำพวกซีเมนต์

EFFECT OF CHROMIUM ON THE STRENGTH OF CEMENT-BASED MATRICES

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บทคัดย่อ

โครเมียมซึ่งปะปนอยู่ตามพื้นดินของแหล่งที่อยู่อาศัยนั้นเชื่อกันว่าอาจทำให้เกิดอันตรายต่อสุขภาพได้ มีหลักฐานที่แสดงว่านอกจากจะเป็นอันตรายต่อมนุษย์แล้ว ยังทำลายสิ่งก่อสร้างที่เป็นคอนกรีตด้วย อาคารคอนกรีตหลายแห่งที่มีโครเมียมสะสมอยู่ตามพื้นดิน พบว่าเกิดความเสียหาย ดังนั้นเพื่อตรวจสอบว่าความ

เสียหายของคอนกรีตนี้เกิดมาจากโครเมียม งานวิจัยนี้จึงนำโครเมียม III และโครเมียม VI ไปผสมในส่วนผสมของมอร์ต้าและคอนกรีต โดยใช้อัตราส่วนโครเมียมเท่ากับร้อยละ 5 ของน้ำหนักปูนซีเมนต์ จากนั้นทำการทดสอบกำลังอัดและ Leachate ของวัสดุจำพวกซีเมนต์เหล่านี้ การทดสอบ Leachate ใช้ตัวอย่างมอร์ต้าขนาด 2" x 2" x 2" โดยใช้น้ำ Deionized กับกรด Acetic (0.5 N) เป็นตัว Extractant และทดสอบที่อายุ 1 วันจนถึง 56 วัน การตรวจหาโครเมียมที่อยู่ใน Extractant ทั้ง 2 ชนิดนี้จะใช้เครื่อง Atomic Absorption Spectrometer เป็นเครื่องทดสอบ ส่วนการทดสอบค่ากำลังอัดนั้นจะทำการทดสอบที่อายุ 1 3 7 14 28 56 90 และ 180 วัน

ผลจากการวิจัยพบว่าการ Leaching ของโครเมียม III และ VI นั้นแตกต่างกันอย่างมาก เพราะเมื่อใช้น้ำ Deionized เป็นตัว Extractant นั้นไม่พบโครเมียม III เลย แต่พบว่าโครเมียม VI นั้นจะมีค่า Leachate สูงในช่วงแรก ๆ และมีค่าต่ำลงเมื่อตัวอย่างที่ทดสอบมีอายุมากขึ้น กรณีเมื่อใช้กรด Acetic (0.5 N) เป็นตัว Extractant สามารถตรวจพบโครเมียม III และโครเมียม VI โดยที่ตัวอย่างที่ใช้โครเมียม VI จะมีค่า Leachate สูงกว่าตัวอย่างที่ใช้โครเมียม III สำหรับทางด้านกำลังอัดนั้นพบว่า การใช้โครเมียม III ในอัตราส่วนร้อยละ 5 ของน้ำหนักปูนซีเมนต์ ไม่ทำให้กำลังอัดของมอร์ต้า หรือคอนกรีตลดลงแต่อย่างไร นอกจากนี้ยังพบว่า คอนกรีตที่มีโครเมียม III ผสมอยู่จะให้ค่ากำลังอัดสูงกว่าคอนกรีตที่ไม่มีโครเมียมผสมอยู่ด้วย ในกรณีที่ใช้โครเมียม VI พบว่ากำลังอัดของคอนกรีตต่ำลงอย่างมาก เนื่องจากคอนกรีตที่มีโครเมียม VI ผสมอยู่ จะมีความเสียหายเกิดขึ้นภายในโครงสร้างระดับจุลภาคของคอนกรีต เพราะฉะนั้นโครเมียม VI จึงเป็นสารที่มีผลกระทบทางด้านลบ ต่อทั้งคอนกรีตและมอร์ต้าโดยเฉพาะอย่างยิ่งต่อกำลังอัด

