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# Agglomeration of atmospheric fluidized bed residue and fly ash mixtures

Jaydeep Dinkar Wagh  
*Iowa State University*

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Agglomeration of Atmospheric Fluidized Bed Residue  
and Fly Ash Mixtures

by

Jaydeep Dinkar Wagh

A Thesis Submitted to the  
Graduate Faculty in Partial Fulfilment of the  
Requirements for the Degree of

**MASTER OF SCIENCE**

Department: Civil and Construction Engineering  
Major: Civil Engineering (Civil Engineering Materials) and  
(Geotechnical Engineering)

Signatures have been redacted for privacy

Iowa State University  
Ames, Iowa

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## I. INTRODUCTION

Increasing concern with environmental issues and pollution control has resulted in a number of emerging technologies to enhance thermal power production, one of which is the atmospheric fluidized bed combustion (AFBC) process. Its main advantage over the other processes lies in its greatly reduced sulfur dioxide emissions and operating temperatures. The reduced gaseous emissions are achieved by combusting crushed coal in a bed of limestone or dolomite which has been fluidized by hot air. The sulfur dioxide which in normal circumstances would be released freely into the atmosphere, reacts with the limestone bed to form calcium sulphate.

The amount of waste residue (AFBC residue) obtained from this advanced technology however, is very high and has been estimated to be about four times that obtained from a conventional coal fired combustion facility. If this process is to be successful, ways of using the waste residue must be obtained.

Past research has indicated that hydrated mixtures of cementitious high calcium fly ashes and AFBC residues are capable of achieving high strengths (4). It is suggested that the high strengths may be due to formation of certain chemical compounds in the hydrated mixture. Observations so far indicate a wide range of applications of this cementitious mixture. Its suitability for each specific application has to be evaluated before full scale commercial application. This motivated the present research which investigates one specific application of the mixture, namely agglomeration to produce artificial aggregates.

Agglomeration is the process by which small particles of the raw material bind together to form larger aggregate sized particles. Agglomeration is brought about by agitating the raw material and the simultaneous addition of a wetting liquid, usually water. The individual particles bind together either due to natural forces such as capillary and molecular forces or due to formation of cementitious compounds.

An understanding of the hydration mechanism is necessary in order to evaluate any application of the mixture and due consideration is given to this. The success of this research could possibly make it feasible to utilize the agglomerates of AFBC residue/fly ash mixtures in highway base or sub-base systems.

## II. OBJECTIVES

The objective of this research is to investigate agglomeration of Ottumwa fly ash/AFBC residue mixtures, and evaluate the potential of these agglomerates for use as artificial aggregates in highway base and sub-base systems. If the agglomerates could be used as a substitute for conventional aggregates in highway systems, this could result in potential economical savings as well as solve a tremendous environmental waste disposal problem related to both fly ash and AFBC residue. Physical and chemical properties of the hydrated mixture of Ottumwa fly ash and AFBC residue have to be understood before any large scale utilization of their agglomerates is attempted. This research is directed at evaluation of the agglomeration process, physical and chemical properties of the agglomerates and an evaluation of their potential use in highway base systems.

### III. LITERATURE REVIEW

#### Introduction

Agglomeration in this case involves hydration of the chemical compounds present in the raw materials, forming cementitious compounds which cause agglomeration. The raw materials, namely, class C fly ash and AFBC residue will be described in this chapter in order to understand the hydration reactions and agglomeration process described later. The compounds supposedly responsible for cementing action in the binder under study, namely, ettringite, silicate hydrates and alumino-silicate hydrates are discussed.

#### Class C Fly Ash

Fly ash that is produced from lignite or sub-bituminous coal is termed as Class C fly ash. They have cementitious properties in addition to pozzolanic properties. This research involves this type of fly ash. The other type of fly ash produced from burning anthracite or bituminous coal is termed Class F fly ash. They lack the cementitious properties of the Class C fly ashes but do exhibit pozzolanic properties.

The chemical and physical composition of fly ash is a function of many factors such as (5),

- 1) Coal rank

- 2) Coal source
- 3) Degree of coal preparation, cleaning and pulverization
- 4) Design, type and operation of power plant boiler unit
- 5) Loading and firing conditions
- 6) Additives to assist combustion or improve precipitator performance
- 7) Collection, handling and storage methods

Characteristics of a fly ash reflects its origin from incombustible mineral matter in pulverized coal. The nature of the coal clearly dictates the nature of fly ash produced (10). The fly ash particles are usually uniformly graded in the silt size range and have a specific gravity ranging from 2.3 to 2.6.

Roy, Luke and Diamond (19) have described the structure and composition of fly ashes. They described fly ash particles to be mostly spherical due to rapid cooling and solidification of molten droplets of inorganic coal residue. Fly ash consists of two phases, a crystalline phase and an amorphous glassy phase in the form of spheres. The crystalline phase of fly ashes is dominated by the four oxides silica ( $\text{SiO}_2$ ), alumina ( $\text{Al}_2\text{O}_3$ ), hematite ( $\text{Fe}_2\text{O}_3$ ) and calcium oxide ( $\text{CaO}$ ). However, these components occur in different combinations and forms. Some of these oxides may reside in the glassy spheres. Most of the aluminium and silicon oxide is locked up in the form of an inert phase in the glass. One form of alumino-silicates very often found in fly ash is inert mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ). It is the calcium oxide in the free state that is mainly responsible for the cementing action. The  $\text{CaO}$  is capable of reacting with the glass itself in a self-pozzolanic reaction. The  $\text{CaO}$  component is also observed to be the most variable in percentage of all four oxides. Alkali sulphates sometimes found in the form of a powder on the glass surfaces can also react with certain components of the glass or with another

component tricalcium-aluminate ( $C_3A$ ) to form ettringite. Rod like crystals of ettringite are capable of cementing the fly ash spheres together. However, the glass and not the crystalline phase is found to be the major phase, constituting about 60 to 90 percent of most fly ashes. This glassy phase is the cause of the amorphous scattering hump seen in the X-ray diffraction pattern of a fly ash. The position of the maxima of this hump gives an idea about whether the glass is rich in silica or calcium. Silica and calcium components may occur in the glass matrix or on the surface of the glass.

#### **Atmospheric Fluidized Bed Combustion Residue (AFBC residue)**

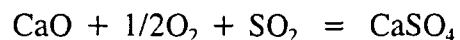
Increasing concern over environmental issues have resulted in an emerging technology of burning coal formed the atmospheric fluidized bed combustion (AFBC) process which results in reduced gaseous emissions. It achieves this by combusting the coal in a bed of limestone. The emitted sulfur dioxide reacts with the bed of limestone to form calcium sulphate and is thus captured in the furnace as bed residue.

The reactions occurring in the furnace are as follows (2, 4):

The limestone ( $CaCO_3$ ) in the bed first calcines to form porous lime ( $CaO$ ).



This lime then reacts in-situ with oxides of sulfur emitted during combustion to form calcium sulfate,



The disadvantage of this process is the amount of waste residue obtained (AFBC residue).

The amount of waste residue has been estimated to be about four times that obtained from a conventional coal fired combustion facility (4). It has been reported that a substantial difference exists in the composition between residues from different sources and even from different batches making it difficult to characterize the AFBC residues. The nature and properties of AFBC wastes depend on a number of interacting variables (2)

including,

- 1) The basic design of the combustion unit.
- 2) The nature and characterization of the feed materials (limestone and coal).
- 3) Sulfur content of the coal.
- 4) The absorption potential of the bed material.

Collins (4) has cited residues from the AFBC process to be composed of:

- $\text{CaSO}_4$  (anhydrite)
- $\text{CaO}$
- $\text{CaCO}_3$
- $\text{MgO}$
- Silicates and Aluminates (derived from clays)
- $\text{SiO}_2$  (from sand or quartz impurities)
- $\text{Fe}_2\text{O}_3$
- ferrites and other iron compounds, and
- minor and trace elements in various states of combination

Observations on the scanning electron microscope and reduced reactivity rate of lime ( $\text{CaO}$ ) has shown that the bed drain material is composed of a core of lime surrounded by a coating of  $\text{CaSO}_4$  (2). This has been explained on the basis of chemical reactions occurring in the furnace during combustion (2,4). The  $\text{CaSO}_4$  formed in the fluidized bed covers the unreacted  $\text{CaO}$  leaving behind an unreacted core of  $\text{CaO}$  coated with  $\text{CaSO}_4$ , as bed residue. Si and Al presumably originating from clay or shale fed with the coal was seen to dominate the rest of the bed residue. A substantial amount of

research has already been done and a number of potential uses of this material have been investigated (2, 4). Their application has been said to be limited due to their variability, lack of pozzolanic properties and the elevated sulphate content. The few promising applications now singled out are (2, 4):

- agriculture;
- lime substitute in acidic waste neutralization;
- waste stabilization agent in lime/pozzolan systems;
- low strength backfill applications (with or without portland cement);
- soil stabilization and soil cementing;
- asphaltic concrete aggregate.

#### **Hydrated Mixture of AFBC Residue and Fly Ash**

Recently it has been realized that significant compressive strength are developed by addition of AFBC residue in stabilized road base mixture components containing conventional aggregates and pulverized fly ash (4). The hydrated mixture of AFBC residue and fly ash has been evaluated on a limited basis. Blocks made up of hydrated mixtures of 80 percent AFBC residue and 20 percent fly ash were seen to develop high strengths on curing (4) and hence exhibit a high potential for utilization. Significant attention has been directed towards understanding the hydration mechanism of this mixture. Analogies with other well understood cementing systems like portland cement have helped evolve theories to explain the origin of cementing action in this binder system. The following general background of the chemical processes responsible for the cementing action provides a theoretical basis for understanding the hydration mechanism



of the mixture under study, namely fly ash and AFBC residue.

Gypsum is supposed to play an important role in the binder system as AFBC residues have large amounts of anhydrous calcium sulfate which hydrates to gypsum on addition of water. The slight cementing capability of gypsum relies on the formation of acicular, or blade like-crystals that interlock and form secondary bonds during precipitation (1). An optimum proportion of gypsum resulting in higher strengths in portland cement pastes is well established (18). Further a different optimum gypsum content is observed at different ages. This concept of optimum gypsum content is still not well understood and few convincing theories have evolved to explain it. One theory attributes this to the reduction in calcium ions due to formation of AFm phase (a alumino-ferrite phase that is mono substituted) in low gypsum mixtures which prevents nucleation of CSH (calcium silicate hydrate) or CASH (calcium alumino silicate hydrate) (18). The low strengths in high gypsum mixtures is attributed to disruptive expansions due to the formation of ettringite after the paste has set. Another theory is based on the acceleration of alite hydration by gypsum and simultaneous lowering of strength of CSH by incorporation of sulfate in its structure (20).

A near complete study of the hydration mechanism of the AFBC residue/fly ash mixture has been carried out by Matex Consultants (1). They have used several techniques including X-ray diffraction, thermal analysis, scanning electron microscopy and pore fluid analysis, to investigate the hydration mechanism of the mixture. They have shown that the compounds present in the binder system as predominantly gypsum, AFt (alumino-ferrite phase formed that is tri substituted) and calcium hydroxide along

with the inert quartz, mullite, hematite, and ferrite spinel initially present in the raw materials. Minor amounts of calcium silicates or calcium alumino-silicate hydration products are estimated to be present. Exceptionally high levels of Si, Al, Ca and  $\text{SO}_4$  in pore fluids suggest large scale precipitation of CSH/CASH and AFt.

Observations on the scanning electron microscope have been conducted by Matex Consultants (1). They describe the matrix material as well densified and having an amorphous, web like character. It is composed mainly of the elements calcium, aluminium and sulphur along with small amounts of silicon. The spherical particles of pulverized fly ash (PFA) appear to be etched although they still preserve their characteristic shape. The etched PFA spheres are possibly only the silicate framework and have been proposed to reinforce the matrix through a web like AFt growth.

Matex Consultants (1) combined results from a quantitative X-ray diffraction analysis with thermo-gravimetric analysis on this binder system to obtain a quantitative indication of reactions occurring. They found formation of gypsum to occur sometimes up to 7 days after which it declined. The rate of AFt formation increased and calcium-hydroxide reduced markedly during the period from 1 to 7 days. Ettringite formation was seen to start at about 3 days and ceased after about 28 to 56 days. Ettringite formation was also indicated by reduction in the  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  ion concentration in solution. In some binders the AFt phase made up 35% to 40% of the hydrated mixture after 90 days.

Matex Consultants (1) also observed that  $\text{Ca}(\text{OH})_2$  was consumed in quantities more than that required for stoichiometric formation of AFt. They attributed this to the

possible formation of CSH or CASH. This was further supported by their finding of exceptionally high levels of Si in pore fluids. Diffusion of silicate ions through sulfo aluminate zones to form CASH has been reported in cement pastes (24, 25). However, the formation of the hydrates was not indicated by X-ray diffraction results.

The absence of the above hydrates in the X-ray diffractograms might be due to the amorphous nature of these hydrates (32, 33). The limitations of X-ray diffraction to detect weak peaks resulting from poor crystallinity make it impossible for detection of the hydrates. Flint and Wells (32) have further complicated this matter by synthesizing a phase of composition CASH which exhibits a X-ray diffractogram similar to that of ettringite in spite of having a different morphology. Carlson and Berman (26) have also described a calcium silico-aluminate composition that produces an X-ray diagram similar to that of ettringite.

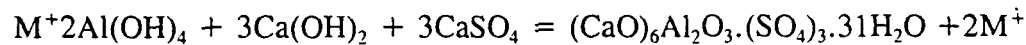
The similarity of temperatures over which dehydration occurs in ettringite, calcium silicate hydrates and calcium alumino-silicate hydrates makes it difficult to identify the presence of these compounds even by thermo-gravimetric (TGA) analysis (1).

In conclusion, Matex Consultants (1) proposed the cementing action in binders to result from formation of mainly alumino-sulfates and hydrated silicates (CSH) or alumino-silicates (CASH) from pozzolanic reactivity, accounting for early and late strength development.

Formation and properties of these compounds is described below;

### Ettringite

When aluminium ions are available in an aqueous system containing  $\text{Ca(OH)}_2$  and  $\text{CaSO}_4$ , it can be expected that sulfo-aluminates ( $\text{CaO}_6.\text{Al}_2\text{O}_3.(\text{SO}_4)_3.31\text{H}_2\text{O}$ ) also called as ettringite will precipitate. Midgley and Pettifer (20) and later, Uchikawa and Tsukiyama (21) showed that ettringite strongly contributed to the mechanical strength of hydrated portland cement at early stage. Ettringite formation is possibly the most important reaction occurring in the binder system under study in view of the large amount of reported sulphate and Ca oxide in AFBC residue (1, 2, 3, 4).



where  $\text{M}^+ = \text{a cation}$

The possible sources of aluminium have been listed as calcined clays in the AFBC residue, aluminium silicate glass in the PFA or trace phases such as  $\text{C}_3\text{A}$  (1). Scanning electron microscope observations conducted on these binders (1) showed AFt crystals to be formed on the surface of PFA particles suggesting that surface glass in the PFA may be the chief Al source. Matex Consultants (1) have further inferred that Al ions may be removed from the glass by alkaline hydrolysis followed by diffusion and subsequent precipitation as AFt. Absence of association of AFt particles with gypsum crystals, suggests that aluminium ions may not be diffusing far from the source before being precipitated. A second factor may be continued dissolution of gypsum as indicated by the presence of more rounded, smaller gypsum crystals in the mature binders.

Mehta (12) has carried out extensive studies of ettringite under a scanning electron

microscope and reported morphology of ettringite as short hexagonal prisms with a thickness to length ratio of about 1:3. Mehta (12) later found that presence of lime enhanced formation of ettringite and also altered the crystal structure of ettringite. The thickness to length ratio of ettringite was seen to be about 1:4 in presence of lime. Moreover, morphology of ettringite was also seen to be dependant on the pore volume available for its formation. Lower available pore volumes result in short prismatic crystals.

Moore and Taylor (27) have described the structure of ettringite in detail. The hexagonal prismatic crystals of ettringite (12) are formed by columns and channels oriented parallel to prism axis. The composition of the columns is  $\text{Ca}_6(\text{Al}(\text{OH})_6)_2 \cdot 24\text{H}_2\text{O}^{6+}$ . Sulfate and  $\text{H}_2\text{O}$  groups are present in the channels. Each column is a chain of alternating polyhedra of one Al polyhedra and three Ca polyhedra. Each Ca atom is linked to four water molecules and four OH groups. A Ca polyhedra is shaped as a trigonal prism with two additional apices in which water molecules are located. In the transverse direction three OH groups bond together three Ca polyhedra, thus imparting the column bond strength in the transverse direction. Also four (OH) groups located at four apices of Ca polyhedra are common to the Al polyhedra. The same OH groups imparting the column bond strength in the transverse direction, can be considered responsible for the column bond strength in the longitudinal direction. Each water molecule interacts with only one Ca atom and therefore they only form the column surface without taking part in the binding action. It can be assumed that water molecules take part in the joining the columns into a single crystal. The positive charge of a

column is distributed among all water molecules and negative among sulfate groups. The interactions of the groups with the surface of more than one column cause the columns to bind into a crystal.

Skoblinskaya and Krasilnikov (29) have correlated the thermal properties with the structure of ettringite. The principal dehydration process for AFt occurs in the range 100-110°C. In differential thermal analysis (DTA), dehydration of AFt is reported to give rise to a large peak at 160°C; a further small peak at 300°C is attributed to decomposition of the hydroxyl groups bound to aluminium (1).

Dissolution in ethylene glycol is an effective way of quantifying amount of ettringite present in a hardened paste, as ettringite is soluble in ethylene glycol.

The structure of ettringite, as described by Moore and Taylor (27) cite the sulfate ions to be present in the space between the channels of ettringite. This might be considered consistent with the observation that sulfate ions can be replaced by other anions. Carlson and Berman (26) have described substitution of sulfate by carbonate, while Flint and Wells (32) have described replacement of sulfate by silicate. The presence of the former has been well established. A study carried out by N. B. Singh (28), has shown the formation of calcium carbo-aluminates. The hydration of C<sub>3</sub>S with gypsum which would form ettringite has been shown to be retarded further by formation of carbo-aluminates in the presence of carbonates. A decrease in carbonate observed in the binder system under study was attributed to possible replacement of sulfate ions in ettringite by carbonate ions (1). There are literature reports of oxyanion substituted ettringites having sulfate substituted by other oxyanions. More recently substitution of

sulfate by silicate ions has been indicated (18, 15). W. Lukas (14) has reported substitution of part of aluminium by silicate ions. The AFt complexes containing  $\text{Fe}_2\text{O}_3$ ,  $\text{SO}_4$ ,  $\text{CO}_3$ , Cl and  $\text{SiO}_3$  may be relevant to the binder system under study (1).

Ettringite formation is supposed to be responsible for causing certain detrimental properties such as retardation of cement paste hydration and sulphate attack.

Forsen (31) attributed strength retardation to two possibilities;

- (1) Repression of the solubility of  $\text{C}_3\text{A}$  in sulfate solutions
- (2) Protective coating around  $\text{C}_3\text{A}$ .

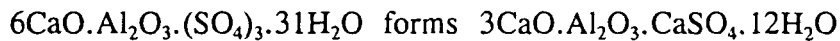
The tendency of ettringite to be strongly associated with the surface of the PFA spheres had been noted (12). Retardation due to a protective coating of ettringite had been proposed. Later observation of ettringite away from the reacting grains, coupled with the relatively higher permeability of ettringite has made the theory of reduced solubility of  $\text{C}_3\text{A}$  in sulfate solutions more convincing (12). The retardation is seen to be more effective in presence of lime. The smaller crystals of ettringite in presence of lime (12) may be more effective in covering the unhydrated core.

Ettringite has also been determined to cause detrimental expansions (11).

Expansive cements relying on ettringite to impart expansive characteristics have been developed. Direct correspondence of maximal AFt precipitation with expansions in the binder system under study has been observed (1). Different theories have evolved to explain the basis for deleterious expansions due to ettringite in the past. The expansions may be due to the anisotropic thrust caused by the needle-like ettringite crystals during their formation (23). Another convincing theory attributes the expansions to the

adsorption of water molecules on the ettringite surfaces, thus causing the crystals to move apart (12).

Ettringite is unstable in the absence of sulfate ions and converts to platy calcium mono sulfo-aluminate ( $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaSO}_4\cdot 12\text{H}_2\text{O}$ ).



This phase is mostly observed in fly ash pastes due to limited availability of sulfate.

