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FLY ASH AND FLY ASH CONCRETE

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16. ABSTRACT

Fly ash is a residue that results from the combustion of ground or powdered coal. Historically, fly ash has been referred to as a pozzolan and is used to reduce the amount of portland cement in concrete. However, in many Western States fly ashes have cementitious properties as well as pozzolanic properties, and they are capable of producing good strengths without portland cement. This study discusses test results of several ashes according to ASTM: C 618, *Standard Specification for Fly Ash and Raw or Calcined Natural Pozzolan for Use as a Mineral Admixture in Portland Cement Concrete.* Many changes are suggested. The replacement of 15 to 25 percent by mass of portland cement in concrete is examined. A few highly cementitious ashes were used to make concrete without portland cement. A new cement was developed that consists of over 90-percent fly ash and anhydrous $CaSO_4$. Test data for most concretes include: mix proportions, compressive strength, elasticity, drying shrinkage, sulfate resistance, and freeze-thaw durability. Other results included are adiabatic temperature rise, alkali-aggregate reaction, and modulus of rupture.

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by
Edwin R. Dunstan, Jr.

May 1984

Concrete & Structural Branch
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Engineering and Research Center
Denver, Colordo

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UNITED STATES DEPARTMENT OF THE INTERIOR ★ BUREAU OF RECLAMATION

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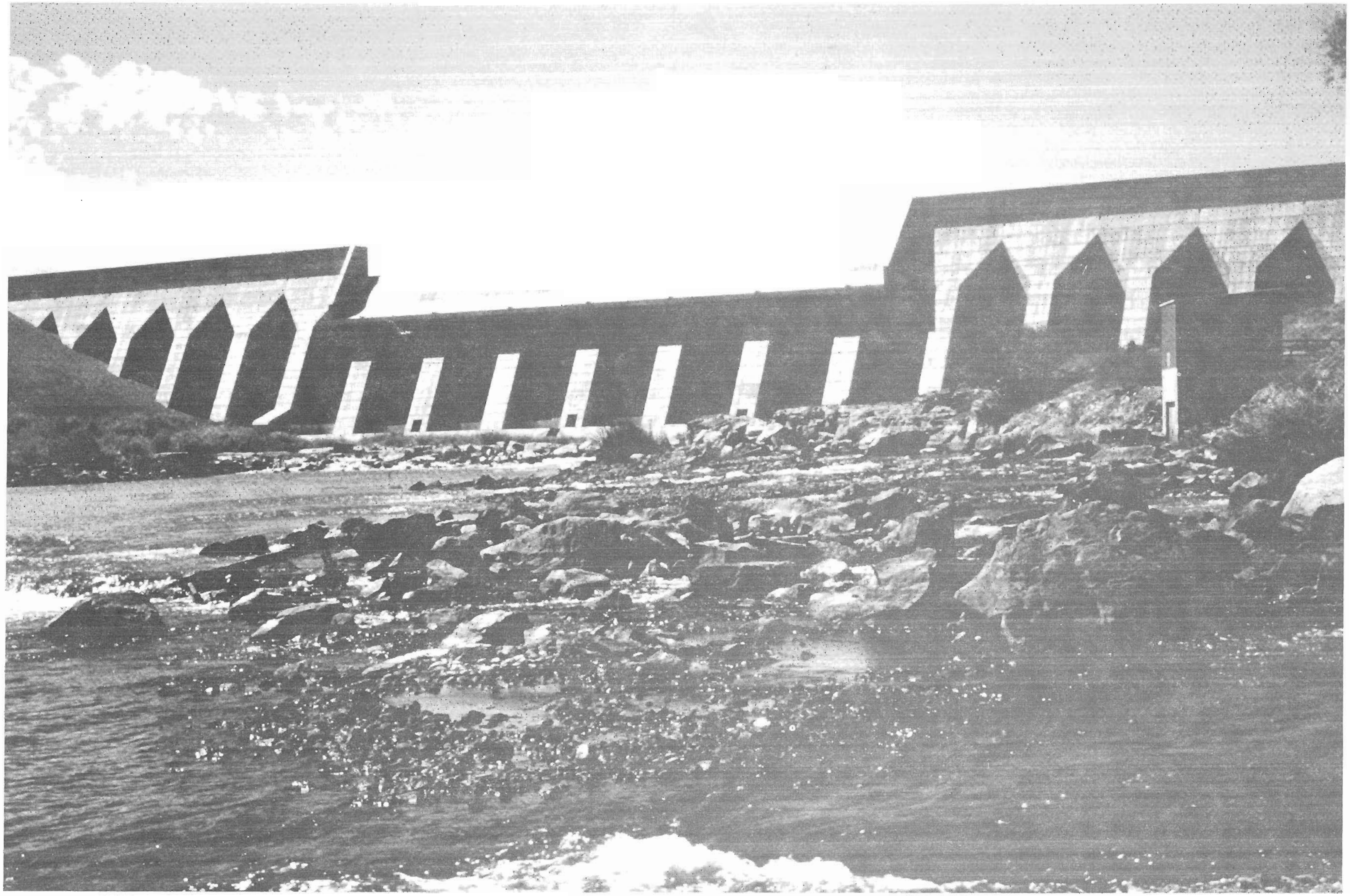
Data reported in this document were measured in the inch-pound system and converted to SI (System International, designation ASTM E 380-79, *Standard for Metric Practice*) metric units.



Frontispiece. — Pueblo Dam is the terminal storage feature for the Fryingpan-Arkansas Project. The concrete dam and massive-head buttress-type spillway structure is the principal control structure for the reservoir. The concrete section is 1,750 feet wide having a maximum structural height of 250 feet.

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INTRODUCTION

Fly ash is a residue resulting from combustion of ground or powdered coal. Historically, fly ash has been referred to as a pozzolan and used to reduce the amount of portland cement required in concrete. The ASTM (American Society for Testing and Materials) has issued a standard specification for using fly ash in portland cement concrete *ASTM: C 618* standard specification.[1] This specification defines pozzolans as:

> siliceous or siliceous and aluminous materials which in themselves possess little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties.

The *ASTM: C 618* specification has two classifications of fly ash *class F* and *class C*; each must meet certain chemical and physical requirements. Class F fly ash normally is produced by burning anthracite or bituminous coal. Class C fly ash normally is produced from burning lignite or subbituminous coal. Class F ash possesses pozzolanic properties; whereas, class C may have a substantial degree of cementitious properties in addition to pozzolanic properties. The Bureau of Reclamation has used class F ash in mass concrete for many years. However, many powerplants within the Bureau's area of operation produce class C ash. The Bureau's initial study was directed toward the use of class C fly ash as partial replacement of cement in concrete. From 1973, the scope of this study has increased greatly. Both class F and class C fly ashes from different locations were evaluated in this study. Predetermination was not made to see if they met the standard specification *ASTM: C 618*.

RESEARCH HISTORY

Table 1 is a list of fly ashes evaluated in this study. The list also includes one calcined class N (natural) pozzolan M-6907. When this research began in 1973, five randomly selected ashes were used in concrete and compared to a control concrete without fly ash and to a concrete containing a control fly ash M-6498 (class F). The control ash was a blend of ashes from the Chicago area which had been collected prior to the use of lignite coals in that area. This ash had been tested previously and its charactertics in concrete were known [1, 2].[2] The five randomly selected ashes were M-6510, M-6514, M-6535, M-6569, and M-6577. A progress report was published in 1976 [3]. Concretes containing those ashes were found to have adequate compressive strength, reduced drying shrinkage, and satisfactory freeze-thaw durability; but, in some cases, they exhibited drastically reduced resistance to sulfate attack. Data from the 1976 progress report are revised and included in this report. To further investigate sulfate resistance, five blended ashes, M-6679, M-6680, M-6681, M-6682, and M-6683 were fabricated from the above ashes. Tests were repeated on ash M-6535 because of its poor resistance to sulfate attack and another sample, M-6734, was obtained from the same source (Comanche Powerplant, Pueblo, Colorado). Ashes M-6730 and

Table 1. – Fly ashes investigated.

Sample No.	Date obtained	Source and comments
M-6498	1963–65	Chicago, Area Powerplants–Blend of Ashes.
M-6510	11-26-73	Basin Electric Power Cooperative, Stanton, N. Dak.
M-6514	12-06-73	Montana Dakota Utilities Plant, Sidney, Mont.
M-6535	02-20-74	Public Service Co. of Colorado, Comanche Plant, Pueblo, Colo.
M-6569	07-23-74	Salt River Project, Navajo Generating Plant, Page, Ariz.
M-6577	08-12-74	Minnkota Power Company, Center, N. Dak.
M-6679	08-13-75	*Blended ash* 76 % M-6535 14 % M-6569 10 % M-6510
M-6680	08-13-75	*Blended ash* 52 % M-6535 28 % M-6569 20 % M-6510
M-6681	08-13-75	*Blended ash* 28 % M-6535 42 % M-6569 30 % M-6510
M-6682	08-13-75	*Blended ash* 58 % M-6569 42 % M-6510
M-6683	08-13-75	*Blended ash* 81 % M-6569 19 % M-6498
M-6730	04-05-76	Southern California Edison, Mohave Plant, Laughlin, Nev.
M-6734	04-12-76	Public Service Co. of Colorado, Comanche Plant, Pueblo, Colo.
M-6754	06-00-76	Nevada Power Company, Reid-Gardner Station, Moapa, Nev.
M-6880	06-20-77	Public Service Co. of Colorado, Comanche Plant, Pueblo, Colo.
M-6907	09-12-77	Calcined Pozzolan, Hallelulah Junction, Calif.
M-6976	05-03-78	Pacific Power and Light, Jim Bridger Plant, Rock Springs, Wyo.
M-6979	05-12-78	Public Service Co. of Colorado, Comanche Plant, Pueblo, Colo., Soda ash (Na_2CO_3) used during collection.
M-7094	04-02-79	Public Service Co. of Colorado, Comanche Plant, Pueblo, Colo., Sodium Sulfate (Na_2SO_4) used during collection.
M-7129	06-13-79	Public Service Co. of Colorado, Comanche Plant, Pueblo, Colo., Sodium Sulfate (Na_2SO_4) used during collection.
M-7143	07-11-79	Southwestern Electric Power Co., Flint Creek Powerplant, Gentry, Ark.

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[1] *Fly Ash and Raw or Calcined Natural Pozzolan for Use as a Mineral Admixture in Portland Cement Concrete.*

[2] Numbers in brackets refer to the bibliography.

M-6754 were added to expand the study. Further study resulted in a method to predict sulfate resistance from the chemical composition of the ash. To verify the method, a new control cement was used and a new ash M-6976 was added to supplement the list of fly ashes. Sulfate resistance of Comanche ash (a third sample, M-6880) with other cements was then investigated. For comparison, a calcined natural pozzolan M-6907 was included in the study. About this time, the ash collection operations at the Comanche Powerplant were changed to meet Environmental Protection Agency regulations. Soda ash (Na_2CO_3) was used to improve the precipitator collection efficiency. Erratic *time-of-set* problems developed when such fly ash was used with some cements and admixtures. Sample M-6979 was obtained to study this problem.

The highly cementitious characteristics of a few of these ashes were investigated further to determine if they could be used to make concrete without portland cement. Sample M-7094 was obtained for this purpose. Mortar tests with ash M-6535 (one of the original ashes) indicated that a combination of ash and $CaSO_4$ (anhydrite) could produce good cement. This combination was investigated with sample M-7129, an ash containing Na_2CO_4 added during collection. Ash M-7143, from another powerplant and without Na_2SO_3 or Na_2SO_4, was obtained to confirm that a cement could be made with ash from other powerplants burning similar coal.[3]

This report summarizes the research which has been accomplished since 1974.

CONCLUSIONS

Conclusions are based on results of tests of mortars and concretes containing fly ashes representative of both class F and class C ashes cited in *ASTM: C 618.*

Conclusions Concerning ASTM: C 618:

1. Pozzolanic activity of fly ash—measured as partial replacement of the control cement—is a good test for predicting concrete strength. The lime-pozzolan test has little relation to concrete strength.

2. Chemical limit on the MgO content for fly ash has little—if any—relation to concrete soundness. The autoclave expansion test should be used to measure soundness, and the limitation of MgO content should be dropped.

3. Chemical limit for SO_3 in fly ash has little—if any—relation to concrete soundness. A maximum SO_3 for each ash should be determined similar to the optimum SO_3 test for portland cements.

4. Compressive strengths at 28 days, of fly ash and $CaSO_4$ mortar combinations, appear promising for predicting sulfate resistance of concrete.

5. Alkali content of fly ash appears to have little relation to alkali-aggregate reaction when tested with a reactive aggregate. A test is needed to determine a *pessimum*[4] limit for pozzolans for alkali-aggregate reaction.

6. The rapid setting of some high-calcium ashes is postulated to be the reaction of glass having a calcium-alumina composition corresponding to approximately $C_{12}A_7H_X$.

Conclusions Concerning Portland Cement/Fly Ash Concretes:

1. With similar mix designs; that is, slump, sand content, etc., fly ash concretes have a lower water requirement than normal portland cement concretes.

2. The AEA (air-entraining admixture) dosage for fly ash concretes is related roughly to the *loss-on-ignition* of the fly ash. When the loss-on-ignition of fly ash exceeds about 1 percent, the AEA dosage requirement will be greater than that for ordinary portland cement concrete.

3. Compressive strength of concrete containing fly ash is related to the calcium content of fly ash. High calcium ashes exhibit higher early-age strength; whereas, low calcium ashes show higher late-age strengths.

4. The strength-gaining pattern of fly ash concrete is lower early-age strengths and higher late-age strengths, as compared to normal portland cement concrete.

5. Compressive strength of fly ash concrete is related to the ratio of W to C plus P (water to cement plus pozzolan). The relation of concrete strength to this ratio is different for each ash.

6. Elasticity of fly ash concrete is similar to that of ordinary portland cement concrete.

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[3] A patent (United States patent 4,256,504: *Fly-Ash-Based Cement)* was issued March 17, 1981 on ash M-7143 and $CaSO_4$ combination.

[4] *Pessimum* as it has been applied to pozzolans in concrete [32] is defined as the amount of pozzolans (fly ash) causing the maximum reactive expansion. Usually the word is used in describing those situations where a small (pessimum) amount of a pozzolan will cause an increase in expansion due to alkali-aggregate reaction but larger amounts result in a decrease in expansion.

7. Resistance of fly ash concretes to sulfate attack can be predicted from fly ash oxide analysis. The ratio *R*, (CaO-5) to (Fe_2O_3), relates to resistance, the lower the ratio the higher the resistance to sulfate attack.

8. Freeze-thaw durability of fly ash concrete is excellent—provided adequate strength and proper air entrainment are attained. Air-entraining admixtures vary in their effectiveness in obtaining the proper air entrainment and thus affect freeze-thaw durability.

9. Drying shrinkage of fly ash concrete normally is less than that of ordinary portland cement concrete.

10. Fly ash reduces the rate of heat generation in concrete (except during early hydration with high calcium fly ash). Rate of heat generation in fly ash concrete is related to the ash calcium content.

Conclusions Concerning Nonportland Cement Concrete:

1. Low-strength backfill and subbase concrete can be made with some high calcium ashes.

2. Very good compressive strengths [34.5 MPa (5000 lb/in^2)] can be achieved using combinations of high calcium ashes and $CaSO_4$ (anhydrite).

3. Sulfate resistance of concrete that contains at least 90-percent fly ash is very good—better than concrete containing only type II portland cement.

4. Excellent freeze-thaw durability can be achieved using 90-percent fly ash concretes—provided proper air entrainment is achieved.

5. Concrete with 90-percent or more fly ash has low-surface abrasion resistance—possibly due to carbonation of the surface.

FLY ASH PROPERTIES

Generally, all ashes used in this investigation were tested for compliance with *ASTM: C 618*.[1] The results are shown on table 2. The specifications for either *class C* or *class F* are shown at the bottom of the table. Additional test data, such as total lime and free lime, etc., are included in the table. Only some of these data will be discussed; however, rather significant results are highlighted.

Characterization — Crystalline Phases

Under magnification shown on figure 1, fly ash appears very fine, primarily consisting of glassy spheres and a small percentage of irregularly shaped particles. Fly ashes have been the subject of many investigations [4, 5, 6]. XRD (X-ray diffraction) examinations by others have revealed crystalline phases such as:

- quartz (SiO_2)
- hematite (Fe_2O_3)
- free lime (CaO)
- mullite ($3Al_2O_3 \cdot 2SiO_2$)
- magnetite (Fe_3O_4)
- at times periclase (MgO)
- anhydrite ($CaSO_4$)

Dicalcium silicate has been found in ashes having very high calcium contents (47 percent) [6, 7]. Other crystalline phases presumed in high calcium ashes were previously indicated to be tricalcium aluminate (C_3A) and tetracalcium trialuminate sulfate (C_4A_3S).[5]

In this study ashes were examined by XRD. Phases identified were:

SiO_2	Fe_3O_4	$CaSO_4$
MgO	Fe_2O_3	CaO

and possibly C_4AS.

C_3A and C_2S were not detected.

The amounts and significance of many of these phases are discussed where applicable.

Characterization — Glass In Fly Ashes

The compositions of the ashes vary extensively; only general characterizations can be made on the basis of oxide compositions, such as high-calcium or low-calcium ashes, and the minimum on the SiO_2 plus Al_2O_3 plus Fe_2O_3 as defined by *ASTM: C 618* contents. Referring to the **CaO, Al_2O_3, SiO_2** equilibrium diagram in figure 2 facilitates some comparisons of the properties of the fly ashes. Expressing compositions of ashes only on the basis of total amounts of CaO, Al_2O_3 and SiO_2 has some limitations. In this study the total amounts of these oxides

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[5] Letter to Dr. G. Frohnsdorff, National Bureau of Standards, Washington, D.C., from Mr. Bryant Mather, Corps of Engineers, Waterways Experiment Station, Concrete Laboratory, Vicksburg, Mississippi, January 23, 1978, and followup letter January 26, 1978.

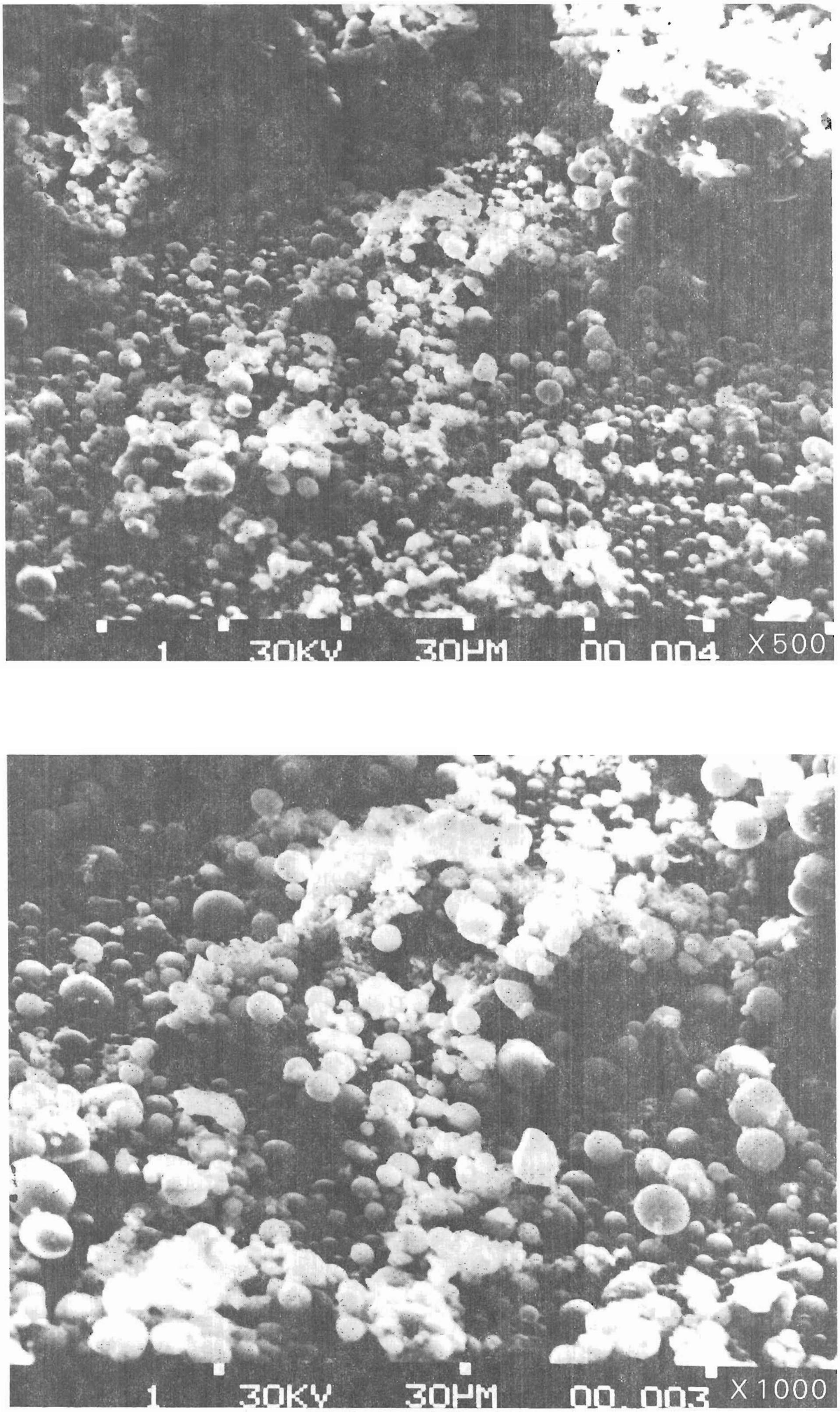

Figure 1. — Fly ash, a residue as fine as talcum powder, resulting from the combustion of ground, powdered coal. P801-D-80299, P801-D-80302, P801-D-80301, and P801-D-80300, respectively.