SUMMARY

Chromium is believed to cause serious health problems when presents in soil in residential premises. There were evidences indicated that chromium even damaged concrete structures and threatened human health. Several concrete buildings have recently found to sustain severe damage due to concrete deterioration. These damages were attributed to the presence of chromium within and around the building premises. To verify whether chromium is harmful to concrete structures, chromium III and chromium VI were used to mix with cement to form mortar and concrete. The percentage of chromium compound in the mix was 5% by weight of cement. Leachate and compressive strength of cement-based matrices were investigated. The 2"x2"x2" mortar cube samples containing chromium in the mix were used to test for leaching and compressive strength. Two kinds of extractant were used: in the 500 ml deionized water and in the 500 ml acetic acid (0.5 N). The leachates were tested from 1 day to 56 days. The Atomic Absorption Spectrometer was employed to detect the leaching of chromium. The compressive strength of cement mortar and concrete were tested at the age of 1, 3, 7, 14, 28, 56, 90, and 180 days.

The results observed from this study indicate that the leaching characteristic of chromium III and VI mortars are very different. With deionized water as an extractant, very little of chromium III leached from the samples. However, for chromium VI mortar, leachate concentrations were high initially and decreased as the specimen became older. When acetic acid (0.5 N) was used as an extractant, both chromium III and VI mortar had a high rate of leaching. Samples containing chromium VI produced higher leachate than those of chromium III. The presence of chromium III up to 5% by weight of cement does not seem to have any effect on the strength of concrete or mortar. The compressive strength of concrete and mortar containing chromium III is higher than the control samples. On the contrary, chromium VI caused severe damage to the microstructure of concrete, resulting in a low compressive strength of cement-based matrices. The presence of chromium VI in the mix clearly affects the long term compressive strength both of concrete and mortar.

INTRODUCTION

Chromium and its compounds are hazardous heavy metal materials and on the Community Right To Know List [1]. Potential source of chromium in industrial waste streams include metal cleaning and chromium plating, encompass pigments, tanning and textile chemicals synthetic rubies for lasers, synthetic emeralds, wood preservatives, catalysts, stainless steels, etc [2]. Chromium can cause serious injuries like burns to the skin, nose, throat and prolonged exposure can cause lung cancer. It can damage the liver and kidneys and has mutated the DNA in the laboratory. Hexavalent compounds are more toxic than the trivalent [1]. Some people believe that chromium is not only threaten human health but also damage concrete structure. This problem can be seen in some places in Jersey City, New Jersey where there are failure of buildings and pavements, being believed to cause by chromium contamination [3]. The results of analyzing the soil from that site showed the chromium concentration was as high as 53,000 ppm [4]. This amount of chromium is much higher than the limit permitted by the Department of Environmental Protection (DEP), which requires to clean up all sites contaminated with more than 75 milligrams of chromium per kilogram of soil [5].

Previously, studies conducted focused on the leaching characteristics of treating sludge or contaminated soil bound into a cement matrix. Little research, however, has been devoted to the effect of chromium itself on the mortar and concrete strength. Sripathi [6] shows that the compressive strength of cement mixing with contaminated soil of chromium

III increases little when the present of chromium is not more than 6% by weight of cement. This means that soil cement mortar containing certain amount of chromium III is not dangerous to its strength. The same study also reveals that the leachate results of trivalent chromium compound did not exceed the Environmental Protection Agency (EPA) standard of 5.0 ppm and solidification of contaminated soil can be made using cement and fly ash. In concrete, the use of chromates as potential corrosion inhibiting admixture in concrete was reported by ACI 212 Committee [7]. But, the effect of addition of chromates to concrete on its performance is not yet fully known. There is ample evidence to suggest that the strength of concrete decreases with increased quantities of potassium chromate [3]. It is therefore recommended that a chromate treatment is required to apply it to the galvanized surfaces rather than add chromates to concrete mixture [8].

Most of the work collected from the literatures mentioned the effect of chromium on the strength of concrete and mortar in the field. Actually, there is not the only chromium that has the influence on the compressive strength, other materials such as sulfate, sulfuric and nitric acid which present in the soil can also cause a serious damage on the concrete and mortar. To verify just only the effect of chromium on the strength of concrete and mortar, others facters are excluded from this investigation.