### **Pozzolanic Reactions Forming Silicates and Alumino-Silicates**

A pozzolan is defined as a siliceous or alumino-siliceous material that in itself possesses little or no cementing value but that in finely divided form and in the presence of moisture will chemically react with alkali and alkaline earth hydroxides, at ordinary temperatures, to form or assist in forming compounds possessing cementitious properties. The constituents of the AFBC residue/PFA system, include pozzolans of two types showing two distinct reaction mechanisms with lime:

- calcined natural pozzolans
- pulverized fuel ash (PFA, or fly ash)

Matex Consultants (1) expect the alumino-silicates in AFBC residues to have properties similar to the calcined shales or clays, due to favorable temperatures occurring in the AFBC process. The calcination is probably responsible for activating the pozzolanic properties.

The chief known products formed from lime-pozzolan reactions are listed below



(1);

- Calcium silicate hydrates (CSH)
- AFt
- Tetracalcium hydrate ( $C_4AH_x$ )
- AFm
- hydrated gehlanite ( $C_2ASH_8$ )
- calcium carbo-aluminate hydrate

In most cases the pozzolanic properties are attributed to alumino-silicate glass in the PFA. This has been proved by Watt and Thorne who showed a progressive increase in reacted silica and aluminium in fly ash reacted with lime. The pozzolanic reaction has been described (1) to occur due to the breaking of the three dimensional network of alumino-silicates existing in the fly ash glass and subsequent leaching of aluminium into solution. The overall matrix is still maintained by the silica skeleton, but not for long. Soon the outer silica also dissolves and reacts with calcium ions in solution to form cementitious calcium silicate hydrates. The process is repeated for the new internal surfaces exposed.

CSH and CASH have been found to contribute significantly to the ultimate strength and its understanding is fundamental to studying the mechanistic basis for cementing action in this binder. Flint and Wells (32) have synthesized CASH and shown it to be in the form of small hexagonal plates which in three years in contact with lime is converted to needle shaped prisms. The needles gave essentially the same composition as ettringite with silicate instead of sulfate. i.e. they were silicate analogs of ettringite. A thin layer of CASH is also seen to form underlying the ettringite layer. The formation of gehlenite hydrate or hydrogarnets which are particular forms of CASH, depend on the

relative silica and lime content of the system. Dron has shown that gehlenite hydrate cannot co-exist with  $\text{Ca}(\text{OH})_2$ . The mono silico-aluminates were seen to contain 2.5% sulfate, while only 1% sulfate is reported in tri silico-aluminates. However, Carstanje, Stein and Stevels (24) found that silico-aluminates are unstable in presence of more than 20% sulfate ions. Preferential formation of ettringite and mono sulfo-aluminate over gehlenite hydrate in presence of gypsum is also known to occur (33). A PFA containing 1.39%  $\text{SO}_3$  is also reported to form ettringite. Interestingly an addition of about 3% gypsum to calcined clay-lime mixes has been found to accelerate strength development. In the absence of sufficient sulfate to form ettringite it is possible that the silico-aluminate hydrates, such as gehlenite hydrate ( $\text{C}_2\text{ASH}_8$ ) could be formed as reported by Verhasselt.

The most important reactions are considered to be those between reactive silicate forms and calcium hydroxide that produce calcium silicate hydrates (CSH). In contrast to lesser known CASH, calcium silicate hydrates (CSH) are an essential component in almost all cementitious mixtures and have been well studied. They are responsible for the high strengths developed in portland cement pastes. The different types of CSH are proposed to have different morphology ranging from amorphous to a semi-crystalline form called jennite. Gard and Taylor (22) have proposed a structure for CSH. According to them CSH is a semi-crystalline compound containing meta silicate chains and pyro silicate groups and has a disordered layered structure. While the exact structure has not been determined, it is likely that they have a layered structure with layers parallel to (001) made of negatively charged hydro silicates. Additional  $\text{Ca}^{2+}$  ions and sometimes water molecules occur between these layers.

Sulfate ions have been found to be incorporated in CSH matrix (16). The incorporated amount increases with the increase in total sulfate in the system. A bad quality gel is obtained on addition of excess sulfate and consequently lower compressive strengths. The optimum gypsum content for maximum strength development has been explained by the interactions between CSH gel and the unreacted aluminium and iron bearing phases (16).

### **Agglomeration**

One of the utilization alternatives of this high strength mixture is agglomeration. Agglomeration is a process which involves binding together of individual particles of a material into aggregate sized particles which might then be used as a substitute for conventional aggregates. Small particles of fly ash and AFBC residue could be converted to large aggregate-sized particles by agglomeration which would then facilitate easy handling for disposal or use in highway base systems.

Agglomeration can be accomplished by either of three processes:

1) Agitating or Pelletizing

This involves agitating the material and providing adequate moisture so that the material particles collide and adhere to each other resulting in the formation of larger particles.

2) Compaction or compression

This involves the use of a mechanical force to compact the individual particles of the raw material into larger particles.

### 3) Heat treatment or sintering

This involves the application of heat to the material to cause its sintering. The molten material is then solidified which results in formation of larger solidified particles.

Agitating or pelletizing is best suited for use with a cementitious material and as such is well suited for use with the binder system under study. In this agglomeration is achieved simply by agitating the material in presence of adequate moisture. The material is usually agitated using balling devices, disc pelletizers, drums and cones (7). Different types of agitating agglomeration devices are shown in Figure 1-1. The shallow pan disc is the most commonly used. The use of the inclined disc pelletizer can be traced back to well before the turn of the century (7). This method involves agitating the individual particles by placing them in a rotating disc pan and coating them with a thin film of liquid, usually water. Particle size enlargement occurs by collision and successful adherence of primary feed particles into discrete granules. The particles are held together by cohesive forces at contact points. These forces may arise from,

- 1) Particle-particle attraction
- 2) Surface tension of liquid film coating the particles
- 3) Formation of cementitious compounds

The type of bonding determines the final properties of the product. In the initial stage the moist feed material particles roll and slide down the surface of the pan during agitation and collide randomly forming nuclei. This stage is called nucleation. The thin

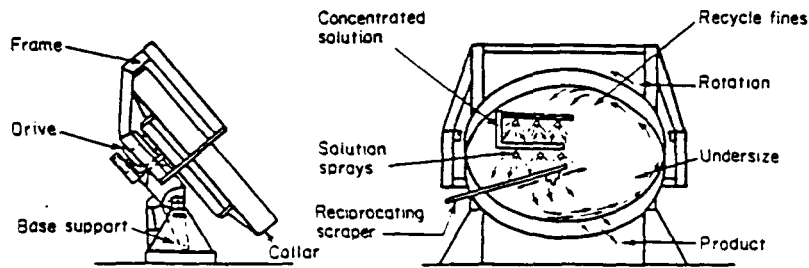
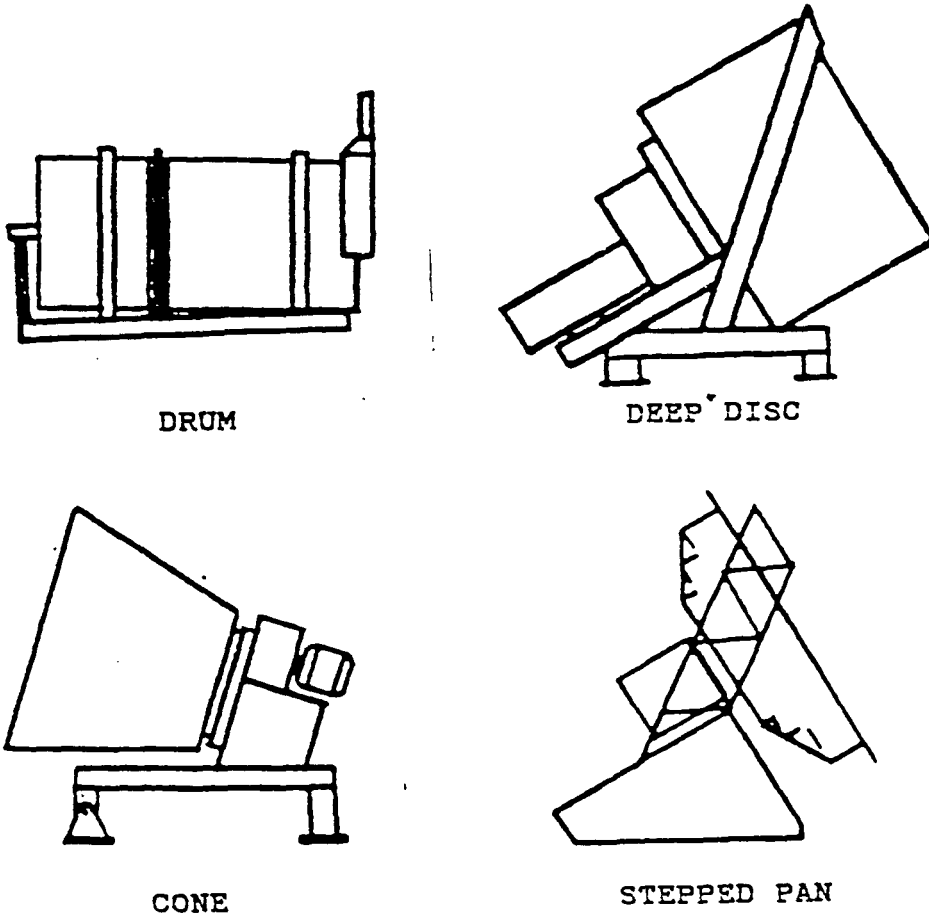


Fig. 38. Dish granulator.<sup>99</sup>

Figure 1-1: Different types of agitating agglomeration devices (7, 8, 9)

film of liquid surrounding the particles have an inward force called surface tension associated with it. This surface tension captures other colliding particles forming a single larger particle. Water is the most commonly used moistening liquid because of its high surface tension. The reduction in the total surface free energy of the system accompanying the decreased air-liquid interface area is the driving force (8). This nucleation phenomenon may account for agglomerate growth up to 1 or 2 mm diameter depending on operating conditions. After the nucleation stage, the growth mechanisms are

- 1) Coalescence
- 2) Layering

Both may occur simultaneously but, in general one mechanism will predominate (7). Initial growth takes place by random coalescence. Large granules would then pick up fines and continue to grow by layering. As the size of the particles increases, the intensity of collision also increases leading to a steady increase in the granule breakage rate (8, 9). This set a limit on the maximum particle size obtained from a specific process for specific settings. Agglomeration of a cementitious material such as Class C fly ashes would also involve a chemical reaction of the particles with the moistening liquid. Formation of cementitious compounds would assist other forces described above in providing a strong bond between individual particles. By far the largest group of materials formed into pellets by agitative agglomeration methods involve a chemical reaction between the powdered material and the liquid. A scraper is almost always provided with a disc pelletizer to scrape particles which stick to the surface of the disc.

The size of the final particles obtained is a function of a number of variables including water content, feed rate, disc inclination and speed of the disc. The agglomeration process is also sensitive to the location of the feed material, moisture and the retention time. These variables can be adjusted depending on the type of raw material and size of agglomerates required. Water content is most frequently varied to control the agglomeration process. The role and judgement of the operator of the agglomeration device has also been emphasized. Many agglomeration devices have only lasted as long as the inventor or promoter was active (7). The procedure of scaling up of pilot plant equipment to production sized equipment using empirical formula cannot be applied for most agglomeration devices (7). Sometimes production size equipment has failed even though the pilot plant size equipment was successful in producing the same product. Operating parameters for field applications thus have to be established for different agglomeration devices.

The process of agglomeration has been well studied and reported for fly ash (6). Kilgour et. al. (6) have studied the variation in size and shape of the agglomerates of fly ash obtained with the rotating disc pan agglomerator, with a number of variables such as feed rate, rotation speed and water content. The effect of increase in water content is to increase the particle sizes obtained.

Escalating costs and dwindling resources of conventional aggregates are making agglomeration more and more economically feasible (6).

## IV. PROCEDURE, RESULTS AND ANALYSIS

### Introduction

Not much is known about the hydrated mixture, of high calcium fly ashes and AFBC residues, although the potential for its utilization has been recognized. Research carried out on this binder system has attributed the high strength development to formation of certain chemical compounds. Understanding the hydration mechanism of the mixture and associated strength development is a prerequisite to any large scale utilization. This motivated the first half of this research which consisted of a study of the hydrated mixture of Class C fly ash and AFBC residue. AFBC residue from Iowa State University's power plant in Ames, Iowa, was used for this research. Ottumwa fly ash and reclaimed hydrated Ottumwa fly ash that had been reground were the Class C fly ashes used in this research. Ottumwa fly ash is obtained from the coal combustion plant located near Ottumwa, Iowa, while reclaimed fly ash is the fly ash obtained by grinding hardened Ottumwa Class C fly ash. The second phase of this research consisted of a study of actual agglomeration process and evaluation of the agglomerates for potential utilization in highway base and sub-base systems.

Thus experiments were carried out in two parts:

- (1) the study of Ottumwa fly ash/AFBC residue system. This is described in sections 3.2.
- (2) preparation of agglomerates and evaluating their properties. This is described in section 3.3.



### Ottumwa Fly Ash/AFBC Residue System

Physical and chemical properties of the raw materials, namely, Ottumwa fly ash and AFBC residue were studied. The strength development of hydrated mixtures of Ottumwa fly ash and AFBC residue, along with the influence of several parameters such as water-content, temperature, particle size and physical and chemical properties of the hydrated mixture were investigated.

#### Properties of raw materials

Physical and chemical properties of raw materials are known to eventually dictate ultimate properties of the hydrated mixture. Properties of the hydrated mixture can be better understood and predicted if an understanding of the basic raw materials exists. It is the chemistry of raw materials that dictates formation of different chemical compounds in the mixture, which in turn affects morphology and other physical properties. Physical properties of raw materials can affect the chemistry of the final hydrated mixture, for example smaller particle sizes of raw materials provide larger surface areas for chemical reactions to occur, resulting in increased chemical activity. Knowledge of the physical and chemical properties of raw materials, namely Ottumwa fly ash and AFBC residue will assist in the understanding of hydration mechanism of the mixture.

The specific gravity of the two raw materials, namely Ottumwa fly ash and AFBC residue was determined by the procedure specified in ASTM-C188 to be 2.65 and 3.0 respectively.

Chemical composition Chemical composition of the two raw materials, namely, Ottumwa fly ash and AFBC residue were determined by using X-ray fluorescence (XRF) method. This method works on the principle that an element emits (fluorescence) a characteristic line spectrum when bombarded with high energy X-rays. The two most intense lines of a spectrum ( $K\alpha$  and  $K\beta$  lines) are unique to the emitting element and can be used to identify that element. The sample was fused before analysis so that most of the elements present in the sample are converted to their respective oxides. The chemical compositions as determined by X-ray fluorescence (XRF) analysis is shown in Table 4-1. The chemical composition gives the total amount of chemical elements present in the substances irrespective of the state or combination in which they occur. The classification of Ottumwa fly ash as a high calcium fly ash is evident considering the high amount of calcium oxide present in it. Aluminium and silica are also present in large amounts in the Ottumwa fly ash. In view of this, Ottumwa fly ash can be predicted to act as a potential source of calcium, aluminium and silica.

However, the chemical composition as determined above, does not give good correlation with predicted reactivity as part of the elements may be in the form of largely inert phases. A major part of aluminum in Ottumwa fly ash for example, may be locked up in the form of inert mullite ( $3Al_2O_3, 2SiO_2$ ). The reactivity of CaO in the AFBC residue is also subdued due to a protective coating of  $CaSO_4$  surrounding it (2, 3, 4).

X-ray diffraction tests were conducted on Ottumwa fly ash and AFBC residue to determine the chemical compounds present in them. X-ray diffractograms of raw Ottumwa fly ash and raw AFBC residue are shown in Figures A-1a and A-1b

Table 4-1: Chemical composition of raw materials used.

OXIDE	CORRECTED WEIGHT %	
	OTTUMWA FLY ASH	AFBC RESIDUE
SiO <sub>2</sub>	33.28	27.79
Al <sub>2</sub> O <sub>3</sub>	20.40	5.87
Fe <sub>2</sub> O <sub>3</sub>	5.35	14.89
SO <sub>3</sub>	2.62	12.57
CaO	25.44	30.10
MgO	4.66	0.84
P <sub>2</sub> O <sub>5</sub>	1.57	0.24
K <sub>2</sub> O	0.43	0.61
Na <sub>2</sub> O	2.74	0.00
TiO <sub>2</sub>	1.50	0.30
SrO	0.44	0.04
BaO	0.85	0.03
LOI	0.43	6.12
TOTAL	99.69	99.39

respectively in the Appendix. The Ottumwa fly ash shows the presence of very few crystalline compounds. A major part of the Ottumwa fly ash is in the form of a glass as indicated by the amorphous hump in the X-ray diffractogram. The position of the maxima of the amorphous hump indicates that the glass is rich in calcium and is most probably a calcium-aluminate glass. Small quantities of crystalline silica and calcium oxide are indicated by the sharp peaks in the diffractogram. In contrast the AFBC residue does not exhibit the presence of a glassy phase and several crystalline compounds are seen to be present. A major volume of the AFBC residue is seen to be composed of quartz, alumina, iron oxide, calcium oxide and anhydrous calcium sulphate.

## Strength development

### Hydrated mixtures of Ottumwa fly ash and AFBC residue

Procedure Raw Ottumwa fly ash and AFBC residue were combined in various proportions forming eleven different mixtures. The light particulate nature of the raw materials and associated dusting problems during mixing, made hand mixing a necessity. The two materials were mixed for about five minutes until a uniform homogenous mixture was obtained. Water content for each mixture was adjusted so as to obtain a thick workable paste of similar consistency, as determined visually. Different proportions used and water contents are given in Table 4-2 and are shown graphically in Figure 4-1.

The mixtures were then molded into 1 " cubes. The cube molds were thoroughly cleaned before use and mixtures were properly tamped into cube molds to remove any air voids that might remain. These 1" cubes were then cured in plastic bags so that loss or ingress of moisture was prevented. Their crushing strengths were determined after 1, 3, 7, 14 and 28 days of curing in an unconfined compression testing device. Three cubes of each proportion were tested at each day and the average strength was determined.

