การใช้เถ้าถ่านหินในการป้องกันการกัดกร่อนของคอนกรีต

โดย

สมหมาย สว่างกิจ
เอนก ศิริพานิชกร
ชัย จาตุรพิทักษ์กุล
จารุรัตน์ วรนิสรากุล
เมธี เวชารัตนา

ภาควิชาวิศวกรรมโยธา
สถาบันเทคโนโลยีพระจอมเกล้าธนบุรี

RP-74

การใช้เถ้าถ่านหินในการป้องกันการกัดกร่อนของคอนกรีต
CORROSION RESISTANCE OF FLY ASH CONCRETE

สมหมาย สว่างกิจ
เอนก ศิรพานิชกร
SOMMAI SWANGKIT
ANEK SIRIPANICHKORN

และ
AND

ชัย จาตุรพิทักษ์กุล
จารุรัตน์ วรนิสรากุล
CHAI JATURAPITAKKUL
JARURAT WORANISALAKUL

Department of Civil Engineering
King Mongkut's Institute of Technology Thonburi
Bangmod, Rasburana, Bangkok 10140, Thailand

และ

เมธี เวชารัตนา
METHI WECHARATANA
Department of Civil and Environmental Engineering
New Jersey Institute of Technology
Newark, New Jersey 07102, U.S.A.

บทคัดย่อ

ในสภาวะที่มีการกัดกร่อนสูง คอนกรีตโดยทั่วไปมักจะผุพังอย่างรวดเร็วเนื่องจากทั้งคอนกรีตและเหล็กเสริมถูกกัดกร่อนจากสารเคมี ทำให้เสียค่าใช้จ่ายในการซ่อมแซมและบำรุงในแต่ละปีเป็นจำนวนมาก เพื่อแก้ไขปัญหาดังกล่าวจึงได้มีการพัฒนาส่วนผสมของซีเมนต์ขึ้นมาใหม่ เช่น โพลีเมอร์คอนกรีต คอนกรีตต้านทานซัลเฟตและอื่นๆ เพื่อเพิ่มคุณสมบัติความต้านทานการกัดกร่อนของคอนกรีต เนื่องจากคอนกรีตดังกล่าวส่วนใหญ่มีราคาแพงมาก จึงทำให้คอนกรีตที่พัฒนาขึ้นมาใหม่นี้ประสบปัญหาในการนำไปใช้งาน ดังนั้นการพัฒนาคอนกรีตที่มีความต้านทานการกัดกร่อนสูงให้มีราคาต่ำ และนำไปใช้ประโยชน์ได้คุ้มค่าเป็นสิ่งที่จำเป็นอย่างมากโดยเฉพาะอย่างยิ่งในสภาพการณ์ที่มีการขยายตัวอย่างรวดเร็วของภาคอุตสาหกรรมในโครงการอีสเทอร์นซีบอร์ด