OBJECTIVES

The objective of this study is to determined the effects of trivalent chromium, Cr (III), and hexavalent chromium, Cr (VI), on the compressive strength of mortar and concrete. Investigations are made to discover whether the chromium, a hazardous heavy metal, will destroy the concrete structures or not. In addition, the leaching of chromium mortar in deionized water and acetic acid (0.5 N) has also been studied.

EXPERIMENTAL PROGRAM

Material

Materials used in this study consist of standard portland cement type I, siliceous sand (river sand), coarse aggregate with the maximum size of 3/8", Cr (III) in the form of $CrCl_3.6H_2O$ and Cr (VI) in the form of $K_2Cr_2O_7$, and water.

Mix Proportion

In this test, Cr (III) and Cr (VI) were mixed in the cement-based matrices to form mortar and concrete. First, the chromium was added into the water and mixed until it dissolved completely. Next, the mortar or concrete was mixed and cast in the usual way. After 24 hours, the specimens were removed from the mold and cured in water. The compressive strength of mortar and concrete was tested at the age of 1, 3, 7, 14, 28, 56, 90, and 180 days. The amount of chromium as $CrCl_3.6H_2O$ (Cr(III)) and as $K_2Cr_2O_7$ (Cr(VI)) used was 5% of cement by weight. The water to cement ratio is 0.5 for mortar and 0.5625 for concrete. The mix proportions for mortar and concrete are shown in Tables 1 and 2, respectively.

CMC is the control mortar sample without any chromium. CMC3 and CMC6 are the mortar samples with Cr (III) and Cr (VI), respectively. In concrete, CMY is the control concrete sample while CMY3 and CMY6 are the concrete samples with Cr (III) and Cr (VI), respectively.

Table 1 Mix Proportion of Chromium Mortar

Sam. No.	Cement (g)	Sand (g)	Chromium (g)	Water (ml)
CMC	500	1375	0	250
CMC3	500	1375	25 (Cr III)	250
CMC6	500	1375	25 (Cr VI)	250

Table 2 Mix Proportion of Chromium Concrete (kg/m^3)

Sam. No.	Cement (kg)	Sand (kg)	Aggregate (kg)	Chromium (kg)	Water (l)
CMY	365	730	1080	0	205
CMY3	365	730	1080	18.3 (Cr III)	205
CMY6	365	730	1080	18.3 (Cr VI)	205

Leaching Test Procedure

The 2"x2"x2" cubes were suspended separately in the 500 ml deionized water and 500 ml acetic acid (0.5 N) extractant and gently stirred by means of magnetic stirrers for 24 hours. The leachates were filtered through 0.45 microns membranes for analyses. The process repeated for 1, 3, 7, 14, 28, and 56 days for the samples in deionized water and 3, 7, 14, 28, and 56 days for the samples in acetic acid extractant. The leachate was detected by using the Atomic Absorption Spectrometer.

RESULTS AND DISCUSSIONS

Effect of Chromium on the Strength of Mortar and Concrete

Table 3 shows the results of the compressive strength of control and chromium mortar. The relationship between the compressive strength and age is presented in Fig. 1. For concrete, these results are shown in Table 4 and Fig. 2.

Table 3 Compressive Strength of Chromium Mortar

Sam. No.	Compressive Strength (MPa)							
	1-d	3-d	7-d	14-d	28-d	56-d	90-d	180-d
CMC	19.6	35.6	42.9	47.5	52.0	54.9	56.0	57.2
CMC3	23.3	44.4	49.3	51.7	54.9	57.5	60.6	65.0
CMC6	20.9	32.3	37.0	40.6	43.4	45.6	48.2	51.4