Results and analysis Figure 4-2 shows strength developed by the mixtures of Ottumwa fly ash and AFBC residue as determined above. Addition of AFBC residue to Ottumwa fly ash increases strength proportionately until an optimum proportion is reached, after which further addition of AFBC residue reduces the strength. Another interesting feature observed is that there exists a different optimum proportion for

**Table 4-2: Water content of hydrated mixtures of Ottumwa fly ash and AFBC residue**

<b>Mixture Number</b>	<b>% Ottumwa fly ash</b>	<b>% AFBC residue</b>	<b>% water content</b>
1	100	0	24.6
2	90	10	29.0
3	85	15	32.0
4	80	20	33.0
5	75	25	36.0
6	70	30	39.0
7	65	35	41.0
8	55	45	44.6
9	40	60	50.4
10	25	75	56.0
11	10	90	63.0

different ages. At 1 day, the peak strength is shown by the mixture having 35 % AFBC residue, but with time the peak is seen to shift towards mixtures with higher percentages of AFBC residue. Mixtures having larger percentages of AFBC residue show retarded strength development but are characterized by a sudden dramatic increase in strength after the end of the induction period. The induction period lasts for about 7 days in the mixture having 45% AFBC residue. AFBC residue thus seems to retard strength development. Mixtures more than 45% of AFBC residue do not gain strength until 28 days and exhibit significantly lower strengths, possibly due to some permanently existing retarding action. The strength of the mixtures is seen to increase steadily up to 28 days although the rate of strength development reduces with time. Thus after 28 days, the

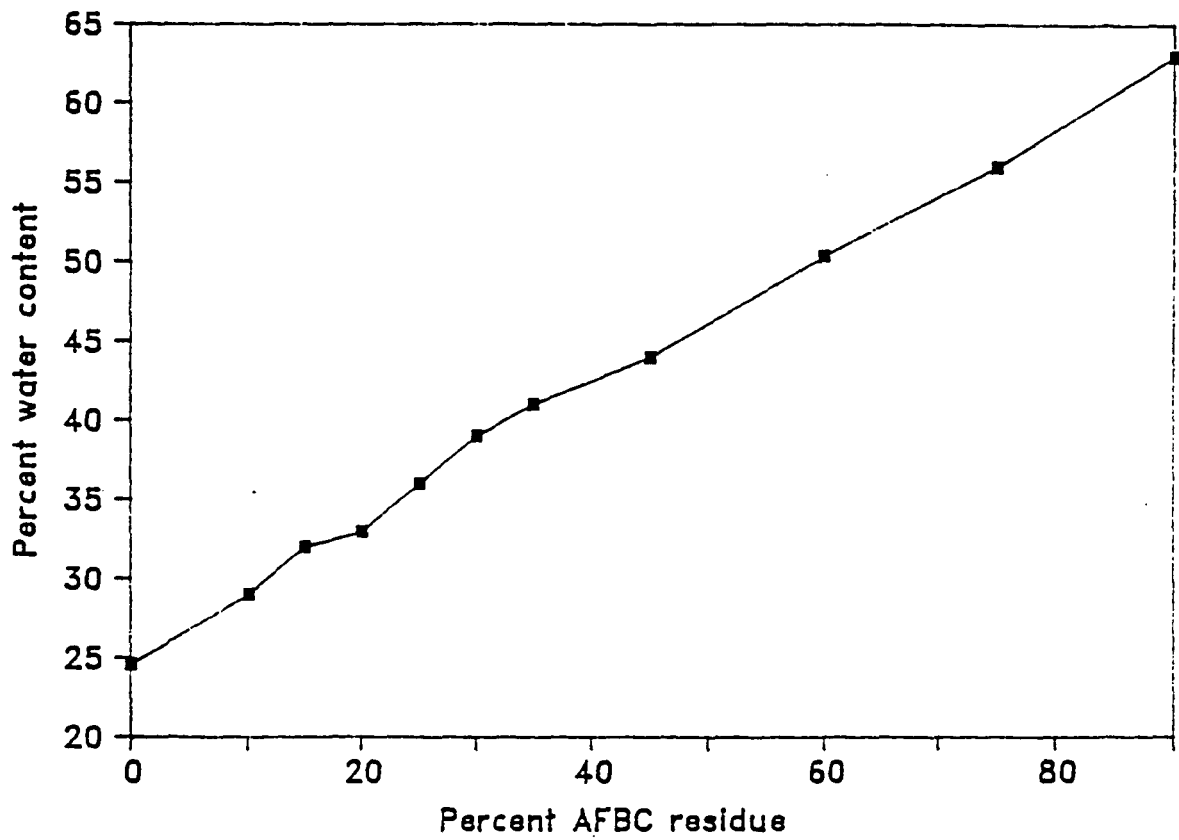


Figure 4-1: Water content of hydrated mixtures of Ottumwa fly ash and AFBC residue

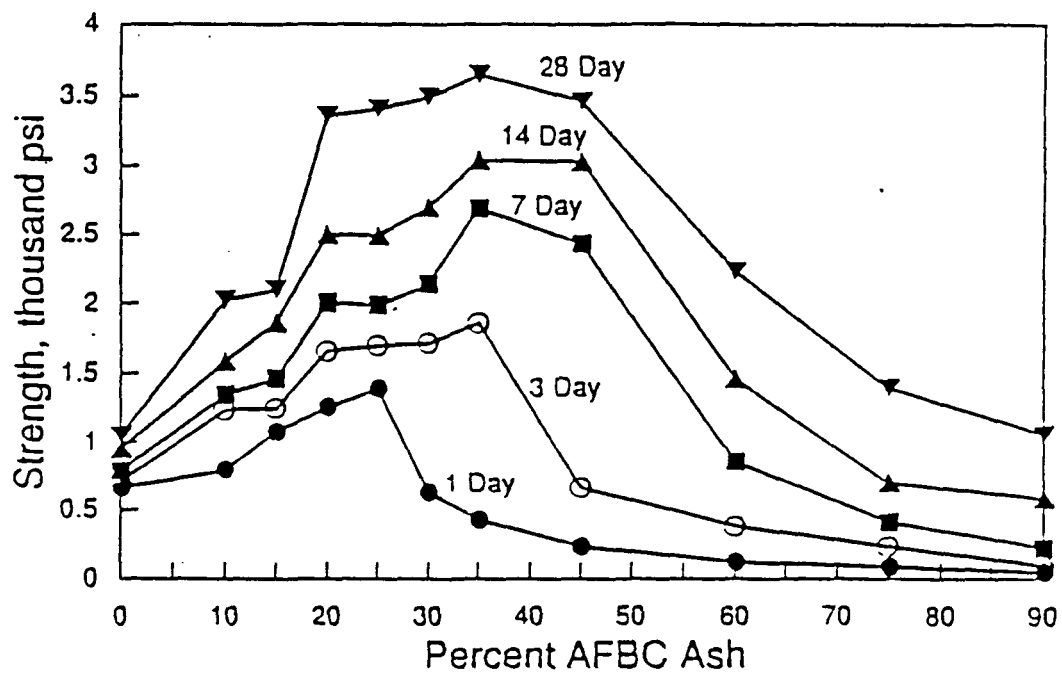


Figure 4-2: Effect of percent of AFBC residue on crushing strength in hydrated mixtures of Ottumwa fly ash and AFBC residue

range of proportions having 20% to 45% AFBC residue are seen to exhibit significantly higher strengths compared to other proportions.

Hydrated mixture of reclaimed fly ash and AFBC residue

Procedure The above procedure was repeated for the hydrated mixture of reclaimed reground Ottumwa fly ash and AFBC residue to compare strength development with the mixture of raw Ottumwa fly ash and AFBC residue. The fraction of hydrated reclaimed fly ash passing through sieve # 80 was used. The ready availability of this size fraction dictated its selection. Five different proportions were prepared in this series of tests. The proportions used and water contents are shown in Table 4-3.

**Table 4-3: Water content of hydrated mixtures of reclaimed fly ash and AFBC residue.**

<b>% Rec. fly ash</b>	<b>% AFBC residue</b>	<b>% Water content</b>
25	75	59
55	45	63.1
65	35	61
75	25	65.2
85	15	63.5

Results and analysis A similar trend of optimum strength range is seen for mixtures of reclaimed fly ash and AFBC residue in Figure 4-3, as seen earlier for mixtures of Ottumwa fly ash and AFBC residue, although overall strengths obtained are



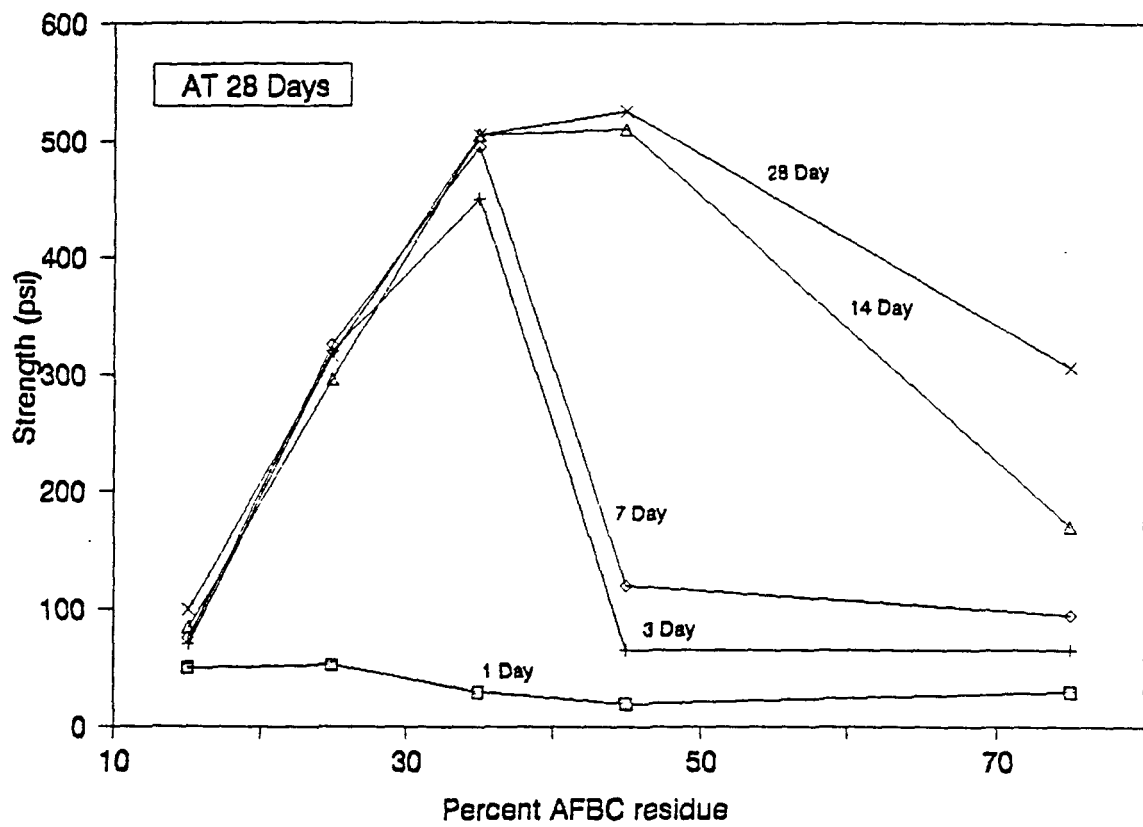


Figure 4-3: Effect of percent AFBC residue on crushing strength in mixtures of reclaimed fly ash and AFBC residue

comparatively lower. The lower strengths are attributed to the different particle sizes and chemical composition of reclaimed fly ash. The retarding action of AFBC residue and the sudden dramatic increase in strength after the induction period as seen in earlier mixtures with Ottumwa fly ash is evident even in these mixtures. The similar trend of strength development observed with reclaimed fly ash indicates that the optimum strength range is not solely a characteristic of mixtures containing Ottumwa fly ash.

Following determination of strengths in the mixtures as described above, the effect of water content, curing temperature and particle size on strength development was studied. It is essential to understand the variations in strength with these parameters as this will then govern the extent of control that needs to be exercised during large scale field applications.

Effect of Water Content One of the most important considerations affecting strength development of any cementing material is the water content utilized. Water content in a cementing material has a great influence on ultimate physical properties attained, including porosity, permeability and strength. In addition, water content also influences the extent of hydration and other chemical reactions occurring in the mixture. A water content striking an appropriate compromise between required workability and strength of a cementing material should be known during its field application.

Procedure To evaluate the effect of water content on strength in the mixtures, hydrated mixtures of 55 % Ottumwa fly ash and 45 % AFBC residue using three different water contents were prepared. This proportion was selected as it exhibits

high strength at a high level of utilization of AFBC residue. Water contents lower than 32 % were seen to result in a dry unworkable mix which could not be molded, while a water content of 44% resulted in a highly flowable mix. The final water contents were selected within this range. The mixtures with different water contents were then molded into 1" cubes and their relative crushing strengths were determined after 1, 3, 7, 14 and 28 days of curing using the same procedure described before. Average strength of three samples was determined for each day. Their relative crushing strengths were compared to evaluate effect of water content on strength development.

Results and analysis The effect of water content on strength development in mixtures of Ottumwa fly ash and AFBC residue as determined above is shown in Figure 4-4. The crushing strength is seen to decrease with addition of excess water. The decrease in strength is attributed mainly to the increased porosity resulting from addition of excess water.

Effect of temperature The effect of temperature on strength development of the mixture was examined as this will influence the field conditions under which agglomeration can be accomplished. Low strength development under cold or hot conditions may require field control of temperatures during the agglomeration process. Understanding variations in strength development as a function of temperature will also help account for the effect of heat liberated due to the exothermic hydration of the mixture, during large scale field applications.

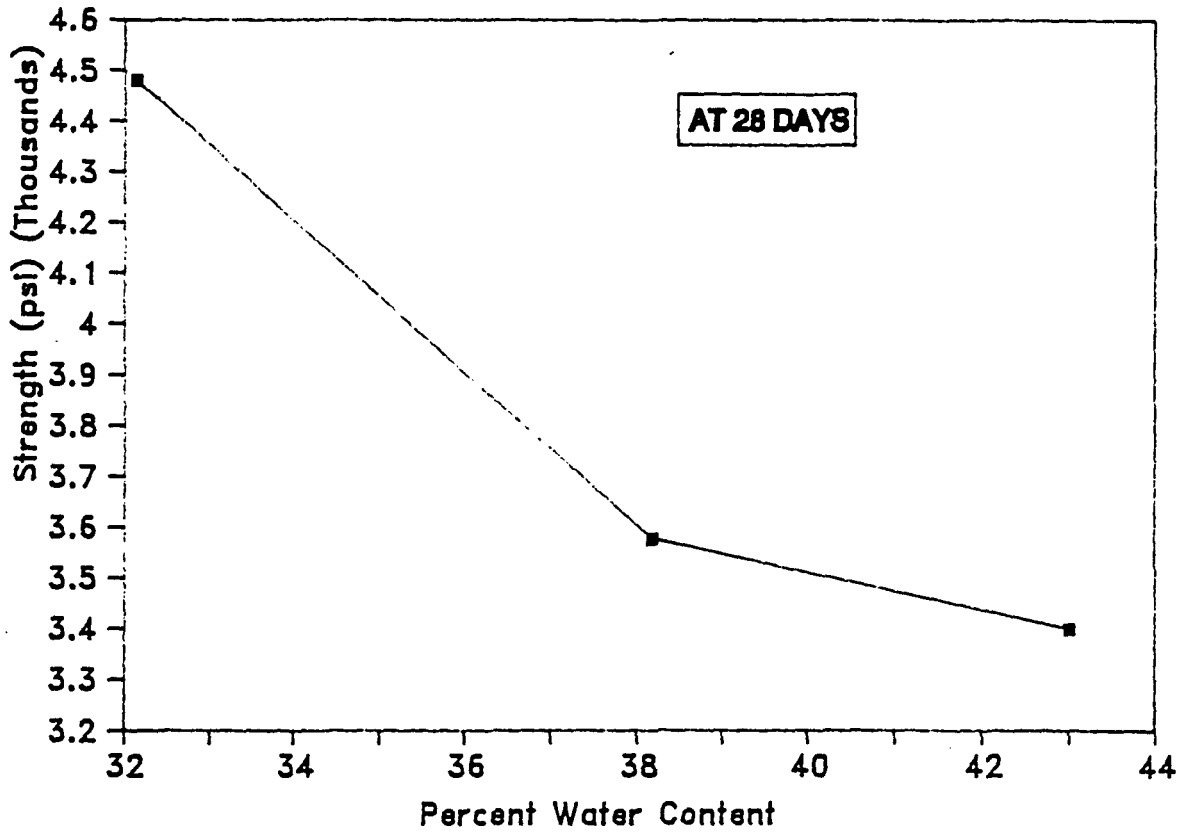


Figure 4-4: Effect of water content on crushing strength in mixtures of Ottumwa fly ash and AFBC residue

Procedure To evaluate the effect of temperature, hydrated mixtures of 55% Ottumwa and 45% AFBC residue were prepared using a water content just sufficient to obtain a workable mix. High strength and maximum use of AFBC residue was used as a basis for selection of this proportion. The mixture was molded into 1" cubes and air cured at four different temperatures ranging from 0°C to 40°C. Curing was achieved by placing the cubes in sealed plastic bags which prevented loss or ingress of water from or into the cubes. The plastic bags containing the cubes were suspended over a water filled container in the oven to ensure adequate relative humidity for curing. Relative crushing strengths of cubes, air cured at different temperatures were determined after 1, 3, 7, 14 and 28 days, using the same procedure described above. Their relative crushing strengths were compared to evaluate effect of temperature on strength development.

Results and analysis Figure 4-5 compares the crushing strength developed by hydrated mixtures of Ottumwa fly ash and AFBC residue, at different temperatures. Strength development of the mixture is rapid at elevated temperatures. However, within 28 days the mixtures at different curing temperatures tend to achieve equal strengths. Higher temperatures are known to act as a catalyst for chemical reactions. This suggests that the increased rate of strength gain in mixtures cured at higher temperatures is due to certain chemical reactions occurring in the mixtures. This also clearly indicates that the basic strength gain phenomenon in the mixtures is due to certain chemical reactions resulting in subsequent formation of chemical compounds which impart the high strengths.

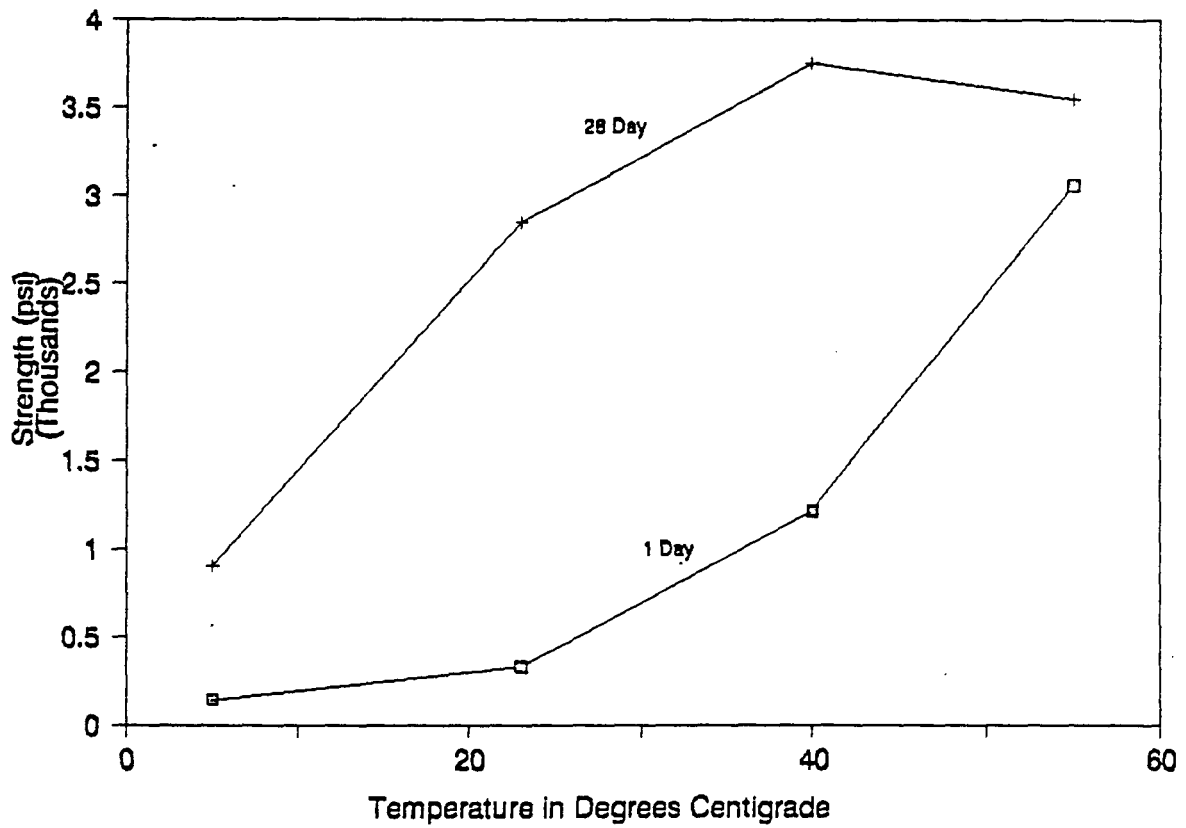


Figure 4-5: Effect of curing temperatures on crushing strength of hydrated mixtures of Ottumwa fly ash and AFBC residue

Effect of particle size Hydrated, reclaimed fly ash that had been reground was available in different sizes and as such the particle size which yields the best strength development needed to be evaluated for potential use in field applications. Strengths development of mixtures of AFBC residue and the fraction of reclaimed fly ash passing through sieve # 80 were described earlier in this chapter (page 37).

Procedure To examine the effect of particle size on strength development, hydrated mixtures of AFBC residue and a smaller particle size of reclaimed fly ash were prepared in two different proportions. The fraction of reclaimed fly ash passing through sieve # 170 was used. Water contents were adjusted so as to obtain the same workable consistency in both proportions, as determined visually. The two proportions and associated water contents are given in Table 4-4.

**Table 4-4: Water content of hydrated mixtures of reclaimed fly ash (# 170 sieve) and AFBC residue.**

<b>Percent reclaimed fly ash</b>	<b>Percent AFBC residue</b>	<b>Percent Water content</b>
65	35	55
55	45	56

The mixtures were molded into cubes and their crushing strength was determined after 28 days of curing using the same procedure as specified above. Crushing strengths developed in these mixtures were compared to those obtained with mixtures using larger particle sizes of reclaimed fly ash.

Results and analysis Figure 4-6 shows that the effect of particle size on strength development in mixtures of reclaimed fly ash and AFBC residue as determined above. The strength is seen to increase with a reduced particle size of reclaimed fly ash. It was determined earlier that strength gain phenomenon in these mixtures is due to formation of certain chemical compounds. Consequently this also explains the higher strengths in mixtures using smaller particle sizes of reclaimed fly ash. Smaller particle sizes have an increased surface area associated with them and thus provide additional sites for chemical reactions to occur. This results in an increased formation of strength giving chemical compounds.