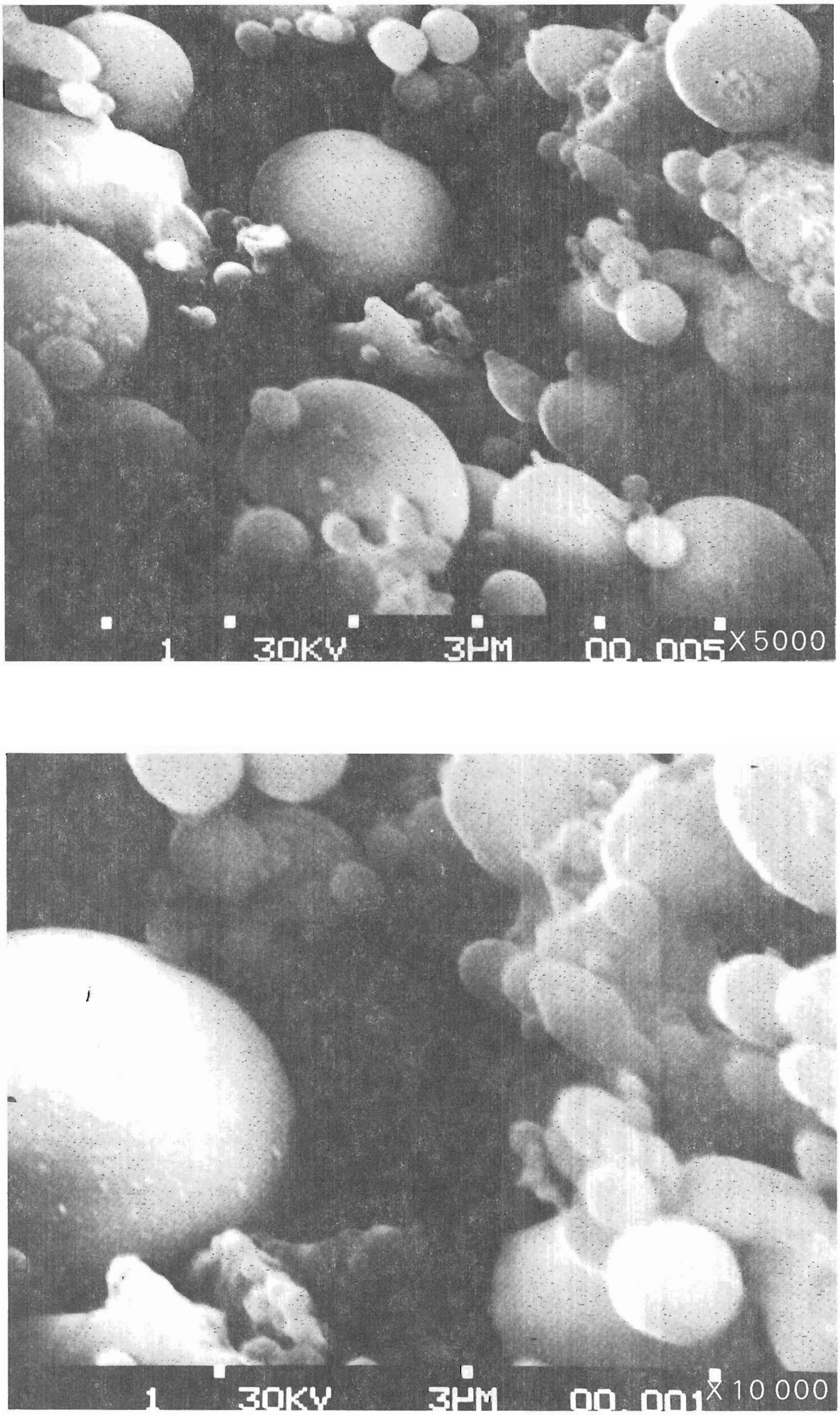

Figure 1. — Fly ash, a residue as fine as talcum powder, resulting from the combustion of ground, powdered coal. P801-D-80299, P801-D-80302, P801-D-80301, and P801-D-80300 — Continued

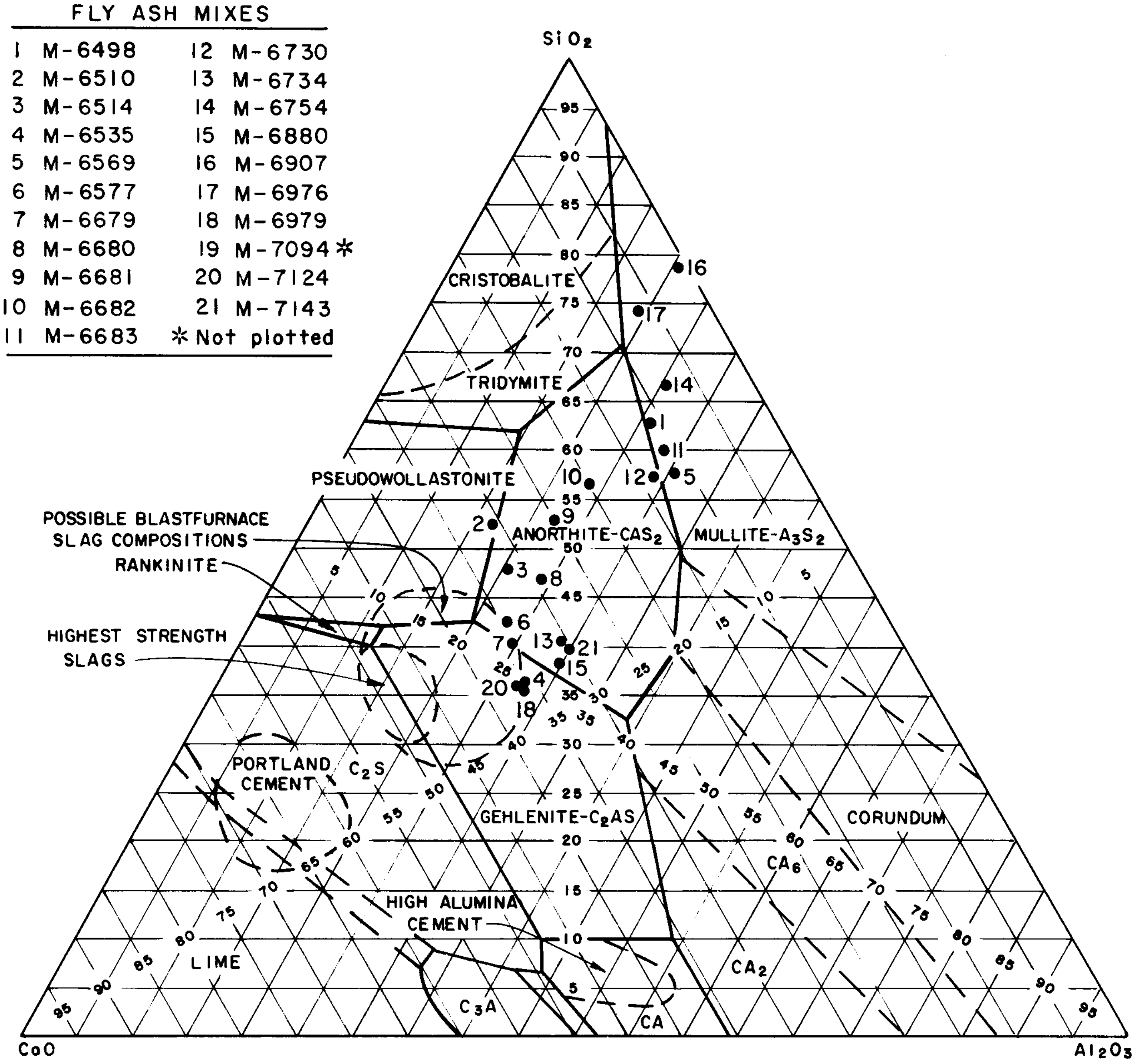

Figure 2. — Relation of fly ash composition to CaO • Al_2O_3 • SiO_2 ternary oxide systems.

in the ashes range between 70 and 92 percent, the balance being Fe_2O_3, MgO, SO_3, and the alkalies. The latter components probably have an effect on some of the properties, but this does not appear to be significant.

Notwithstanding these limitations, systematic studies of glasses in slags [8, 9] have been made and to a limited extent on fly ash glass [10]. These studies have been facilitated by the use of the equilibrium ternary system diagram. Locher [9] prepared slag glasses with 5-percent MgO falling primarily in the C_2AS (gehlenite) field but extending somewhat into the C_2S and CS fields. These glasses when activated with portland cement were tested for compressive strength; ones with the highest strengths plot in an area partly in the C_2AS and C_2S fields. This study and other considerations indicate that expressing the compositions of fly ashes in terms of **CaO, Al_2O_3, and SiO_2** and plotting these compositions in the equilibrium diagram expedite presentation and interpretations of the properties of the ashes.

Properties — According To ASTM: C 618

As stated, *ASTM: C 618* includes two classifications for fly ash—classes F and C. Reference is made in the

Table 2.—Physical and chemical properties of fly ashes.

Sample No.	Chemical composition										Relative mass density		Autoclave expansion	Fineness,[1] retained on No. 325 sieve	Pozzolanic activity with			Water[3] require-ment	Reactivity with cement alkalies[4]	Comment	Control cement
	SiO_2	Al_2O_3	Fe_2O_3	Total S+A+F	Free CaO	Total CaO	MgO	SO_3	Alkalies as Na_2O	Loss on ignition	kg/m^3	lb/ft^3	percent	%	Cement[2]	Lime lb/in^2	Lime MPa	%	percent		
M-6498	46.1	19.0	18.6	83.7	2.2	8.2	1.3	1.6	0.72	2.0	2435	152.0	−0.004	28.5 (7413)	81.8	957	6.60	93.2	0.237	Blended ash	M-6400
M-6510	37.1	11.8	7.3	56.2	0.5	21.8	5.6	2.6	4.23	0.3	2685	167.6	0.0110	44.5 (4729)	56.6	781	5.38	[1] <100	0.321		M-6400
M-6514	37.2	15.5	5.6	58.3	0.2	24.3	11.3	0.9	0.07	0.3	2696	168.3	0.141	19.9 (5616)	102.6	278	1.92	<100	0.388		M-6400
M-6535	28.8	20.0	4.1	52.9	2.1	32.0	6.4	3.8	0.68	0.2	2715	169.5	0.116	17.9 (12 835)	90.7	517	3.56	<100	0.456		M-6400
M-6569	51.8	27.2	2.0	81.0	1.9	10.7	2.1	0.7	0.86	1.2	2316	144.6	0.038	27.4 (3805)	93.6	869	5.99	<100	0.138		M-6400
M-6577	31.1	17.1	7.9	56.1	0.0	25.3	8.1	3.3	1.35	1.1	2704	168.8	0.070	10.3 (12 834)	79.1	808	5.57	<100	0.144		M-6400
M-6679	32.8	19.6	4.1	56.5	0.9	28.0	5.5	3.4	1.54	0.5	2656	165.8	0.079	(11 185)	110.0	1003	6.92	<100	0.282	Blended ash	M-6550
M-6680	36.9	18.1	4.7	59.7	0.8	24.0	4.8	2.8	1.86	0.6	2635	164.5	0.069	(10 042)	103.0	1120	7.72	<100	0.300	Blended ash	M-6550
M-6681	41.1	17.9	4.9	63.9	0.8	20.2	4.4	2.2	2.21	0.8	2545	158.9	0.064	(8244)	89.0	1189	8.20	<100	0.286	Blended ash	M-6550
M-6682	45.7	18.4	5.3	69.4	0.7	15.5	3.8	1.6	2.83	0.9	2486	155.2	−0.037	(6691)	71.0	1018	7.02	<100	0.225	Blended ash	M-6550
M-6683	51.5	24.5	5.7	81.7	0.8	10.2	2.1	0.9	0.96	1.2	2416	150.8	0.027	(8376)	88.0	544	3.75	<100	0.181	Blended ash	M-6550
M-6730	49.6	25.7	3.0	78.3	2.4	11.3	2.1	0.7	1.20	1.3	2335	145.8		(11 230)				101.4			M-6550
M-6734	34.7	24.8	4.2	63.7	0.0	26.1	5.2	1.4	0.81	0.2	2645	165.1	0.024	11.4 (12 443)	126.0	1220	8.41	86.3	0.302		M-6550
M-6754	61.4	23.4	3.7	88.5	NA	7.0	1.2	0.5	0.81	2.5	2236	139.6	0.023	34.9 (5206)		716	4.94	99.6	0.347		M-6550
M-6880	32.0	25.1	5.2	62.3	0.05	27.7	4.9	2.2	0.85	0.7	2585	161.4	0.099			1409	9.71	95.1	0.368		M-6886
M-6907	69.2	18.3	4.3	91.8	NA	2.0	1.2	0.7	2.35	0.6	2406	150.2	−0.029	(34 295)	87.5	2690	18.55	109.0	*92.2 (0.035)	Calcined pozzolan	M-6800
M-6976	64.4	16.8	4.7	85.9	0.4	6.1	2.7	3.2	2.49	0.8	2335	145.8	0.012	(7173)	85.9	1490	10.27	95.1	0.226		M-6800
M-6979	30.0	24.1	2.1	56.2	NA	28.1	4.8	0.5	1.35	1.0	2566	160.2	0.056	(11 343)	87.9	2174	14.99	94.4	0.239		M-6800
M-7094											2624	163.8									
M-7129	28.9	22.9	4.0	55.8	NA	30.7	5.3	4.3	1.53	0.5											
M-7143	33.3	25.8	4.0	63.1	NA	28.1	4.9	2.2	0.96	0.2											
[5]Class C				50 min.			5.0 max.	5.0 max.	1.5 max.	6.0 max.			0.8 max.	34 % max.	75 min.	800 min.	5.52	105 max.	0.020 max.		
[5]Class F				70 min.			5.0 max.	5.0 max.	1.5 max.	12.0 max.			0.8 max.	34 % max.	75 min.	800 min.	5.52	105 max.	0.020 max.		

Note: U.S.A. standard sieve No. 325 is equivalent to 45 micrometers (ASTM E-11).

* Reduction in expansion 14 days (percent).

[1] Blaine fineness cm^2/g.

[2] Percent of the control mortar with portland cement.

[3] Water requirement, percent of control.

[4] 14-day expansion.

[5] Limits prescribed by ASTM designation: C 618.

specification to the type of coal burned that produces each class. Normally, class F ashes are produced from burning anthracite or bituminous coal and class C from lignite or subbituminous coal. However, disagreement exists as to the significance or use of the reference in specifications. A portion of a letter discussing this point follows:[6]

> The question that I desire to address has to do with ASTM specification: C 618-78 and particularly the part in section 3 thereof that deals with the classification of fly ash and pozzolans and particularly class C and class F fly ash as defined in section 3.3 and 3.2, respectively. Both of these classes are defined as fly ash "normally" (sic) produced from a kind of coal, and goes on to say that in addition to being "normally produced" from that kind of coal the stuff must obviously meet "the applicable requirements as given herein."
>
> There are some users of fly ash who specify that the ash they want must be class F. I have argued that, if that is the case, the ash cannot be ash produced by burning subbituminous coal regardless of whether or not the resulting product complies with the requirements for class F as given in C 618; to which I receive the answer: "but C 618 says 'normally' produced from * * * meaning that it doesn't have to be produced from burning anthracite or bituminous coal so long as it meets the applicable requirements."
>
> If a fly ash may be classed as class F regardless of what kind of coal is burned to produce it so long as it meets the requirements of class F then it seems to me the definition ought to be stated the other way around as follows:
>
> > *Class F— Fly ash that meets the applicable requirements for this class as given herein. Such ash is normally produced from burning anthracite or bituminous coal but may be produced from burning lignite or subbituminous coal.*
>
> Since this issue has been raised, I also inquire as to whether, since at present I believe all ashes that meet class F also meet those for class C, if those who want a class C, because, as stated in C 618, section 3.3 it "has some cementitious properties" they may be assured, of such, simply by ordering class C. Most class F ashes are not cementitious. If I want a class C cementitious fly ash, there's no way under a C 618-78 that I can specify it.

Therefore, the author will describe ashes by physical and chemical properties and not by coal type.

ASTM: C 618 — Strength Gaining Properties

Fly ash strength properties relate largely to the amount of oxides of SiO_2 plus Al_2O_3 plus Fe_2O_3, in the fly ash [11]. *ASTM: C 618* requires the minimum content, of the sum of these three oxides, must be 70 percent for a class F ash and 50 percent for a class C ash. Ashes that meet class F requirements have a low calcium content. A small amount of the silica is crystalline quartz and partly combined as mullite, but most is in the glassy phase. A small amount of alumina is combined as crystalline mullite, but most is also in a glassy phase. The iron (Fe_2O_3 and Fe_3O_4) is present largely as hematite and magnetite, but some is also in the glass.

The portion of the oxides of silica, alumina, and iron that exists as glass is recognized as being the largest contributor to strength development. The physical condition of the glass also affects its reactivity [4, 12]. Class F ashes contain glasses that have compositions in or near the mullite field on figure 2.

Class C ashes having the sum of the oxides of SiO_2 plus Al_2O_3 plus Fe^2O_3 near the minimum of 50 percent have higher calcium oxide contents and have compositions in or near the gehlenite field shown in figure 2. Many of these ashes are self-hardening without addition of lime or portland cement. More calcium oxide appears to increase, while more iron oxide decreases the reactivity [12]. Investigators have described this self-hardening property as being due to the hydration of free lime CaO [13, 14], but this does not appear to be the case with the ashes in this study. High calcium contents in the ashes in this study do not necessarily correlate with high free lime contents [15]. For example, ash M-6498—with little self-hardening capacity—has about the same amount of free lime as ash M-6535 does which has very rapid and extensive self-hardening capacity (table 2), accompanied by rapid heat evolution. To illustrate the relation between fast setting and heat evolution, a *time-of-set* paste was made with ash M-6535 according to *ASTM: C 191*.[7] A 60-mm (2-1/2-in) diameter ball was molded by hand and a thermometer placed in the center. In 15 minutes, a *flash set* had taken place and the temperature had increased 16 °C (60 °F).

Investigations to date have not disclosed a good correlation between compressive strength and chemical composition [4, 11]. Empirical test methods, therefore, have been developed that are based on

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[6] Letter to Prof. J. F. McLaughlin, School of Civil Engineering, Purdue University, Lafayette, Indiana, from Mr. B. Mather, Waterways Experiment Station, Corps of Engineers, Concrete Laboratory, Vicksburg, Mississippi, April 8, 1980.

[7] ASTM: C 191: *Time of Setting of Hydraulic Cement by Vicat Needle.*

mechanical strength development properties. Current requirements in *ASTM: C 618* include pozzolanic activity with lime and with portland cement.

Pozzolan reactivity with lime may correlate with concrete strength when the ashes have glasses with compositions in the mullite field; however, the correlation is very erratic for high calcium ashes. Lime-fly ash mortar strengths are plotted versus concrete strength on figure 3a. The concretes (table 3) are mixes 2, 4, 6, 8, 11, and 13—all containing 25-percent fly ash with comparable mix proportions. Comparable data from later mixes were not used because some ashes are blends and part of the data for later mixes is not available. Data indicate—if anything—that lime-fly ash mortars generally have an inverse relation to compressive strength of concretes containing 25-percent fly ash.

The rate of strength development of fly ash-portland cement mortars is regarded [11] as the most direct and reliable method for determining reactivity of the fly ash with cements. This method appears to have a direct correlation to concrete after at least 28 days as shown on figure 3b.

Strength Versus Reaction Products. — Reaction products that produce strength in cement-fly ash combinations have been studied by many investigators [12, 16]. However, almost all studies have been performed on ashes that have glasses of composition in or near the mullite field of figure 2. Very little work has been done on high calcium ashes; specifically on the very rapid self-hardening ashes that have compositions in or near the gehlenite field of figure 2.

Reaction products of low calcium ashes are mainly hydrous calcium silicates and calcium aluminates [12, 16]. Products of hydration are not essentially different from those formed in hydration of portland cement [17].

High Calcium Ash and Water Hydration. — A minimal study of the early hydration products of high calcium ashes has been made; however, long time studies are needed. When mixed with water, ash M-6535 exhibited flash set. This reaction is highly exothermic, similar to that of a quicklime slurry. To investigate the initial reactions, ash M-6535 was hydrated with excess water for 3 days at room temperature and then dried for several days in a vacuum oven at 49 °C (120 °F). This temperature was selected to remain below the drying temperature [54 °C (130 °F)] used in the sulfate-resistance test discussed later in the subsection *Resistance to Sulfate Attack*. The sulfate resistance test is severe on high calcium ashes. To identify products susceptible to temperature alteration by higher temperatures, drying was performed at the lower temperature

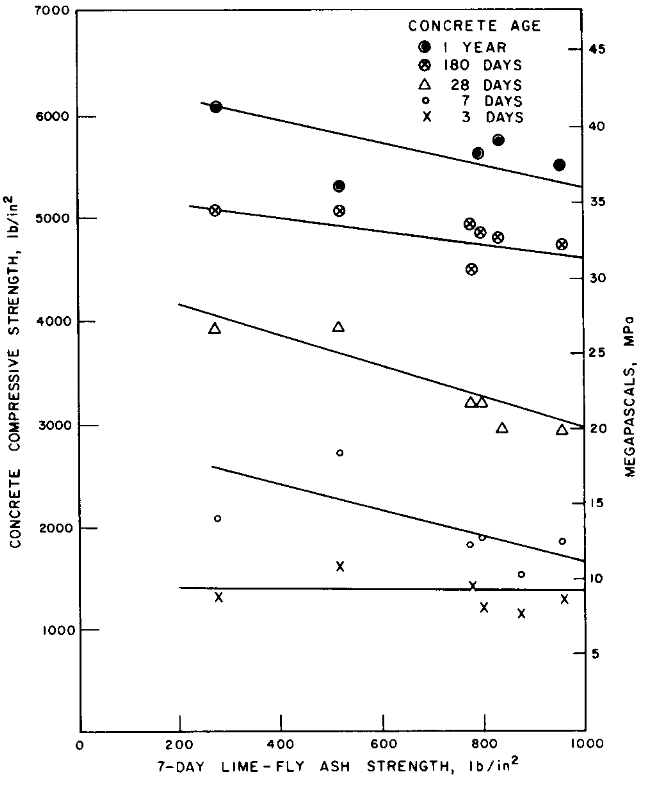

Figure 3a. — Comparison of 7-day, lime-fly ash strengths to concrete strengths — 25-percent fly ash.

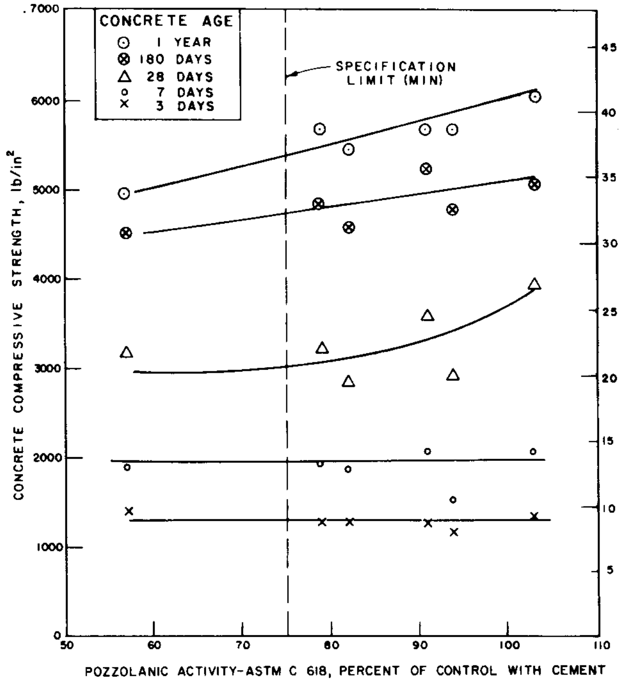

Figure 3b. — Comparison of pozzolanic activity with cement to concrete strength, 25-percent fly ash.

Table 3. — *Concrete mix quantities, compressive strength, and elastic properties.*