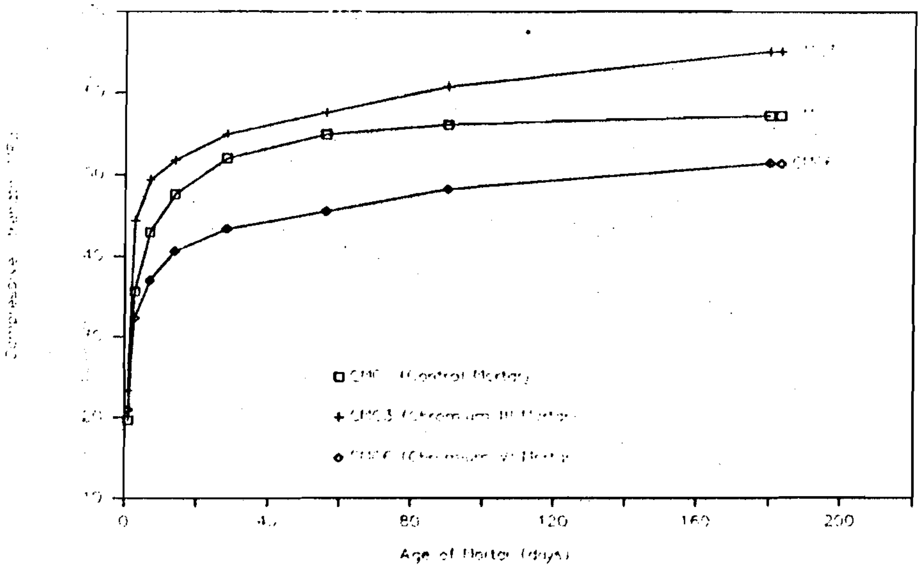

Fig. 1 Relationship Between the Compressive Strength of Chromium Mortar and Age

The difference in compressive strength can be observed throughout the test. The test results indicate that different valences of chromium in mortar have different strengths for the same mix proportions. Up to the age of 180 days, the Cr (III) mortar has a higher compressive strength compared to the control mortar. The compressive strength of Cr (VI) mortar, however, is less than that of the control mortar at all ages up to 180 days. This means that the amount of Cr (III) in mortar up to 5% by weight of cement has a positive effect on the compressive strength up to 180 days. The experimental data obtained from Sripathi [6] also revealed that the compressive strength of soil cement mixture containing Cr (III) increased when Cr (III) content was used from 2% to 6% by weight of cement. Similar results can be observed in chromium concrete containing Cr (III).

The compressive strength of mortar and concrete containing Cr (VI) is always lower than the control and the Cr (III) samples. This means that Cr (VI) is harmful to cement-based matrices. The results was also confirmed by looking at the specimens after being broken. The color of the control and the Cr (III) samples is the same color, it is light gray color. But the color of the Cr (VI) specimen is light yellow and the texture of concrete or mortar is softer than that of the control. For concrete or mortar containing Cr (VI), the heavy metal hydroxide crystals grow too big, it swells the C-S-H gel structure and destroys or looses the structure of the C-S-H gel. That is, the crystallization of salts from supersaturated solutions produces pressures which may cause cracking in the concrete thereby reducing the mortar or concrete strength. Also, because Cr (VI) in cement mixture may form $CaCr_2O_7$, Cr(VI) is leached from cement mixtures readily and results in a decrease in strength of the cement matrix. Laboratory tests indicate that chromium migrates into the pores filled by capillary action over a period of time and causes swelling to occur, resulting in damage to slabs, parking lots, and other structures [3].

Table 4 Compressive Strength of Chromium Concrete

Sam. No	Compressive Strength (MPa)							
	1-d	3-d	7-d	14-d	28-d	56-d	90-d	180-d
CMY	13.0	24.4	31.5	38.9	41.9	45.5	48.6	55.1
CMY3	14.1	33.9	43.7	46.9	50.8	55.1	58.0	62.7
CMY6	9.0	19.6	25.3	30.4	34...	38.4	40.5	44.2