#### Pore volume

Pore structure is a basic parameter influencing physical properties of any material, including strength, and as such should be adequately understood. It was thought that the significant differences in strengths exhibited by air cured hydrated mixtures of Ottumwa fly ash and AFBC residue as seen above may be due to differences in pore volume. Mixtures of Ottumwa fly ash and AFBC residue having higher amounts of AFBC residue had consumed larger amounts of water for the same consistency (Figure 4-1). This is expected to result in increased porosity in mixtures with higher percentages of AFBC residue. A large difference in pore volume might partly explain the reduction in strength on addition of AFBC residue in excess of the optimum proportion.



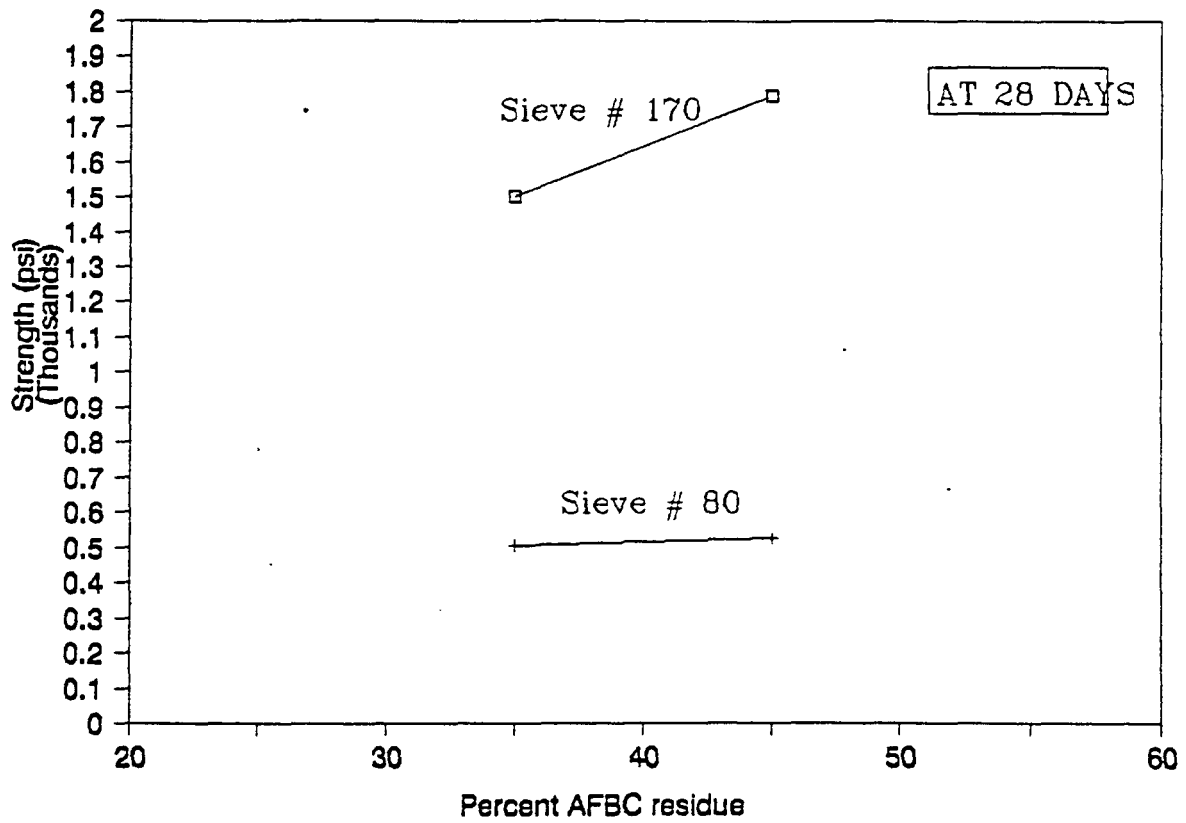


Figure 4-6: Effect of particle size of reclaimed fly ash on crushing strength in mixtures of reclaimed fly ash and AFBC residue

Procedure The pore size distribution of two hydrated mixtures of Ottumwa fly ash and AFBC residue, in proportions having 45 % and 75 % AFBC residue, was determined after 28 days of curing. These two proportions were selected because of the significant strength differences exhibited by them. An extremely large difference in pore characteristics between the mixtures may help explain in part, the significant strength difference. Pore size distribution was determined using the mercury porosimetry technique which enables the determination of pore size distribution. The principle of this technique is the known relation between pressure applied to mercury to intrude pores of the sample, radius of the pores and intruded volume. The mercury porosimeter used in this experiment has a maximum pressure capability of 60,000 psi. Pore diameters ranging from 200 micro meters to 3.5 nm can be determined using this instrument. In this technique a sample of the hydrated mixture is immersed in mercury. The mercury is forced to intrude the sample pores by application of a known pressure. The change in intruded volume of mercury with pressure is continuously monitored. Knowing the intruded volume and applied pressure, the pore size distribution of the sample is obtained. A contact angle of  $140^\circ$  was used and mercury pressure was increased in 3 stages:

- 1) from 0 to 1200 psi
- 2) from 1200 to 6000 psi
- 3) from 6000 to 60,000 psi.

The pore size distribution of the two mixtures was then compared.

Results and analysis Figures 4-7 and 4-8 show that the pore sizes or pore-radii are almost the same in two mixtures having 45% and 75% AFBC residue respectively.

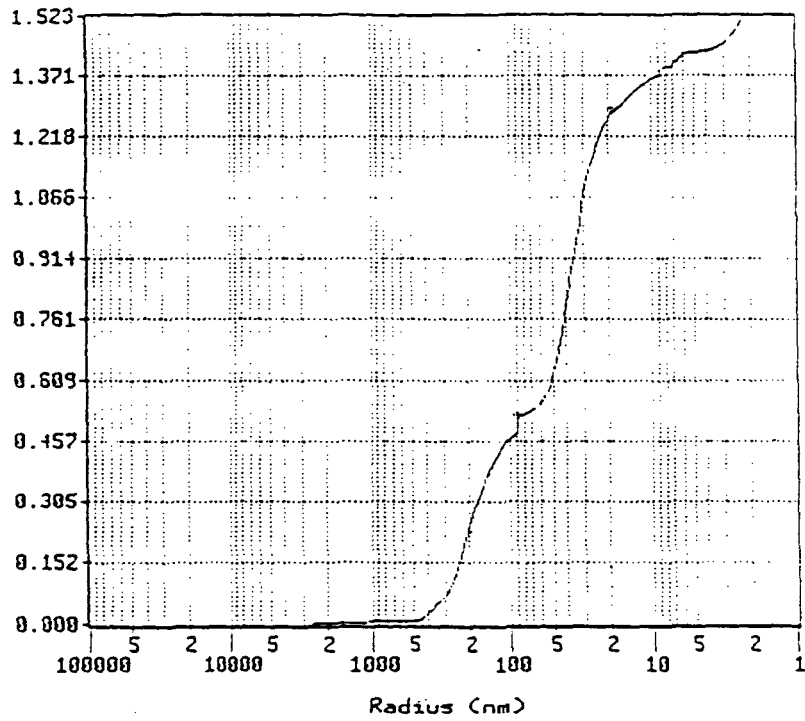


Figure 4-7: Cumulative pore volume in hydrated mixture of 55% Ottumwa fly ash and 45% AFBC residue

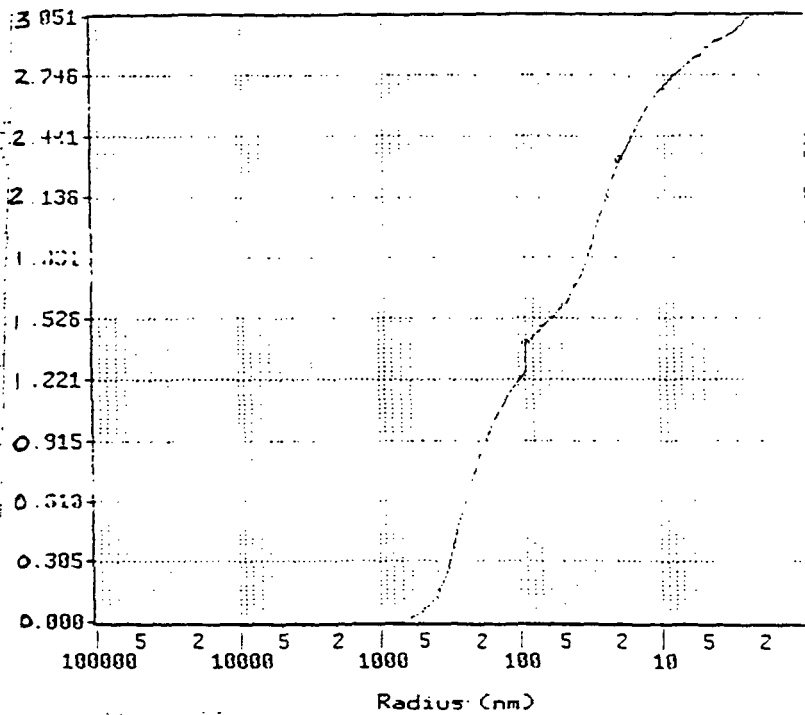


Figure 4-8: Cumulative pore volume in hydrated mixture of 25% Ottumwa fly ash and 75% AFBC residue

However, total intruded volume is only 0.1523 cc for the mixture having 45% AFBC residue, while it is much higher (0.3051 cc) for the mixture having 75% AFBC residue. The increased pore volume is due to higher water content used by mixtures having larger amounts of AFBC residue. It is noted that the mixture having 75% AFBC residue had a water content of 56% in comparison with the mixture having 45% AFBC, which used only 44%.

### Chemical compounds

In cementitious materials, the cementing ability and resulting strength development is usually due to formation of certain chemical compounds. Comparison of chemistry of hydrated mixtures of different proportions might indicate the chemical compounds responsible for imparting high strengths.

Procedure The chemical compounds formed in hydrated mixtures of Ottumwa fly ash and AFBC residue mixed in different proportions, after 28 days of curing were determined. X-ray diffraction techniques were used for this purpose. This involves the measuring of the intensity and position of a beam of X-rays diffracted from a substance. These measurements are fundamental physical properties of a crystalline substance allowing for its identification. The mixtures in different proportions were ground to a powder form and were then subjected to a  $\text{Cu K}\alpha$ , radiation in the X-ray diffraction apparatus. Peaks in the diffraction pattern obtained from mixtures were used in identifying crystalline chemical compounds present in the mixtures.

In addition chemical compounds formed in the high strength mixture containing

45% AFBC residue, after 3 and 28 days of curing were also determined using X-ray diffraction techniques. This was done to study qualitative aspects of phase formation or transformations occurring in mixtures during the hydration process. Relating phase transformations with corresponding increases in crushing strengths could help identify a particular compound or compounds contributing to the high strength.

Results A series of X-ray diffractograms for hydrated mixtures of Ottumwa fly ash and AFBC residue in three different proportions, cured for 28 days are shown in Figures A-2a to A-2c in appendix. The chemical compounds detected in the mixtures are mainly :

- 1) Ettringite (AFt phase)
- 2) Mono sulfoaluminate (AFm phase)
- 3) Quartz
- 4) Iron-oxide
- 5) Gypsum
- 6) Calcium-hydroxide

The above list is conspicuous by the absence of the cementitious hydrates such as CSH or CASH, usually found in hydrated cement systems. These cementitious hydrates are also known to form by a lime-pozzolanic reaction and are expected to form in this binder system. Their absence may be due to limitations of X-ray diffraction techniques in detecting these amorphous or poorly crystalline components. This problem is further compounded by the detection of certain calcium silico- aluminates in the past, having x-ray diffraction patterns resembling that of ettringite, although their morphology differs (15, 33). Past research carried out on AFBC residue/fly ash binders from different sources (1) has also not succeeded in detecting the presence of these phases. The

compounds listed above are not present in all proportions of the mixture. Presence or absence of some of these compounds in certain mixtures is governed by the proportion of that mixture. Quartz, and iron oxide are major phases in most of the hydrated mixtures. These are probably the inert quartz and iron oxide present in the AFBC residue and Ottumwa fly ash which have remained unhydrated. Gypsum is a major constituent in mixtures having higher percentages of AFBC residue. The presence of gypsum is expected due to the large amounts of anhydrous  $\text{CaSO}_4$  in the AFBC residue which hydrates to gypsum in the presence of water. Ettringite is seen to be a major component in the mixtures in the high strength range. The other proportions also consist of ettringite, but the relatively low quantities are evident from the diffractograms. Ettringite is known to be stable only in the presence of sulfate ions or in this case, gypsum. In the absence of sulfate ions or gypsum, ettringite converts to monosulfoaluminate (AFm phase). Consequently, the mixtures having lower percentages of AFBC residues show an absence of gypsum and partial conversion of ettringite to the AFm phase. The peaks corresponding to AFm phase are clearly seen in the diffractograms for mixtures having up to 45% AFBC residue. The conversion to AFm phase is more in mixtures having still lower percentages of AFBC residues. For some reason ettringite was formed in relatively low concentrations in mixtures having higher percentages of AFBC residue. This may be due to the diluting effect of the large amounts of inert  $\text{SiO}_2$  and  $\text{Fe}_2\text{O}_3$  present in the AFBC residue. The X-ray diffraction patterns of hydrated mixtures having 20% to 45% AFBC residue indicate possible substitution of sulphate ions in ettringite with silicate or carbonate ions. The substitution was inferred from a minor shift in the

X-ray diffraction peaks of ettringite. Substitution by silicate ions is considered a probability owing to the large amount of quartz present and depletion of sulphate ions available in the system. The depletion of sulphate ions is inferred from the partial conversion of ettringite to an AFm phase which occurs only in the absence of sulphate ions or gypsum. The substitution may have occurred due to the depletion of the source of  $\text{SO}_4^{2-}$  ions, or gypsum and subsequent entering of silicate ions in the channels of unstable ettringite. However, limitations of X-ray diffraction in detecting minor modifications in crystal structure of ettringite, imposed by entry of silicate ions made a definitive conclusion impossible. Silicate and carbonate substituted ettringite have, however, been detected in the past (28, 14, 15).

The domination of gypsum originating from AFBC residue in the mixtures is evident from the above analysis. The chemical compounds formed are seen to change from AFm phases to ettringite to gypsum along the line, with increasing quantities of AFBC residue or gypsum. This suggests that an optimum percentage of gypsum in the mixtures might be responsible for the high strength range exhibited by them. The concept of optimum gypsum content has been realized in the past (18) and seems to be a probability in this case.

X-ray diffraction patterns for the hydrated mixture having 45 % AFBC residue after 3 and 28 days of curing are shown in Figures A-3a and A-3b in the Appendix respectively. The X-ray diffractograms indicate essentially similar chemistry. Contrary to prior expectations, no formation of new chemical compounds corresponding to the strength increase was indicated. This eliminated the theory of formation of a new

compound imparting the high strengths. An increase in the amount of well crystallized ettringite was inferred from the sharper and higher peaks. Few additional peaks for mono-sulfo-aluminate were seen to occur in the mixture after strength development. This indicates depletion of gypsum in the mixture as mono-sulfo-aluminate is formed from conversion of ettringite, only in the absence of sulphate ions. Diffraction patterns at early hydration periods did not indicate any shift in ettringite peaks pointing to sulphate substitution as observed in the well hydrated, high strength mixtures. No other major difference in the diffraction patterns, before and after the strength rise was seen which could account for the strength gain.

Analysis Although quantitative results were not obtained from X-ray diffraction, it is reasonable to assume that mixtures with very high percentages of AFBC residue ( > 45% AFBC residue) are super-saturated with gypsum and calcium ions, due to the high amounts of anhydrous  $\text{CaSO}_4$  and  $\text{CaO}$ , respectively in the AFBC residue. Ettringite is known to form from the reaction of gypsum with aluminate in presence of calcium oxide. The lower amounts of ettringite formed in the mixtures having very high percentages of AFBC residue can only be due to a paucity of aluminum ions. The aluminate ions available are apparently not sufficient to react with the large reserves of gypsum and formation of ettringite is restricted. The source of aluminum is unknown and may be due to leaching from the glassy phase in Ottumwa fly ash or from aluminosilicates in AFBC residue. However, the paucity of available aluminate species in these high AFBC residue, low Ottumwa fly ash mixtures suggest Ottumwa fly ash to be the source of aluminum. In contrast, mixtures with slightly lower percentages of AFBC



residue (20% to 45% AFBC residue) should have lesser gypsum. Sufficient aluminate ions seem to be available in these proportions to react with gypsum, as gypsum is not detected and all the sulphate ions are seen to be locked up in ettringite. Exhaustion of the gypsum source in these proportions can also be inferred from the conversion of a part of the ettringite to AFm phases. This suggests that formation of ettringite in these proportions is governed by the extent of gypsum available, rather than available aluminum. The higher availability of aluminum in these proportions having higher amounts of Ottumwa fly ash confirm the source of available aluminum to be Ottumwa fly ash as proposed earlier. High strength development in these mixtures correspond to high amounts of ettringite indicate ettringite to be responsible for high strengths. The proportions having much lower quantities of AFBC residue ( $< 20\%$  AFBC residue) also shown an absence of gypsum. The ettringite formation in this case is restricted by exhaustion of the available sulfate or gypsum. Part of the ettringite formed is converted to AFm phase in the absence of sulfate source.

### Chemical analysis

The above X-ray diffraction analysis clearly indicates the dominant role played by the gypsum content in the mixtures. The concept of optimum gypsum content in portland cement concrete is well known and cited in the literature (18). Gypsum contents higher or lower than the optimum content causes a drastic reduction in strength of hydrated cements. Significant quantities of gypsum are formed in the hydrated mixtures under study from hydration of anhydrous  $\text{CaSO}_4$  in the AFBC residue. An optimum strength

range possibly due to optimum formation of ettringite from gypsum was also observed in the hydrated mixtures. This led to the belief that the optimum strength range in the mixtures, might be related to an optimum gypsum content. To investigate this hypothesis, experiments were performed with pure gypsum. The effect of addition of gypsum to the raw materials, namely, Ottumwa fly ash and AFBC residue was investigated. Variations in strength development with gypsum content will provide some insight into the role played by gypsum or sulfate ion content in causing high strengths in the mixtures.

Hydrated mixture of AFBC residue, Ottumwa fly ash and gypsum Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) was added to a raw mixture of 75% Ottumwa and 25% AFBC residue in increasing quantities. Water content was adjusted so as to obtain a workable mix. Water contents used are given in Table 4-5.

**Table 4-5: Water content of hydrated mixtures of Ottumwa fly ash, AFBC residue and gypsum.**

<b>% Ott. fly ash</b>	<b>% AFBC residue</b>	<b>% Gypsum</b>	<b>% Water content</b>
70.5	23.5	6	38.1
65	22	13	41.4
44.5	18	37.5	48.5

The mixture was molded into 1" cubes and the crushing strength developed in the mixtures was determined after 1, 3, 7, 14 and 28 days of curing by the procedure described before.

Figure 4-9 shows the strength developed by mixtures of Ottumwa fly ash, AFBC residue and gypsum. The above theory relating the strength development to an optimum sulphate ion or gypsum content was further reinforced by the drastic reduction of strength observed in mixtures of 25% Ottumwa fly ash and 75% AFBC residue on addition of a large amount of gypsum. This is clearly seen in Figure 4-9. Furthermore, addition of a small amount of gypsum is seen to enhance the strength of the mixture.

It is evident from Figure 4-9, that gypsum does have an effect on strength development. However, this experiment could be misleading as the strength effect is attributed solely to gypsum when in actuality it may be acting in combination with certain other compounds present in the AFBC residue. It was deemed essential to test a mixture of Ottumwa fly ash and gypsum exclusively. This would help establish conclusively whether gypsum is the sole component of AFBC residue, imparting high strength to the Ottumwa fly ash.

Hydrated mixture of Ottumwa fly ash and gypsum      A hydrated mixture of raw Ottumwa fly ash and gypsum was prepared. The proportion of two substances used, resembled a high strength mixture of Ottumwa fly ash and AFBC residue assuming all other phases in AFBC residue to be inert. This proportion was achieved by estimating amount of gypsum present in an optimum percentage of AFBC residue and adding it to an optimum percentage of Ottumwa fly ash. The water content was adjusted to obtain a thick workable paste. The proportions used are given in Table 4-5. The mixture was molded into 1" cubes and strength developed in the mixture after 28 days of curing was determined by the procedure described before.