การวิจัยครั้งนี้ ได้นำเถ้าถ่านหินซึ่งเป็นผลพลอยได้จากการเผาถ่านหินเพื่อผลิตกระแสไฟฟ้าไปผสมในซีเมนต์มอร์ต้าในปริมาณมากๆ เนื่องจากเถ้าถ่านหินมีคุณสมบัติทางพอซโซลานิค และมีขนาดอนุภาคที่เล็กมากซึ่งอนุภาคเหล่านี้จะเข้าไปอุดตามช่องว่างของคอนกรีต ทำให้คอนกรีตดังกล่าวมีความหนาแน่นมากกว่าคอนกรีตธรรมดา และทำให้มีคุณสมบัติในการซึมผ่านต่ำ ด้วยคุณสมบัติดังกล่าวคอนกรีตที่ผสมเถ้าถ่านหินจึงมีอัตราการกัดกร่อนต่ำ หรืออาจกล่าวได้ว่าคอนกรีตดังกล่าวมีความสามารถทนต่อการกัดกร่อนได้ดีกว่าคอนกรีตธรรมดา การวิจัยครั้งนี้จึงได้เน้นศึกษาในด้านความต้านทานต่อการกัดกร่อนของคอนกรีตที่ผสมเถ้าถ่านหิน เนื่องจากช่วงเวลาที่ใช้ทดสอบน้อยกว่าสภาพการกัดกร่อนที่เป็นจริง จึงต้องใช้กรดที่มีความเข้มข้นสูงเพื่อจะเร่งอัตราของการกัดกร่อนของสารเคมี ในการทดลองเบื้องต้นชี้ให้เห็นว่าคอนกรีตที่มีเถ้าถ่านหินผสมแทนซีเมนต์ 50 % มีความต้านทานต่อการกัดกร่อนมากกว่าคอนกรีตธรรมดา ขณะที่คอนกรีตทั่วไปถูกกัดกร่อนจนเป็นผง คอนกรีตที่ผสมเถ้าถ่านหินยังคงสภาพเดิมโดยมีความเสียหายตามบริเวณมุมเพียงเล็กน้อย ในการวิจัยครั้งนี้ได้พิจารณาค่าการสูญเสียน้ำหนักระหว่างกระบวนการกัดกร่อนของคอนกรีตที่ผสมเถ้าถ่านหินและคอนกรีตธรรมดา จากผลการวิจัยจะเห็นได้ชัดว่าคอนกรีตที่ผสมเถ้าถ่านหินจะทนทานกว่า และควรจะใช้ในการก่อสร้างที่มีสภาวะการกัดกร่อนสูง เช่นโครงการอีสเทอร์นซีบอร์ด

SUMMARY

In a highly corrosive environment, conventional concrete often corrodes rapidly due to chemical attack both to concrete and the steel reinforcement, causing enormous amount of money annually for repairs and maintenance of these structures. To improve the resistance of concrete against corrosion, many new cement-based materials such as polymer concrete, sulfate resistance concrete, etc. have been developed. Unfortunately, these products are mostly expensive and economically not feasible to be used in practice. Developing a cheaper and more economical cement-based materials with high corrosion resistance is crucially needed especially for the rapid expansion of industrial facilities along the eastern seaboard.

In this study, fly ash, a by-product or sometimes considered to be a waste product from the coal-burning power plant, is incorporated into cement-mortar in large quantity. The pozzolanic property of fly ash and its very small particle size, which results to the packing characteristics of fly ash in concrete, make fly ash concrete a denser material than conventional concrete. With lower permeability of fly ash concrete, the rate of corrosion of this concrete is then slower, or in other words, fly ash concrete is more durable than normal concrete in the same highly corrosive environment. This investigation puts an emphasis on studying the corrosion resistance of fly ash concrete. Due to time consumption involved in the traditional corrosion test, more concentrated acidic solutions are used in this investigation to accelerate the rate of chemical attack to fly ash concrete. Preliminary test results indicate that fly ash when used as 50% of cement replacement in concrete exhibits excellent durability against chemical attack than normal concrete. While conventional mortar was turned into a pile of sand and powder, the fly ash mortar samples remain consecrated with merely very minor damage to the specimen corners. In this study, weight loss during the corrosion process of fly ash mortar and control mortar was monitored. It is obvious that fly ash concrete is more durable and should be used effectively and economically for structures in the highly corrosive environment such as those along the eastern seaboard.

INTRODUCTION

Concrete structures such as off-shored structures, chemical storage containers, and shore protecting structures, etc. are sometimes used in harsh corrosive environment. The corrosion of concrete by seawater and/or other chemicals and its progress with time is a problem of great importance. To properly design a durable concrete structure requires a thorough understanding on the corrosive process of concrete. However, such a corrosive attack process of chemicals on the integrity of concrete and mortar is very complex. While much of the emphasis in concrete design is given to the strength and the load carrying capacity of the materials, the interrelated factors among its mechanical, physical and chemical properties which control the durability of concrete may have to be closely evaluated and taken into account as part of the design process.

Concrete constituents can easily be attacked by the corrosive environment to which they are exposed. These harsh conditions may be due to weathering, abrupt changes of temperature, abrasion, or attack by chemicals such as sulfates or acids. The more common forms of chemical attack on concrete are the leaching out of cement, attack from sulfate, sea water, and acid solutions. In search for concrete to be used in these harsh environment has led to many durable cementitious composites such as polymer concrete, sulfate resistance concrete, etc. Unfortunately, most of these products are expensive and therefore economically impractical for actual construction projects.