Mix No.	Mix designation series	Mix date	$\frac{w}{c+p}$ ratio	Fly ash No.	Cement No.	Fly ash %	Sand %	Mix quantities per cubic meter (cubic yard)												Properties of fresh concrete								Compressive strength [150- x 300-mm (6 X 12-in) cylinders]										Elastic properties					
								‡AEA		Water		Cement		*Pozz. fly ash*		Sand		Coarse agg.		Temp.		Slump		Unit weight		Air content		3-day		7-day		28-day		180-day		365-day		28-day		180-day		365-day	
								cm^3		kg	lb	kg	lb	kg	lb	kg	lb	kg	lb	$^\circ$C	$^\circ$F	mm	in	$\mathrm{kg/m}^3$	$\mathrm{lb/ft}^3$	*Grav.* %	*meter* %	MPa	$\mathrm{lb/in}^2$	MPa	$\mathrm{lb/in}^2$	MPa	$\mathrm{lb/in}^2$	MPa	$\mathrm{lb/in}^2$	MPa	$\mathrm{lb/in}^2$	$E\mathrm{X}10^{-6}$	r	$E\mathrm{X}10^{-6}$	r	$E\mathrm{X}10^{-6}$	r
		1973																																									
1	LIG-1	Nov. 6	0.46	M-6498	M-6400	15	33	401	–	94.3	208	174.2	384	30.8	68	487.6	1075	978.9	2158	23.3	74	79	3.1	2310	144.2	5.7	4.8	9.7	1410	13.6	1970	22.5	3270	38.0	5510	39.0	5660	3.01	0.14	3.68	0.16	3.64	0.24
2	LIG-2	Nov. 9	.44	M-6498	M-6400	25	33	550	–	89.8	198	151.0	333	50.3	111	494.9	1091	993.4	2190	20.0	68	58	2.3	2327	145.3	5.2	4.5	9.0	1300	12.8	1860	20.0	2900	32.8	4750	37.5	5442	2.75	0.15	3.88	0.18	4.47	0.20
3	LIG-3	Dec. 10	.44	M-6510	M-6400	15	33	302	–	92.1	203	177.4	391	31.3	69	489.4	1079	982.0	2165	18.9	66	74	2.9	2318	144.7	5.8	4.9	10.3	1500	14.2	2065	23.9	3470	31.1	4510	32.3	4680	3.10	0.14	4.05	0.18	4.01	0.16
4	LIG-4	Dec. 10	.46	M-6510	M-6400	25	33	259	–	89.8	198	147.0	324	49.0	108	499.0	1100	1001.5	2208	18.9	66	71	2.8	2335	145.8	5.0	4.8	9.8	1420	12.9	1870	21.7	3150	30.9	4480	34.1	4950	3.14	0.15	4.06	0.18	4.41	0.18
		1974																																									
5	LIG-5	Feb. 8	.45	M-6514	M-6400	15	33	288	–	92.5	204	174.2	384	30.8	68	490.8	1082	984.7	2171	17.8	64	76	3.0	2319	144.8	5.7	5.2	9.7	1400	15.4	2240	29.3	4250	35.3	5120	39.2	5680	NA	NA	4.20	NA	4.20	0.16
6	LIG-6	Feb. 8	.45	M-6514	M-6400	25	33	261	–	91.2	201	152.0	335	50.8	112	499.0	1100	1001.1	2207	18.3	65	69	2.7	2345	146.4	4.6	4.3	9.4	1360	14.4	2090	27.4	3970	35.2	5100	41.5	6020	NA	NA	4.33	0.16	4.33	0.17
7	LIG-7	Mar. 1	.45	M-6535	M-6400	15	33	289	–	93.0	205	175.1	386	30.8	68	493.5	1088	990.2	2183	21.1	70	64	2.5	2332	145.6	5.2	4.6	11.5	1670	18.8	2720	27.5	3990	35.4	5130	34.8	5050	3.13	0.17	3.95	0.23	4.39	0.21
8	LIG-8	Mar. 1	.45	M-6535	M-6400	25	33	262	–	91.2	201	152.0	335	50.8	112	499.4	1101	1002.9	2211	21.1	70	69	2.7	2350	146.7	4.5	3.8	11.0	1600	18.9	2740	27.0	3910	34.9	5060	36.3	5260	3.24	0.19	3.96	0.12	4.42	0.24
9	LIG-9	May 21	.44	–	M-6400	–	33	401	–	102.5	226	232.2	512	–	–	480.4	1059	963.9	2125	21.1	70	81	3.2	2326	145.2	5.0	5.0	12.7	1840	17.9	2600	30.1	4370	41.0	5940	38.3	5560	3.25	0.19	4.33	0.19	4.70	NA
10	LIG-10	Aug. 27	.46	M-6569	M-6400	15	33	423	–	96.6	213	179.2	395	31.8	70	493.5	1088	990.6	2184	25.6	78	66	2.6	2343	146.3	4.2	4.3	9.0	1310	14.5	2100	24.7	3580	39.0	5650	40.3	5850	3.09	0.04	4.25	0.16	4.45	0.22
11	LIG-11	Aug. 27	.45	M-6569	M-6400	25	33	483	–	94.8	209	158.3	349	52.6	116	491.2	1083	986.6	2175	26.7	80	81	3.2	2332	145.6	4.4	4.2	8.0	1160	10.4	1510	20.6	2990	33.1	4800	39.5	5730	3.48	0.07	4.06	0.19	4.43	0.21
12	LIG-12	Sept. 10	.45	M-6577	M-6400	15	33	439	–	94.3	208	178.3	393	31.3	69	489.9	1080	983.4	2168	25.6	78	89	3.5	2326	145.2	5.3	4.3	10.0	1450	14.5	2110	25.4	3680	32.3	4680	39.1	5670	3.28	0.11	3.78	0.16	4.28	0.18
13	LIG-13	Sept. 10	.44	M-6577	M-6400	25	33	478	–	88.9	196	150.6	332	50.3	111	494.9	1091	993.8	2191	25.6	78	79	3.1	2326	145.2	5.5	4.4	8.8	1270	13.3	1930	22.3	3240	33.6	4870	39.4	5710	2.95	0.12	4.10	0.18	4.67	0.19
		1975																																									
14	LIG-14	Nov. 24	.46	M-6535	M-6400	25	33	712	(274)	93.4	206	151.0	333	50.3	111	501.7	1106	999.3	2203	17.8	64	71	2.8	2348	146.6	4.8	NA	9.2	1340	14.2	2060	24.6	3570	36.6	5310	39.3	5700	3.13	0.09	3.76	0.19	4.31	0.17
15	LIG-15	Nov. 24	.45	M-6679	M-6400	25	33	854	(329)	94.8	209	159.2	351	53.1	117	497.1	1096	990.6	2184	17.8	64	64	2.5	2348	146.6	4.7	NA	8.6	1250	14.1	2050	25.3	3670	35.2	5110	40.5	5880	3.33	0.17	3.78	0.18	4.36	0.17
16	LIG-16	Dec. 1	.44	M-6680	M-6400	25	33	826	(318)	94.8	209	161.9	357	54.0	119	492.6	1086	981.1	2163	16.7	62	74	2.9	2334	145.7	5.2	NA	8.9	1290	14.5	2110	25.3	3670	35.0	5080	39.0	5650	3.25	0.21	3.44	0.17	4.32	0.19
17	LIG-17	Dec. 1	.44	M-6681	M-6400	25	33	829	(319)	95.3	210	161.0	355	53.5	118	495.3	1092	987.0	2176	17.2	63	69	2.7	2345	146.4	4.7	NA	9.4	1370	14.2	2060	24.7	3580	38.2	5540	40.3	5840	3.20	0.17	3.86	0.19	4.43	0.21
18	LIG-18	Dec. 5	.45	M-6682	M-6400	25	33	824	(317)	99.8	220	165.6	365	55.3	122	486.7	1073	970.2	2139	17.8	64	81	3.2	2324	145.1	5.0	NA	8.5	1230	12.4	1800	23.2	3370	36.0	5220	41.5	6020	2.73	0.16	3.79	0.18	3.99	0.17
19	LIG-19	Dec. 5	.45	M-6683	M-6400	25	33	858	(330)	100.7	222	167.4	369	55.8	123	484.0	1067	963.9	2125	17.8	64	76	3.0	2316	144.6	5.2	NA	7.9	1150	13.0	1890	22.4	3250	38.7	5610	41.6	6040	2.76	0.14	3.88	0.15	4.16	0.21
		1976																																									
20	1-6734	Sept. 17	.46	M-6734	M-6400	25	33	458	(176)	94.3	208	152.0	335	50.8	112	504.8	1113	1003.3	2212	22.8	73	81	3.2	2361	147.4	4.1	3.6	7.9	1150	15.0	2170	26.3	3820	39.7	5760	39.2	5690	3.15	0.14	3.78	0.18	4.32	0.15
21	2-6730A	Sept. 17	.47	M-6730	M-6400	25	33	516	(198)	102.5	226	162.4	358	54.0	119	509.8	1124	1013.8	2235	23.3	74	53	2.1	2411	150.5	1.3	1.0	–	NA	–	NA	NA	NA	45.8	6640	47.6	6910	NA	NA	3.84	0.17	4.52	0.18
22	2-6730B	Sept. 17	.46	M-6730	M-6400	25	33	1011	(389)	98.9	218	160.0	352	53.1	117	502.1	1107	997.9	2200	23.3	74	48	1.9	2369	147.9	3.1	3.0	–	NA	–	NA	31.0	4490	–	NA	–	NA	3.36	0.16	NA	NA	NA	NA
23	3-6754	Sept. 17	.46	M-6754	M-6400	25	33	1097	(422)	104.8	231	169.6	374	56.7	125	489.0	1078	971.6	2142	23.3	74	66	2.6	2343	146.3	3.5	3.7	7.9	1150	12.0	1740	22.3	3240	37.7	5470	38.0	5510	2.74	0.17	3.54	0.15	4.31	0.19
		1977																																									
24	4-6880	June 22	.42	M-6880	M-6400	20	33	906	(348)	98.0	216	187.3	413	46.7	103	490.8	1082	973.9	2147	15.6	60	71	2.8	2350	146.7	4.4	NA	–	NA	20.1	2920	34.1	4940	44.7	6480	45.2	6560	3.29	0.14	4.39	0.17	4.59	0.29
25	5-6880A	June 22	.43	M-6880	M-6400	15	33	897	(345)	98.4	217	196.9	434	34.9	77	485.3	1070	963.9	2125	15.6	60	66	2.6	2327	145.3	5.3	3.5	–	NA	–	NA	30.8	4460	–	NA	–	NA	NA	NA	NA	NA	NA	NA
26	5-6880B	June 22	.44	M-6880	M-6400	15	33	764	(294)	102.5	226	197.3	435	34.9	77	486.7	1073	965.7	2129	15.6	60	74	2.9	2337	145.9	4.6	3.3	–	NA	19.4	2820	32.4	4700	40.6	5890	46.7	6780	3.41	0.15	4.12	0.19	4.98	0.19
27	6-6886	July 15	.48	–	M-6886	–	33	836	(322)	110.2	243	230.9	509	–	–	476.3	1050	944.8	2083	15.6	60	81	3.2	2305	143.9	5.2	4.2	18.8	2720	22.7	3290	–	NA	34.1	4950	36.7	5320	NA	NA	3.92	0.18	4.42	0.22
28	7-6880	July 15	.44	M-6880	M-6886	20	33	981	(377)	103.0	227	187.3	413	46.7	103	484.4	1068	961.6	2120	15.6	60	81	3.2	2332	145.6	4.4	3.8	19.4	2810	24.3	3530	–	NA	35.0	5080	37.9	5490	NA	NA	3.66	0.16	4.17	0.22
29	8-6880	July 15	.46	M-6880	M-6886	25	33	1050	(404)	101.2	223	166.5	367	55.3	122	486.7	1073	965.7	2129	15.6	60	81	3.2	2323	145.0	4.8	4.3	15.9	2300	22.7	3290	–	NA	36.0	5220	35.8	5190	NA	NA	3.95	0.19	4.18	0.19
		1978																																									
30	LIG-20	Feb. 15	.46	–	M-6880	–	33	949	(365)	108.0	238	236.3	521	–	–	474.4	1046	956.2	2108	17.8	64	89	3.5	2323	145.0	4.9	4.0	–	NA	22.9	3320	31.4	4550	43.3	6280	43.2	6260	3.40	0.25	4.29	0.20	4.30	0.22
31	LIG-21	Feb. 15	.46	M-6907	M-6800	25	33	1517	(583)	129.3	285	210.0	463	69.9	154	447.2	986	901.3	1987	19.4	67	66	2.6	2299	143.5	3.6	3.0	–	NA	23.0	3340	36.5	5290	39.9	5780	39.6	5740	3.42	0.19	3.86	0.19	3.86	0.21
32	LIG-21R	Feb. 22	.47	M-6907	M-6800	25	33	1981	(762)	127.9	282	205.9	454	68.5	151	438.2	966	882.7	1946	15.6	60	74	2.9	2255	140.8	5.3	4.2	–	NA	22.2	3220	34.2	4960	38.3	5550	39.0	5650	3.39	0.18	3.69	0.18	3.88	0.20
33	LIG-22	May 15	.46	–	M-6909	–	–	1002	(385)	107.5	237	232.2	512	–	–	480.4	1059	967.5	2133	22.2	72	76	3.0	2339	146.0	4.4	4.4	15.6	2260	19.7	2850	29.3	4250	35.9	5200	38.4	5570	3.17	0.16	4.45	0.16	4.26	0.14
34	LIG-23	May 15	.46	Interground	M-6918 M-6754	15	33	1619	(623)	104.3	230	226.3	499	–	–	487.2	1074	981.6	2164	20.1	69	25	1.0	2355	147.0	3.5	3.8	15.1	2190	–	NA	30.6	4440	–	NA	39.4	5710	3.33	0.15	NA	NA	4.30	0.17
35	LIG-24	May 15	.47	M-6976	M-6800	25	33	1598	(615)	102.1	225	164.7	363	54.9	121	480.8	1060	968.4	2135	22.8	73	76	3.0	2316	144.6	4.7	4.9	10.3	1500	14.9	2160	24.2	3510	–	NA	38.7	5610	2.93	0.16	NA	NA	5.74	0.25
36	–	July 10	.45	M-6979	M-6800	25	33	262	†(101)	91.6	202	152.9	337	50.8	112	494.9	1091	997.0	2198	20.0	68	76	3.0	2339	146.0	4.9	3.9	11.2	1630	28.7	4160	34.0	4930	–	NA	–	NA	2.93	0.14	NA	NA	NA	NA

† WRA dosage is 530 cm^3; this is the only mix that contained WRA.

‡ Dosages in ( ) represent a calculated dosage for comparison with mixes 1 to 13.

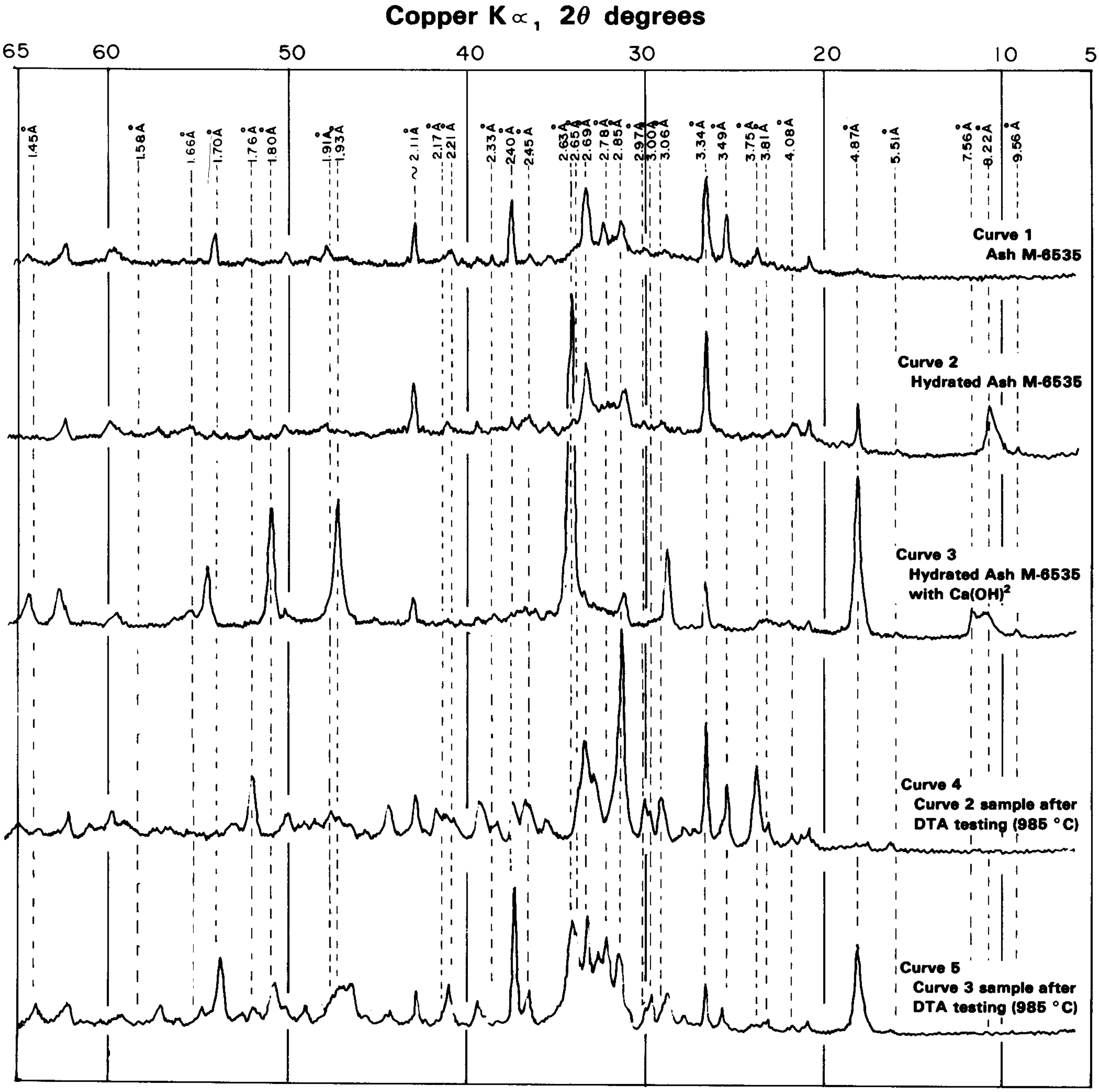

Figure 4. — XRD patterns on ash M-6535 and hydration products— before and after heating to 985 °C (1805 °F).

(49 °C). The reactions were allowed to continue beyond 3 days, so hydration results are indicative of a longer period. The hydration products of two samples were examined by XRD and DTA (X-ray diffraction and differential thermal analysis). The two samples were ash M-6535 and excess water, and ash M-6535, $Ca(OH)_2$, in 50:50 mass proportions, and excess water. The XRD curves are shown on figure 4 and DTA curves are shown on figure 5.

Samples heated to 985 ° C (1805 °F) by DTA were investigated further by XRD. These curves also are shown on figure 4. The benefit of this additional data is discussed at the end of the next subsection.

Hydration or reduction in amount of the crystalline phases is found by comparing curves 1 and 2 on figure 4. Crystalline materials that disappeared or were reduced in amount upon hydration include CaO,

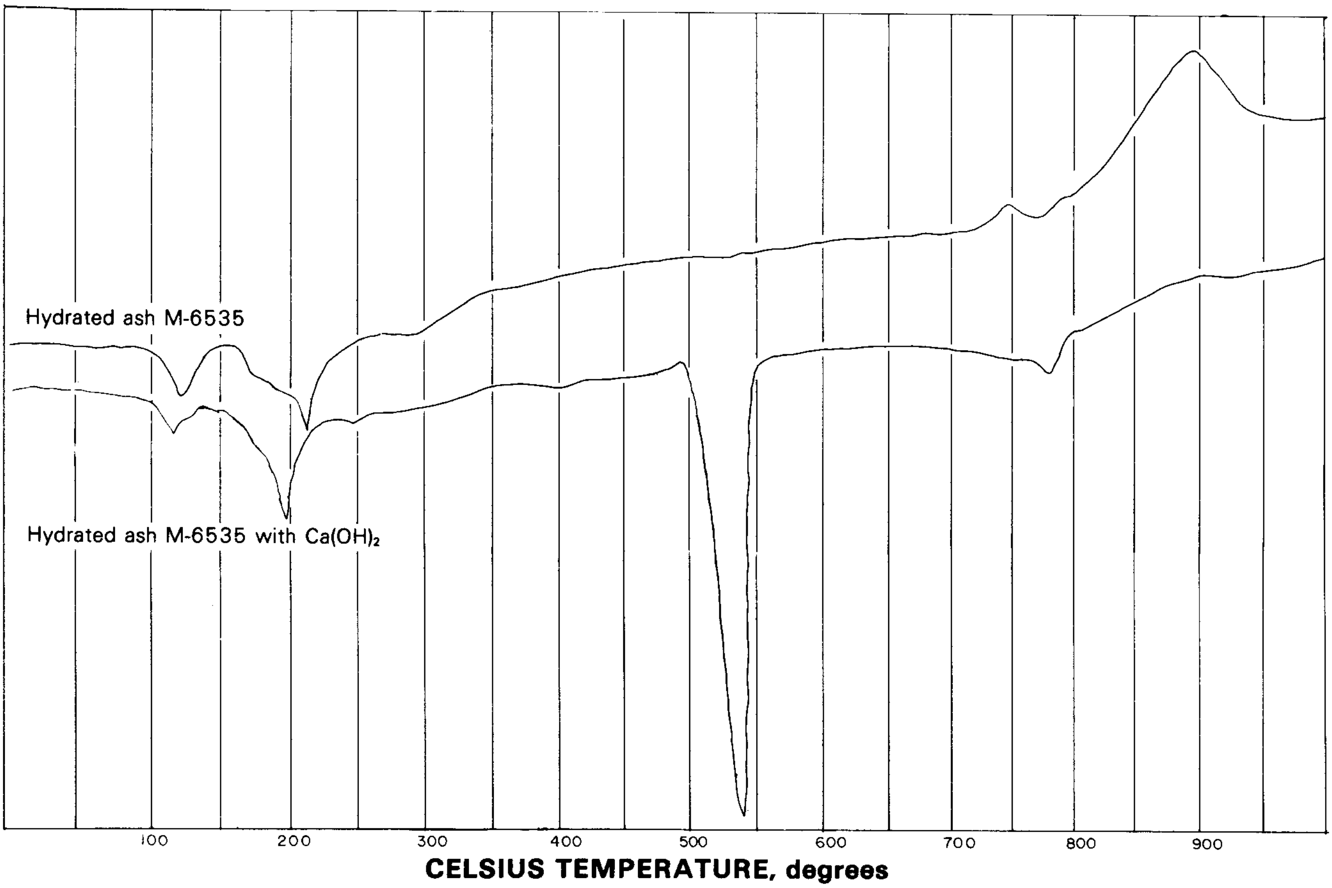

Figure 5. — Hydration study of ash M-6535 — differential thermal analysis curves.

$CaSO_4$, and speculatively $C_4A_3\bar{S}$ as indicated by the peak of 3.75 Å and also weak peaks at 2.65 and 2.17 Å. Hydration of CaO is indicated by marked reductions in the peaks at 2.40, 1.70, and 2.78 Å. Reaction of $CaSO_4$ is indicated by reductions in the peaks at 3.49, 2.33, and 2.21 Å. The peak of anhydrite at 2.85 Å changes very little. The compound showing the 3.75 Å peak and two weak-to-very-weak peaks and assumed to be $C_4A_3\bar{S}$ disappears during hydration.

There is some indication that the 2.69-Å peak (fig. 4, curve 1) for Fe_2O_3 may include C_3A. In any case, the amount of C_3A (if present) is probably less than 2 percent. In comparison to a known quantity, the free lime (CaO) determined chemically is 2.2 percent. The peak for free lime at 2.40 Å is almost equal to the peak at 2.69 Å indicating less than 2.2 percent of Fe_2O_3 and possibly C_3A.

The possibility that C_3A causes the flash set seems remote. Time-of-set pastes, of ash M-6535 and various percentages of gypsum, were made according to *ASTM: C 191*. Gypsum additions—up to 10 percent by mass of this ash—produced little, if any retardation.

The peak at 4.87 Å (fig. 4, curve 2) could be $Ca(OH)_2$; however, the major peak at 2.63 Å indicates that the amount of $Ca(OH)_2$ is small. The DTA curve has no endotherm for $Ca(OH)_2$. The peak at 4.87 Å therefore likely represents a compound other than $Ca(OH)_2$.

The only hydration product positively identified was a $C_4A \cdot 1/2CO_2 \cdot 12H_2O$ or a solid solution variety of it. This identification was made by X-ray peaks at 8.22, 4.08, and 2.90 Å, and with a DTA endotherm at about 215 °C (420 °F, fig. 5). A very small endotherm at 300 °C (570 °F) could indicate a solid solution with a small amount of calcium aluminate monosulfate. However, the very small endotherm at 300 °C may be another compound.

If ettringite were formed, it would account for the disappearance of the SO_3. However, ettringite does not seem to appear on the XRD pattern. Ettringite is characterized by XRD peaks at 9.73, 5.61, and 3.88 Å. Small peaks do appear at 9.60 and 5.53 Å, but these probably indicate thaumasite ($Ca_3CO_3SiO_3SO_4 \cdot 14H_2O$) rather than ettringite. Thaumasite has been found in concrete [18] and is characterized by peaks at 9.56 and 5.51 Å, which is very close to the peaks found here (fig. 4) at 9.60 and 5.53 Å. When found in the natural state, thaumasite has been associated with ettringite [19] and with gehlenite [20]. Thaumasite has been implicated as a cause of deterioration of dolomite aggregate mortars in sulfate conditions [21].

Benton [16] mentioned an unknown product having a peak at 4.85 Å in a lime-gibbsite mix and with a small endotherm at 300 °C (570 °F) in DTA. In these data (figs. 4 and 5) there also appears an XRD peak at 4.87 Å and a DTA endotherm at 300 °C. The following speculation on this unknown product is submitted: It is probably calcium alumina hydrate since Benton's product was found in a lime-gibbsite mix.

The glass of M-6535 may have composition of anhydrous $C_{12}A_7H_x$ which (with water) quickly hydrates to $C_{12}A_7H_x$[22] with generation of heat. The formation of $C_4A \cdot 1/2CO_2 \cdot 12H_2O$ could result from the hydration of $C_{12}A_7H_x \cdot C_4A \cdot 1/2CO_2 \cdot H_2O$ prepared by shaking a slurry of $C_{12}A_7H_x$ and lime [23, 24]. The slurry and M-6535 was agitated continuously for three days and, as shown by XRD, $C_4A \cdot 19H$ is formed first and upon drying converted to $C_4A \cdot 13H_2O$ or if carbonated to $C_4A \cdot 1/2CO_2 \cdot 12H_2O$.

$C_{12}A_7H_x$ has major peaks at 4.89 and 2.68 Å both are present on curve 2. If a small amount of C_3A hydration lowered the peak at 2.69 Å (curve 1) and $C_{12}A_7H_x$ formed restoring the peak at 2.69 Å, the evidence of C_3A hydration would be minimal. It is possible that a small amount of C_3A is present but is overshadowed by this reaction. The reaction of $C_{12}A_7H_x$ with gypsum results in large increases in strength without undergoing retardation [26]. This was found to be true for M-6535 with gypsum or $CaSO_4$ additions [27].

A poorly crystallized calcium silicate hydrate (CSH-1) may be indicated by a broad XRD peak of 3.06 Å and weak peak at 1.82 Å. Ash M-6535 hydrated with $Ca(OH)_2$ showed these two peaks.

The DTA sample heated to 985 ° C (1805 °F) then was examined by X-ray diffraction (fig. 4, curve 4). Gehlenite was found as the most significant crystalline compound (2.85, 1.76 2.40, and 3.07 Å). Garnets such as grossularite have very low peaks; it is possibly indicated by peaks at 2.66, 1.58, 2.97, and 1.92 Å. The questionable compound $C_4A_3\overline{S}$ seems to increase—indicated by increases in the peaks at 3.74, 2.65, and 2.16 Å—indicating further production of this expansive cement compound.

Hydration of a high calcium ash, $Ca(OH)_2$, and water. — Similar to the hydration of M-6535 (discussed previously in preceding subsec.) a second M-6535 sample was hydrated with an equal quantity of $Ca(OH)_2$ (fig. 4, curve 3). The main hydration product was $C_4A \cdot 1/2CO_2 \cdot 12H_2O$, with peaks at 8.22, 4.08, and 2.90 Å, and also $C_4A \cdot CO_2 \cdot 11H_2O$ with major peaks at 7.56, 3.81, and 1.66 Å. These two products were found in about equal quantities. Abundant $Ca(OH)_2$ was detected.