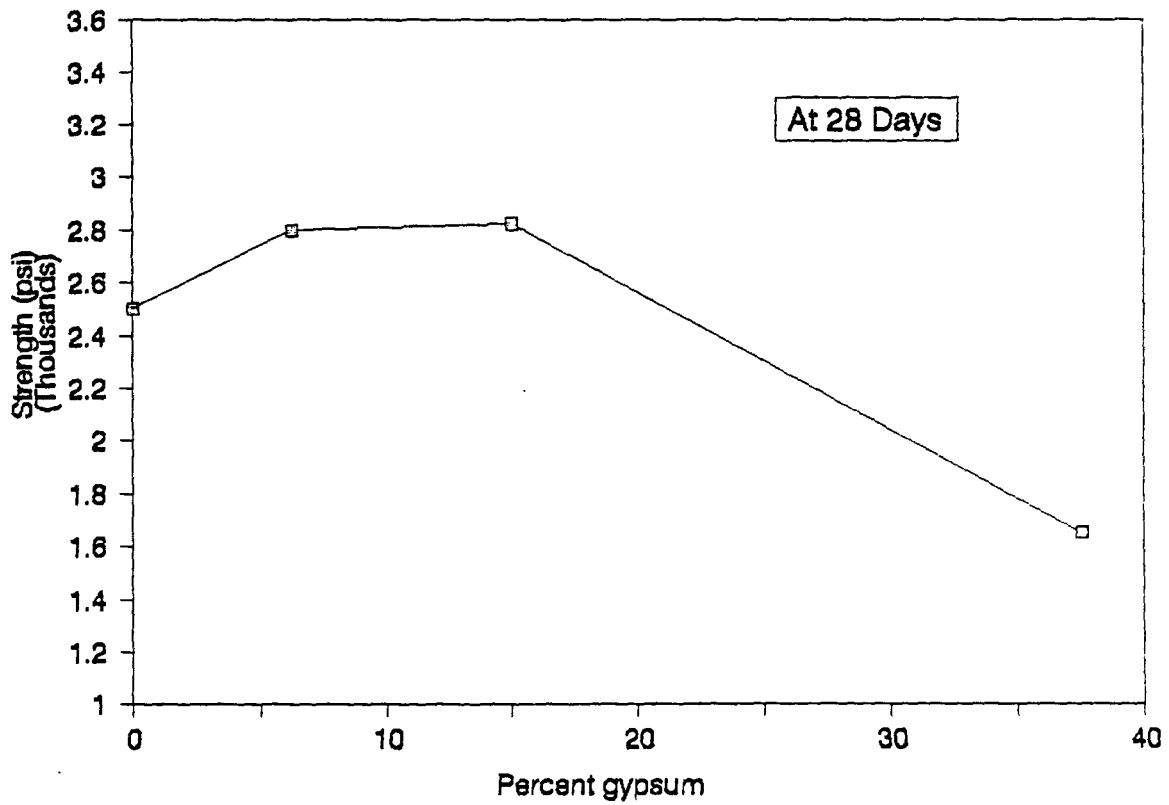


Figure 4-9: Effect of addition of gypsum on crushing strength in hydrated mixtures of 75% Ottumwa fly ash and 25 % AFBC residue

Strengths developed by mixtures of Ottumwa fly ash and gypsum alone are shown in Figure 4-10. Addition of gypsum alone is clearly seen to increase strength of Ottumwa fly ash. Addition of gypsum to Ottumwa fly ash contributes to the formation of ettringite. The increase in strength on addition of gypsum must be related to formation of ettringite as proposed earlier also. However, the strength of the mixture of Ottumwa fly ash and gypsum is much lower than that of the mixture of Ottumwa fly ash and AFBC residue. This implies that gypsum is not the sole component of AFBC residue contributing to the high strengths.

Hydrated mixture of Ottumwa fly ash, CaO and gypsum In addition to gypsum, AFBC residue has one more component which has always been associated with cementing ability, namely calcium oxide (CaO) or free lime. Lime-pozzolanic reactions are cited in the literature to cause significant strength development. Moreover, CaO is also known to assist the formation of sulpho-aluminates which are supposedly the primary strength giving compounds in these binders. It was suggested that CaO may be acting in combination with gypsum, if not singly, with Ottumwa fly ash to contribute to high strengths. To investigate this, strength development in hydrated mixtures of Ottumwa fly ash, CaO and gypsum in different proportions after 1, 3, 7, 14 and 28 days of curing was studied. The proportions used and water content of the mixtures to obtain the same workable consistency (as determined visually) are given in Table 4-6. The mixture of Ottumwa fly ash, CaO and gypsum having 75% Ottumwa fly ash is prepared, so as to closely resemble a high strength mixture of Ottumwa fly ash and AFBC residue based on the chemical composition of the AFBC residue.

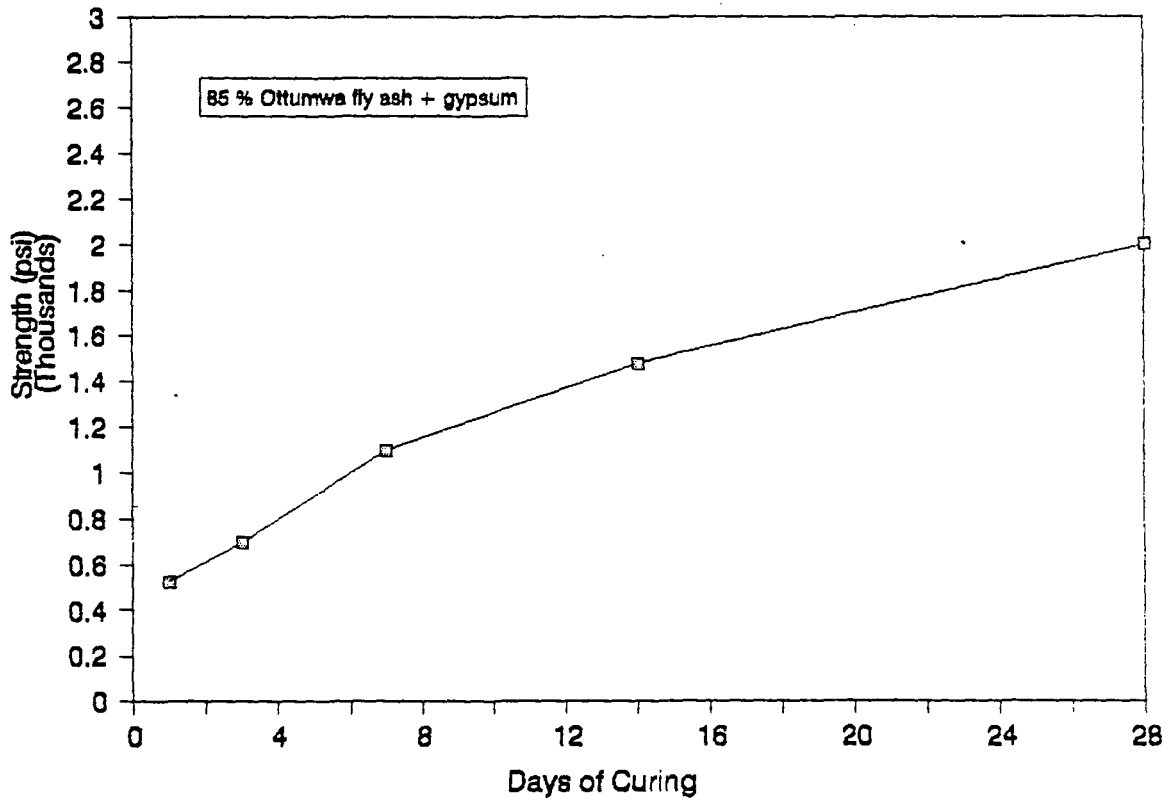


Figure 4-10: Effect of addition of gypsum on crushing strength in hydrated Ottumwa fly ash

**Table 4-6: Water content of hydrated mixtures of Ottumwa fly ash, CaO and gypsum.**

<b>% Ott. fly ash</b>	<b>% CaO</b>	<b>% Gypsum</b>	<b>% Water content</b>
100	-	-	24.6
87	13	-	33
85	-	15	33.6
75	11.2	13.4	40
59.7	17.9	22.3	49

The strengths developed in of Ottumwa fly ash, lime and gypsum mixed in different proportions are shown graphically in Figure 4-11. From Figure 4-11 it is seen that addition of CaO along with gypsum to Ottumwa fly ash imparts significantly high strengths. The addition of CaO along with gypsum to Ottumwa fly ash, has an effect of increasing the calcium ion concentration in solution. Ettringite formation is known to be enhanced with the availability of a high calcium concentration in solution. This results in increased formation of ettringite compared to the earlier mixture of Ottumwa fly ash and gypsum alone. Moreover, the degree to which alumina residing in the glassy phase in fly ash reacts with sulfate to form ettringite is directly related to the CaO content (10). The effect of this should be to cause a further increase in the amount of ettringite formed in the above mixture.

In order to verify the high amounts of ettringite formed in this high strength mixture of Ottumwa fly ash, CaO and gypsum, X-ray diffraction tests were carried out on this mixture. The X-ray diffractogram is shown in Figure A-4 in the Appendix.

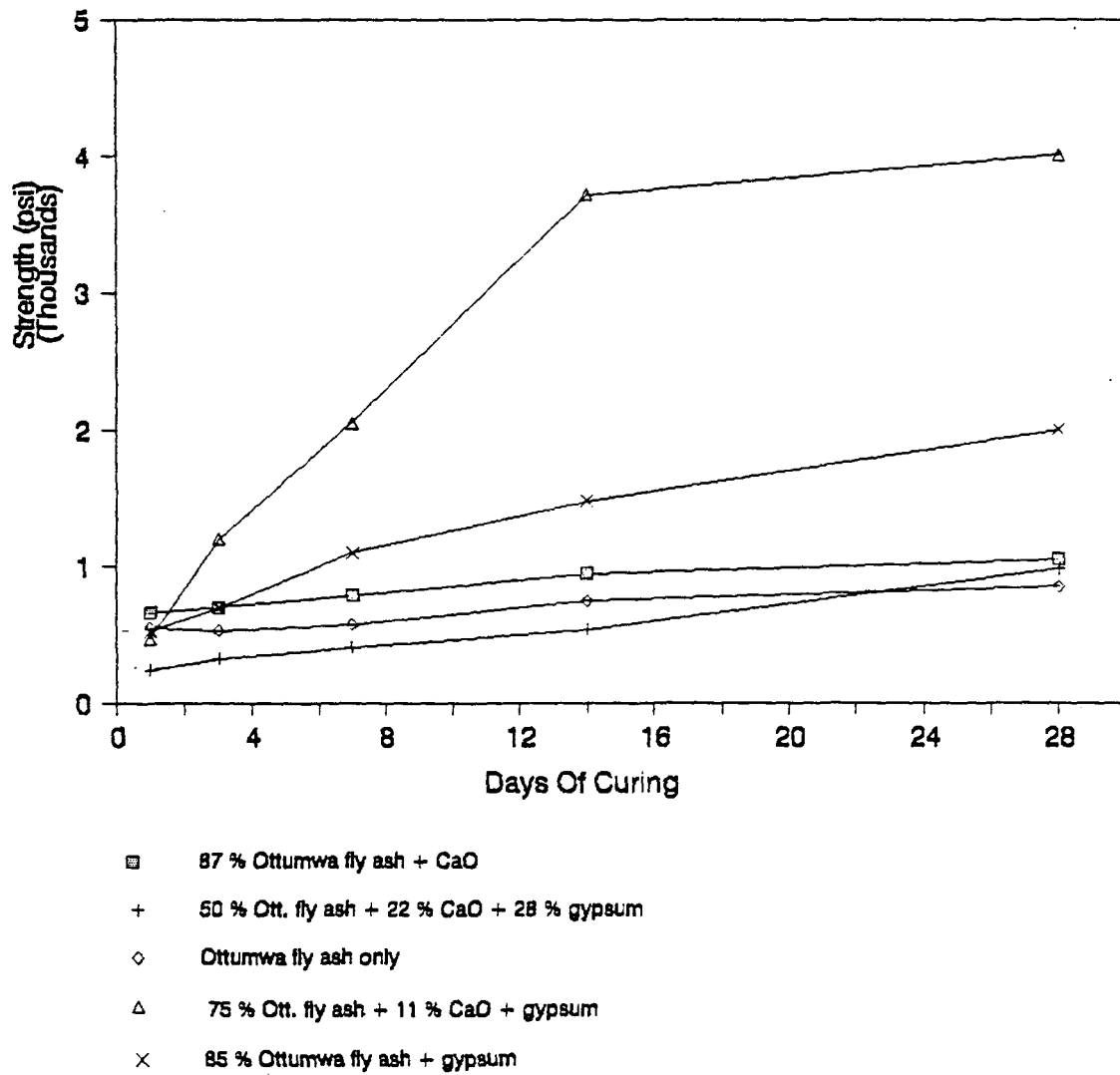


Figure 4-11: Crushing strength developed by hydrated mixtures of gypsum, CaO and Ottumwa fly ash



The large amount of ettringite formed in this mixture as proposed is evident from the diffractogram. Substitution of sulphate ions in ettringite by silicate ions is indicated as a probability by a minor shift in diffraction peaks of ettringite. Partial conversion of ettringite to the AFm phase is also seen. An interesting feature noted is that, this hydrated mixture of Ottumwa fly ash, CaO and gypsum, having supposedly large amount of ettringite formed in it develops strengths more than that developed in Ottumwa fly ash/AFBC residue mixtures. As the mixtures of Ottumwa fly ash and AFBC residue have similar components as this mixture, the high strengths developed by them can also be attributed to formation of ettringite. The presence of large amounts of ettringite in mixtures of Ottumwa fly ash and AFBC residue exhibiting high strengths was confirmed by X-ray diffraction techniques earlier. The slightly lower strengths in Ottumwa fly ash/AFBC residue mixtures as compared to Ottumwa fly ash, CaO and gypsum mixtures may be due to the diluting effect of other inert components of AFBC residue. From Figure 4-11, it is also seen that there is an optimum proportion of Ottumwa fly ash, CaO, and gypsum that results in significantly high strength. Increasing the quantities of any one of the compounds disproportionately drastically reduces the strength. This is expected since increase in any one compound reduces the net percentage of the other compounds in the mixture thus limiting their availability for formation of ettringite. An optimum percentage of the three materials, Ottumwa fly ash, CaO, gypsum results in maximum ettringite formation causing high strengths. As CaO and gypsum are components of AFBC residue, the above results also explain the optimum proportion of Ottumwa fly ash and AFBC residue which result in high ettringite formation and high

crushing strengths. Ettringite formation requires availability of aluminum. The large amount of ettringite formed in the mixtures of Ottumwa fly ash, CaO and gypsum, indicate the availability of large reserves of aluminum. It is evident that Ottumwa fly ash can be the only source of aluminum in the system as CaO and gypsum cannot provide the aluminum. It can be inferred that the aluminum residing in the glassy phase, is mobilized in solution and is responsible for the formation of ettringite. It was proposed earlier that the source of aluminum in mixtures of Ottumwa fly ash and AFBC residue is either the glass in Ottumwa fly ash or the alumino-silicates in AFBC residue. The large amount of ettringite formed in the above mixture of Ottumwa fly ash, CaO and gypsum in absence of alumino-silicates from AFBC residue clearly indicate that the major source of aluminum is the glassy phase in Ottumwa fly ash. The low strengths developed by the mixture of Ottumwa fly ash and CaO as seen in Figure 4-11, eliminates the possibility of a lime-pozzolanic reaction to cause the high strengths in the Ottumwa fly ash/AFBC residue mixtures.

Formation of ettringite is known to retard strength development of portland cement. This suggests that the strength retardation phenomenon in hydrated mixtures of Ottumwa fly ash and AFBC residue may also be associated with ettringite formation.

### Morphology

Crystalline chemical compounds manifest themselves in strength development by virtue of their morphology. The cementing ability of gypsum arises from its intermingling blade like crystals. It was suggested that morphological differences

associated with different chemical compounds, may be the root cause of the significant strength differences between mixtures. A scanning electron microscope (SEM) is the non-destructive apparatus used to determine morphology of a material. In this an electron beam is focussed on the specimen under high vacuum, and a back-scattered electron image is obtained on the screen at desired magnification.

Morphology exhibited by three proportions of the mixture of Ottumwa fly ash and AFBC residue containing 20%, 45% and 75% AFBC residue, after 28 days of curing was compared using SEM. The specimens were analyzed along a failure surface. The specimen surfaces were coated with gold and carefully scanned at different levels of magnification. Photographs were taken of any distinguishing features that were observed. Chemical composition of different crystals seen, was determined using EDS analysis.

The morphology of the three proportions observed in a SEM is described below.

Specimen 1: (80% Ottumwa fly ash + 20% AFBC residue) The compounds formed due to hydration of Ottumwa fly ash alone, predominate in this specimen. Numerous unhydrated fly ash spheres were still seen to be present in the specimen. This is clearly seen in Figure 4-12. These glassy spheres must be rich in silica, which is resistant to chemical attack. An amorphous matrix embedding these unhydrated fly ash spheres was observed at many locations. Its composition was estimated by an EDS analysis to be CASH. Needle-like ettringite crystals were also seen at a few locations. They are mostly seen to be formed on surfaces of fly ash spheres. Figure 4-13 is an interesting micrograph showing the transition from ettringite to platy crystals of mono sulfoaluminate. This indicates the depletion of gypsum in the mixture. Formation of

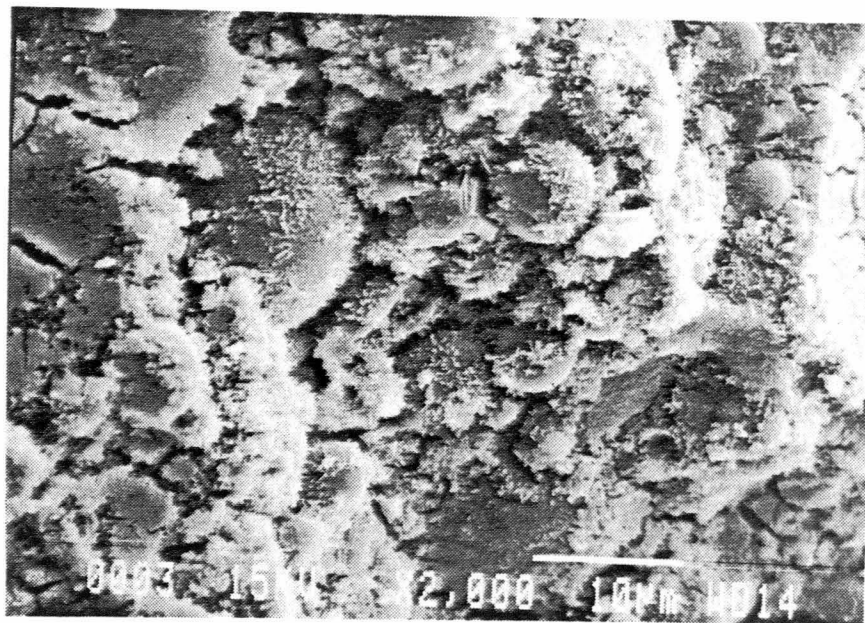


Figure 4-12: Unhydrated Ottumwa fly ash spheres in mixture having 20 % AFBC residue

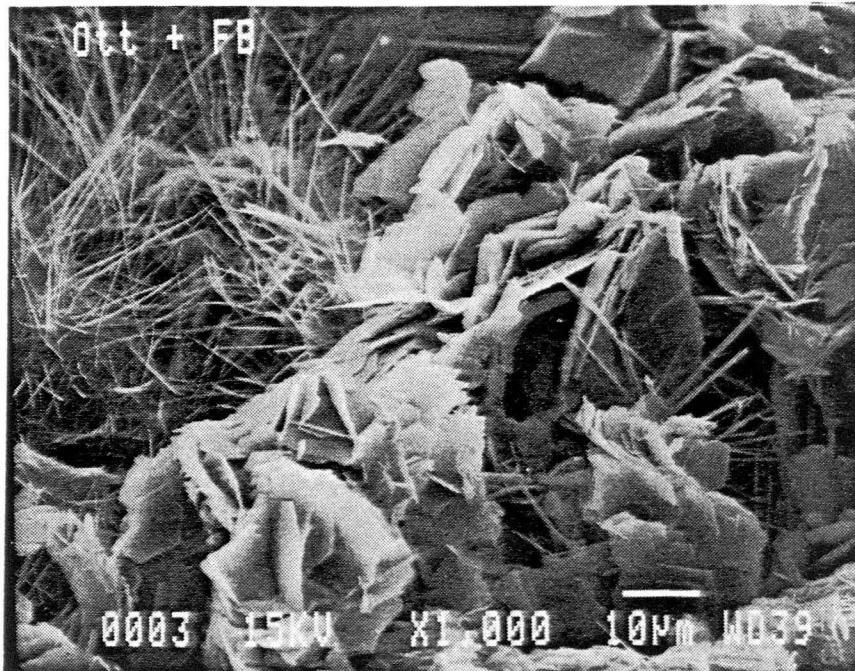


Figure 4-13: Transition from ettringite to mon-sulfo-aluminate in the mixture having 20% AFBC residue (Bob Lapke, 1991)

ettringite crystals away from fly ash spheres suggest a through-solution reaction mechanism.