To improve concrete durability, many methods have been suggested. In general, the durable concrete must be dense and have low permeability. Such low permeability concrete can be obtained by lowering the water/cement ratio of the mixes. ACI 301-84 [1] suggests that to achieve a watertight concrete the water/cement ratio should not be more than 0.50 when concrete is exposed to fresh water and should not exceed 0.44 when exposed to sea water. Other methods suggested to improve the quality of concrete are the use of polymer materials as additive, sulfate-resisting cement, high-alumina cement or pozzolanic materials, etc. These potential solutions can only be feasible depends largely on the economical condition. In so far, these materials are very costly and can only be used in small repair projects.

Perhaps the weakest link of the concrete products that is vulnerable to chemical attack is the calcium hydroxide and calcium carbonate. Calcium hydroxide, $Ca(OH)_2$, is one of the products generated from the hydration process of cement. It is produced during the hydrolysis of calcium silicates C_3S and C_2S compounds in portland cement when the cement reacts with water. Excess lime tends to weaken the concrete mass mainly because it is more vulnerable to acid, carbon dioxide, and sulfate attacks. To prevent calcium hydroxide from these attacks, pozzolanic materials such as fly ash is introduced into concrete. The silica content in the fly ash reacts with free lime or calcium hydroxide generated from the hydration process of cement results to calcium silicate hydrate compound. The gel helps fill up the remaining air voids in between fine aggregates and cement particles, making concrete denser, more impermeable and durable [2,3]. In considering the effect of pozzolans in general, it should be noted that silica in fly ash has to be in the form of amorphous since crystalline silica is inert and has very low reactivity rate.

Many researchers have used fly ash to enhance the ability of concrete to resist chemical attack. Nasser and Lai [4] and Irassar and Batic [5] reported that Class F fly ash was a good source of pozzolan which could improve resistance of concrete from sulfate attack. The data on corrosion resistance of concrete samples monitored for more than three years indicated that concrete samples with 20% of cement replaced by fly ash performed better in resisting the reinforcing bars from corrosion than with plain concrete [6]. Sheu, Quo, and Kuo [7] studied the use of fly ash mortar with different particle sizes which was immersed in sodium sulfate solution. They concluded that among those mortar specimens that were tested, the ones with finer particle size of fly ash have greater resistance to sulfate attack than the control sample (without fly ash). However, the minimum proportion of fly ash required for sulfate resistance in concrete is varied. In general, it is believed that it should not be less than 20% [8].

Acid attack is often found to be another major problem for the durability of concrete. It usually starts by dissolving and removing part of the harden concrete. For values of pH in the range between 3 to 6, the attack of acid progresses at a rate approximately proportional to the square root of time [9]. A severe damage on concrete sewer systems can cause by bacterial action especially in warm climate such as in Thailand. Sulfur-reducing bacteria are able to reduce the sulfates which are present in natural waters and produce hydrogen sulfide as a waste product. These bacteria are anaerobic. Another group of bacteria takes the reduced sulfur and oxidize it back to sulfuric acid [10]. Thus the attack from these sulfuric acid occurs and gradually dissolves and deteriorates the concrete surface.

In this study, attempt was made to improve the durability of concrete from acid attack. Fly ash is introduced as a pozzolan into concrete with the expectation that it will react with the excess lime or calcium hydroxide in concrete. By replacing cement in the mix with fly ash, the process thus reduces the amount of free lime or calcium hydroxide which makes such fly ash concrete less vulnerable to acid attack. Another assumption of this process is that the presence of fly ash tends to tie up the available lime in concrete and therefore prevents it from reacting with the acid. To verify these concepts, two kinds of fly ash, wet and dry bottom fly ash, from a utility in New Jersey, U.S.A. were used as cement replacement in concrete. Another type of fly ash from Mae Moh, Thailand was also used in this investigation. Fly ash mortars with 25% and 50% of cement replaced were cast in a standard 2"x 2"x 2" cube. These fly ash mortar specimens together with a control sample made from normal cement mortar were then immersed into a concentrated H_2SO_4 solution to be evaluated for their resistance to acid attack.