There is speculative evidence for the transient formation of $C_{12}A_7H_x$ (as indicated in preceding subsec.). The small DTA endotherm at 300 °C (570 °F) is not formed; however, a small endotherm at 750 °C (1380 °F) is formed. The $C_4A \cdot H_x$ endotherm has shifted to 200 °C (390 °F), and a large endotherm between 500 and 550 °C (930 and 1020 °F) for $Ca(OH)_2$ is very prominent as are the characteristic XRD peaks. The $Ca(OH)_2$ used probably was carbonated to some extent indicated by an endotherm at 800 °C (1470 °F). The highly carbonated form of C_4AH_x was probably a result of a carbonated $Ca(OH)_2$ reaction with alumina glass. The exotherm at 750 °C (1380 °F) did not occur.

After the sample had undergone DTA testing to 985 °C (1805 °F), it was submitted again to X-ray diffraction. The X-ray pattern (fig. 4, curve 5) indicates CaO and gehlenite are still present, but in a much smaller amount than before being submitted to the high temperature. The presence of C_3A (peaks at 2.70, 1.91, and 1.56 Å) and surprisingly significant amounts of $Ca(OH)_2$ are indicated also (fig. 4, curve 5). One of the characteristics of $C_{12}A_7H_x$ is that it has equal peaks at 4.89 and 2.68 Å. Therefore, the peaks at 4.90 and 2.63 Å probably indicate that $C_{12}A_7H_x$ was formed and makes up part of the 4.90- and 2.69-Å peaks. This belief that $C_{12}A_7H_x$ is formed is supported by the presence of other distinct characteristic peaks of this compound at 3.00, 2.45, and 2.19 Å. The expansive compound $C_4A_3\overline{S}$ is absent. In summary, early rapid hardening of ash M-6535 is probably caused by very reactive glass; it is theorized to have the approximate composition $C_{12}A_7H_x$. The rapid hardening is augmented by hydration of small amounts of free CaO, $CaSO_4$, and C_4A_3S, and possibly C_3A.

Long-time studies of high calcium ash hydration. — Speculatively, in prolonged hydration of the glass, gehlenite hydrate and calcium silicate hydrates should form [7]. This is indicated possibly by the glasses falling in the gehlenite field (none of the glasses had a C_2AS composition) as shown on figure 2 and the fact that gehlenite formed during

DTA testing. There is much evidence for gehlenite hydrate formation as discussed previously [27]. The presence of uncombined $Ca(OH)_2$ and $Ca(SO_4)$ during early hydration prevents the crystallization of gehlenite hydrate [9].

Hydration reactions of a high calcium ash versus pozzolanic activity. — Some high calcium ashes are highly reactive. The early strength gaining mechanism is, in part, similar to that of high alumina cement. At later ages, the mechanism is a combination of pozzolanic reaction and reaction of slag composition glass either with lime or calcium sulfate. Therefore, a test such as *ASTM: C 618* based on strength of lime and pozzolan could produce conflicting results. As was demonstrated (see sec. *ASTM: C 618 — Strength Gaining Properties*) the pozzolanic activity (preferably measured as strength) is best assessed using portland cement. The test also should be modified to allow variable replacement percentages so that an optimum fly ash replacement for strength can be determined.

ASTM: C 618 - Unsoundness Testing

Delayed reactions within hardened concrete can cause disruptive expansion, ordinarily referred to as *unsoundness*. In portland cement the expansion can be due to hydration of uncombined calcium oxide (CaO) or hard burned crystalline magnesium oxide. Other deleterious chemical reactions that can occur include delayed internal sulfate reactions to form ettringite and reactions of alkalies with reactive aggregates.

MgO and CaO potential unsoundness. — The potential unsoundness of portland cement caused by MgO is controlled by limits on chemical composition; however, CaO is not limited by specifications. This analysis has been applied to fly ashes in that a limit of 5-percent MgO is specified in *ASTM: C 618*. The potential unsoundness caused by MgO and/or CaO normally is detected by the autoclave expansion test (*ASTM: C 151*).[8] Several fly ashes in this study have MgO contents in excess of 5.0 percent, yet the autoclave expansion test indicates little unsoundness. For example, ash M-6514 (table 2) has an MgO content of 11.3 percent, and autoclave expansion of 0.141 percent, considerably below the specification limit of 0.8 percent. The MgO and CaO combined in glass do not cause unsoundness.

MgO is combined mostly in glass. It appears to correlate with the amount of calcium in the glass; i.e., glasses high in calcium have a high MgO content and vice versa [15]. High calcium ashes that have compositions near the gehlenite field (fig. 2) have a similarity to blast-furnace slags. The glasses in the blast-furnace slags have compositions approximately of melilite which would represent a mixture of gehlenite (C_2AS) and akermanite (C_2MS_2). The MgO content in blast-furnace slags can be as high as 16 percent before any periclase (crystalline MgO) is detected. Therefore, when furnace slags are used with portland cement, unsoundness attributable to MgO hydration does not result [28]. An autoclave test to determine unsoundness due to MgO in the fly ash would be more appropriate than the limit on chemical composition that now exists in *ASTM: C 618*. The autoclave test could be conducted at the optimum percentage of *fly ash to cement* found for strength.

Unsoundness caused by SO_3. — Unsoundness caused by SO_3 is a complex process. Delayed reaction of SO_3 with lime, alumina, and water causes disruptive expansion through formation of ettringite. The SO_3 that reacts early in the hydration of the cement does not cause problems. Supersulfated cements that consist of blast-furnace slag and $CaSO_4$ can have SO_3 contents near 10 percent and remain sound. The permissible amount of SO_3 appears to be related to the amount of reactive alumina. For example, the SO_3 limit varies with C_3A content in *ASTM: C 150, Standard Specification for Portland Cement*.

As indicated previously, the amount of very reactive alumina in fly ash appears to correlate with the calcium content. The glasses containing both alumina and calcium are the most reactive. Pozzolans or fly ashes containing higher amounts of reactive alumina can tolerate higher percentages of sulfate. In fact, higher percentages of sulfate may be an advantage in that drying shrinkage may be reduced and durability improved—particularly sulfate resistance [29].

Based on results of this study, an optimum SO_3 content test similar to that of *ASTM: C 563, Standard Test Method for Optimum SO_3 in Portland* Cement, should be developed for *fly ash to cement* combinations or for *blended* cements. This suggestion is based on *time-of-set pastes* made according to ASTM: C 191 of five 90-percent fly ash (M-6734, M-6510, M-6577, M-6569, and M-6498) and 10-percent anhydrite cements. Fifty-millimeter (2-in) cubes were cast from each paste. Pastes of ashes M-6510, M-6577, M-6569, and M-6498 underwent varying degrees of expansion. Most also developed different compressive strengths by 28 days; paste of ash M-6498 could not be removed from the molds and was judged to have no strength. The compressive strengths of the remaining pastes varied from 15.2 MPa (2200 lb/in²) for ash M-6577 to over 62.0 MPa (9000 lb/in²) for ash M-6734, and

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[8] ASTM: C 151, *Autoclave Expansion of Portland Cement.*

strengths varied with the (CaO-5) / (Fe_2O_3) ratio, calculated from chemical oxide percentages of the ash.

This ratio was developed [27] to predict the amount of reactive alumina as an indication of the sulfate resistance of fly ash concretes. The compressive strength divided by 1000 compares favorably with the numerical value of this ratio. Ashes having the higher strengths in these tests had the poorest sulfate resistance when used as an admixture in concrete. Sulfate resistance of concretes containing 25-percent replacement of portland cement with ash M-6498, M-6577, M-6569, M-6510, or M-6734, ranged — in order—directly from best to worst, and the strengths ranged from worst to best. The sulfate resistance of those ashes at replacements other than 25 percent may be different [27, 30] from those observed here. The SO_3 content allowed in ash M-6734 could be much higher than in M-6498. It is anticipated that with an optimum SO_3 content, by adding gypsum, sulfate resistance will improve. Based on these observations and considerations, it appears that the *ASTM: C 618* specification for SO_3 content is somewhat arbitrary and at times has little significance [31]. If an optimum SO_3 test is developed, *cement/fly ash* studies on *time-of-set* and *drying shrinkage* should be investigated also.

Alkali-aggregate disruptive reaction.— Alkalies in cement and certain aggregates react to cause disruptive expansion. To reduce this reaction, available alkalies in the fly ash are limited to 1.5 percent (ASTM: C 618). As a further safeguard, a mortar bar expansion test may be specified. At 14 days, the maximum expansion shall not exceed 0.02 percent. There was no definite correlation between available alkalies content and expansion as shown on figure 6. Ash M-6510 has the highest available alkali content of the ashes investigated. The expansions shown in table 2 are with high-alkali cement (1.19 percent Na_2O equivalent). In this study high-alkali cement was used as a companion control for 24 different pozzolans (between November 1973 and April 1980). The 14-day expansion of Pyrex™ bars made with the control cement ranged from 0.268 to 0.565 percent. Further, 22 tests showed expansions exceeding 0.370 percent. For comparison, only two fly ashes (M-6535 and M-6514)—when tested with this cement—produced Pyrex™ bar expansions larger than 0.370 percent. Most fly ashes appear to reduce the 14-day expansion of Pyrex™ bars containing high-alkali cement at 14 days, when tested according to *ASTM: C 441*.[9]

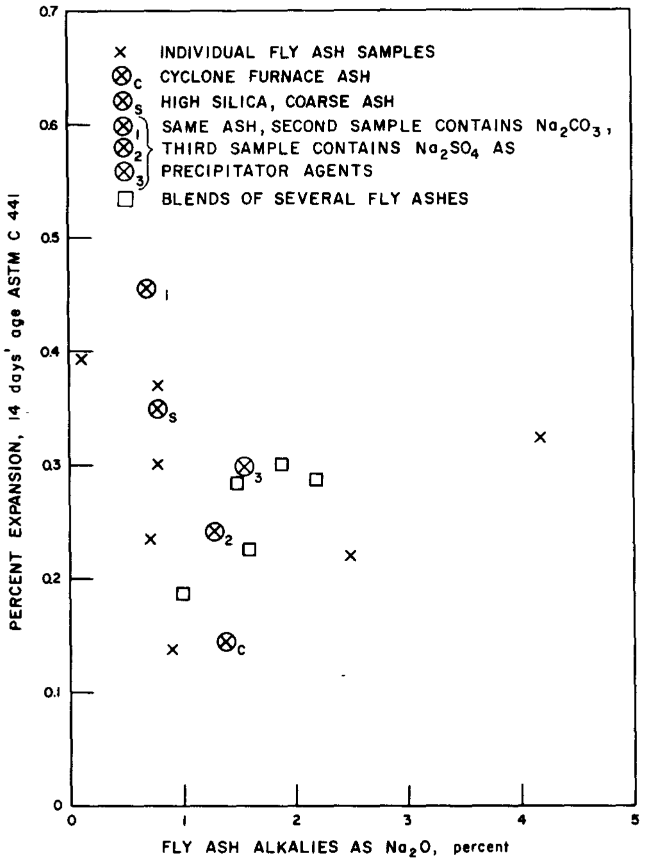

Figure 6. — Effect of fly ash alkalies on alkali-aggregate reaction using the control cement.

The reactive aggregate, Pyrex™ glass, and cement alkalies react to cause expansion. However, the alkalies of fly ash seem to have little effect on these expansions. Expansion data for each fly ash mixed with control cement are plotted against the alkali content of each fly ash (fig. 6). Apparently, there is no relation. Ash M-6510, which has the highest alkali content (4.23 percent), does not have the largest expansion.

It has been shown in previous studies [27, 30] that fly ash affects sulfate resistance. In those studies, calcium oxide content was of prime importance. Similar correlation can be demonstrated with regard to alkali-aggregate reaction. Figure 7 is a plot of fly ash calcium oxide content versus alkali-aggregate (14-day) expansion. There appears to be a correlation. Ash M-6754 may not fit the pattern because it has physical and chemical differences in that it is very coarse and has a very high silica content. Ash M-6577, which was collected from a powerplant having a cyclone furnace, also appears out of line. It has been the exception in many tests [27]. Apparently, this ash has no chemical nor physical difference in relation to the others which makes it an

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[9] ASTM: C 441, *Effectiveness of Mineral Admixtures in Preventing Excessive Expansion of Concrete Due to the Alkali-Aggregate Reaction.*

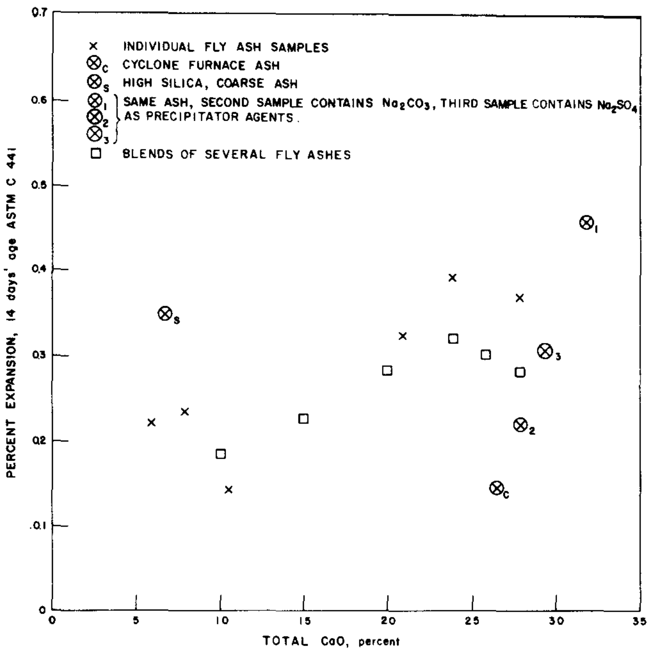


Figure 7. — Effect of fly ash CaO content on alkali-aggregate reaction.

exception. Possible differences in glass structure relating to characteristics of the ashes are discussed elsewhere [27].

Figure 7 indicates that calcium oxide content with a few exceptions (high silica, coarse ash, and the same ash with added Na_2CO_3 and Na_2SO_4) correlates with percent of expansion. It appears, therefore, that CaO content may be a useful parameter to indicate the effectiveness of an ash to combat alkali-aggregate reaction.

The effect of Na_2CO_3 or Na_2SO_4 added to fly ash is interesting. A mortar of a high-alkali cement, ash M-6535 and Pyrex™ glass, had the largest expansion. Ashes M-6979 and M-7129 are from the same source as M-6535 but Na_2CO_3 or Na_2SO_4 was added during collection which increased the available alkalies from 0.68 to 1.35 and 1.53 percent, respectively. This increase did not cause an increase in expansion. The expansion was reduced. Such effect of Na_2CO_3 has been reported by McCoy and Caldwell [33].

Another interesting comparison is that M-6498, M-6577, and M-6976, at 25-percent mass replacement of cement, show improved sulfate resistance of concrete. Lower expansions of Pyrex™ bars with 20-percent replacement of ashes were observed. It has been shown [30] that both sulfate resistance and alkali-aggregate expansion varies with level of fly ash replacement.

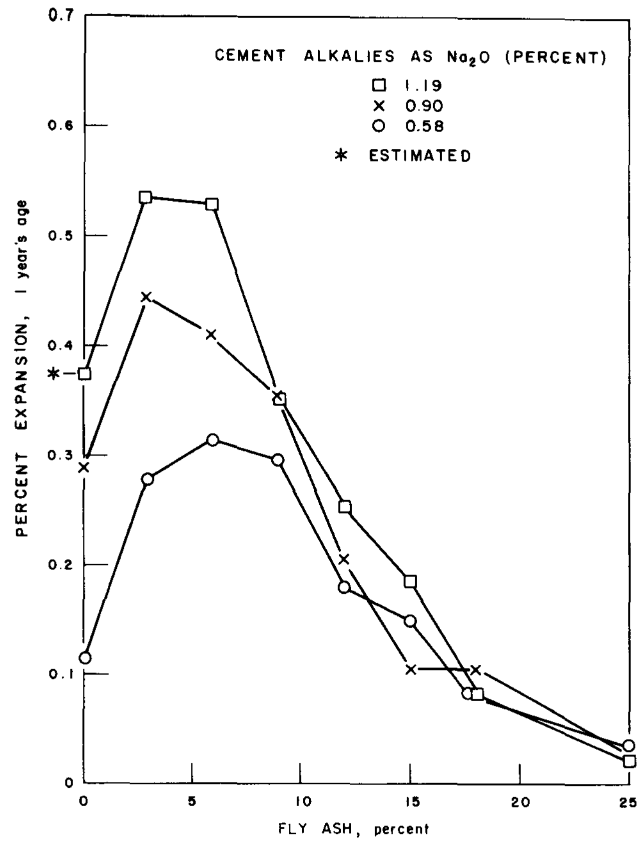


Figure 8. — Effect of cement alkalies and fly ash replacement percentage on alkali-aggregate reaction.

Porter [32] and others indicated a *pessimum* amount for fly ashes with regard to alkali-aggregate reaction. The word "pessimum" is defined as the amount of pozzolan (fly ash) causing the maximum expansion. Usually the word is applied in those situations where a small amount of pozzolan produces an increase in expansion, but larger amounts result in a decrease in expansion. Figure 8 illustrates this condition.

In examining the data used to develop figure 8, together with the data from Porter [32], an idealized plot of alkali-aggregate expansion versus fly ash replacement can be developed for fly ashes of various calcium oxide contents as shown on figure 9. Fly ash M-6498, which has a calcium oxide content of 8.2 percent, shows an expansion almost equal to the CaO equals 10-percent curve (fig. 9) when used in the amount of 10-percent replacement—but shows reduced expansion when used in the amount of 20-percent replacement. Fly ash M-6535, which has 32-percent CaO, produces an expansion—when used in the amount of 20-percent replacement with high-alkali cement in Pyrex™ bars—about twice that of control bars without fly ash. This correlates with the CaO = 30 % curve on figure 9.

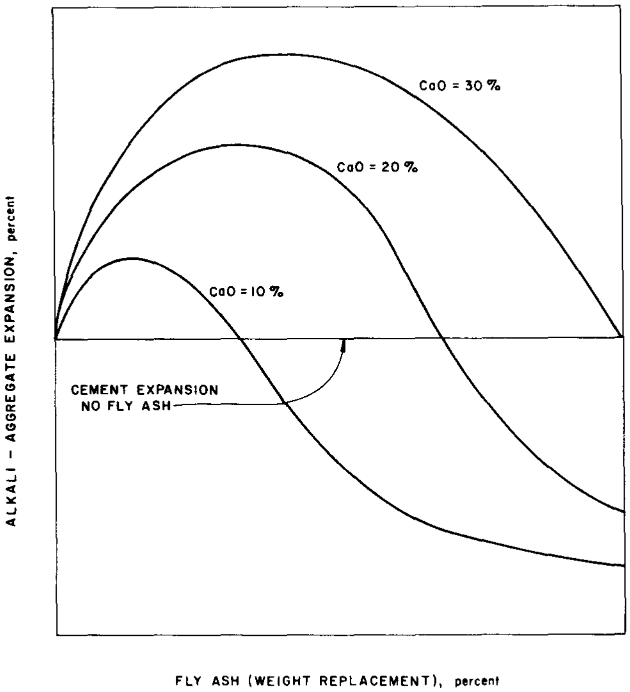


Figure 9. — Theoretical expansion alkali-aggregate reaction.

To verify that a higher percentage of ash M-6535 would indeed reduce expansion, as the curve on figure 9 indicates, a 40-percent replacement was used. Expansion at 14 days was 0.331 percent, which is less than the expansion of 0.370 percent for the cement without fly ash replacement.

Therefore, a minimum replacement to reduce expansion for high calcium ash M-6535 is somewhere between 20 and 40 percent. Those not familiar with high calcium ashes may feel this is too high a replacement; however, adequate strengths can be obtained with high calcium ashes with replacements in excess of 50 percent.

In conjunction with the particular high-alkali cement of this study, the minimum replacement to reduce expansion appears to be very close to the calcium oxide content; i.e., the minimum replacement for M-6498 is about 10 percent (CaO equals 8.2 percent) and the minimum for M-6535 is about 30 percent (CaO equals 32.0 percent).

ASTM: C 618 - Miscellaneous Tests

Fly ash pozzolans usually reduce the water requirement of concrete. All fly ashes in this study require less water than the control to produce the same flow. In the column headed "Water requirement" in table 2, those ashes for which data show <100 were tested under Federal Specification for Pozzolan SS-P-570B. This test method measures change in flow for the same water requirement, whereas *ASTM: C 618* measures the change in water requirement to produce the same flow.

The relative mass density of fly ashes generally parallels the amount of calcium oxide. High calcium ashes have higher specific gravities than lower calcium ashes. At equal calcium contents, specific gravity varies with ferric oxide contents.

Chemical and physical properties having various finenesses [passing 45μm (U.S.A. Standard Sieve No. 325) and Blaine fineness] are shown in table 2. Generally, the finer the ash the more reactive it is with portland cement. Fineness and pozzolanic activity with portland cement show a fair degree of correlation. Comparisons with strengths in concrete show less correlation—especially for high calcium ashes. Low calcium ashes, however, may require a higher fineness to produce higher early strengths (see strengths for ash M-6754, table 3). These ashes require reaction of cement to produce $Ca(OH)_2$ before reaction of the fly ash can begin. A finer material speeds up reaction. As discussed, some high calcium ashes develop strength very rapidly; in such instances the fineness may *not* be as critical.

FLY ASH CONCRETE

A total of 36 concrete mixes were made that contained portland cement or portland cement and pozzolan combinations. Material quantities for each mix are shown in table 3. Physical and chemical properties of the cements are shown in table 4. Chemical and physical properties of the fly ashes were discussed earlier and are shown in table 2. All mixes were made with a maximum-size aggregate of 37.5 mm (U.S.A. Standard 1-1/2 in). Aggregate properties are shown in table 5. Generally, mixes were designed for the concrete to have 5.0 percent entrained air and a 75-mm (3-in) slump. These targets were not achieved in all cases, but most results fall close to those values. Replacement by mass of fly ash or pozzolan was normally 15 or 25 percent. A few mixes were made slightly different. These include mixes 24 through 28 which will be discussed later. Water to cement ratio, or water to cement plus pozzolan ratio was controlled to 0.45 plus or minus 0.01. Concretes were mixed for 5 minutes in a revolving drum mixer and then measured for slump, air content, temperature, and density.

Concrete Tests

For most mixes, testing included compressive strength, elasticity, drying shrinkage, freeze-thaw durability, and sulfate resistance. Tests for adiabatic

Table 4. — Physical and chemical properties of cements.

	M-6400	M-6550	M-6800	M-6886	M-6909	M-6918
Physical properties						
Relative mass density	3.18	3.15	3.17	3.10	3.20	3.04
Air content, %	8.39	9.3	8.59	9.8	12.80	3.7
Autoclave expansion, %	0.063	0.060	−0.018	0.071	−0.018	0.005
Specific surface, m^2/kg	344.0	328.0	362.0	379.0	352.0	– –
Normal consistency, %	25.0	27.2	24.4	25.7	30.8	– –
Water, cm^3	126.0	136.0	122.0	154.0	154.0	– –
Penetration, mm	9.0	9.0	9.0	11.0	10.0	– –
Time of setting—initial:	170.0	210.0	200.0	144.0	180.0	180.0
(Vicat)—final	285.0	375.0	335.0	210.0	270.0	240.0
Compressive strength, MPa (lb/in^2):						
3-day	16.45	13.27	19.56	25.65	16.69	– –
	(2388)	(1925)	(2837)	(3721)	(2421)	– –
7-day	25.74	17.96	29.13	34.79	22.86	– –
	(3733)	(2605)	(4225)	(5046)	(3316)	– –
28-day	38.21	27.72	43.44	– –	– –	– –
	(5542)	(4021)	(6300)	– –	– –	– –
90-day	44.27	35.92	48.38	– –	– –	– –
	(6421)	(5210)	(7017)	– –	– –	– –
False set—penetration, mm:						
Initial	33.0	34.0	32.0	35.0	– –	35.0
5-minute	28.0	16.0	29.0	– –	– –	11.0
Remix	26.0	– –	– –	30.0	– –	40.0
Remix 5-minute	21.0	– –	– –	24.0	– –	37.0
Chemical analysis						
Oxide analysis, %						Clinker only
SiO_2	22.53	22.28	21.30	20.40	21.6	23.6
Al_2O_3	5.11	4.51	4.47	5.82	4.65	4.15
Fe_2O_3	3.3	3.66	3.87	2.22	5.05	3.29
CaO	62.56	62.91	64.90	64.90	62.40	64.70
MgO	3.14	2.64	0.90	1.35	1.00	3.29
SO_3	2.20	2.35	2.69	3.05	2.54	– –
Percent alkalies—paste method:						
Na_2O	0.06	0.06	0.35	0.11	0.22	0.19
K_2O	0.27	0.038	0.22	0.64	0.58	0.57
Al as Na_2O	0.24	0.31	0.49	0.53	0.60	0.57
Loss-on-ignition	0.80	1.62	1.04	1.06	0.96	1.04
Insoluble residue	0.40	0.034	0.27	0.18	0.32	10.12
Compound composition, %						Clinker only
C_3S	38.06	44.47	59.02	58.13	44.10	54.72
C_2S	35.96	30.41	16.63	14.72	28.74	23.13
C_3A	7.96	5.76	5.31	11.69	3.79	5.44
C_4AF	10.03	11.13	11.76	6.75	15.35	10.00
$CaSO_4$	3.74	4.00	4.57	5.19	4.32	– –

Table 5. – Properties of laboratory aggregate, M-3864.