Specimen 2 (55% Ottumwa fly ash + 45% AFBC residue) Figure 4-14 shows the typical morphology of the mixture as seen under the SEM. Other than the needle-like crystals of ettringite seen scattered throughout the specimen, several other distinct features were observed. An uniform matrix was clearly seen at many locations. An EDS analysis indicated the matrix to be CASH and CSH at some locations. A typical EDS spectrum of this matrix material is shown in Figure A-5a in the appendix.  $C_2ASH_8$  (Stratlingite) and CSH have been shown to have strength giving properties. A few silica rich, spherical particles of unhydrated Ottumwa fly ash having diameters ranging to a maximum of 15 micro-meters were scattered throughout the specimen. But by far the most frequently seen crystals are needle-like crystals scattered throughout the surface. They are mostly formed on surfaces of hydrated or partially hydrated fly ash spheres. These crystals were identified by an EDS analysis to be ettringite. These ettringite needles were seen to develop radially outwards from the grains. These intersect and combine with other crystals on adjacent grains forming a network. These ettringite crystals are shown in Figure 4-15. The ettringite crystals are shown at a greater magnification in Figure 4-16. An EDS analysis carried out on several ettringite crystals show the presence of silicon. Incorporation of silicate ions in the needle like crystals of ettringite was indicated by X-ray diffraction results. A typical EDS spectrum of silicate ettringite is shown on Figure A-5b in the Appendix. However, the silicate ions detected by EDS analysis may be present underlying the ettringite crystals. The electron beam

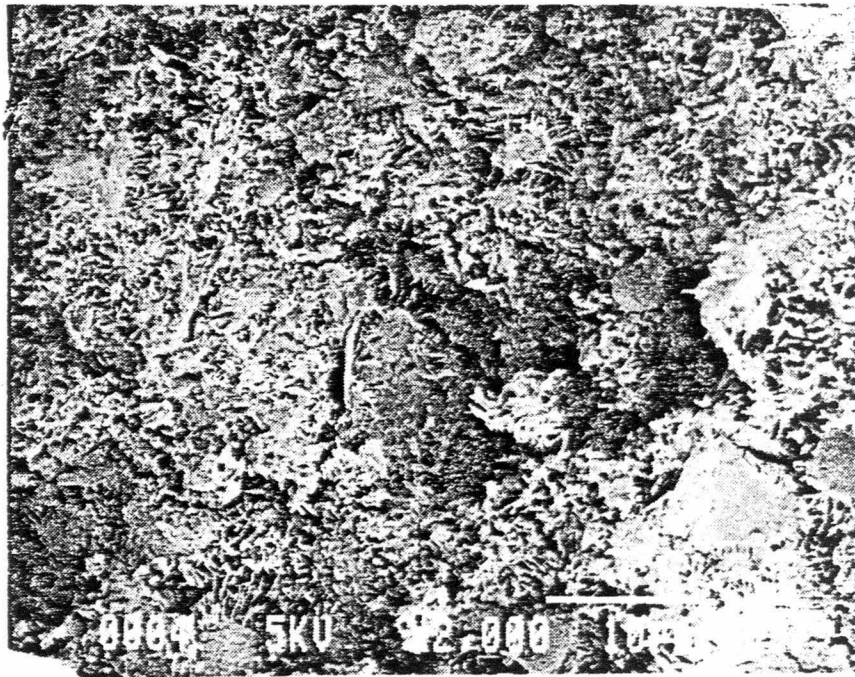


Figure 4-14: Typical morphology of hydrated mixture of 55 % Ottumwa fly ash and 45% AFBC residue

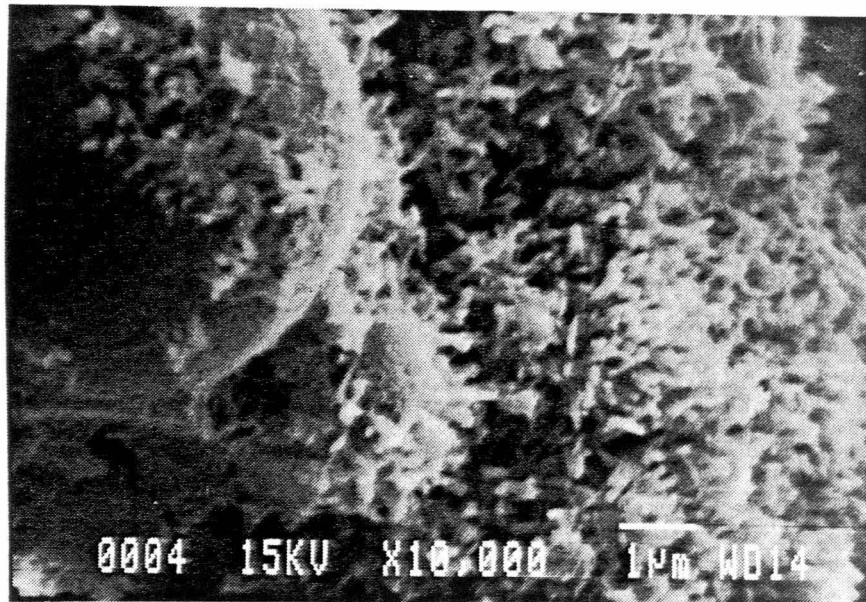


Figure 4-15: Needle crystals of ettringite

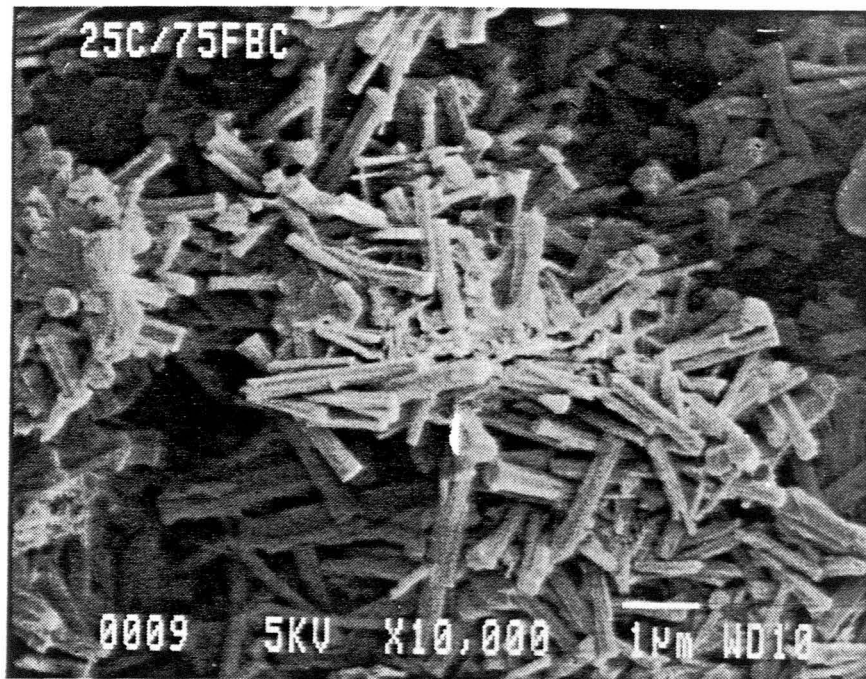


Figure 4-16: Ettringite at greater magnification



utilized by the EDS analysis could have easily passed through the small ettringite crystals and picked up traces of silicate from beneath the ettringite crystals. To resolve this difficulty, a needle crystal of ettringite lying at the edge of the specimen and protruding beyond the specimen was selected. This eliminates the presence of any underlying chemical compounds which might alter the EDS spectrum of ettringite. The EDS spectrum of one single ettringite crystal is shown in Figure A-5c in the Appendix. The carbon peak is due to the carbon stub on the which the specimen was resting. This EDS spectrum also indicates the presence of silicate ions in ettringite. However, the silicate ions may be present on the surface of ettringite rather than within it. But in any case this observation further reinforced the earlier theory of silicate ion substitution in ettringite on depletion of gypsum. The ettringite crystals seen in this binder are much smaller and thinner than the usual ettringite crystals reported in hydrated Portland cement. The smaller size is attributed to the presence of lime in the system, which is known to reduce the size of ettringite crystals (12). This may explain the retarding action observed in mixtures having higher amounts of AFBC residue, as smaller crystals of ettringite would be more efficient in covering the hydrating grains. Clusters of these needle crystals of ettringite were also seen throughout the specimen. The frequent ettringite clusters seen throughout the specimen clearly established the large amount of ettringite present in the mixture. This is consistent with X-ray diffraction results and results from chemical tests obtained earlier. The clusters of ettringite crystals were seen to form in pore spaces close to partially hydrated fly ash spheres. Their close proximity to the fly ash spheres suggests that aluminate required for their formation may have

leached from fly ash spheres. The aluminate leached from aluminosilicate glass in fly ash may have reacted with calcium hydroxide and gypsum in the pore solution, resulting in subsequent formation of ettringite. This is further supported by the observation of severely etched and dissolved fly ash spheres. The possible leaching of aluminate from these spheres may have left them in this condition. Despite the severe etching and dissolution of fly ash spheres, they retain their original spherical form and structure. In many places these severely etched and dissolved fly ash spheres were seen to be strongly connected to the binder matrix. They appear to reinforce the binder matrix. The micro-reinforcing provided by these skeletal fly ash spheres, as proposed by Matex Consultants (1) appears to be true. Very few thick plates of gypsum were detected. This indicates that gypsum has been consumed in the formation of ettringite. Hexagonal, platy crystals of mono sulfoaluminate were also seen occasionally. EDS on these crystal is shown on Figure A-5d in the Appendix. These must have formed from ettringite on depletion of gypsum. These mono-sulfo-aluminate crystals are shown on Figure 4-17. Few crystals of calcium hydroxide were observed.

Specimen 3 (25% Ottumwa fly ash + 75% AFBC residue) The morphology of this specimen is seen to be significantly different from the earlier specimens. Spherical particles of fly ash were absent, while many small thick plates of gypsum were observed. This was expected as this specimen has only 25% Ottumwa fly ash and a large percentage of AFBC residue (75%), which is loaded with anhydrous calcium sulphate ( $\text{CaSO}_4$  anhydrite). EDS analysis carried out on these gypsum crystals is shown on Figure A-5e in the Appendix. The matrix material in this case was seen to be much more amorphous

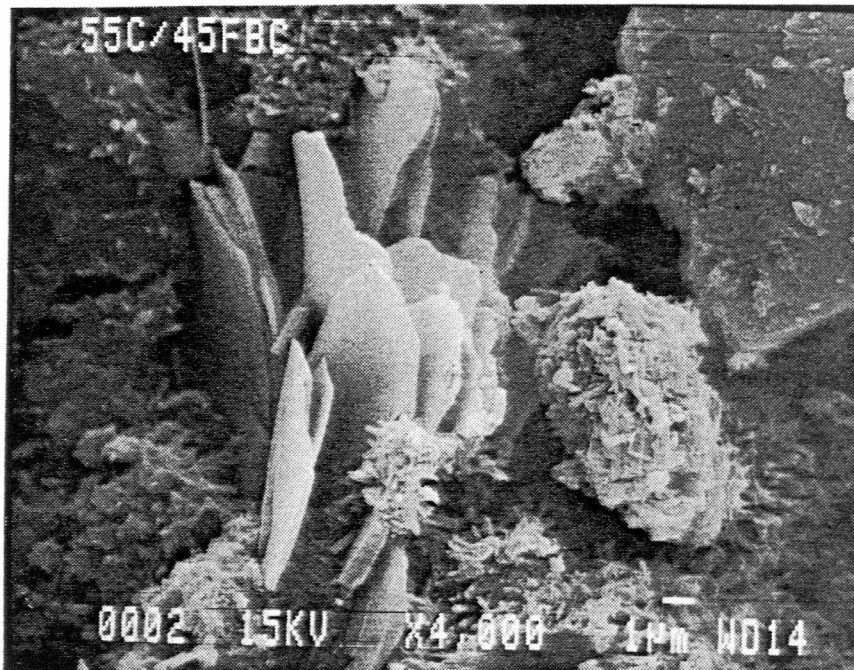


Figure 4-17: Platy crystals of mono sulfo-aluminate

than the earlier mixture. The EDS analysis showed this to be composed of CASH at certain locations. This composition as obtained from EDS is shown in Figure A-5f in the Appendix. Needle-like crystals of ettringite were seen concentrated at certain locations. However, no presence of silicate ions was detected by an EDS analysis in most of the ettringite crystals. Even the crystals of mono sulfoaluminate were absent in this specimen. However, this was expected as the abundant supply of gypsum does not facilitate the conversion of ettringite to mono sulfoaluminate.

The above observations on the SEM were consistent with earlier findings.

#### Thermal gravimetric analysis (TGA)

When solid substances are heated in an inert atmosphere, resultant reactions form new phases. This is accompanied by weight changes and is the basis for TGA. In TGA the weight losses exhibited by a sample heated in any required atmosphere can be measured and from this the compounds present in the sample can be determined.

Procedure Two proportions of the mixture of Ottumwa fly ash and AFBC residue, having 35% and 75% AFBC residue respectively were selected to be tested in a TGA apparatus. It was expected that this would give an indication of the chemical compounds formed in the mixtures. The TG analysis was carried out after 3 and 28 days of curing, so that an idea of the chemical changes occurring in the mixtures could also be evaluated. The TGA apparatus has a capability of being heated to a maximum of 1100°C. The two samples were heated in air and the weight losses exhibited by them was measured.

Results and analysis The TGA results for the above two proportions after 3 and 28 days of curing are shown in Figures A-6 and A-7 respectively. The differential thermogravimetric (DTG) graphs superimposed on the same plots is the derivative of the TGA graphs. DTG graphs show the change in rate of weight loss as distinct sharp peaks which help in identifying the exact temperature at which the weight loss occurs. The initial weight loss seen in the sample having 75% AFBC residue cured for 3 days is due to drying or evaporation of the moisture still retained in the pores of the mixture. The wet nature of this sample was evident visually, before being tested in the TGA apparatus.

The 28 day old samples of both proportions show essentially similar TGA curves. Only one major peak was observed in the samples. This is attributed to the loosely held water in the AFt phase and/or gypsum. The mixture having 35% AFBC residue does not exhibit any drastic change in its TGA graphs from 3 to 28 days of curing. However, a major change was seen in the TGA curves for the mixture having 75% AFBC residue from 3 days to 28 days. The calcium carbonate peak shown by this proportion after 3 days of curing, at about 650°C to 750°C, was absent in the TGA results of the same mixture after 28 days of curing. The disappearing of this peak implies that the initially present calcium carbonate is consumed during the hydration process. This depletion of carbonate may be due to the partial substitution of sulfate ions in ettringite by carbonate ions. The presence of calcium carbonate was seen to be minimal in the sample having 35% AFBC residue even at 3 days as inferred from the small peak in the DTG graph.

## **Agglomeration Process and Agglomerate Properties**

The main objective of the entire research was to utilize agglomerates of Class C fly ash and AFBC residue as aggregates in highway base and sub-base systems. Following investigation into the physical and chemical properties of the mixture, efforts were then directed toward actually preparing the agglomerates and carrying out laboratory tests to determine their suitability for use in actual field conditions.

The agglomeration process was studied and the agglomerates were prepared in three different proportions. Physical and chemical properties of agglomerates were investigated. The durability characteristics of the agglomerates, including: (1) abrasion resistance; (2) resistance to freeze-thaw; (3) volume expansions; (4) sulphate attack and, (5) leachability were also evaluated.

### Agglomeration process

Agglomeration of Ottumwa fly ash and AFBC residue was accomplished using a bench scale rotary pan agglomerator manufactured by Mars Mineral Corporation, model no. DP 14" Agglomiser. This consists of a stainless steel, shallow rotating pan having a depth of 15.5 cm and an inside pan diameter of 36 cm. The inclination of the pan could be varied from 35° to 90° with the horizontal and its rotational speed could be varied from 0 to 50 rpm. Raw material was fed into the rotating pan slowly but continuously using a vibratory feeder crafted by Syntron FMC corporation (Model FTOC). It was

observed that water content, feed rate and rotational speed had a high influence on particle size of the agglomerates obtained. The agglomeration process was sensitive to the water feed rate and to the location where water and the raw material was fed to the pan agglomerator. Water content and feed rate, were seen to be proportional to the particle size obtained. No combination of the variables yielded uniformly graded agglomerates. However, the maximum size of the agglomerates obtained could be controlled by exercising proper control over the variables affecting the process as specified above. These variables differed for different proportions of the AFBC residue/Ottumwa fly ash mixture. The effect of varying the feed rate and the rotational speed of the pan on the agglomeration process was studied. The settings that resulted in well graded agglomerates of the mixture of Ottumwa fly ash/AFBC residue for a fixed water content were determined. The rotational speed of the disc pan was selected so that the motion of the material in the pan closely approximated that shown in Figure 4-18. The feed rate and the rotational speed of the pan was kept constant and the water content was varied to obtain the required particle size of agglomerates. Water was sprayed manually on the raw material with a calibrated spray bottle. The calibrations served to measure the water content used in the agglomeration process. Water was sprayed alternately at two locations periodically as shown in Figure 4-18. Brook (9) has reported location 2 to have a slight advantage over location 1 as it results in close contact of moist particles. Care was taken to ensure that the water did not fall on the pan surface as this would result in adhering of the material to the surface. A hand trowel was used to scrape the material adhering to the pan surface.

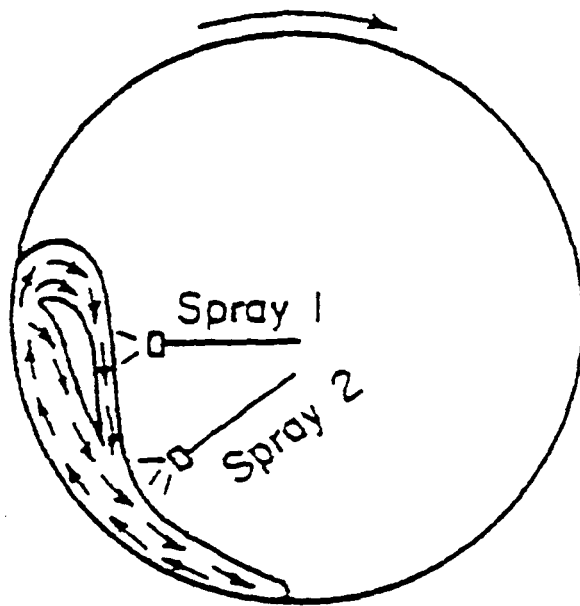


Figure 4-18: Motion of raw material in agglomerator with water feed locations

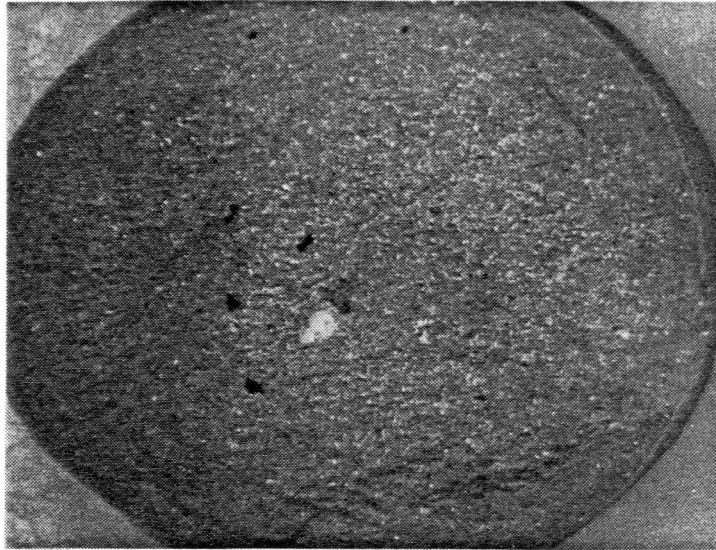


### Morphology of the agglomerates

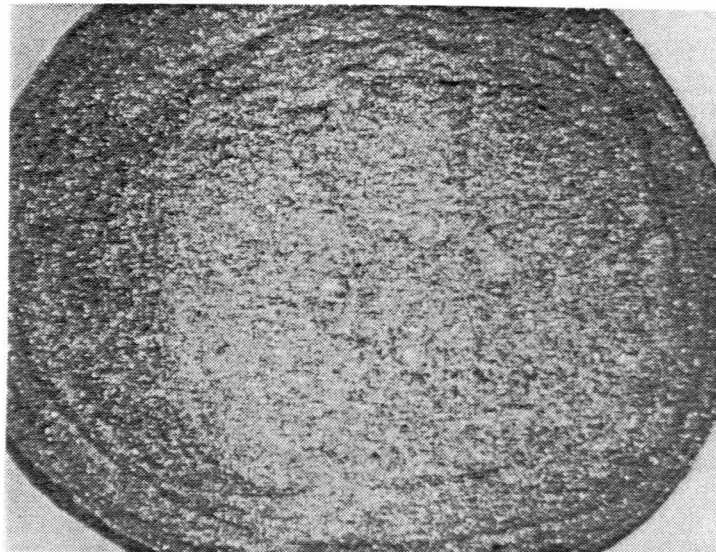
The morphology of agglomerates of Ottumwa fly ash and AFBC residue in two proportions having 35% and 75% AFBC residue, cured for 28 days were studied under a SEM. The agglomerate samples were observed along their failure surface. A silver coating was used on these samples. An EDS analysis was carried out on any distinguishing crystals.