EXPERIMENTAL PROGRAM

Source of Fly Ash

The types of fly ash used in this study were from two utilities, one from the Public Service Electric and Gas (PSE&G) Company in New Jersey, U.S.A., and another from the Electric Generation Authority of Thailand (EGAT) at Mae Moh, Lumpang, Thailand. Fly ash from the United States can further be divided into two classes: one from the wet bottom boiler and another from the dry bottom boiler. The difference between these two types of fly ash is that the wet bottom one was burned above the ash fusion temperature while the dry bottom ash was generated below that same temperature. As a result, crystallization of these two ashes were different so as its reactive characteristics. In this study, fly ash samples designated with 6F and HO represent ashes from the dry bottom boiler which are the fractionated 15 micron ash and the original unfractionated ash. Similarly, the 16F and MO were from the wet bottom boiler and also have the fractionated 15 micron size as well as the original ash respectively. The sample designated as "LIG" represents the original fly ash from Mae Moh, Thailand. Since there are eleven boilers at the Mae Moh Power Plant, there is no way of knowing from which boiler the ash we used were obtained. Furthermore, the chemical composition of fly ash from Mae Moh cited from literature review reveals that there are large variation of the ash collected. This probably indicates that there are problems involved with the quality assurance on the operation of the utility. Although this factor may affect the result of this study, it is, nonetheless, not the objective of this study to discuss the efficiency of the operation here.

Table 1 shows the chemical composition of these fly ashes and the cement used in this experiment. It should be noted that although the 6F and HO fly ashes were from the same boiler with its minor difference on the particle size, the chemical composition tends to vary, particularly on the LOI (Loss on Ignition) content. Other major differences in these ashes are the CaO content and the amount of Silica. LIG fly ash has more than 12% of CaO while the ashes from the U.S. have only 2.5 to 6.5%. The SiO_2 of the dry bottom ash is 10% higher than the wet bottom and the LIG fly ashes. Most ashes generally consist of up to 40 or 50% of SiO_2 with less than 10% of CaO while the cement has up to 60 of CaO but has only 20% of silica. It is important to note that for fly ash to have the same cementitious properties as cement these chemical compositions may have to be compatible. In addition, glassy phase versus crystallization of fly ash particle will also have to be taken into account. Fig. 1 shows the particle size distributions of the dry and wet bottom fly ash: two series of original unfractionated fly ashes versus two series of 15-micron fractionated ashes.

Physical properties such as specific gravity, fineness, and mean diameter of the dry and wet bottom ash as well as cement are summarized in Table 2. It can be seen that most fly ashes are lighter than cement, but tend to have a larger surface or, in other words, have a finer particle size than cement. The finer particle size allows fly ash to fill into the void between the cement grain making the cement composites denser. This phenomenon is commonly known as packing effect.

Table 1. Chemical Composition of Fly Ashes and Cement

	Chemical Composition (%)								
Sam.	LOI.	SO_3	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	MgO	Na_2O
CEM.	0.73	2.53	20.07	8.84	1.41	60.14	0.86	2.49	0.28
6F	3.12	1.09	51.40	26.54	4.91	2.72	1.71	0.74	0.31
HO	2.75	0.98	52.25	26.72	5.43	2.41	1.67	0.69	0.28
16F	2.06	3.05	40.65	24.92	13.26	6.55	2.09	1.41	1.26
MO	2.05	3.13	41.54	24.74	14.83	6.89	2.07	1.43	1.17
LIG	0.40	2.36	40.39	22.75	16.06	12.65	2.37	2.06	0.52