Property	Sand	Coarse aggregate
Relative mass density	2.65	2.63
Absorption, %	0.81	1.07
NaSO$_4$ soundness, % loss in 5 cycles	4.25	5.38
Los Angeles abrasion (A grading)		
100 revolution, % loss	– –	10.88
500 revolutions, % loss	– –	42.08
Color	Clear	
Percent silt [passing 75 μm (No. 200) sieve by washing]	0.44	

Sand grading, % retained

SI Standard	Alternative	Percent
2.36 mm	No. 8	15.0
1.18 mm	No. 16	15.0
600 μm	No. 30	25.0
300 μm	No. 50	25.0
150 μm	No. 100	15.0
Pan		5.0
Fineness modulus, 2.75		
4.75 mm	No. 4	22
9.5 mm	3/8 in	33
19.0 mm	3/4 in	45
37.5 mm	1-1/2 in	0

temperature rise were made on a few mixes. Test specimens were made as follows:

Ten 150- by 300-mm (6- by 12-in) cylinders were cast from each mix for compressive strength testing at 3, 7, 28, 180, and 365 days. The cylinders were cured at 100-percent relative humidity (fog room) and 23 plus or minus 1.7 °C (73.4 plus or minus 3 °F) until tested. Two cylinders were tested at each age.

Two 100- by 100- by 760-mm (4- by 4- by 30-in) prisms were cast from each mix for measuring drying shrinkage. The prisms were cured for 14 days in the fog room and then placed in an atmosphere of 50-percent relative humidity (50-percent room) at 23 plus or minus 1.7 °C for measurements of drying shrinkage.

Six 75- by 150-mm (3- by 6-in) cylinders were cast from each mix for freeze-thaw durability testing. The concrete was wet-screened to remove material over 19.0 mm (3/4-in) size from these cylinders. Three of the specimens were cured for 28 days in the fog room and then exposed to freeze-thaw cycles. The other three cylinders were cured for 14 days in the fog room, followed by 76 days in the 50-percent room, and then exposed to freeze-thaw cycles. These six cylinders were tested in water; the freezing portion of the cycle was maintained for 1-1/2 hours at −12 °C (10 °F), and the thawing portion for 1-1/2 hours at 21 °C (70 °F). Freeze-thaw failure was considered to have occurred when 25 percent of original mass was lost.

Six 75- by 150-mm cylinders were cast from each mix for measuring resistance to sulfate attack. The plus 19.0-mm aggregate was removed from the mix by wet-screening. The cylinders were cured for 14 days in the fog room, followed by 14 days in the 50-percent relative humidity room, and then placed in a sodium sulfate solution. Three cylinders were exposed to continuous soaking in a 10-percent sodium sulfate solution (hereinafter designated 10-percent soak) at room temperature and the remaining three cylinders were exposed to an accelerated test consisting of cycles of 16-hours soaking in a 2.1-percent sodium sulfate solution at room temperature and 8-hours drying at 54 °C (130 °F). Length measurements were made periodically; a total expansion of 0.5 percent was considered failure.

The 10-percent continuous soak is also an accelerated test considered to be comparable in severity to alternate immersion in 2.1-percent solution and drying in air. Continuous soak in 2.1-percent solution is the standard nonaccelerated test.

Concrete Mixes — Significant Differences

Water requirements to produce 75-mm (3-in) slump for fly-ash concretes are less than those for the control-cement concretes. Water requirement is reduced for higher replacements (15 to 25 percent by mass replacement) of cement with fly ash. Calcined natural pozzolan M-6907 used in mixes 31 and 32 had a higher water requirement than the control. Mixes having M-6400 cement as a control (1 through 26) with a 0.45 plus or minus 0.01 water-cement ratio, or water to cement plus pozzolan ratio illustrates the various water requirements. The control (mix 9) required 134 kg/m^3 (226 lb/yd^3) of water. With 15-percent fly ash, the average is 126 kg/m^3 (212 lb/yd^3). For 25-percent fly ash, the average is 124 kg/m^3 (209 lb/yd^3). The reduced water requirement is independent of the source of the fly ash. The only ash requiring more water than the control was M-6754; however, entrained air for this mix was a little low. Raising the air content to comparable levels would lower the water requirement. Ash M-6754 is a coarse ash which does not meet the current fineness requirements of *ASTM: C 618*.

Since the concretes were made at constant *W* to (*C* plus *P*) ratios, the reduction in water content resulted in an average cement plus pozzolan content which is less than the amount of cement in the control mix [304 kg/m^3 (512 lb/yd^3)]. For example, mix 8 contains a total cementitious content of 265 kg/m^3 (447 lb/yd^3). Mixes 24 through 29 were made to investigate the properties of concretes containing equal totals of cementitious materials rather than equal *water* to *cement plus pozzolan* ratios.

Air was entrained by a neutralized vinsol resin. For mixes 1 through 13, a proprietary admixture was used. Mixes 14 through 36 contained a 5-percent solids neutralized vinsol resin prepared in the laboratory. The dosage shown in parentheses for mixes 14 through 36 equates the percent solids of the laboratory vinsol to the proprietary vinsol. Dosage requirements investigation follow. For comparison, mixes 1 through 26 were selected. They all have cement M-6400 as the control. The gravimetric air content data are complete so they were used for comparison. Table 6 shows a comparison of the dosages. The comparison factor is AEA (air-entraining admixture) dosage per kilogram of cementitious material per percent entrained air. Generally, dosage requirement increases with higher fly ash replacement. However, it is not necessarily true that fly-ash concrete requires more AEA than concrete without fly ash. Interestingly, ashes which have higher total $SiO_2 + Al_2O_3 + Fe_2O_3$ contents and meet the requirements of *ASTM: C 618* for type F require more air entraining admixture than the class C type ashes. However, the relation may be that class C ashes normally have a lower loss-on-ignition indicating less unburned carbon (table 1). When loss-on-ignition exceeds 1 percent, the AEA dosage exceeds that for the control concrete (fig. 10). Ignition loss of the control cement M-6400 is 0.8 percent. Ash M-6730 had erratic behavior even though its *loss-on-ignition* is not excessive. To the author's knowledge, it is the only ash in this study from a powerplant where the coal is transported to the powerplant by a water slurry pipeline.

Table 6. – Air-entraining admixture dosages for fly ash concretes.

Mix No.	Fly ash sample No.	Fly ash replacement %	AEA[1] dosage factor	Exceeds control yes, no
1	M-6498	15	0.343	No
2	M-6498	25	.525	Yes
3	M-6510	15	.249	No
4	M-6510	25	.120	No
5	M-6514	15	.112	No
6	M-6514	25	.127	No
7	M-6535	15	.122	No
8	M-6535	25	.130	No
9	Control	–	.157	–
10	M-6569	15	.217	Yes
11	M-6569	25	.236	Yes
12	M-6577	15	.179	Yes
13	M-6577	25	.196	Yes
14	M-6535	25	.129	No
15	M-6679	25	.150	No
16	M-6680	25	.128	No
17	M-6681	25	.143	No
18	M-6682	25	.130	No
19	M-6683	25	.129	No
20	M-6734	25	.096	No
21	M-6730	25	.319	Yes
22	M-6730	25	.268	Yes
23	M-6754	25	.242	Yes
24	M-6880	20	.154	No
25	M-6880	15	.127	No
26	M-6880	15	.125	No

Note: AEA is air-entraining admixture.

[1] Dosages cubic centimeters per pound of cementitious material per 1.0 percent air. (Multiply dosages by 2.205 to give cc per kg per 1.0 percent air.)

Another interesting comparison is AEA dosage versus relative mass density. Generally speaking, the higher the density the lower the AEA dosage requirement.

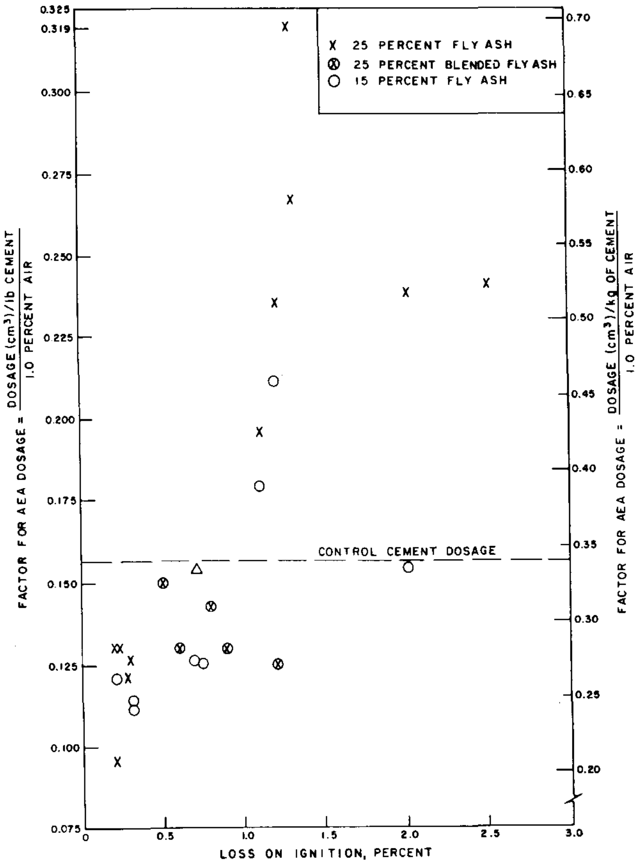


Figure 10. — Loss-on-ignition versus AEA dosage.

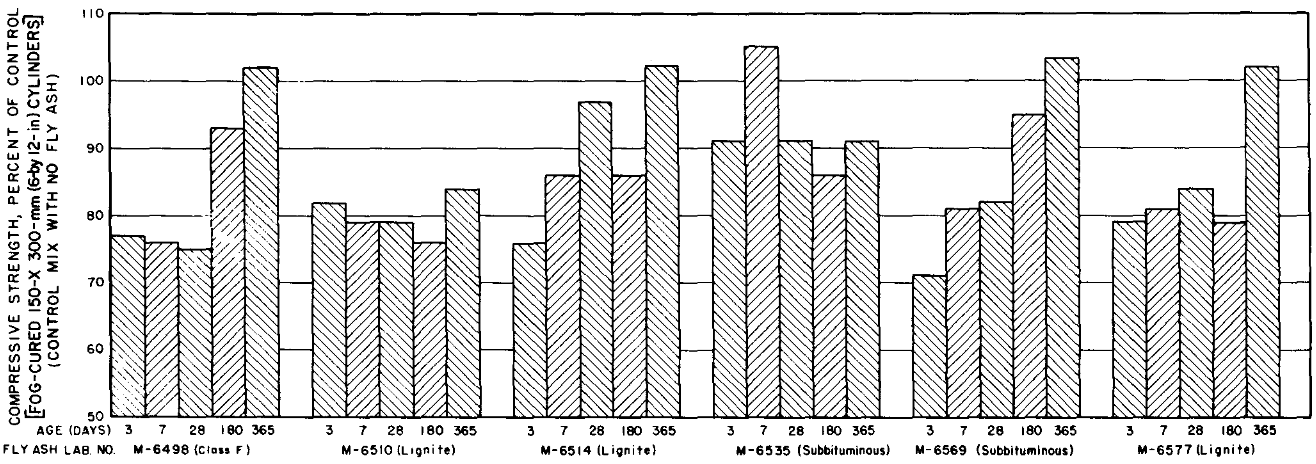
Compressive Strength

Compressive strength results are shown in table 3. Compressive strengths of mixes 1 through 13 are shown on figure 11.

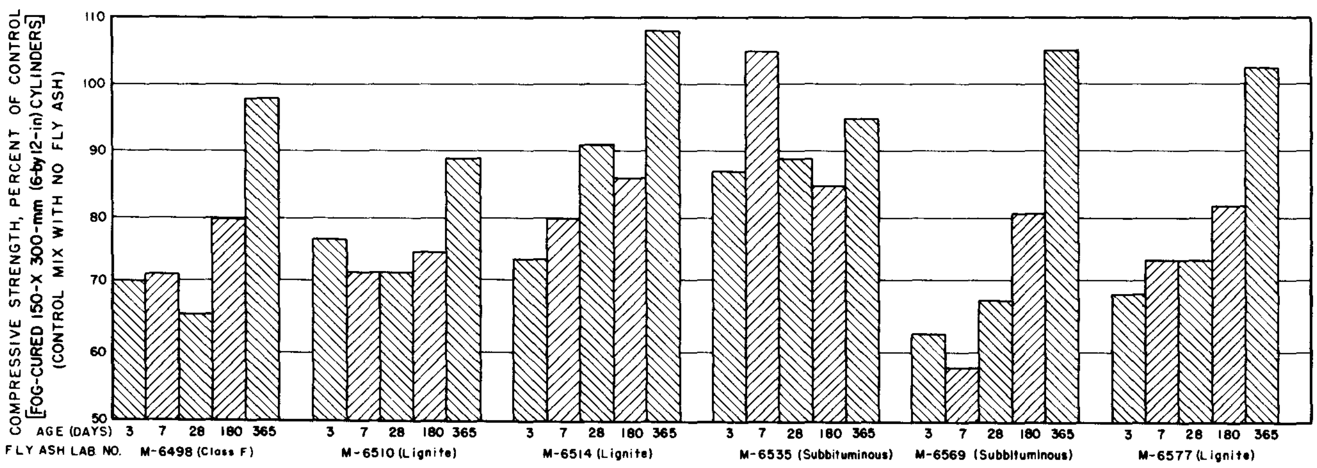
Concrete containing 15-percent fly ash averaged 25.6 MPa (3710 lb/in²) at 28 days and those with 25-percent ash averaged 24.3 MPa (3530 lb/in²), these strengths being 85 and 81 percent, respectively, of the control concrete. When comparing compressive strengths, note that the mixes were made at constant *W* to *C water* to *cement* ratio or *W* to (*C* plus *P*) *water* to *cement* plus pozzolan ratio. Fly ash concretes reduced the water requirement; thus, at constant *W* to *C* or *W* to (*C* plus *P*) ratio, they contained less total cementitious material than did the control concrete (mix 9). Even with this difference in cementitious content, the general strength-gain pattern expected—when using fly ashes—is apparent. The strength gain tends toward low early-age strength, with later development approaching that of the control (fig. 11). This is apparent especially in the 25-percent fly ash concrete that had an overall average compressive strength of 83 percent of the control at 28 days, and 99 percent of the control at 1 year.

Generally, concretes containing high calcium ashes have higher strengths through 28 days than concretes containing low calcium ashes. The reverse is true at later ages. This is seen on figure 12 which shows the compressive strengths of concrete 14 through 19.

To obtain equal strength at a particular early age, fly ash concrete should have a slightly lower *W* to (*C* plus *P*) ratio than the *W* to *C* ratio of straight portland cement concrete. For early-age strengths, the ratio must be lowered more for low calcium ashes than for high calcium ashes. For later ages (greater than 90 days) the reverse is true. Replacing



15 PERCENT FLY ASH REPLACEMENT



25 PERCENT FLY ASH REPLACEMENT

Figure 11. — Comparison of compressive strengths of concrete — with and without fly ash.

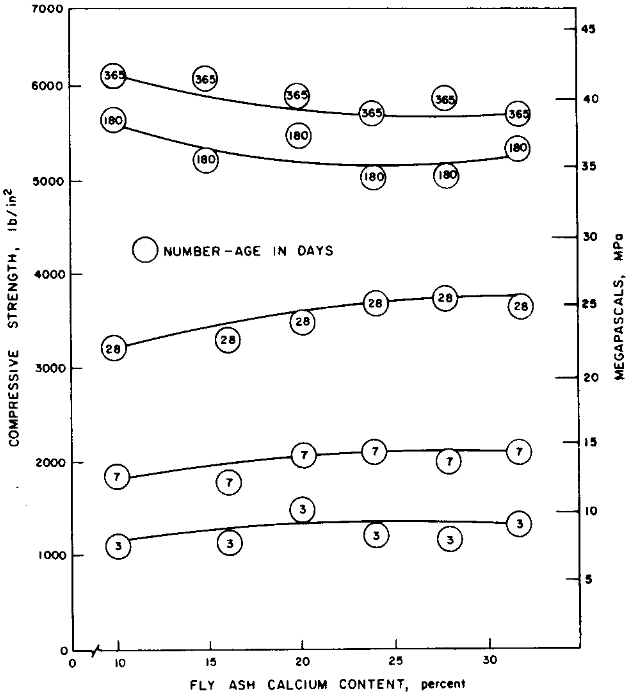


Figure 12. — Fly ash calcium content versus compressive strength of concrete containing 25 percent fly ash.

0.45 kg (1 lb) of cement with more fly ash, 0.50 to 0.59 kg (1.1 to 1.3 lb), effectively reduces the *W* to (*C* plus *P*) ratio [34].

With a type I cement (mixes 27, 28, and 29), 1 to 1 replacement again is demonstrated. Equal quantities of cementitious materials can be used for high calcium ashes. Mix 28 was made with the cementitious material quantity comparable to the control (mix 27) and the strengths are similar from 3 days to 1 year. However, when total cementitious material is less (mix 29), early strengths are reduced but later-age strengths are similar.

New materials were added (mixes 30 to 35) to the program mainly for testing sulfate resistance. Table 3 shows compressive strengths at various ages. The calcined natural pozzolan (mixes 31 and 32) produced strengths comparable to their control (mix 30); however, at an equal *W* to (*C* plus *P*) ratio, calcined pozzolan requires more water and, thus, more total cementitious material. It does give very good strength-gain between 7 and 28 days and has higher strengths at 28 days. The overall cementitious material required for equal strengths could be reduced and better comparisons could be made.

Concrete mix 36 was made to illustrate the erratic set that can take place when various admixtures conflict with each other. When Na_2CO_3 was added at the powerplant to improve collection of ash M-6979, setting problems with some cements and WRA's (water reducing admixtures) were reported by some field offices. The Na_2CO_3 appears to affect only the setting characteristics; the compressive strengths are good. The 1- and 7-day strengths are very high. The 1-day strengths are as high as that normally expected at 3 days. Activation of the glass in high calcium ashes is increased by high alkali content.

The Na_2CO_3 caused erratic setting. A *false set* would occur in various degrees, and the *final set* was delayed up to 48 hours. Use of such materials in powerplants continues to be a problem to fly ash suppliers. It is the author's theory that the *erratic set* was a combination of the complex sodium salts in the WRA, the Na_2CO_3 from the ash, and may occur when acetic acid is used in cement to prevent bulking. Research is needed to find materials to improve collection of ashes in the powerplant which do not impair the properties of this very good resource material. Since this problem has been recognized, Na_2SO_4 has been substituted for Na_2CO_3 and it appears to be a compromise material (ash M-7129).

Elastic Properties

Modulus of elasticity and Poisson's ratio of various concretes are shown in table 3. For most concretes, results are shown at 28, 180, and 365 days. The trends found were as expected. Modulus of elasticity like compressive strength increased with age. Poisson's ratio also increased with age in most concretes. Modulus of elasticity varies from a low at 28 days of 18.8 GPa (2.73 x 10^6 lb/in²) to a high at 365 days of 39.6 GPa (5.74 x 10^6 lb/in²). Poisson's ratio varies from a low of 0.04 at 28 days to 0.29 at 365 days.

Modulus of elasticity and Poisson's ratio (averages) for all concrete

Age, days	Modulus of elasticity, GPa	lb/in² X 10^{-6}	Poisson's ratio
28	21.72	3.15	0.15
180	27.30	3.96	0.18
365	30.06	4.36	0.20

Resistance to Sulfate Attack

This area of study has produced more data than any other area. Two reports, one in ASTM [27] and one in ACI [30], have been published using the data from the first few years of this research program.

The progress report published in 1976 [3] concluded that some high calcium fly ashes drastically reduce sulfate resistance. Since that time, the reason for poor resistance has been theorized [27] and practical use of the theory and data was demonstrated [30]. High calcium ashes contain very reactive alumina present primarily in the glass. Figure 2 indicates that the composition of very high calcium ashes falls in or near the gehlenite field. The ASTM paper [27] discussed the characteristics of gehlenite composition glass and its possible contribution to sulfate attack. The sulfate expansion data for mixes 1 through 13, 20, 22, and 23 were used in the ASTM report. The sulfate resistance was found to relate to the ratio *R* termed resistance factor, and calculated as $(CaO-5)/(Fe_2O_3)$. As the ratio increases, the amount of sulfate reactive alumina increases. Table 7 is a tabulation of some of the data from figures 13 through 21. These data indicate a direct relation between the *R* value and sulfate resistance (expansion).

The numerator of this ratio is used to indicate that as the calcium content increases, the amount of reactive alumina increases. This holds true whether the alumina is combined as $C_{12}A_7H_x$ or C_2AS or combined with calcium in any other way such as C_3A or $C_4A_3\overline{S}$. The higher the amount of sulfate reactive alumina remaining at late ages, the more susceptible a concrete will be to sulfate attack. Susceptibility of high calcium ashes to sulfate attack is probably due to both calcium-alumina combination ($C_{12}A_7H_x$ C_3A, and $C_4A_3\overline{S}$) and calcium-alumina-silica combination (C_2AS).

Table 7 and figures 13 (A and B) through 21 (A and B) indicate differences in the two test methods (wetting and drying versus 10-percent soak). This is probably due to alumina combined as calcium-alumina-silica form [27] and also may be due to the formation of thaumasite ($Ca_3CO_3SiO_3SO4 \cdot 14H_2O$) (discussed under *Hydration of a high calcium ash, $Ca(OH)_2$, and water*). Thaumasite may be a hydration reaction product of high calcium ashes. In the continuous-soaking test this compound probably does not form because CO_2 from the air could not reach the concrete. However, the drying portion of the wetting and drying test is done in air. These specimens possibly could form thaumasite.

Table 7. – Resistance factor *R* versus expansion of concretes in sodium sulfate solutions.

Ash at 25% replacement	Expansion percent at 700 and 1200 days: Wetting and drying test, 700	Wetting and drying test, 1200	10% soak test, 700	10% soak test, 1200	[2]R, $\frac{(CaO-5)}{Fe_2O_3}$
M-6498	0.02	0.04	0.00	0.02	0.17
M-6754	.02	[1] NA	.03	.07	1.05
M-6730	.02	[1] NA	.03	.06	1.67
Control, no ash	.05	.15	.05	.10	. . .
M-6510	.08	.18	.02	.05	2.33
M-6577[3]	.07	.09	.05	.05	2.57
M-6569	.06	.17	.03	.05	2.86
M-6514	.35	[4]1100	.05	.10	3.45
M-6734	[4].50	[4]350	[4].50	[4]500	5.00
M-6535	[4].50	[4]250	[4].50	[4]500	6.67

[1] NA is not available.
[2] R equals $(CaO-5)$ / (Fe_2O_3) percentage from fly ash oxide analysis.
[3] Cyclone furnace ash, possibly different in its glass structure.
[4] Days to failure at 0.5 percent expansion.

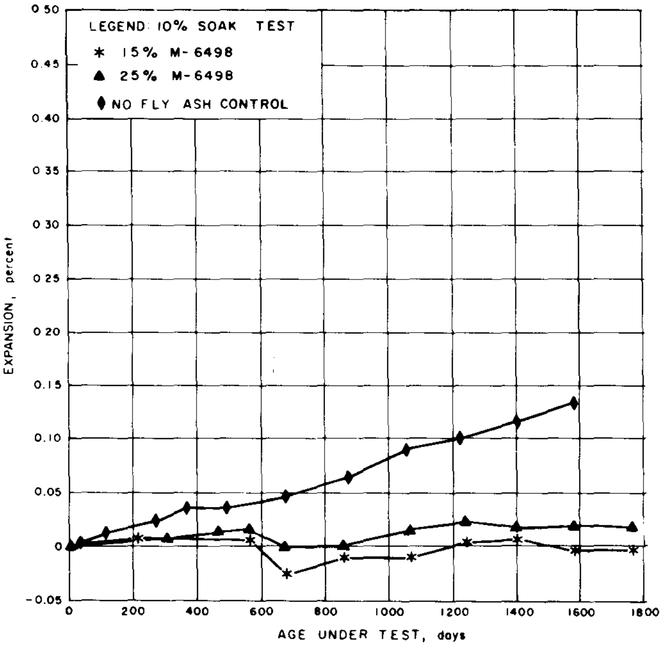


Figure 13a. — Sulfate expansion plot — age versus expansion 75- by 150-mm (3- by 6-in) cylinders, 10-percent soak test, ash M-6498.