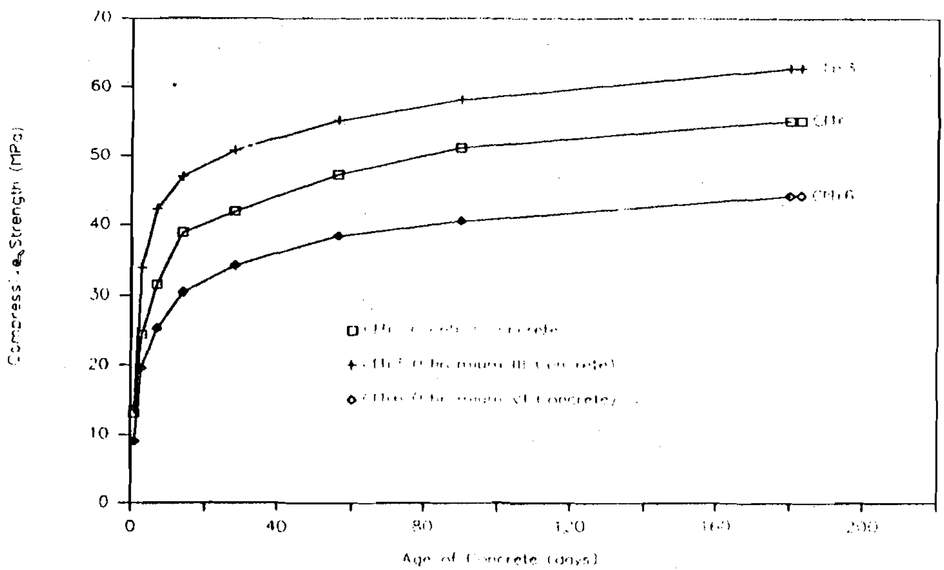

Fig. 2 Relationship Between the Compressive Strength of Chromium Concrete and Age

Leaching Characteristics with Deionized Water Extractant

The significant differences in the leaching characteristics of Cr (III) and Cr (VI) mortar can be seen in Fig. 3. Leaching tests using deionized water as an extractant on cement-based matrices with Cr (III) show that cement is very good for immobilizing Cr (III) as a result of the formation of $Cr(OH)_3$. With deionized water as an extractant, there is no detectable leaching of chromium from the Cr (III) mortar specimen determined by Atomic Adsorption Spectrometer. But leaching of chromium from the Cr (VI) mortar specimens was clearly observed. Fig. 3 also indicates that the leaching of Cr (VI) decreased with the development of strength of mortar. Before 14 days, the concentration of Cr (VI) was higher than the EPA standard of 5 ppm but was lower than the standard after 14 days.