Testing Procedure and Mix Proportions

Fractionated fly ashes, 6F, 16F, and the original feed of the dry bottom ash (HO), and wet bottom ash (MO) are mixed with cement to form the fly ash cement mortar. Standard 2-inch cubes were cast and cured in lime-saturated water about 60 days before being put into the acid pond. The mix proportions used are tabulated in Table 3. The percentage of fly ash used in the mixes was 25 and 50 percent by weight of cementitious material (cement + fly ash). Fly ash was used as cement replacement. The water to cementitious ratio of all mixes was kept constant at 0.5. Fly ash cement-mortar samples and the control samples (no fly ash) were then immersed in the H_2SO_4 acid solution with a concentration of 100 ml/l. All samples were kept under the same corrosive environment until the day of testing. To evaluate the extent of the damage caused by acid attack, the samples were removed from the acid pond and washed with tab water. The samples were then weighed at the saturated surface dry condition. The weight loss will then be determined as compared to the weight of original sample recorded earlier. Sample designated "CF" is the control mix which contains no fly ash in the mix. The number "25" and "50" stand for the percentage of cement replaced by fly ash.

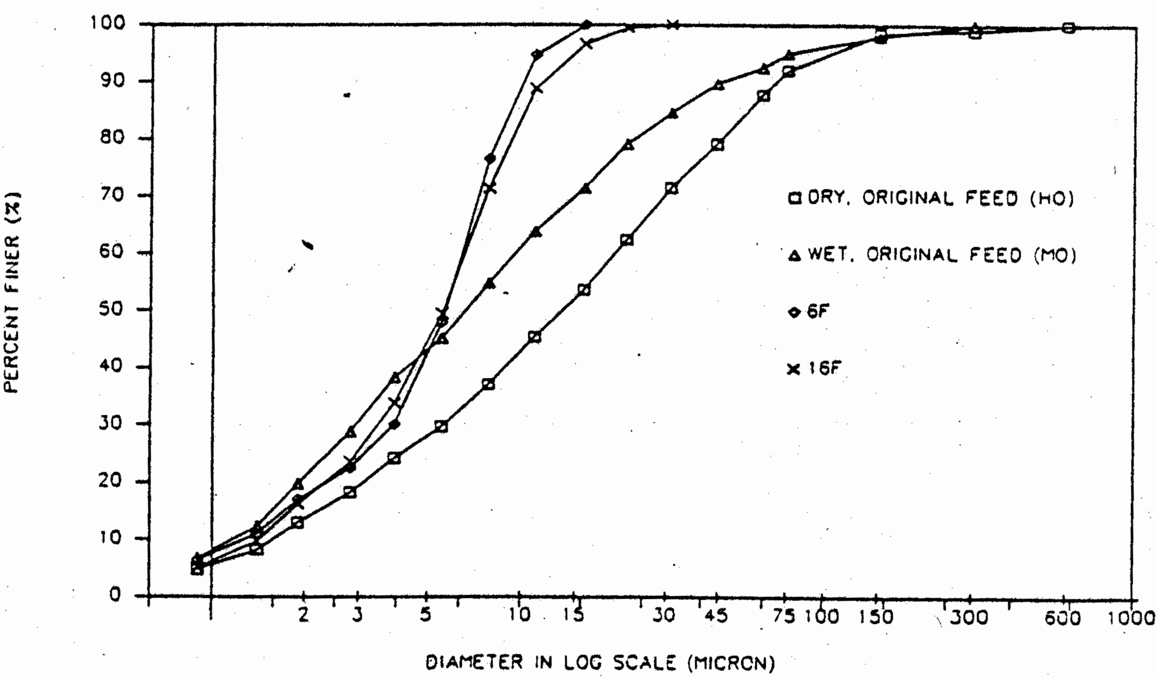

Fig. 1 Particle Size Distributions of Dry and Wet Bottom Ash

Table 2 Physical Properties of Cement and Fly Ashes

Sam. No.	Specific Gravity g/cm^3	Fineness Retained 45 um. (%)	Fineness Blaine (cm^2/g.)	Mean Diameter (um)
CEM	3.122	-	3815	-
HO	2.343	20.0	3235	13.73
MO	2.500	10.0	5017	6.41
6F	2.488	0	4478	5.66
16F	2.609	0	5171	5.54