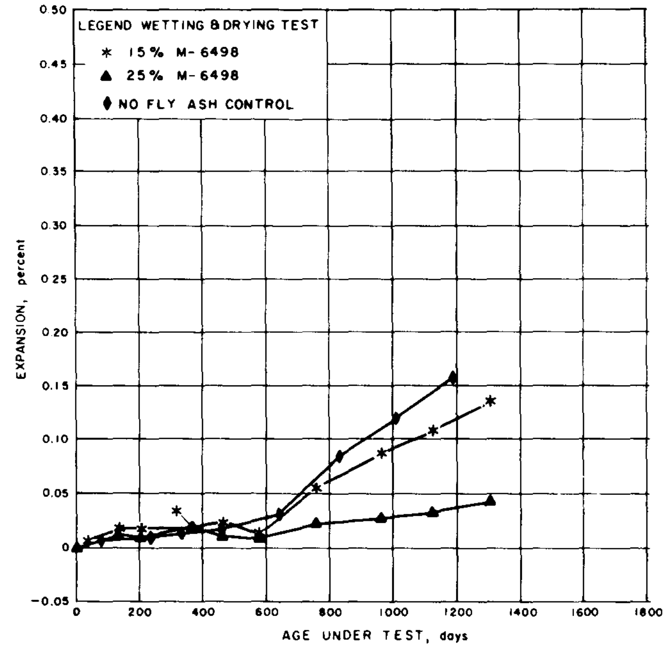


Figure 13b. — Sulfate expansion plot — age versus expansion 75- by 150-mm (3- by 6-in) cylinders, wetting and drying test, ash M-6498.

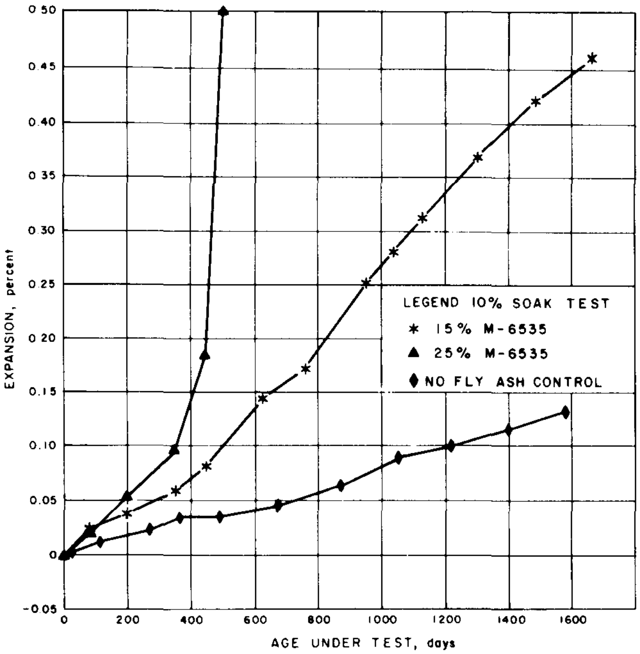


Figure 14a. — Sulfate expansion plot — age versus expansion 75- by 150-mm (3- by 6-in) cylinders, 10-percent soak test, ash M-6535.

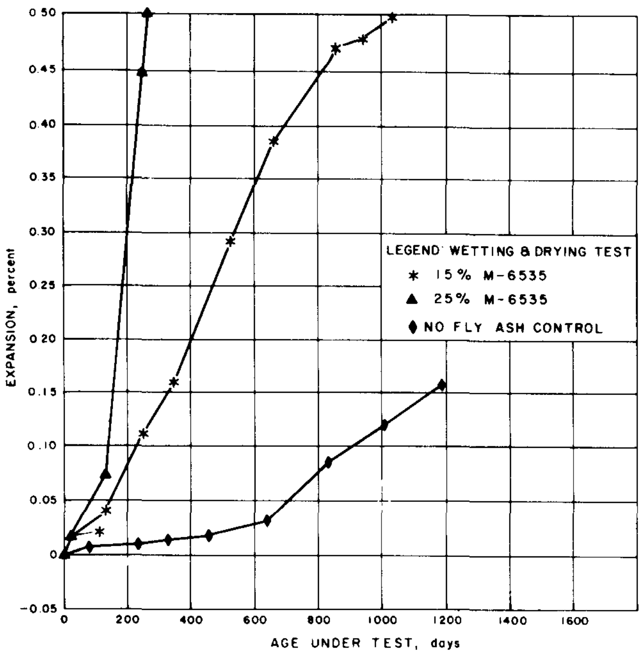


Figure 14b. — Sulfate expansion plot — age versus expansion 75- by 150-mm (3- by 6-in) cylinders, wetting and drying test, ash M-6535.

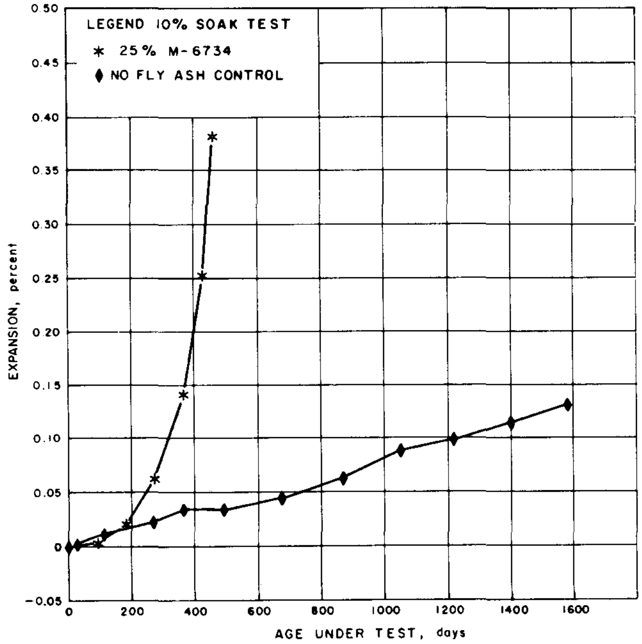


Figure 15a. — Sulfate expansion plot — age versus expansion 75- by 150-mm (3- by 6-in) cylinders, 10-percent soak test, ash M-6734.

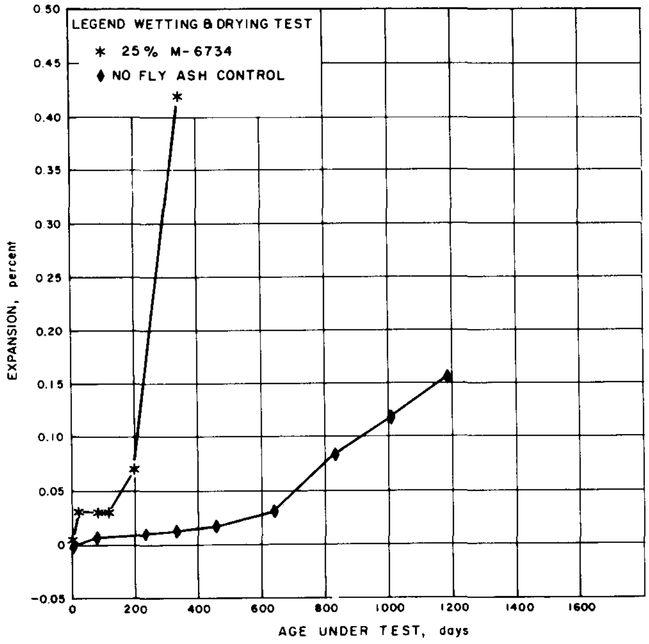


Figure 15b. — Sulfate expansion plot — age versus expansion 75- by 150-mm (3- by 6-in) cylinders, wetting and drying test, ash M-6734.

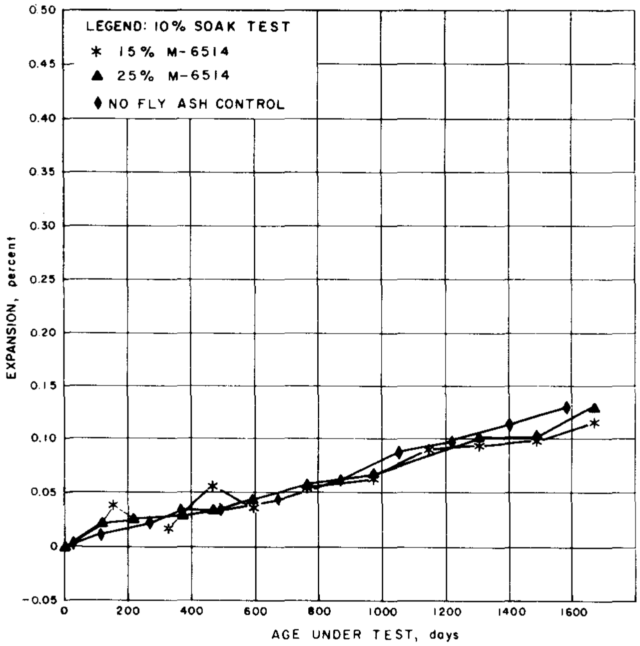


Figure 16a. — Sulfate expansion plot — age versus expansion 75- by 150-mm (3- by 6-in) cylinders, 10-percent soak test, ash M-6514.

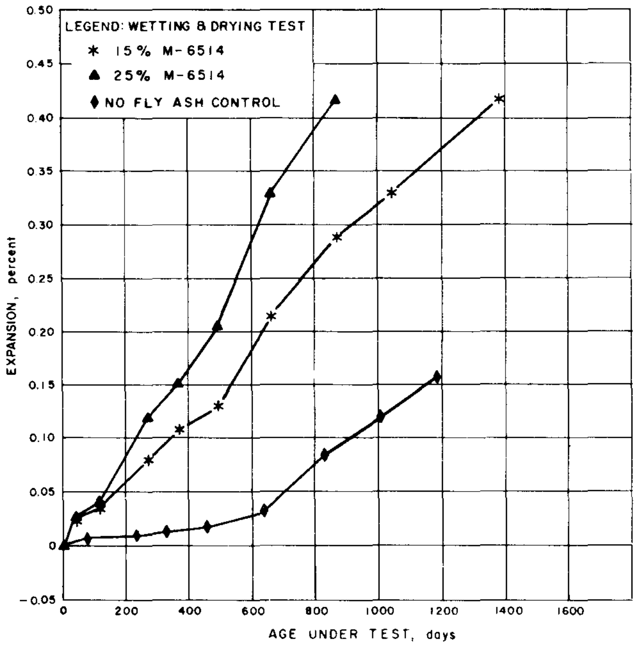


Figure 16b. — Sulfate expansion plot — age versus expansion 75- by 150-mm (3- by 6-in) cylinders, wetting and drying test, ash M-6514.

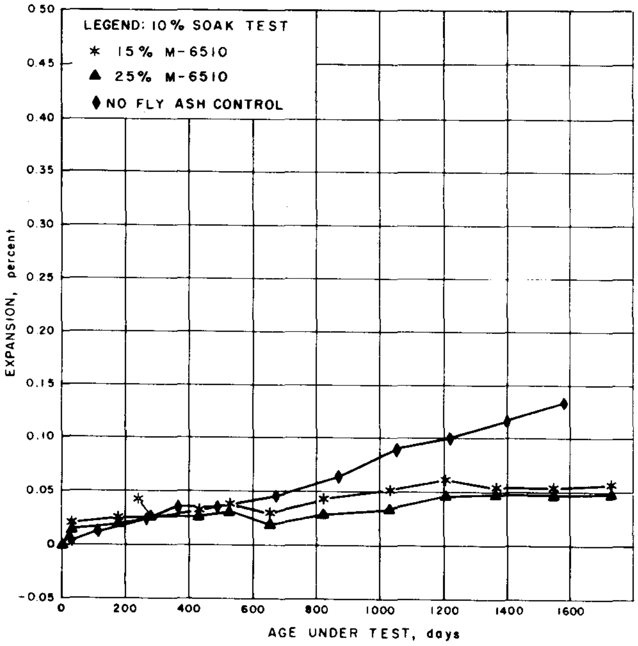


Figure 17a. — Sulfate expansion plot — age versus expansion 75- by 150-mm (3- by 6-in) cylinders, 10-percent soak test, ash M-6510.

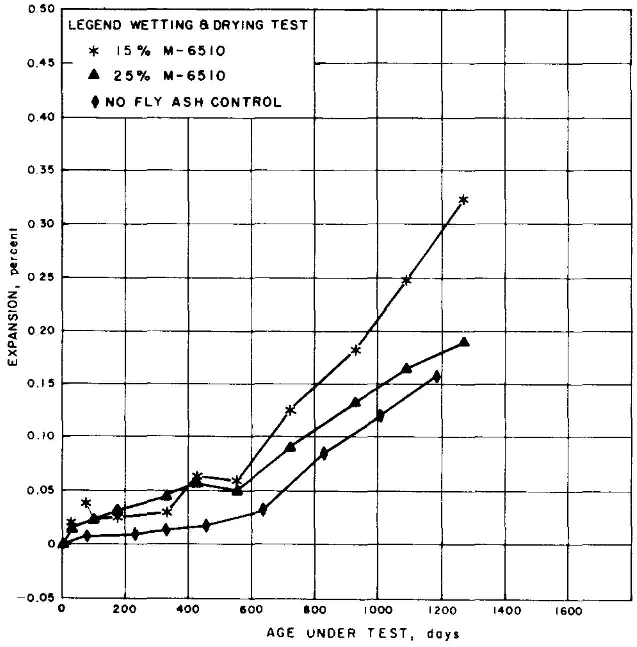


Figure 17b. — Sulfate expansion plot — age versus expansion 75- by 150-mm (3- by 6-in) cylinders, wetting and drying test, ash M-6510.

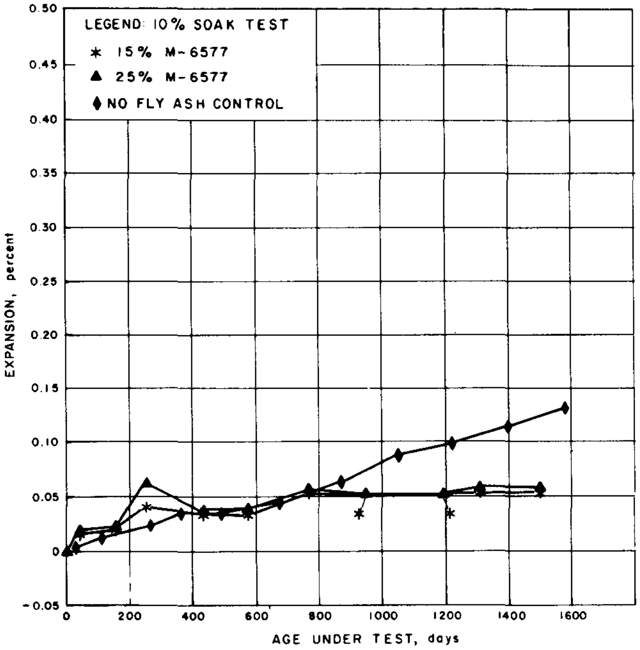


Figure 18a. — Sulfate expansion plot — age versus expansion 75- by 150-mm (3- by 6-in) cylinders, 10-percent soak test, ash M-6577.

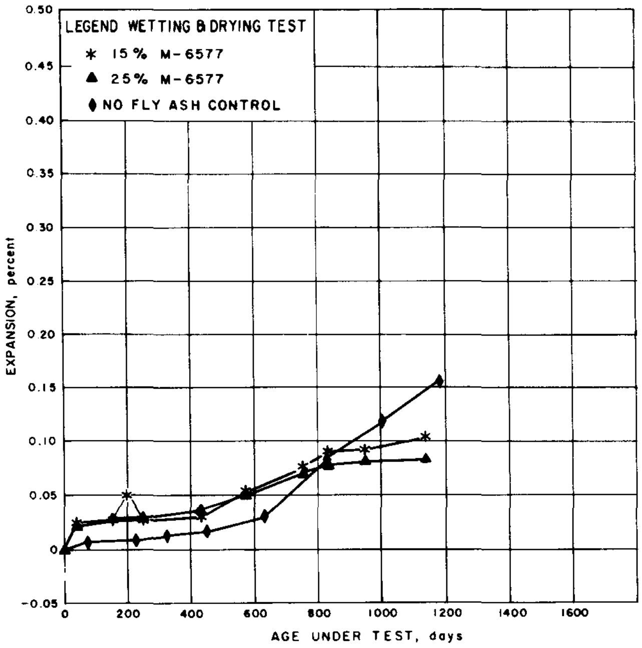


Figure 18b. — Sulfate expansion plot — age versus expansion 75- by 150-mm (3- by 6-in) cylinders, wetting and drying test, ash M-6577.

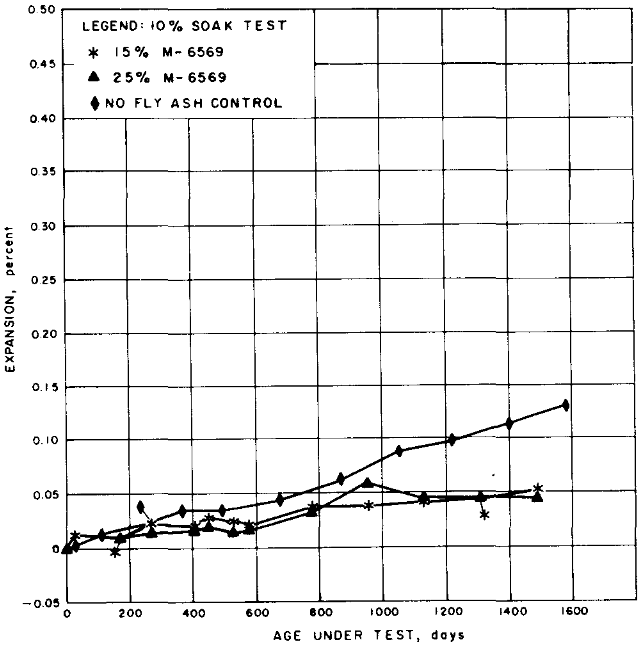


Figure 19a. — Sulfate expansion plot — age versus expansion 75- by 150-mm (3- by 6-in) cylinders, 10-percent soak test, ash M-6569.

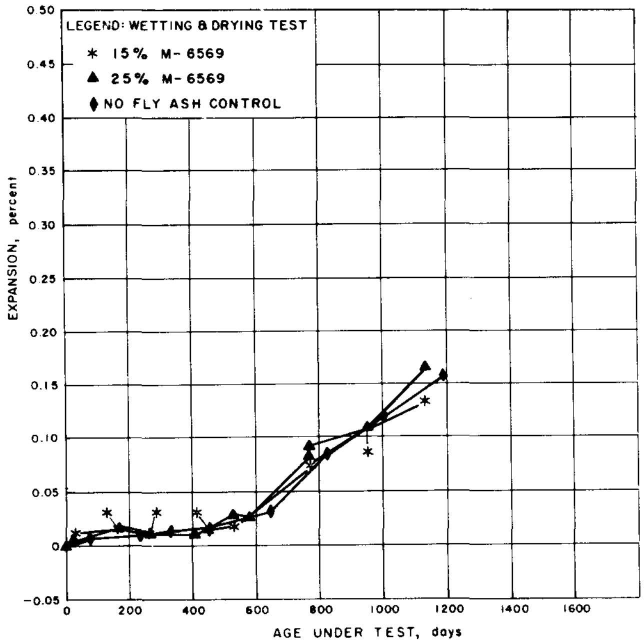


Figure 19b. — Sulfate expansion plot — age versus expansion 75- by 150-mm (3- by 6-in) cylinders, wetting and drying test, ash M-6569.

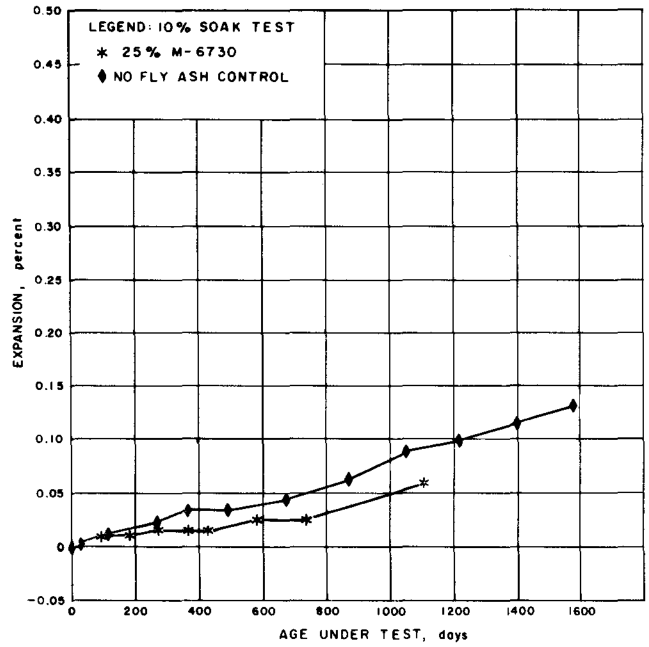


Figure 20a. — Sulfate expansion plot — age versus expansion 75- by 150-mm (3- by 6-in) cylinders, 10-percent soak test, ash M-6730.

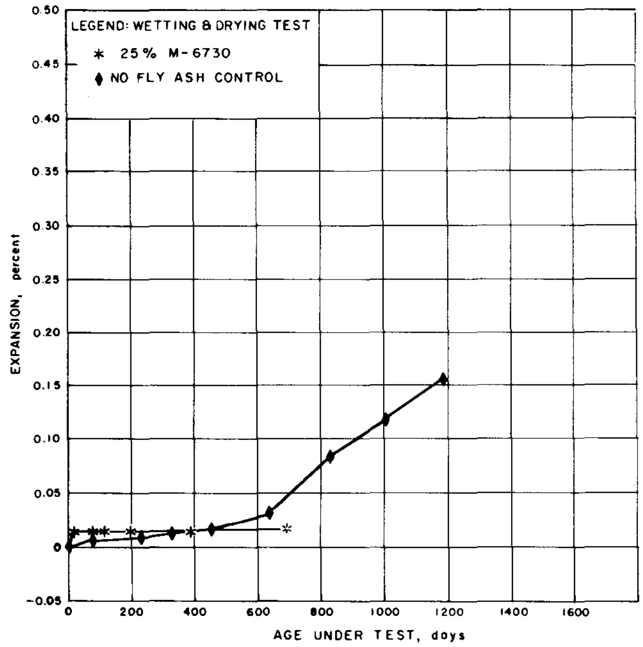


Figure 20b. — Sulfate expansion plot — age versus expansion 75- by 150-mm (3- by 6-in) cylinders, wetting and drying test, ash M-6730.

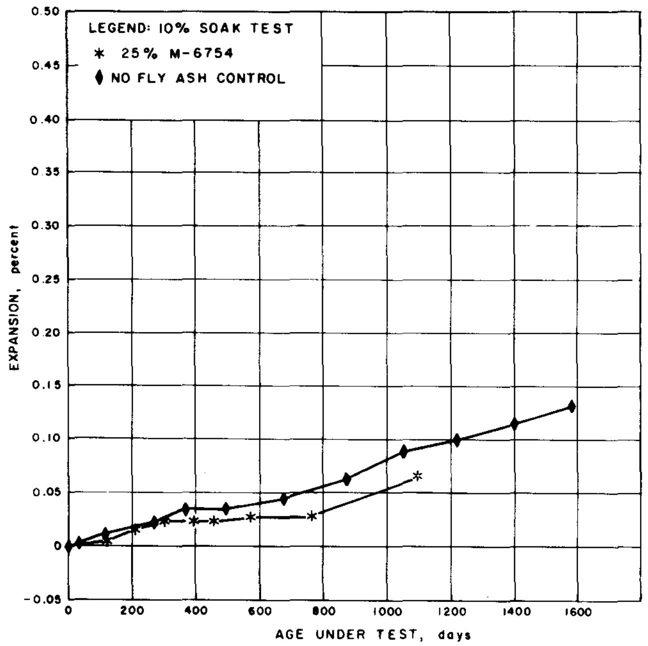


Figure 21a. — Sulfate expansion plot — age versus expansion 75- by 150-mm (3- by 6-in) cylinders, 10-percent soak test, ash M-6754.

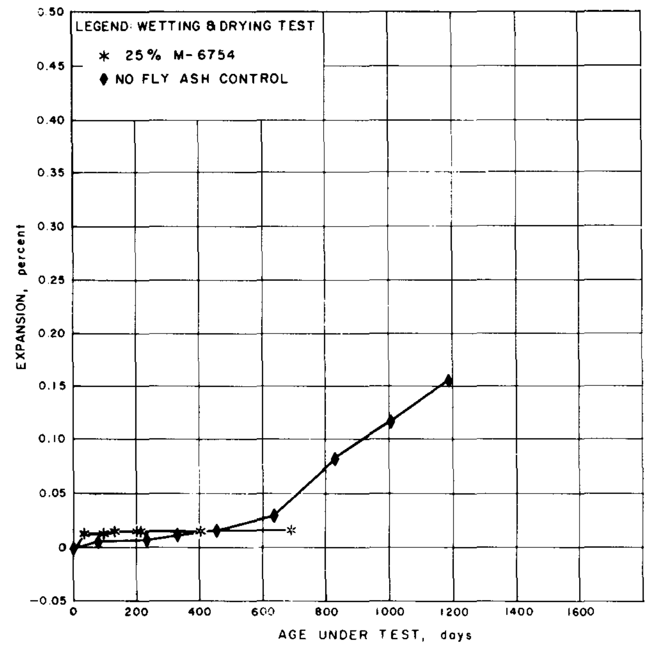


Figure 21b. — Sulfate expansion plot — age versus expansion 75- by 150-mm (3- by 6-in) cylinders, wetting and drying test, ash M-6754.