The agglomerates of Ottumwa fly ash and AFBC residue having 35% and 75% AFBC residue and a size of about 3/4 " are shown in Figures 4-19. Dark circular rings are seen at the edges of the agglomerate. Few circular rings are visible even in the interior of the agglomerate having 75% AFBC residue. These rings seem to encapsulate the remaining material to form the agglomerates. These dark rings are either relatively well hydrated layers or an accumulation of AFBC residue which is relatively dark in color.

Elemental distribution at center and edge of agglomerates To determine whether there is any preferential accumulation of AFBC residue at the outer edges, elemental dot mapping was carried out at the edges and at the center of the agglomerate having 35% AFBC residue. This was done using EDS by focussing the electron beam on a larger area. Concentrations of sulfur would imply an accumulation of AFBC residue. The dot mapping showing relative distribution of elements at the edges on the dark rim and at the center of the agglomerate are shown in Figures 4-20a and 4-20b respectively. The elemental distribution was seen to be uniform and no specific pattern is detected. The distribution of sulfur was not seen to change from the edge to the center.



(a)



(b)

Figure 4-19: Agglomerate of Ottumwa fly ash and AFBC residue showing dark circular rings; (a) 65% Ottumwa fly ash and 35% AFBC residue; (b) 25% Ottumwa fly ash and 75% AFBC residue

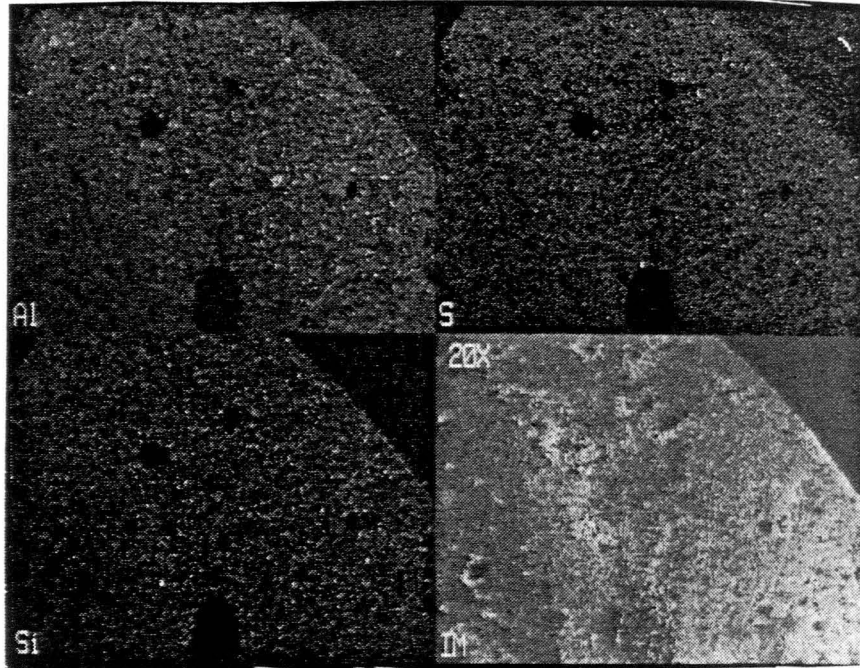


Figure 4-20a: Elemental distribution at edge of agglomerate having 35% AFBC residue

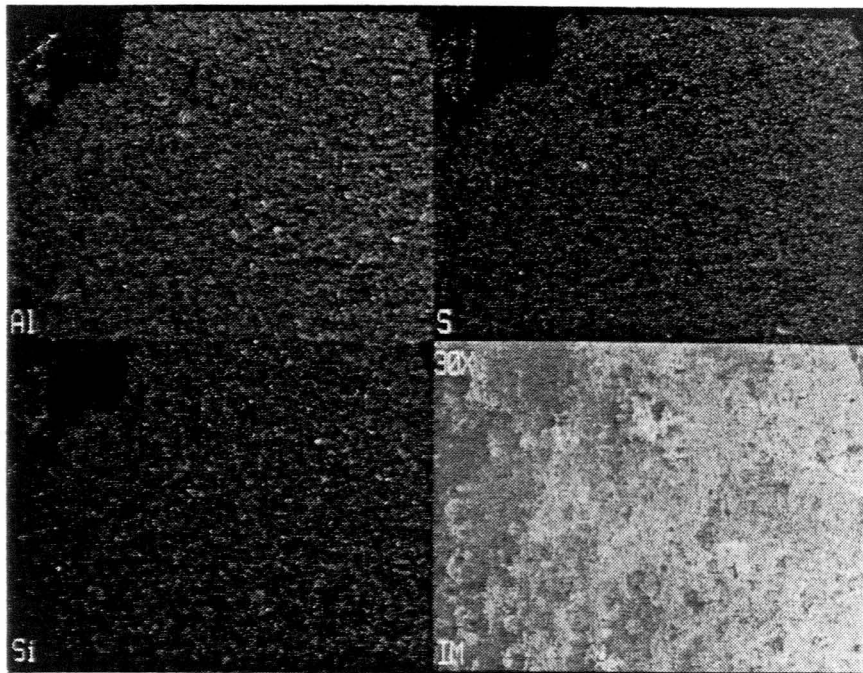


Figure 4-20b: Elemental distribution at center of agglomerate having 75% AFBC residue

The dark outer rim at the edges of the agglomerate was then concluded to be a relatively well hydrated layer which encapsulates the remaining relatively unhydrated particles to form agglomerates. The rings of hydrated layers seen in the interior of the agglomerates must be due to covering of already formed pellets by raw material fed into the agglomerator.

Micro-structure The agglomerate having 35% AFBC residue observed under a SEM showed essentially similar morphology as the hydrated mixture of the same proportion analyzed earlier. A major difference between the two was the large number of unhydrated fly ash spheres in the agglomerates. Most of the raw mixture used in the agglomeration process has remained unhydrated owing to the lesser quantities of water used in agglomeration. The edge of the agglomerate shows an absence of unhydrated fly ash spheres. This confirms the presence of a well hydrated layer encapsulating relatively raw material in the agglomerate. The compounds present in the paste of the same mixture were also detected in the agglomerates. Ettringite crystals were seen to develop mostly on the surfaces of fly ash spheres in the agglomerates. This is clearly seen in Figure 4-21a. Presence of silicon ions in ettringite was detected by an EDS analysis. However, the silicon ions located around the ettringite crystals may have contributed to the ettringite spectrum. At a few locations a uniform matrix was seen, embedding the fly ash spheres. One such location is shown in Figure 4-21b. The matrix has a composition CASH, as determined by the EDS analysis. One interesting observation was the presence of large number of intermingling thick plates of gypsum at the edges of the agglomerate. Figure 4-21c is a micrograph showing gypsum crystals at the edge. In contrast, the

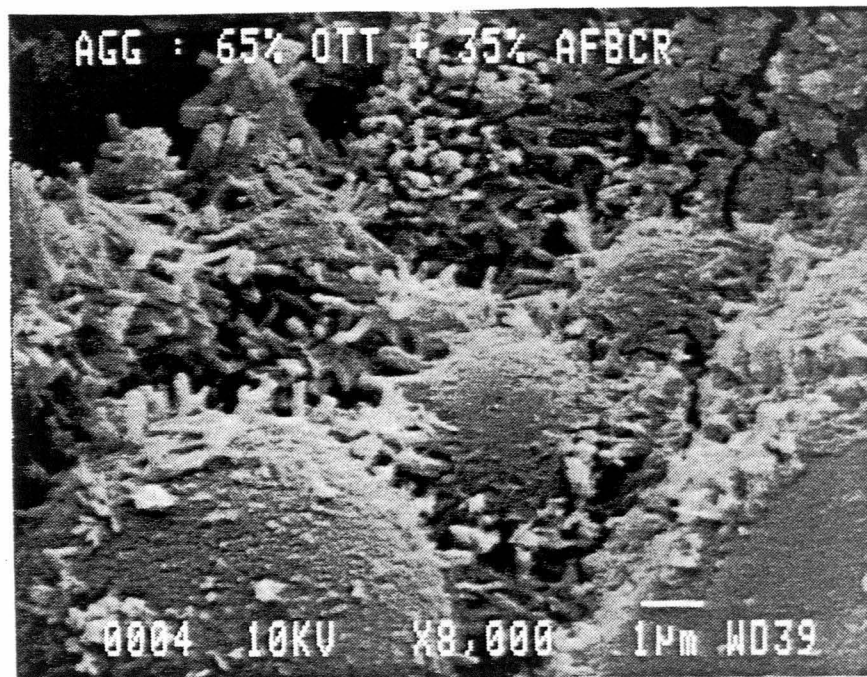


Figure 4-21a: Ettringite crystals formed on surfaces of fly ash spheres in agglomerates having 35% AFBC residue

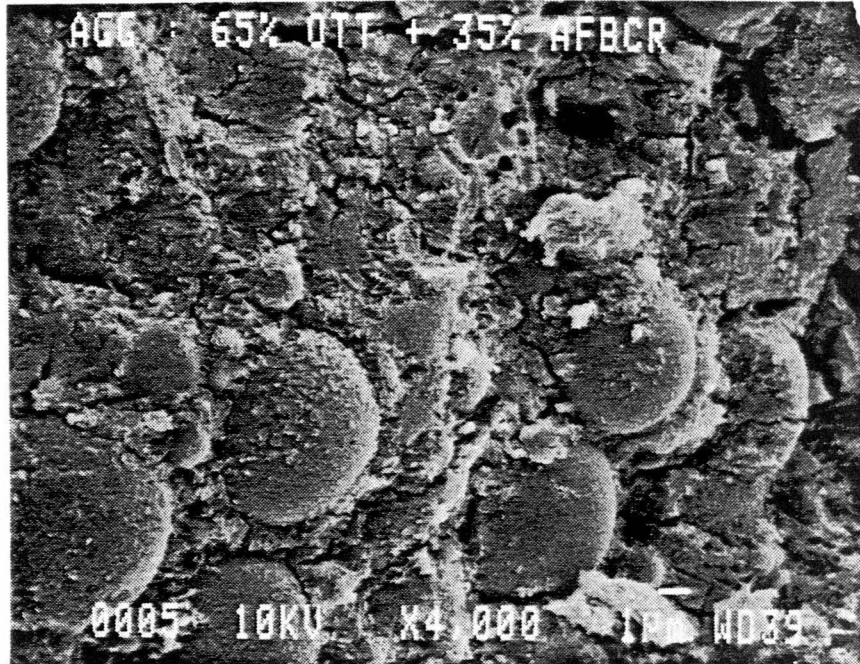


Figure 4-21b: Uniform massive matrix having imbedded fly ash spheres in agglomerates having 35% AFBC residue

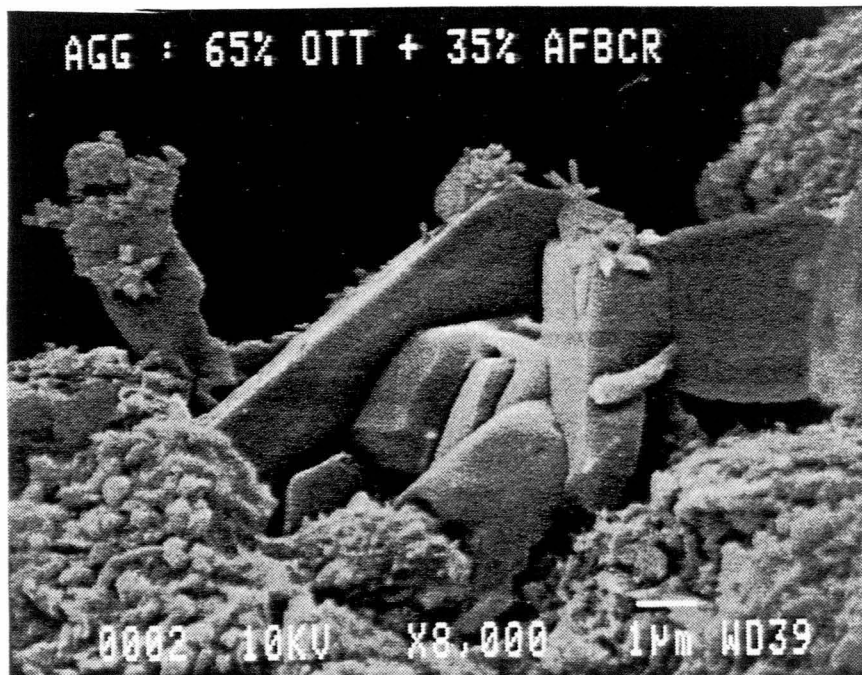


Figure 4-21c: Thick plates of gypsum at edge of agglomerates

presence of gypsum crystals was negligible in the interior of the agglomerate. This encapsulating the remaining material indicates that the gypsum crystals play a major role in encapsulating the raw mixture into agglomerates. Other than gypsum crystals an amorphous mass was seen to be present at the edges of the agglomerate. This is determined to have a composition of CASH.

Line scan from center to edge of agglomerate A line scan showing the elemental distribution at 100 points at equal intervals from the center to the edge of the agglomerate was plotted. The purpose of this was to study transition of elemental distribution from the edges to the center of the agglomerate cross-section. Distribution of sulfate ions was of special interest as it is known to originate mostly from the AFBC residue. The distribution of sulfate ions might also provide an indication about the location of AFBC residue in the agglomerates. From this, the role played by AFBC residue in the agglomeration process can also be evaluated. With the help of this, quantitative aspects of distribution of elements from the center to the edge of the agglomerate could be studied. Calculating the ratios of counts of different elements at every point might help evaluate the chemical compounds formed at the different points from the center to the edge of the agglomerate.

The line scan showing elemental concentrations at 100 points at equal intervals, from the center to the edge of the agglomerate is shown in Figure A-8a in the appendix. Calcium is clearly seen to dominate the composition chart. Aluminum and silicon also occur in high concentrations. No specific pattern of elemental distribution is indicated. A few locations show a very high concentration of silicon (almost up to 80%). These

must be quartz particles or silica rich glassy spheres of Ottumwa fly ash. A striking correlation was seen between aluminum and silicon concentrations. Their concentrations were seen to change proportionately. This is clearly seen in Figure A-8b in the appendix, where only the concentration of these two elements at every point are shown. To eliminate effect of voids on the agglomerate surface, where concentration of all elements reduce proportionately and to better perceive the composition changes, ratios of elements were plotted. However, these results must be viewed with caution as the penetrating electron beam used in the analysis may be picking up traces from underlying elements also, thus altering the composition of the surface features. Ratios of the dominating elements at every point are shown on Figures A-8c to A-8g. The ratio of silicon to aluminum is seen to be constant at 1.3, except for minor fluctuations. This suggests the presence of an alumino-silicate hydrate or clay minerals in coal which are still preserved in the coal combustion residues. This also supplements the theory of silicate substitution in ettringite. Even at places where the amount of calcium increases significantly the silicon to aluminum ratio stays the same. The aluminum to sulfur ratio is also seen to fluctuate narrowly between 0.6 and 1.6, except at a few points where it is seen to increase significantly. This suggests the presence of ettringite which has a aluminum to sulfur molar ratio of 1. Calcium is seen to be by far the most variable of all these elements. The ratios of calcium and the other elements also show wide fluctuations. the calcium silicon ratio generally varies between 0 and 3 except for few high calcium points. The ratio of calcium to sulfur mostly varies between 2 and 3.5. However, many points having lower and higher calcium-sulfur ratios are also seen.



Calcium and sulfur exist together in the form of mostly ettringite and gypsum having calcium to sulphur molar ratio at 2 and 1 respectively. The observed calcium to sulfur ratios indicate the absence of gypsum and formation of ettringite. The higher calcium to sulphur ratios may correspond to an AFm phase or silicate substituted ettringite. All the elements exist in small amounts at points showing very high calcium concentrations. This implies the presence of crystals of calcium hydroxide or calcium carbonate at those locations.

#### Pore volume

The pore size distribution of agglomerates of Ottumwa fly ash and AFBC residue having 25 % and 75 % AFBC residue was determined using a mercury porosimetry. The intruded pore volume in the agglomerates having 25% and 75% AFBC residue are shown in Figures 4-22a and 4-22b. The pore volume of the agglomerates is an important factor which would dictate their resistance to freeze-thaw damage and thus their durability. The cumulative pore volume in the agglomerates having 25% AFBC residue is seen to be much lower than that in the agglomerates having 75% AFBC residue. This may be due to the lower water content used by the agglomerates containing 25% AFBC residue. It is also noted that the pore volume in the agglomerates is also much lower than the pore volume in the hydrated paste of the same proportions as described earlier in the same chapter (page 49). This is also due to the reduced water content used in the agglomeration process.

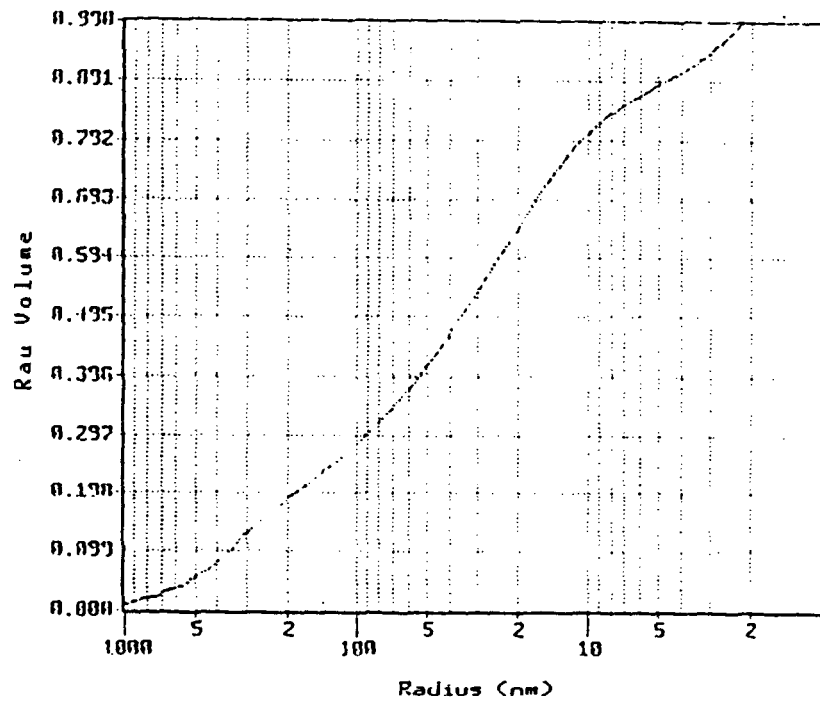


Figure 4-22a: Cumulative pore volume in agglomerate having 25% AFBC residue

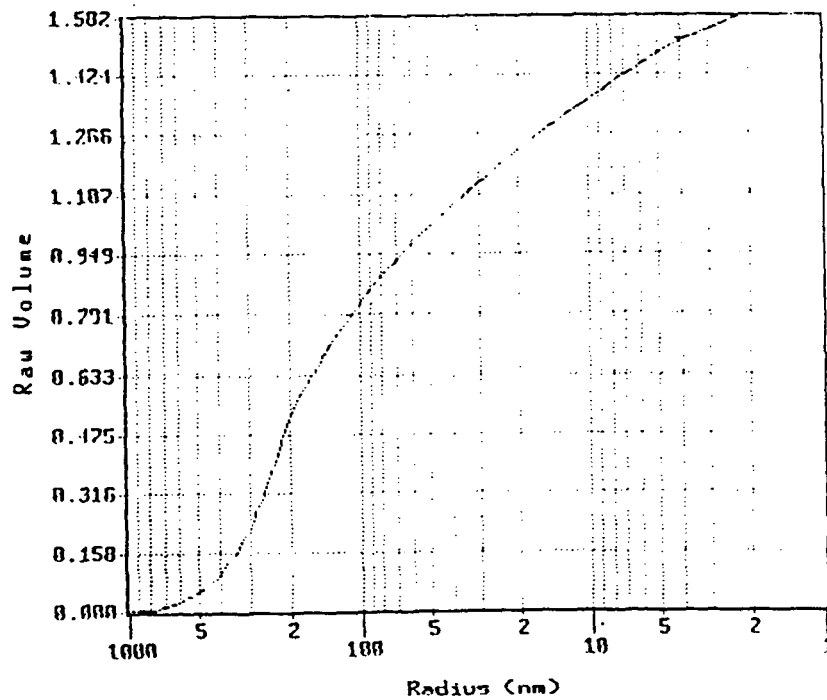


Figure 4-22b: Cumulative pore volume in agglomerates having 75% AFBC residue

The agglomerates of Ottumwa fly ash and AFBC residue in three different proportions having 25%, 45%, and 75% AFBC residue and having a maximum particle size of 3/4" were prepared in the pan agglomerator to evaluate their durability properties. Water contents used to agglomerate different proportions of Ottumwa fly ash and AFBC residue to obtain a maximum particle size of about 3/4" are given in Table 4-7.