Table 3 Mix Proportion

Sample	Cement	Fly Ash	Sand	W/(C+F)	Type of Fly Ash
CF	1.00	-	2.75	0.50	-
HO25	0.75	0.25	2.75	0.50	DRY ORIGINAL FEED
MO25	0.75	0.25	2.75	0.50	WET ORIGINAL FEED
6F25	0.75	0.25	2.75	0.50	6F
16F25	0.75	0.25	2.75	0.50	6F
LIG25	0.75	0.25	2.75	0.50	LIG
HO50	0.50	0.50	2.75	0.50	DRY ORIGINAL FEED
MO50	0.50	0.50	2.75	0.50	WET ORIGINAL FEED
6F50	0.50	0.50	2.75	0.50	6F
16F50	0.50	0.50	2.75	0.50	16F
LIG50	0.50	0.50	2.75	0.50	LIG

RESULTS AND DISCUSSIONS

Fly Ash-Cement Mortar in H_2SO_4 Solution

A) Fly Ash from New Jersey, U.S.A.

The weights of sample at different age after being submerged in the concentrated 100 ml/l-H_2SO_4 solution are tabulated in Table 4. The compressive strength of these fly ash mortar prior to being immersed in H_2SO_4 solution are also presented in this table. For the normal cement samples, the corrosion due to acid attack is rather obvious. The weight losses of this control sample is 30% at 7 days and 67% at 21 days. This rate of decay on the integrity of cement mortar is rather alarming. It seems that the free lime or calcium hydroxide in the cement control sample is rather vulnerable to the acid attack. Can fly ash tie up these calcium hydroxide compounds and prevent them from being attacked from the sulfuric acid ? The results presented in Table 4 indicate that the 25% fly ash mortar samples sustained similar damage as the control cement sample, but with a little lesser extent regardless of the type of fly ash or its particle size. However, for high volume fly ash samples, the extent of weight loss was significantly reduced to practically 0% at 7 days and only 6% at the age of 21 days. Once again, the type of fly ash and its particle size play no significant role on the corrosion resistance of fly ash mortar. Figs. 2 and 3 are the relationship between the weight loss of the samples and immersed time for the 25 and 50% fly ash mortar. At the age of 30 days, Fig. 3 shows the influence of particle size of fly ash on the corrosion resistance. The original feed of fly ash seems to sustain more damage than the fractionated 15-micron ash samples. The wet bottom ash shows a better resistance than the dry bottom ash. Fig. 4 shows the remains of the fly ash mortar samples after being immersed in the H_2SO_4 for 30 days. Control and fly ash mortar samples which have 25% of fly ash in the mix show severe loss of weight due to acid attack by the 100 ml/l H_2SO_4 solution. With 50 percent fly ash in the mix, the attack is much less effective than on the control and the 25 percent fly ash cement samples. Consider in terms of compressive strength, the samples with 25% cement replacement gives a higher compressive strength than the 50% one. Based on the compressive strength, we can divide the samples into 2 groups. The first is the control and the 25% fly ash samples which have the compressive strength more than 65 MPa (about 650 ksc) and the second group of the 50% fly ash mortar samples which have strength below 55 MPa. It can be seen that the compressive strength of the sample is not the correct measured parameter which can indicate the ability of the cement-based composites in resisting acid attack. But rather, it is the amount of fly ash in the mix that governs the resistance. From our investigation, it seems that the limit of fly ash content to provide a reasonable corrosion resistance against acid attack is about 35%. This is believed that the resistance was a result of $Ca(OH)_2$ being tied up by the pozzolanic content in the ash which reacts to form a more stable C-S-H.

B) Fly Ash From Mae Moh, Thailand

The similar experiment was carried out in Thailand using the Mae Moh fly ash. The results observed so far also lead to the same conclusions. With fly ash of 35% and 50% as cement replacement, the fly ash mortars exhibited better resistance to acid attack than the control cement mortar.