The reader may wonder why the numerator in the ratio is CaO–5 instead of only CaO. Some of the calcium is not combined with alumina—for example, CaO and $CaSO_4$. If the amount not combined with alumina could be readily determined, it could be used instead of 5 which is assumed to be a representative percentage value for most ashes.

The relation of the resistance factor *R* and sulfate resistance is demonstrated dramatically on figures 22 and 23. Blends M-6979 through M-6983 and concrete mixes 15 through 19 are compared to a rerun of concrete containing ash M-6535 (mix 14) and the control mix (mix 9). Large sulfate attack expansions for high *R* value ashes are dramatically shown. Expansions in both tests are lower for lower *R* values.

These data could be very beneficial when both a high calcium and a low calcium ash are available. By blending the ashes, so that the *R* value is lowered to around 2.0, the ash would neither increase nor decrease sulfate resistance. Theoretically, $CaSO_4$ could be blended with a high calcium ash to achieve the same effect. This needs to be verified by experimentation. Blending may improve the sulfate resistance of a high calcium ash and also improve its strength-gaining properties.

In addition to measuring expansion caused by sulfates on mixes 14 through 19, compressive strengths were measured through 3 years' age. Cylinders, 75 by 150 mm (3 by 6 in), were fog-cured 28 days, then half were placed in a 10-percent solution of Na_2SO_4 and half were placed in tap water—both at room temperature. The results are shown in table 8. The trend (except for mix 14) is that at early ages specimens immersed in sulfate solutions have increased strength over the water-cured specimens. With time, internal expansion disrupts the integrity of the concrete and the strength is reduced. Comparing the strength results of mix 16 with the expansion results shown on figure 22 indicates that when expansion reaches 0.15 percent the strength is reduced to 93 percent of the control; however, only 0.05 percent expansion causes equal reduction in strength for mixes 18 and 19. It appears that, on an average, an unconfined expansion of 0.05 percent will cause reduced strength. However, the reduction is not significant (less than 10 percent) until expansion exceeds 0.15 percent.

High calcium ashes such as M-6535 reduce the sulfate resistance of type II cement concrete. This was found for mixes 7, 8, and 14, and again for mixes 24, 25, and 26. Data for mixes 24, 25, and 26 are not reported here; they are, however, shown in the ACI report [30]. The lower water to cement ratio of mixes 24, 25, and 26 and the slightly lower *R* value of ash M-6880 (compared to M-6535) extends the age to failure slightly over that found for mixes 8 and 14. Even though ash M-6880 reduces the resistance

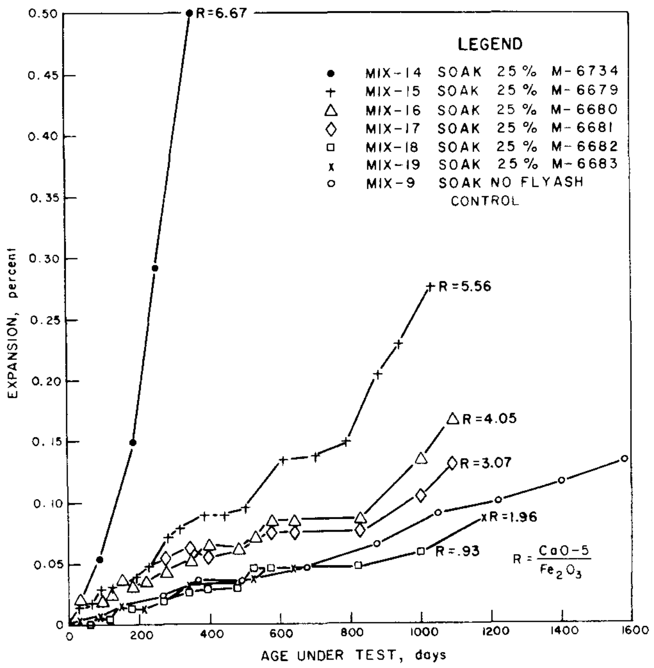


Figure 22. — Sulfate expansion plot — age versus expansion (ashes with various *R* -values), 10-percent soak test.

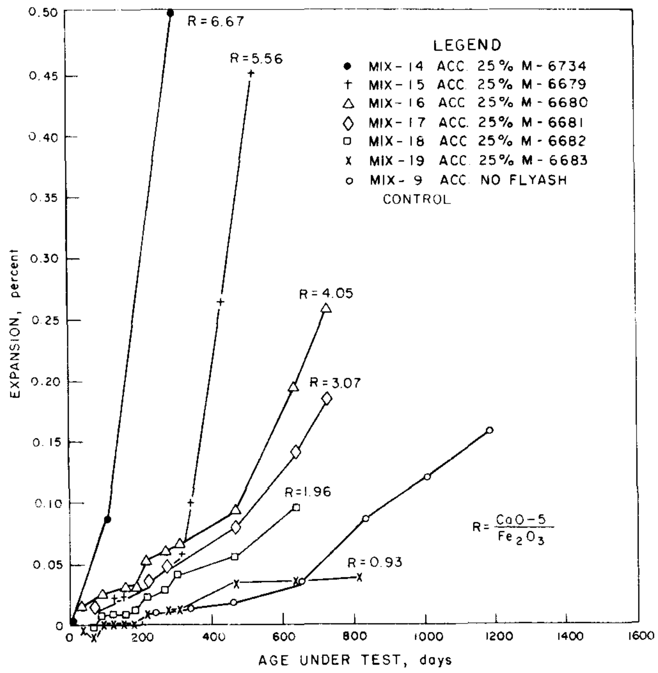


Figure 23. — Sulfate expansion plot — age versus expansion (ashes with various *R* -values), wetting and drying test.

Table 8. — Strength of concretes in sulfate solutions as percent of water-cured specimens.

Mix No.	Age 90 days	180 days	1 year	1-1/2 years	3 years
14	100	72	70	30	15
15	90	100	91	90	86
16	101	103	105	102	93
17	102	102	102	104	91
18	99	108	104	109	86
19	100	98	99	91	94

Table 9. — Proposed limits of resistance factor R for concretes containing fly ash at 25 percent mass replacement.

R limits[1]	Sulfate resistance[3]
<0.75	Greatly improved
0.75 to 1.5	Moderately improved
1.5 to 3.0	No significant change[2]
>3.0	Reduced

[1] R equals (CaO−5) / (Fe_2O_3) percentage from fly ash oxide analysis; for very severe cyclic conditions of wetting and drying or for $MgSO_4$, reduce the R value by 0.50.

[2] Ranges from slightly improved to slightly reduced.

[3] Compared to a type II cement control at 0.45 water to cement ratio.

of a type II cement concrete, this is not necessarily true with type I cement concrete.

Mixes 30 and 35 were used to verify that sulfate resistance can be predicted. The R value for fly ash M-6976 is 0.23. Ashes having R values below 1.5 should improve the sulfate resistance of concrete when used at 25-percent replacement [27] (table 9). A different type II cement, M-6800, and an ash, M-6976, of unknown sulfate resistance were used. Its R value indicated that it should improve resistance and, as expected, improvement was found for both tests (figs. 24 and 25).

Fly ashes are formed at very high temperatures in the powerplant. Pozzolan M-6907 is a calcined material that was heated in a rotary kiln similar to one in a portland cement plant. Thermal history of this material may make it comparable to fly ash with regard to sulfate resistance. The R value for M-6907 is:

$$\frac{CaO-5}{Fe_2O_3} = \frac{2.0-5.0}{4.3} = -0.70$$

Theoretically, the amount of sulfate reactive alumina is a minimum of zero rather than negative. Probably, for this material, the R value is zero. This pozzolan has improved resistance over the control similar to ash M-6976 (figs. 24 and 25). Figures 24 and 25 also show the expansion data for a modified type II cement M-6909. This cement has a low C_3A content of 3.79 percent but too high a C_4AF content (15.35 percent) to meet requirements for a type V cement. Generally, ashes and pozzolans that improve sulfate resistance of a type II cement as shown on figures 24 and 25 have equal or better resistance than a type V cement [1, 36].

Also shown (figs. 24 and 25) is the expansion of a blended cement M-6918, containing 18-percent interground fly ash. The clinker used had 5.44 percent C_3A. The fly ash is from the same source as M-6754.

The possible number of combinations of cements and fly ashes and other pozzolans is astronomical. A practical approach to the problem of predicting sulfate resistance of any combination is described in ACI report [30].

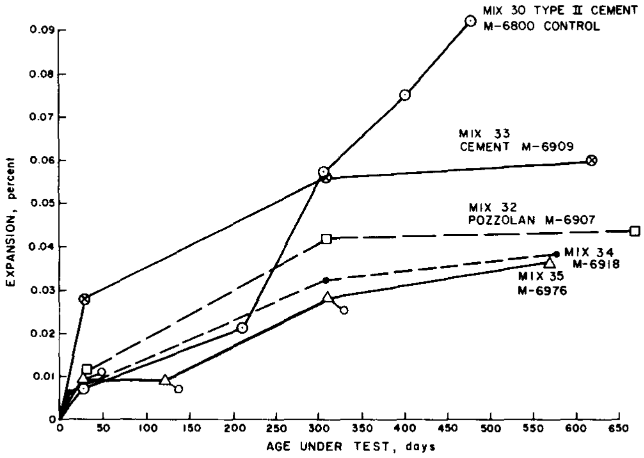


Figure 24. — Sulfate expansion plot soak test — age versus expansion — additional cements and pozzolans.

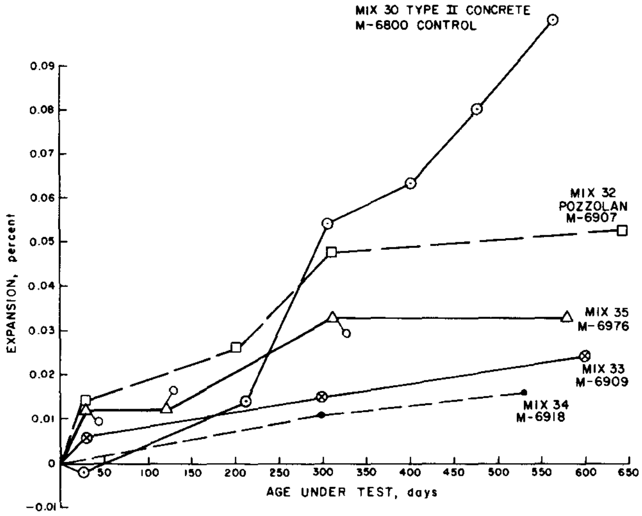


Figure 25. — Sulfate expansion accelerated test — age versus expansion — cements and pozzolans.

Freeze-Thaw Durability

The results of freeze-thaw durability tests reported in figure 26 show the number of cycles to failure for concretes cured for 28 days in fog, and 14 days in fog plus 76 days at 50 percent relative humidity. The failure criterion for concrete is when the specimens lose 25 percent of their original mass.

All concretes, except for the 28-day, fog-cured concretes made with ash M-6569, have excellent freeze-thaw durability. The cycles to failure appear to be much higher for ashes beginning with sample No. M-6734 in figure 26 and with those tests to the right of it. This probably corresponds to a change in AEA. The AEA has more effect than fly ash on durability of concrete. Even fly ash M-6730, the most difficult in which to entrain air (mixes 21 and 22) and which had a low air content, 3.1 percent (mix 22), still shows excellent durability with the laboratory-prepared vinsol resin. The lowest air content found for the proprietary vinsol resin was for mixes 10 and 11 which contained ash M-6569. These concretes, for 28-day, fog-cured specimens, show the lowest durability of all concretes.

For a comprehensive interpretation of present data, information on the size and spacing of the entrained air bubbles would be required. Such tests were not conducted. However, the air-void system is an inherent characteristic of the concrete mixture, influenced by physical and chemical properties and by the proportion and efficiency of the AEA [37]. It appears likely that a better air-void system was obtained at low air contents for the laboratory-prepared admixture—mixes 20 and higher—than for the proprietary admixture—mixes 1 through 13.

Properly mixed and placed fly ash concretes with AEA will have excellent freeze-thaw durability. An ordinary neutralized vinsol resin AEA can provide proper air-entrainment. The dosage of AEA was shown earlier to be roughly related to loss on ignition of the ash (fig. 10). Concretes containing ashes having ignition losses higher than 1 percent require more admixture than concretes without ash.

Drying Shrinkage

Drying shrinkage test results are shown on figure 27. Ashes M-6498, M-6510, M-6514, M-6535, M-6569, and M-6577 have the same control cement M-6400. All of these ashes except M-6535 have less shrinkage than the control concrete without fly ash. Drying shrinkage is at least partially a function of water content in concrete; it would be expected that reduced water requirement when fly ash is used would result in decreased drying shrinkage. This also is evident in that concretes containing 25-percent ash contain less water than concretes containing 15-percent fly ash and, thus, have less drying shrinkage.

Ash M-6535, which does not exhibit reduced shrinkage, was shown in the hydration studies to have a high portion of reactive alumina glass. The alumina content may be related to the shrinkage in that cements with higher amounts of reactive alumina in the form of C_3A have higher optimum SO_3 contents to lower shrinkage [38]. Highly reactive alumina fly ashes also may need higher SO_3 contents to reduce shrinkage. Allowances for higher SO_3 contents with certain highly reactive alumina glass fly ashes should be added to *ASTM: C 618*.

Calcined pozzolan M-6907 and ash M-6976 have the same control cement M-6800. Natural pozzolan increases the water requirement and increases shrinkage; the ash reduces water and decreases shrinkage.

Drying shrinkage results for cement M-6800, M-6909, and M-6918 are similar. These cements have similar water requirements, and the C_3A content also is similar. (The C_3A content has some effect on shrinkage [39].) It is surprising that cement M-6918 does not have a lower shrinkage because of its fly ash constituent. Grinding of fly ash may break down the glassy spheres and negate some of the workability imparted by such spheres.

Additional tests were made on the drying shrinkage bars after completion of 365-days drying. The bars were tested to determine; dynamic modulus of elasticity, flexural strength, and compressive strength of modified 100- by 100-mm (4- by 4-in) cubes. Results of the tests are shown in table 10.

Adiabatic Temperature Rise

Excessive temperature rise in mass concrete can cause cracking. Fly ash has been used to reduce the rate of heat generation. The rate of heat development parallels the rate of strength development. Class F ashes which are not self-hardening can be of great benefit in lowering the rate of heat generation [40]; however, as noted, a few high calcium ashes react very rapidly and generate much heat. To investigate the heat generation of high calcium ash, three concretes were made. These were placed in an insulated container inside a room at a temperature the same as that of the fresh concrete. The temperature of the concrete is monitored and the room temperature is automatically and continually maintained at the temperature of the concrete. In this way heat is not lost from, nor added to the concrete; i.e., the concrete is cured adiabatically. Temperature rise for the three concretes (mixes 8,

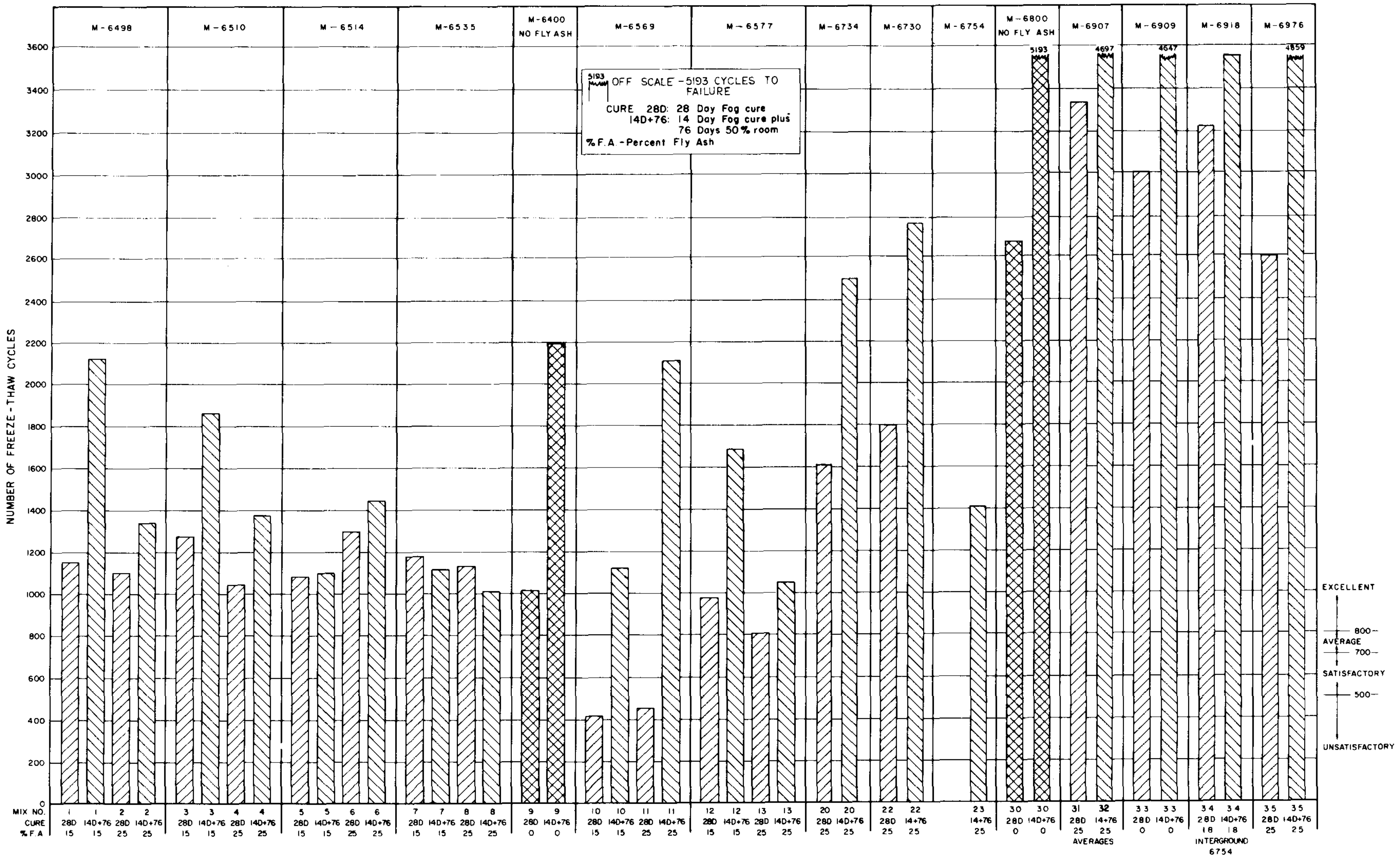


Figure 26. — Cycles of freezing and thawing to failure.

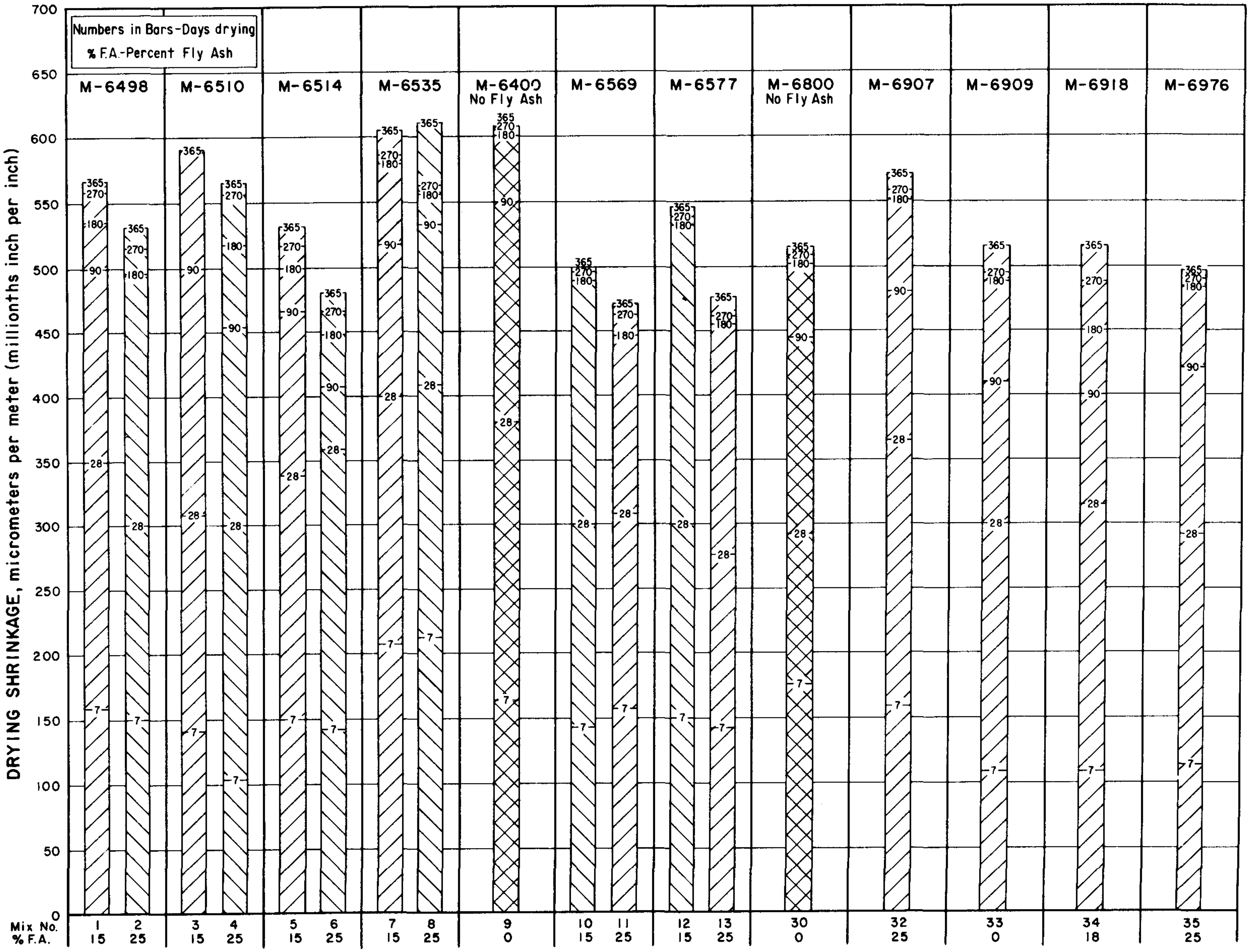


Figure 27. — Drying shrinkage of 100- by 100- by 760-mm (4- by 4- by 30-in) concrete prisms.

9, and 11) is shown on figure 28. Temperature rise is plotted against age for each 45.4 kg (100 lb) of cementitious material (cement or cement plus fly ash). The high calcium ash M-6535 generates nearly as much heat as the control without fly ash. Ash M-6569—a low calcium ash—shows reduced heat generation.

In mass concrete placements where heat may be a problem, a low calcium ash or an ash of low heat generation should be used. Ashes having a low *R* value, as discussed for sulfate resistance, will have lower heat generation. The early heat of portland cement is, in part, a function of the amount of C_3A. Similarly, lower *R* value ashes have lower amounts

Table 10. — Tests on 100- by 100- by 760-mm (4- by 4- by 30-in) drying shrinkage prisms after 1 year's drying.