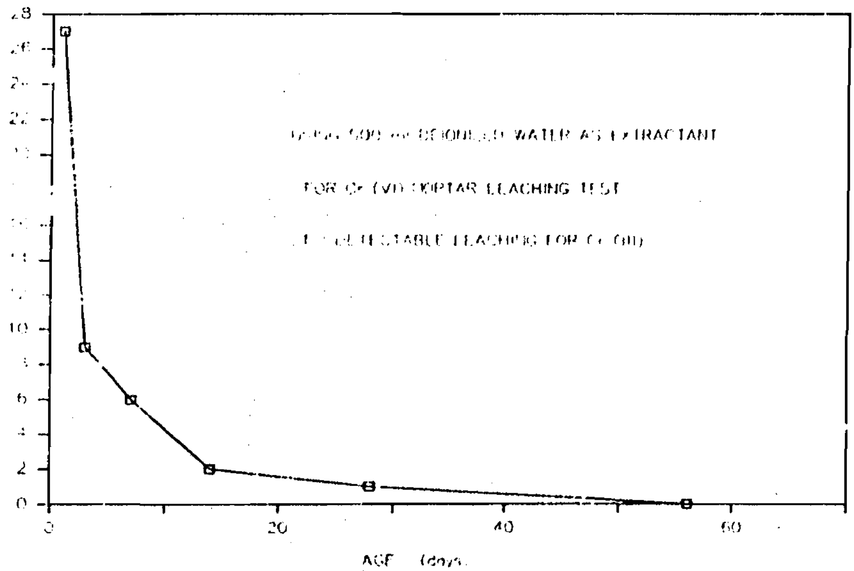

Fig. 3 Relationship between the Leachates of Chromium and Age in Deionized Water

Leaching Characteristics with Acetic Acid (0.5 N) Extractant

The leaching test results of Cr (III) and Cr (VI) mortar using acetic acid (0.5 N) as an extractant are shown in Fig. 4. There is considerably chromium leaching from both Cr (III) and Cr (VI) mortars when using acetic acid as an extractant. The concentrations of both Cr (III) and Cr (VI) in leachates decreased with the development of compressive strength. Chromium leaching from Cr (VI) mortar was much higher than that of Cr (III) mortar at all ages. The maximum chromium concentration in the leachates of Cr (VI) mortar is 420 ppm while those from Cr (III) is only 130 ppm. This may be due to the fact that the strength of Cr (VI) mortar is lower than that of Cr (III) mortar at the same ages. Another season is that the present of Cr (VI) swells the C-S-H gel and destroys the formation of C-S-H gel which makes mortar more permeable and results in a high leachate.

It is noted that both trivalent and hexavalent chromium leach more readily in low pH extractant (in acetic acid, 0.5 N). It is also noted that chromium leaches from Cr (VI) mortar at a relatively high concentrations compared to Cr (III). Thus, the pH and the concentration of hydroxyl ions, has a significant effect on the stability of the heavy metal. In the absence of calcium hydroxide, the pH of the system would be even lower, perhaps affecting the solubility of the heavy metals in a manner unlike a system containing calcium hydroxide. Roy et al [9] showed that the calcium hydroxide in heavy metal (including chromium) cement mixtures is lower than that of conventional mortar.

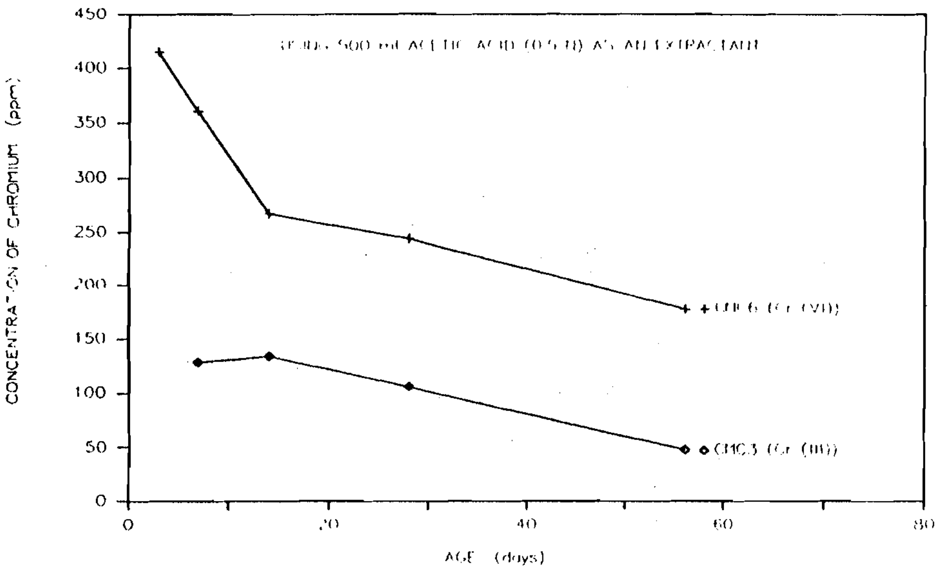

Fig. 4 Relationship between the Leachates of Chromium and Age in Acetic Acid (0.5 N)

CONCLUSIONS

The following conclusions may be drawn from the present investigations.

1. The effect of Cr (III) and Cr (VI) on mortar and concrete strength is quite different when chromium is presented in the cement-based matrices at rate of 5% by weight of cement. The strength of Cr (VI) mortar and concrete is lower than that of the control mortar while the strength of Cr (III) mortar and concrete is higher.

2. The leaching characteristic of Cr (III) and Cr (VI) in cement-based matrices are very different. They have different behaviors with changes in pH and type of extractants. With deionized water as an extractant, no chromium leached from Cr (III) mortar specimens. But chromium clearly leached from Cr (VI) mortar samples and the leaching amount of chromium decreased with the development of the compressive strength.

3. When acetic acid (0.5 N) was used as an extractant, both Cr (III) mortar and Cr (VI) mortar have a great deal of leaching. The chromium leached from Cr (VI) mortar at a relatively high concentration with a maximum of 420 ppm.

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