Table 4 Effect of Fly Ash Cement-Mortar in H_2SO_4

Sample No.	Weight at Different Ages (g) 0-day	1-day	3-day	7-day	14-day	21-day	30-day	Comp. (MPa)
CF	301.7	289.3	262.2	206.5	139.5	100.1	69.9	71.4
HO25	297.1	287.0	263.0	212.7	166.5	125.5	92.7	65.6
MO25	297.8	286.8	260.7	212.3	164.6	122.1	89.3	66.7
6F25	299.6	287.6	260.3	208.6	153.4	110.6	79.2	74.0
16F25	297.0	284.6	255.5	197.7	135.4	90.6	60.9	75.3
HO50	295.8	295.4	293.6	289.5	280.1	276.8	257.8	44.7
MO50	291.9	291.8	291.3	291.1	291.3	276.8	233.5	51.7
6F50	294.8	294.7	294.8	293.6	294.3	292.6	287.2	48.3
16F50	298.3	298.2	298.0	298.2	298.5	290.8	269.3	53.9

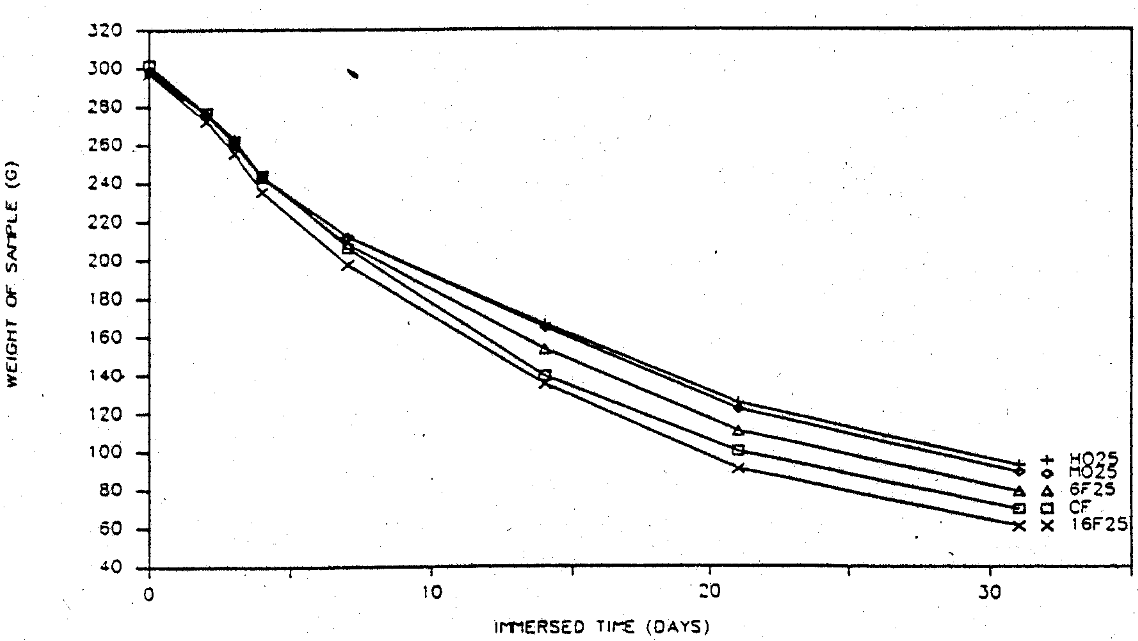

Fig. 2 Relationship between the Weight of Fly Ash Mortar Samples and Immersed Time When using Fly Ash 25% as Cement Replacement