Mix No.	Fly ash No.	Fly ash %	Flexure modulus GPa	Flexure modulus $lb/in^2 \times 10^{-6}$	Dynamic modulus of elasticity GPa	Dynamic modulus of elasticity $lb/in^2 \times 10^{-6}$	Modulus of rupture MPa	Modulus of rupture lb/in^2	Modified cube compressive strength MPa	Modified cube compressive strength lb/in^2
1	M-6498	15	2.18	3.16	2.56	3.72	2.77	402	26.8	3890
2	M-6498	25	2.25	3.26	2.55	3.70	3.12	452	22.6	3280
3	M-6510	15	2.25	3.27	2.70	3.92	3.07	445	23.6	3430
4	M-6510	25	2.40	3.48	2.85	4.14	3.21	465	26.9	3900
5	M-6514	15	2.40	3.48	2.79	4.05	3.23	468	27.1	3930
6	M-6514	25	2.70	3.91	2.88	4.17	3.12	453	28.5	4130
7	M-6535	15	2.45	3.55	2.87	4.16	3.11	451	27.0	3910
8	M-6535	25	2.44	3.54	2.87	4.16	3.61	524	28.7	4160
9	— —	0	2.43	3.53	2.94	4.27	3.56	517	33.4	4850
10	M-6569	15	2.53	3.67	2.93	4.25	3.63	526	34.5	5000
11	M-6569	25	2.74	3.98	2.77	4.02	3.03	440	23.9	3460
12	M-6577	15	2.62	3.80	2.83	4.11	3.42	496	31.4	4550
13	M-6577	25	2.70	3.91	2.92	4.23	3.34	485	33.6	4870

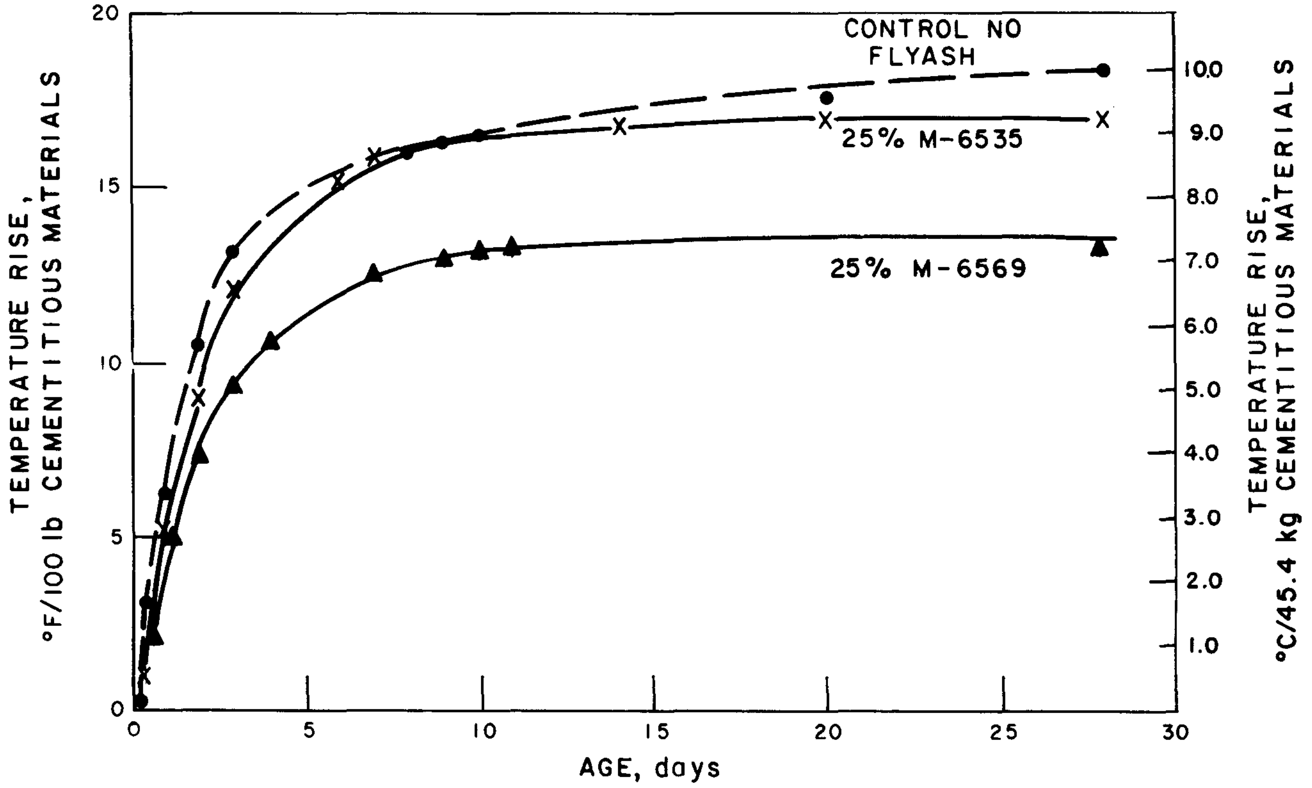


Figure 28. — Adiabatic temperature rise.

of very reactive heat generating alumina compounds.

Mix design also must be considered when making temperature rise comparisons. Different strength levels can be achieved by different mix proportions, dependent upon the cementitious materials; i.e., cement and class F or C fly ash. Therefore, comparisons on a pound-for-pound basis, as shown on figure 28, may be misleading.

NONPORTLAND CEMENT CONCRETES

Combinations of high calcium ashes, such as M-6535, and water set rapidly and gain strength. With this reaction, obvious questions are: "How much strength do they gain?" and "Can they be used to make concrete without portland cement?"

100-Percent Fly Ash Cement Concrete — Strength

Concrete mixes were made to answer those questions (table 11). The first series of mixes, FA-1 through FA-5, with 37.5-mm (1-1/2-in) maximum-size aggregate were mixed and handled similarly to concretes discussed earlier (portland cement—fly ash combination). In a previous mix (mix 20), ash M-6734 was used as a 25-percent replacement of portland cement. That mix contained 203 kg (447 lb) of cementitious material. Mixes FA-1 through FA-3 have a similar cementitious mass except the cementitious material is all fly ash.

Laboratory mortar mixes confirmed that large dosages of a WRA (Daratard™ 17) could be used to retard the very rapid setting of these ashes and, therefore, were used. When an ash contains Na_2CO_3 (M-7094) as an aid for collection, the amount of retarder must be increased (mix FA-3). This series of mixes gained very little strength. The total fly ash content was greatly increased for mixes, FA-4 and FA-5. With these mixes, strengths of 20.7 MPa (3000 lb/in^2) were obtained at 1 year. This type of concrete could be used for backfill concrete, or for subbase work for roads, etc. The concrete can be air-entrained. No special effort was made to control the air content or slump. However, the WRA dosages with 100-percent fly ash were unpredictable. The retarder (sodium citrate) used in later studies would probably afford much better control.

The setting time in the laboratory could be controlled so that the concrete set was much like that of portland cement concrete.

Sulfate-Ash Cement Concretes — Strength

An early attempt to control set was to add gypsum. Results were negative; it was discovered, however, that strength was greatly increased. Further tests indicated that anhydrous $CaSO_4$ produced the best strength (table 1).

Retarders for 100-percent ash mixes also worked well with $CaSO_4$ and ash combinations. Here too the amount of retarder required had to be increased if the ash collection system is modified by adding Na_2CO_3 or Na_2SO_4. Interestingly, these two materials act as accelerators for calcium alumina cements [41]. They probably react the same on calcium-alumina glass of high calcium ashes. Greater quantities of the retarder are needed to combat the effect of these accelerators.

Recent work by this investigator has shown that sodium citrate will not effectively retard ashes having Na_2SO_4 as a collection agent. A retarder that seems to work with most ashes and collection agents is borax.

Mixes DHC-1 through DHC-7 contain combinations of high calcium ash and various forms of $CaSO_4$. The strengths obtained cannot be compared directly because these concretes have a 19.0-mm (3/4-in) maximum-size aggregate instead of 37.5-mm (1-1/2-in). The compressive strength specimens were 75- by 150-mm (3- by 6-in) cylinders rather than 150- by 300-mm (6- by 12-in). Mixing was made in a pan mixer because limited quantities of materials mandated smaller mixes. However, multiplying the strength of the DHC series concretes by 0.95 should give an expected strength for a 150- by 300-mm cylinder [42]. The best strength obtained for DHC-7 at 28 days was 35.3 MPa (5120 lb/in^2). The equivalent strength would be 0.95 times 35.3 MPa or 33.5 MPa for a 150- by 300-mm cylinder [0.95 (5120 lb/in^2) = 4860 lb/in^2]. The highest 28-day strength obtained without $CaSO_4$ was 12.0 MPa (1750 lb/in^2). With $CaSO_4$ a comparison strength of 33.5 MPa (4860 lb/in^2) was obtained. This is almost a threefold increase.

A 28-day compressive strength of 33.5 MPa (4860 lb/in^2) is higher than that of any of the portland cement, or portland cement and fly ash combinations discussed earlier (table 3). An unusual characteristic of these concretes is that curing at a lower humidity (50 percent) gives equal or higher 28-day strengths than curing in 100-percent relative humidity.

An interesting result (DHC-6) indicates that a final strength upon drying may be the same regardless of

Table 11. – Nonportland cement concretes: mix quantities, compressive strength, and elastic properties.

							Mix quantities												Properties of fresh concrete							
	Mix		Fly	WRA[1]	Fly	Sand	AEA	Water		Fly ash		Admixture			Sand		Coarse agg.		Temp.		Slump		Unit weight		Air content	
Date	Designation	W/C ratio	ash No.		ash %	%	cm^3	kg/m^3	lb/yd^3	kg/m^3	lb/yd^3	kg/m^3	lb/yd^3	[2]No.	kg	lb	kg	lb	°C	°F	mm	in	kg/m^3	lb/ft^3	Grav. %	Meter %
1979																										
Apr. 3	FA-1	0.37	M-6734	977 cm^3	100	33	1630	97	164	263	443				589	993	1192	2009	17.2	63	200	8.0	2142	133.7	12.5	10.0
Apr. 3	FA-2	.38	M-6734	508 cm^3	100	33	1691	101	170	266	448				618	1042	1251	2108	17.2	63	110	4.5	2236	139.6	8.7	6.0
Apr. 4	FA-3	.38	M-7094	1975 cm^3	100	33	146	100	168	260	439				634	1069	1283	2163	17.2	63	230	9.0	2279	142.2	7.1	6.0
Apr. 13	FA-4	.26	M-7094	3640 cm^3	100	33	162	125	210	480	809				587	990	1188	2002	18.3	65	230	9.0	2379	148.5	1.7	2.0
Apr. 13	FA-5	.22	M-7094	3590 cm^3	100	33	160	103	173	473	798				579	976	1172	1975	18.3	65	230	9.0	2327	145.3	5.1	3.9
July 24	DHC-1	.31	M-7143	1642 cm^3	91.5	45	794	106.1	234	309.8	683	29.0	64	1	819.2	1806	699.9	1543	21.1	70	170	6.8	2260	141.1	6.3	NA
Aug. 7	DHC-2	.31	M-7143	1694 cm^3	91.5	45	819	98.0	216	319.3	704	29.9	66	2	601.9	1327	721.7	1591	23.3	74	90	3.5	2316	144.6	4.9	NA
Aug. 7	DHC-3	.29	M-7143	2515 cm^3	91.5	45	804	99.3	219	313.9	692	29.0	64	2	591.0	1303	709.0	1563	23.3	74	170	6.5	2278	142.2	6.3	NA
Aug. 21	DHC-4	.31	M-7143 80% M–7129 20%	408 g	91.5	45	825	107.5	237	321.6	709	29.0	66	2	606.0	1336	726.7	1602	22.2	72	100	4.1	2344	146.3	3.1	NA
Aug. 21	DHC-5	.31	M-7129	680 g	91.5	45	824	107.5	237	321.1	708	29.9	66	2	605.5	1335	726.2	1601	22.2	72	70	2.8	2342	146.2	3.2	NA
Aug. 23	DHC-6	.31	M-7129	680 g	91.5	45	1069	108.9	240	317.5	700	29.5	65	2	598.3	1319	717.6	1582	17.8	64	100	4.1	2318	144.7	3.9	NA
Aug. 23	DHC-7	.31	M-7129	680 g	91.5	45	1069	109.8	242	319.8	705	29.9	66	3	602.3	1328	722.5	1593	17.8	64	110	4.4	2334	145.7	3.3	NA

		Compressive strength [150- by 300-mm (6- by 12-in) cylinders]										Elastic properties					
		3-day		7-day		28-day		180-day		365-day		28 days		180 days		365 days	
Date	Mix Designation	MPa	lb/in^2	MPa	lb/in^2	MPa	lb/in^2	MPa	lb/in^2	MPa	lb/in^2	$E \times 10^{-6}$	R	$E \times 10^{-6}$	R	$E \times 10^{-6}$	R
Apr. 3	FA-1	1.6	240	2.3	340	2.6	380	4.1	600	9.2	1340	NA	NA	NA	NA	NA	NA
Apr. 3	FA-2	2.6	380	3.2	460	3.2	470	5.4	790	5.2	760	NA	NA	NA	NA	1.96	0.19
Apr. 4	FA-3	1.4	200	1.9	280	2.6	370	4.4	640	9.2	1330	NA	NA	NA	NA	2.12	0.21
Apr. 13	FA-4	6.0	870	8.4	1220	12.1	1750	19.4	2810	21.4	3100	2.53	0.16	NA	NA	NA	NA
Apr. 13	FA-5	5.0	730	7.0	1020	11.6	1680	16.5	2400	17.9	2600	2.53	0.16	NA	NA	3.15	0.17

			Compressive strength [75- by 150-mm (3- by 6-in) cylinders]										Elasticity	
		Cure	1-day		3-day		7-day		28-day		13-month		$E \times 10^{-6}$ lb/in^2	
Date	Mix Designation	type[3]	MPa	lb/in^2	MPa	lb/in^2	MPa	lb/in^2	MPa	lb/in^2	MPa	lb/in^2	28 days	57 days
July 24	DHC-1	Fog	12.7	1840	16.8	2440	17.9	2590	21.3	3090	25.2	3650	3.30	
		S. No. 1	7.6	1100	7.9	1140	9.9	1430						
Aug. 7	DHC-2	Fog	18.4	2670	21.6	3140	20.9	3030	25.0	3620			3.42	
		S. No. 2	23.2	3370	27.4	3980	30.8	4460					3.42	
Aug. 7	DHC-3	Fog	17.9	2590					22.9	3320			3.41	
		S. No. 3							30.6	4440				
Aug. 21	DHC-4	Fog	11.8	1710			21.5	3120	24.0	3480			3.25	
		S. No. 2	11.6	1680			24.2	3510	29.0	4200			3.16	
Aug. 21	DHC-5													
											57 days			
Aug. 23	DHC-6	S. No. 4	12.9	1870			19.0	2750	23.9	3470	34.5	5010	2.92	3.47
		S. No. 5	14.8	2140			23.2	3360	32.0	4640	33.9	4910	3.15	3.51
Aug. 23	DHC-7	Fog	14.7	2130			24.3	3530	31.9	4630			3.44	
		S. No. 2	16.5	2400			29.6	4300	35.3	5120			3.42	

[1] CC–Daratard 17, manufactured by W.R. Grace & Co.
g–Sodium citrate–United States Gypsum Co.

[2] No. 1–Anhydrous $CaSO_4$, prepared by heating tech grade $CaSO4 \cdot 2H_2O$ (200 °C for 24 hours).
No. 2–United States Gypsum, No. 1 molding plaster, plaster of paris.
No. 3–Anhydrous $CaSO_4$, snow white filler, United States Gypsum.

[3] Cure type–S=special
Fog- 100-percent relative humidity, 73 °F.
Special No. 1–130 °F in water.
Special No. 2–1-day fog, then 50-percent room.
Special No. 3–1-day specimen broken and placed on a desk for 28 days and then retested.
Special No. 4–Fog cured 28 days, then 28 days 50-percent room.
Special No. 5–1-day fog, then 27 days 50 percent, then 28 days fog room.

the cure. Compare the special cures for DHC-6 and the strengths at 57 days.

The most surprising strength of all was for DHC-3. A sample was tested at 1 day. The load was removed immediately at failure when the sample would not take a higher load. The sample was not broken down completely and remained intact. The sample was tested again at 28 days and the strength was higher than for a sample fog-cured for 28 days—comparable to 28-day strength in air without previous testing (DHC-4). This test represents a one-time occurrence and the test has not been repeated; however, a previously tested 28 days' age specimen from DHC-1 was tested again at 13 months. It tested 3.9 MPa higher at 25.2 MPa (560 lb/in^2, 3650 lb/in^2).

Curing at high temperatures and high humidity reduces strength (DHC-1). This may be the same as that for supersulfated cements which have similar hydration products [43]. A study of the hydration products of $CaSO_4$ and ash M-6734 at 90 days indicates that ettringite is the main hydration product. A poorly crystallized calcium silicate hydrate may be present also [44].

Sulfate Resistance

Sulfate resistance of these nonportland cement concretes appears good. Figures 29 and 30 show the expansions of a few concretes in comparison to type II cement. The expansions of FA-1 and FA-2 are interesting. These concretes are made with fly ash M-6734. It was shown earlier (fig. 15) that this fly ash reduces the sulfate resistance of a type II cement concrete. In fact, at 25-percent replacement of type II, M-6400 cement, expansion to failure was rapid (350 days). At the same approximate age (300 days), the expansion of FA-1 and FA-2 is only 1 percent of that for mix No. 20 containing 25-percent M-6734.

Freeze-Thaw Durability

Freeze-thaw durability of nonportland cement concretes is a function of air-entrainment (fig. 31). Durability of mix FA-4 is poor due to a very low air content, 1.7 percent. Mix FA-5, a similar mix with 5.1-percent air, had excellent durability. With proper air entrainment, these nonportland cement concretes can have durability comparable to that of portland cement concretes.

A microscopic study of the air-void system was made on concrete DHC-1 as prescribed in *ASTM: C 457.*[10] The air content was 5.9 percent. The spacing factor was 0.0061, and the specific surface was 769 per inch.[11] Both of these parameters are within recommended limits [37]for durable concrete.

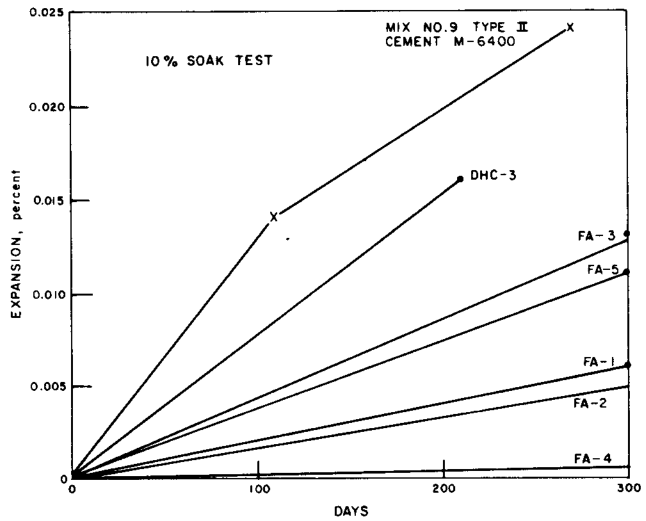


Figure 29. — Sulfate expansion plot — age versus expansion — 10 percent soak test — nonportland cement concretes.

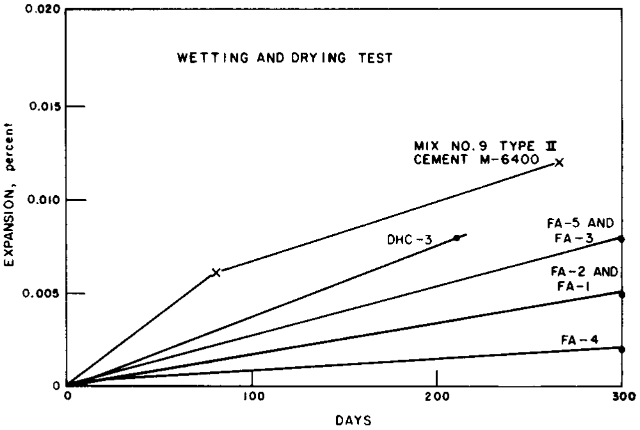


Figure 30. — Sulfate expansion plot — age versus expansion — wetting and drying test — nonportland cement concretes.

Drying Shrinkage

Nonportland cement concretes consisting mainly of fly ash have little drying shrinkage (fig. 32). Mix DHC-3 has a water requirement of 130 kg/m^3 (219 lb/yd^3) which is close to that of mix 9, 134 kg/m^3 (226 lb/yd^3); however, shrinkage is much less.

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[10] ASTM: C 457 *Microscopical Determination of Air-Void Content and Parameters of the Air-Void System in Hardened Concrete.*

[11] *Spacing factor*— A useful index related to the maximum distance of any point in the cement paste from the periphery of an air void.
Specific Surface — 769 square inches per cubic inch of air void volume, the surface area of air voids.

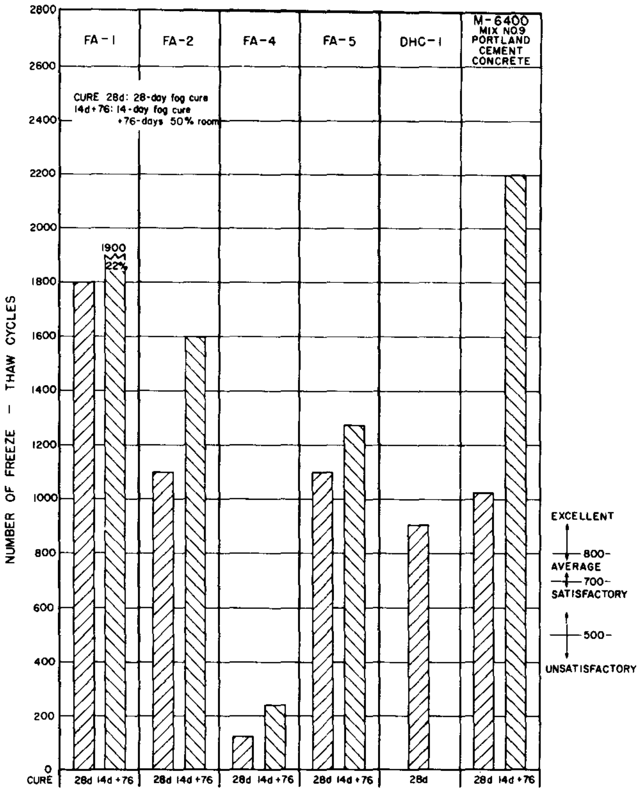

Figure 31. — Cycles of freezing and thawing to failure — nonportland cement concretes.

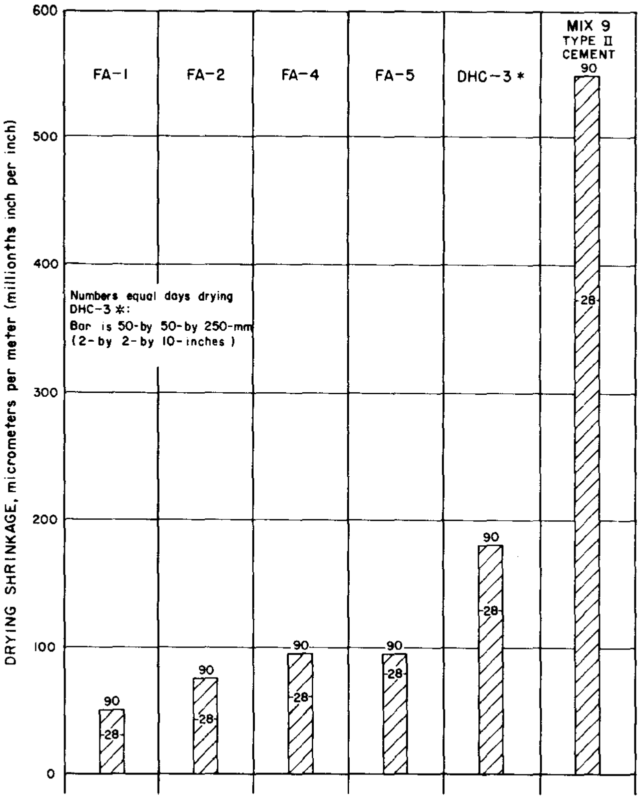

Figure 32. — Drying shrinkage of 100- by 100- by 760-mm (4- by 5- by 30-in) — nonportland cement concretes.

Surface Abrasion

The concretes with high fly ash content have poor resistance to surface abrasion. Carbon dioxide in the atmosphere reacts with the surface concrete to form a carbonated layer which causes dusting. This softening has not been investigated in detail but it may be similar to that of supersulfated cements [45]. However, this problem should only preclude their use in flat work which will not be protected. The surface also could be improved by treating it with hardeners, etc.

SUGGESTED RESEARCH

In view of the limited extent of research discussed in this report and the many still unanswered questions, further research efforts should be done in the following areas:

1. The rapid self-hardening reaction products of high calcium ashes need further investigation for ages 15 minutes through 1 year.

2. To a limited degree, this study examined high calcium ashes as 25-percent mass replacement and as 100 percent of the cementitious material of concrete. It is likely that 50-percent and possibly up to 75-percent fly-ash concretes can be made which will gain good strength. Another series of concrete mixes should be made with 25-, 50-, 75-, and 100-percent fly ash replacements. Three designs for different *water to cementitious* ratios should be made at each replacement level. If setting time can be controlled, accelerated, or retarded—as required—high replacement mixes can produce very economical and energy-efficient concrete.

3. Fly ash used to control alkali-aggregate reaction needs to be investigated further. A *pessimum* limit for low calcium and high calcium ashes should be investigated.

4. A limit, similar to the pessimum for alkali-aggregate reaction, needs to be determined for high calcium ashes in sulfate environments. A concrete that has only high calcium ash as cementitious material has good sulfate resistance. A concrete with 75-percent portland cement and 25-percent high calcium ash often has poor resistance. One can ask, "At what percentage of ash is the effect neither worse nor better than the control with 100-percent portland cement?"

5. The SO_3, MgO, and Na_2O limits for soundness of high calcium ashes seem to be unrelated to fly ash characteristics. A new approach to test soundness of fly ash is needed.

6. Ash blending can greatly modify fly ash characteristics. Where more than one ash is available, consideration of developing a high quality controlled ash by blending the materials should be considered.

7. The possibilities that $C_4A_3\overline{S}$ can be found in some high calcium ashes and that the amount $C_4A_3\overline{S}$ can be increased upon hydrating and heating makes these high calcium ashes candidates for use in making expansive cements similar to type K cement.

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