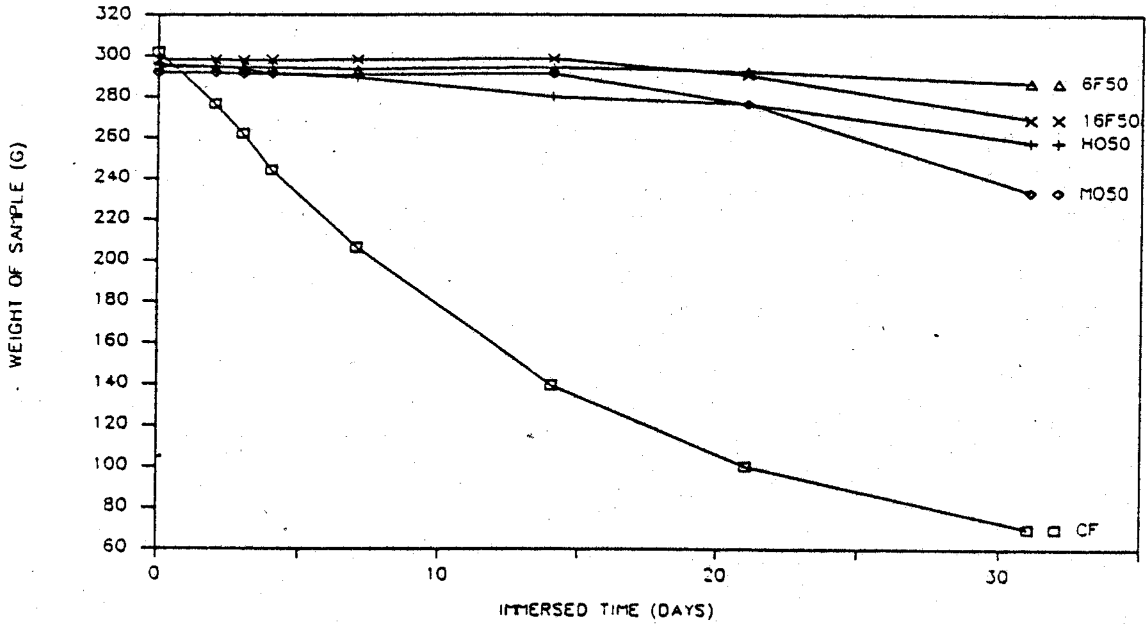

Fig. 3 Relationship between the Weight of Fly Ash Mortar Samples and Immersed Time When using Fly Ash 50% as Cement Replacement

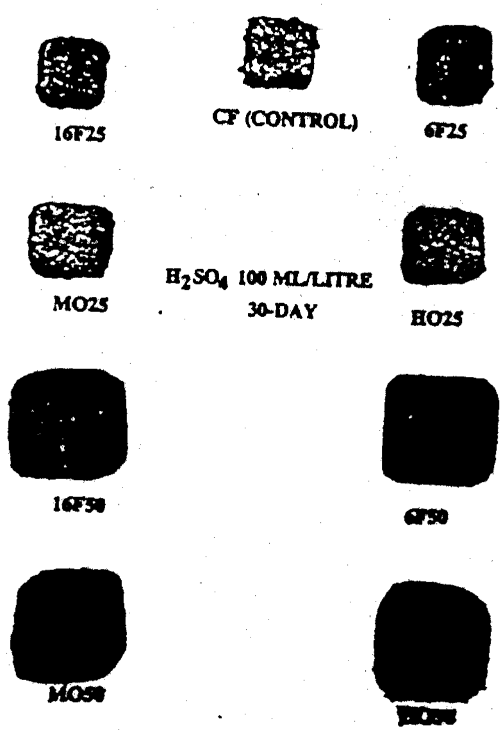

Fig. 4 Fly Ash Mortar After Immersed in H_2SO_4 for 30 Days

CONCLUSIONS

The results obtained through this investigation can lead to the following conclusions:

1. The type of fly ash does not have any significant effect on corrosion resistance against acid attack. Wet bottom ash showed a slight better resistance than the dry bottom ash. The Mae Moh fly ash mortars have almost the same acid resisting properties as the fly ashes from the United States.

2. The amount of fly ash needed in the mix to provide for corrosion resistance is about 35% and higher. The data presented here are only for the 50 percent samples. With these high volume content of fly ash in the mix, the fly ash mortar samples exhibit excellent corrosion resistance, against H_2SO_4 acid, in particular.

3. The compressive strength of mortar is not the correct measured on the durability or corrosion resistance of concrete. It is rather the amount of fly ash in the mix which governs the corrosion resistance properties of the fly ash mortar.

4. Finer particle fly ash tends to exhibit better corrosion resistance that the coarser particle one when used in the cement-based materials.

ACKNOWLEDGEMENTS

This research was supported by grants from the Public Service Electric and Gas Company of New Jersey (Program Director: Mr. Jeffrey Hynds) and the U.S. Department of Energy (DOE), grant No. DOE-DE-FG-22-90PC90299 (Program Director: Mr. Jerry L. Harness). Their financial supports are gratefully acknowledged here.

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