**Table 4-7: Water content for different proportions of agglomerates.**

<b>% Ottumwa fly ash</b>	<b>% AFBC residue</b>	<b>% Water content</b>
75	25	18
55	45	23
25	75	25

The particle size gradation used for testing durability of the agglomerate proportions is shown in Table 4-8.

**Table 4-8: Particle size gradation of agglomerates for durability testing.**

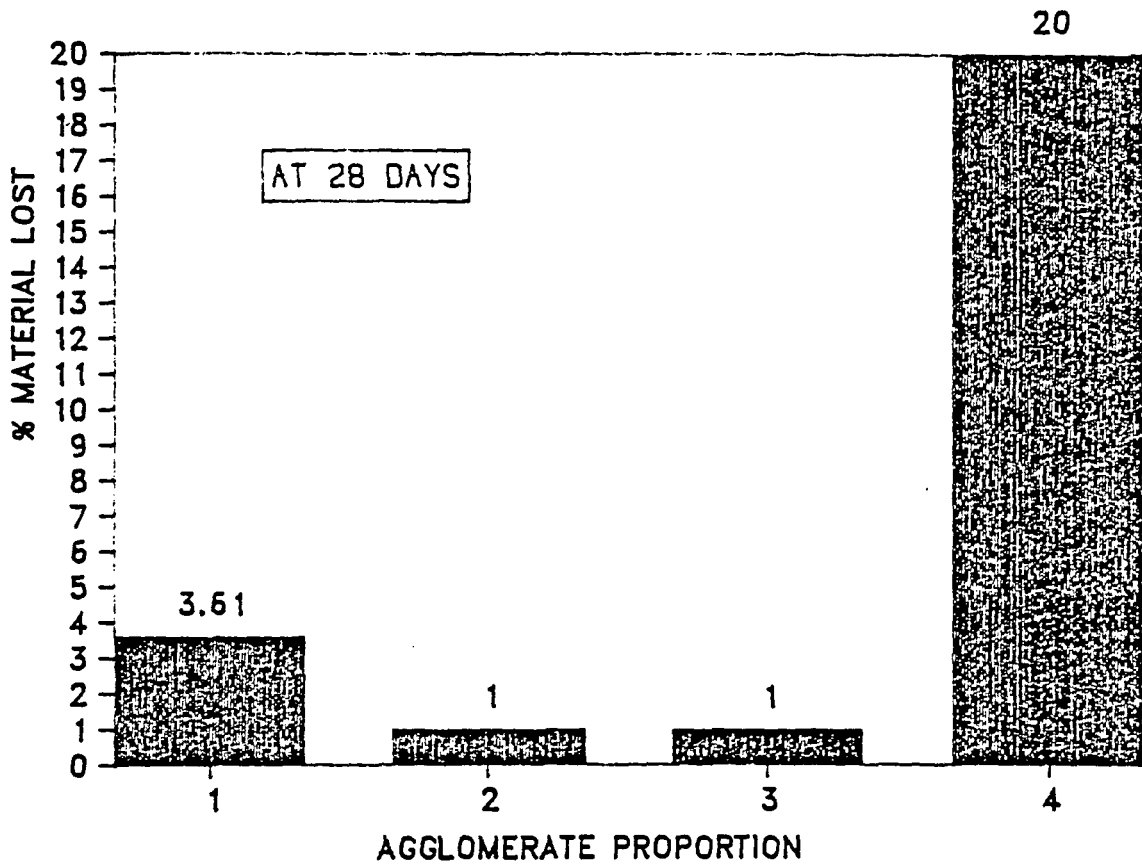
<b>Size</b>	<b>% Wt. retained</b>
3/4 "	31.25
5/8 "	27.08
1/2 "	22.91
3/8 "	16.66
0.187"	2.08

### Abrasion resistance

Adequate resistance to abrasion is one of the main consideration for use of aggregates in road base systems. The main objective of this study was to determine the relative resistance to abrasion of the three agglomerate proportions compared to limestone aggregates from Martin Marietta's Ames mine.

Procedure To evaluate the resistance to abrasion, agglomerates of the three proportions cured for 28 days, having similar size gradation retained over sieve # 4, were subjected to abrasion by a charge of steel spheres in a rotating drum for a period of 12 hours. The abrasion loss was expressed as the percent material by weight passing through sieve # 4, after the abrasion test. The particle size gradation used is given in Table 3-7. Material lost by each proportion was compared to the loss of limestone aggregates of a similar particle size gradation.

Results and analysis Figure 4-23 compares the material lost due to abrasion in the three agglomerate proportions and limestone aggregates. The material lost is actually the percent material by weight passing through sieve # 4 after subjecting the aggregates to abrasion. It is clearly seen that the abrasion was not very effective in altering the particle sizes of the agglomerates. The material loss in all the three agglomerate proportions is seen to be almost the same. The small material loss is believed to be only due to abrasion of the dry loosely held grains on the surface of the agglomerates. Differences in material lost between the three agglomerate proportions is too small to draw conclusions about their relative resistance to abrasion. All the three agglomerate proportions have a much lower material loss than limestone aggregates, indicating higher abrasion resistance.



Agglomerate proportion 1: 75 % Off. fly ash + 25 % AFBC residue  
 Agglomerate proportion 2: 55 % Off. fly ash + 45 % AFBC residue  
 Agglomerate proportion 3: 25 % Off. fly ash + 75 % AFBC residue  
 Agglomerate proportion 4: Limestone aggregates

Figure 4-23: Abrasion resistance of agglomerates, relative to limestone aggregates

The limestone aggregates were seen to have suffered a drastic reduction in particle size and were severely abraded compared to all the three proportions of agglomerates.

However, the higher material loss in limestone aggregates may be in some part due to their angular shape in contrast to spherical shape of the agglomerates.

### Freeze-thaw resistance

All aggregates to be used in highway base systems in Iowa will be subjected to numerous cycles of freeze and thaw over the years due to its extreme climate. This tends to break down the aggregates, sometimes resulting in complete failure. This makes it necessary to utilize aggregates having a strong resistance to freeze and thaw damage.

This experiment was carried out to evaluate resistance of three proportions of the agglomerates to freeze-thaw as compared to limestone aggregates from Martin Marietta's Ames mine.

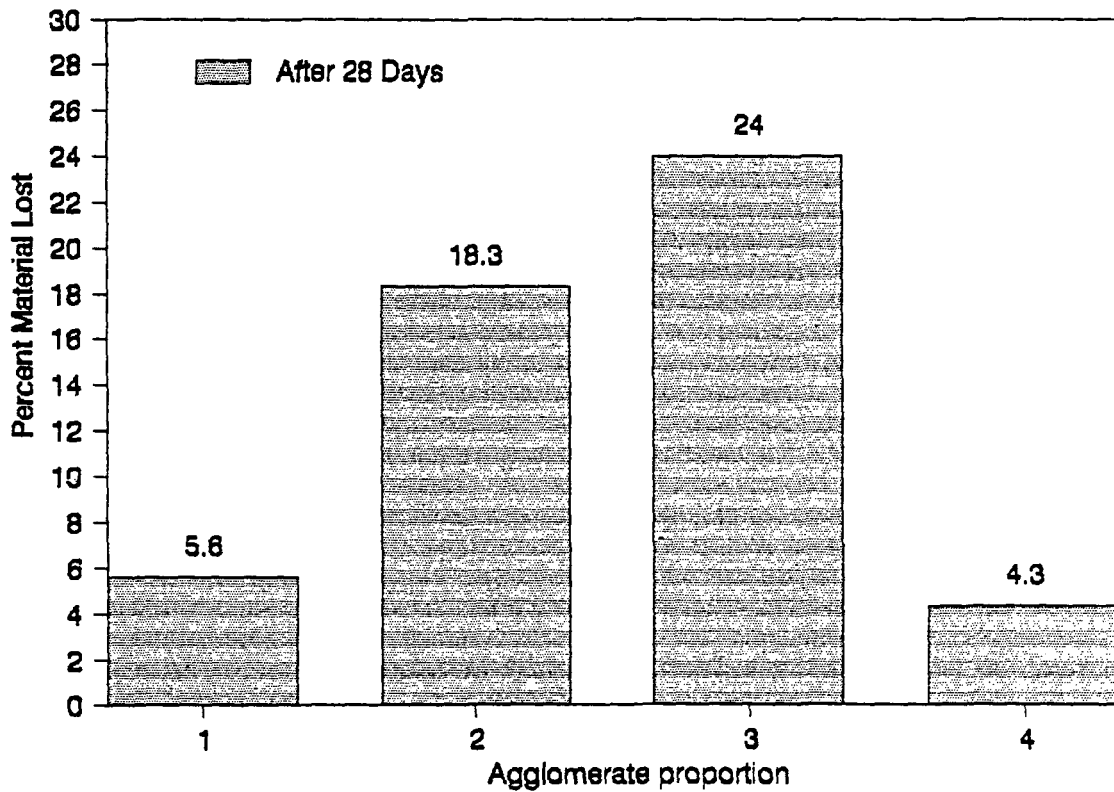
Procedure The experimental procedure was in accordance with the method specified by Iowa Department of Transportation (IDOT) Materials Department for testing aggregates (Test Method No. Iowa 211-A). Method "C" which uses water as the thawing medium was used. The agglomerates of three different proportions cured for 28 days, and limestone aggregates having similar gradations as shown above, were tested using this method. The water saturated agglomerates and limestone aggregates were subjected to 25 cycles of alternating freeze-thaw patterns with temperatures ranging from 0°F to 45°F. The loss due to freeze-thaw was expressed as the percent material by weight passing through sieve # 4, and compared to the loss of limestone aggregates of a

similar gradation. Comparison of the relative damage gives a direct indication of the resistance to freeze-thaw of the agglomerates relative to limestone aggregates.

Results and analysis The three agglomerate proportions subjected to 28 cycles of freeze-thaw were seen to be heavily fractured and broken down. Figure 4-24 shows the relative material loss or degradation in agglomerates and the limestone aggregates due to freeze-thaw action. A distinct difference in the degree of degradation of the samples is seen. Comparatively the limestone aggregates are seen to be highly resistant to freeze-thaw. Agglomerates containing only 25% AFBC residue are seen to have a high resistance to freeze and thaw even as compared to limestone aggregates. However, the degradation due to freeze-thaw is more in agglomerates containing higher percentages of AFBC residue. From Figure 4-24 it can be inferred that agglomerates containing more than 45% AFBC residue are unsuitable for use in road base systems where freeze-thaw durability is a criteria. On the basis of this test, it was deduced that the agglomerates made with 35% AFBC residue would have an acceptable resistance to freeze-thaw and would even result in maximum permissible use of AFBC residue. Further durability tests in this research centered on this selected proportion.

#### Volume expansions

Large volume expansion of aggregates in highway bases can lead to cracking and as such are detrimental to the pavement. AFBC residues have been reported to show significant volume expansions probably due to expansive hydration of CaO and sulfate components. It is necessary to investigate volume expansions of the agglomerates if they



Agglomerate proportion 1: 75 % Ott. fly ash + 25 % AFBC residue

Agglomerate proportion 2: 55 % Ott. fly ash + 45 % AFBC residue

Agglomerate proportion 3: 25 % Ott. fly ash + 75 % AFBC residue

Agglomerate proportion 4: Limestone aggregates

Figure 4-24: Resistance of agglomerates to freeze-thaw, relative to limestone aggregates



are to be used as aggregates in highway bases.

Procedure Difficulty in measuring the volume of irregularly shaped agglomerates made it necessary to carry out the tests on hydrated mixtures molded into rectangular bars. For this purpose, two hydrated mixtures of Ottumwa fly ash and AFBC residue having 35 % and 75 % AFBC residue, were molded into rectangular bars of 1" X 1" X 11". These bars were then cured in 3 different curing environments: air curing, moisture curing and oven curing. Changes in length of the bars were measured as a function of time.

Results and analysis Figure 4-25 shows the changes in length of the bars as measured above. It is seen that hydrated mixtures made with 35% AFBC residue show much lower volume expansions than the specimens having 75% AFBC residue under humid and oven curing. However, the specimens cured in air do not show much difference in expansion. The higher volume expansions in mixtures having higher percentages of AFBC residue is probably due to the expansive hydration of the CaO and CaSO<sub>4</sub> components of AFBC residue. Part of the expansions may also be due to the anisotropic growth of needle-like ettringite crystals. The large expansions seen in mixtures under humid curing conditions is due to more effective hydration of the AFBC residue components in presence of adequate moisture. A large part of the expansions in mixtures under humid curing conditions can also be explained on the basis of the theory of expansion proposed by Mehta (11). Mehta has proposed that the high specific surface of ettringite and its negatively charged, peculiar crystal structure attracts a large number of water molecules. These adsorbed water molecules which surround the ettringite

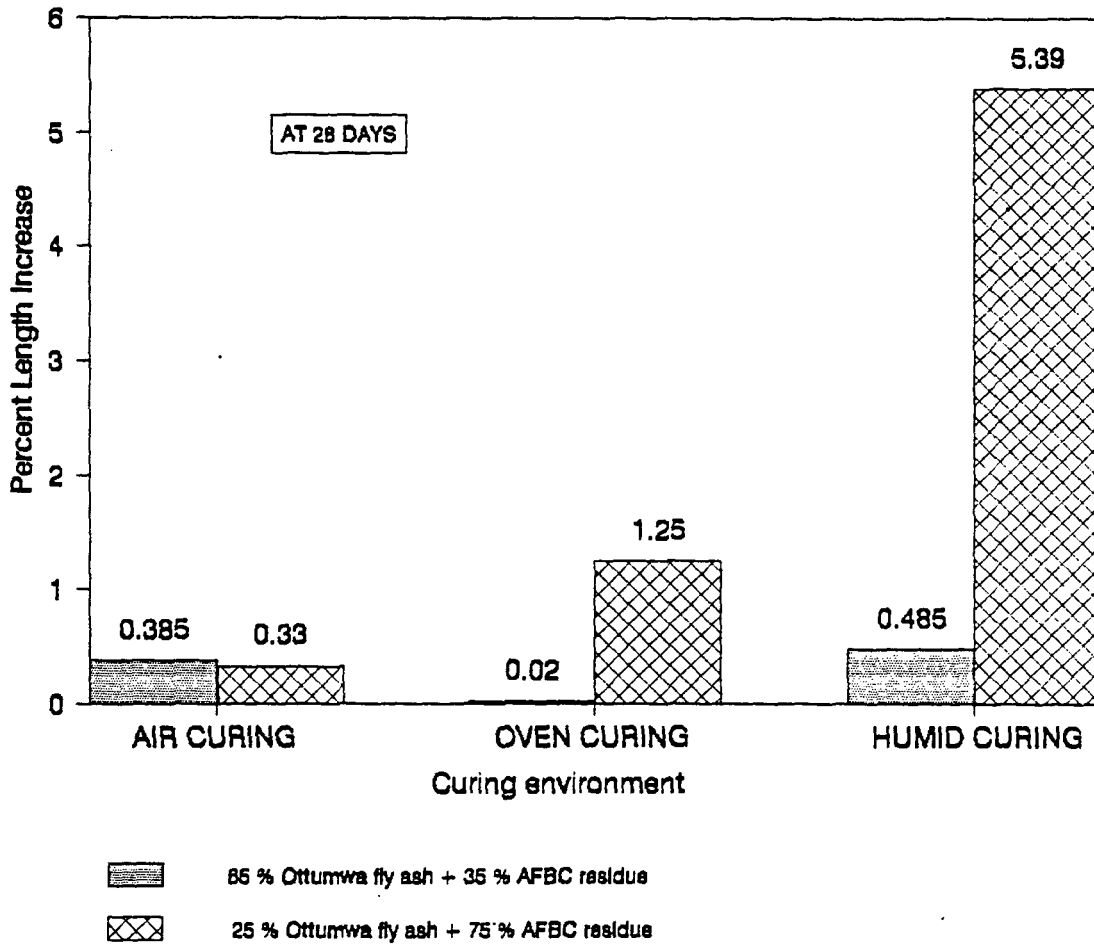


Figure 4-25: Volume expansions of hydrated mixtures of Ottumwa fly ash and AFBC residue

crystals cause interparticle repulsion, thus causing an overall expansion of the system, without any change in crystal lattice of ettringite. As the presence of large quantities of ettringite in the mixtures has been shown earlier, the above theory describing the contribution of ettringite to expansion may be valid for these mixtures. The low expansions of the mixtures, cured under high temperatures is attributed to the accelerated rate of hydration at high temperatures and completion of hydration while the mixture was still in the mold. The mixtures were kept in the mold for 24 hours and expansions accompanying hydration may have been restrained by the mold.

Generally the mixture having 35% AFBC residue showed expansions well below the limit of 0.6% expansion specified for use in highway bases. These results serve as an additional basis for elimination of mixtures having larger percentages (greater than 35 %) of AFBC residue for use in highway bases.

#### Resistance to sulfate attack

Class C fly ash concretes may exhibit low resistance to sulfate attack. This research was conducted to evaluate resistance to sulfate attack, of Ottumwa fly ash and AFBC residue mixtures.

Procedure Test procedure ASTM C1012 was used. Two mixtures of Ottumwa fly ash and AFBC residue having 20% and 35% AFBC residue were molded into rectangular bars 1" X 1" X 11". Simultaneously 1" cubes of the same mixtures were also cast. At the time when crushing strength of the cubes reached 2850 psi, two rectangular bars of that proportion were exposed to mixed sodium and magnesium

solutions. Two more rectangular bars of the same proportion were exposed to saturated lime water, to serve as control specimens. Volume ratio of bars to solution was maintained at 1:4. Length changes of these rectangular bars were measured as a function of time. Length changes may then be used as an indication of volume expansions.

Results and analysis Percent length increase observed in the bars of the two proportions exposed to sulfate solution, and saturated lime solution for two months are shown in Figure 4-26. No major length changes are observed in the specimens. The minor initial length changes observed up to 15 days are supposed to be due to the imbibition of water by the hydrated compounds of the specimen. No conclusion can be drawn at this stage as sulphate attack is known to occur sometimes after many months. However, sulfate attack is not expected to cause any problems in these mixtures which are already super-sulfated.

#### Leachate analysis

The agglomerates to be used in field applications might have to be stockpiled for long periods. These agglomerates and the agglomerates utilized in road base mixtures might be subjected to leaching, causing possible contamination of groundwater.

Procedure The leachability of the agglomerates composed of 65% Ottumwa fly ash and 35% AFBC residue cured for 60 days, was evaluated by the Toxicity Characteristic Leaching Procedure (TCLP) as specified by the Environmental Protection Agency (EPA). The sample of the agglomerate was agitated with an acid solution and the collected leachate was analyzed for potential contaminants. The maximum

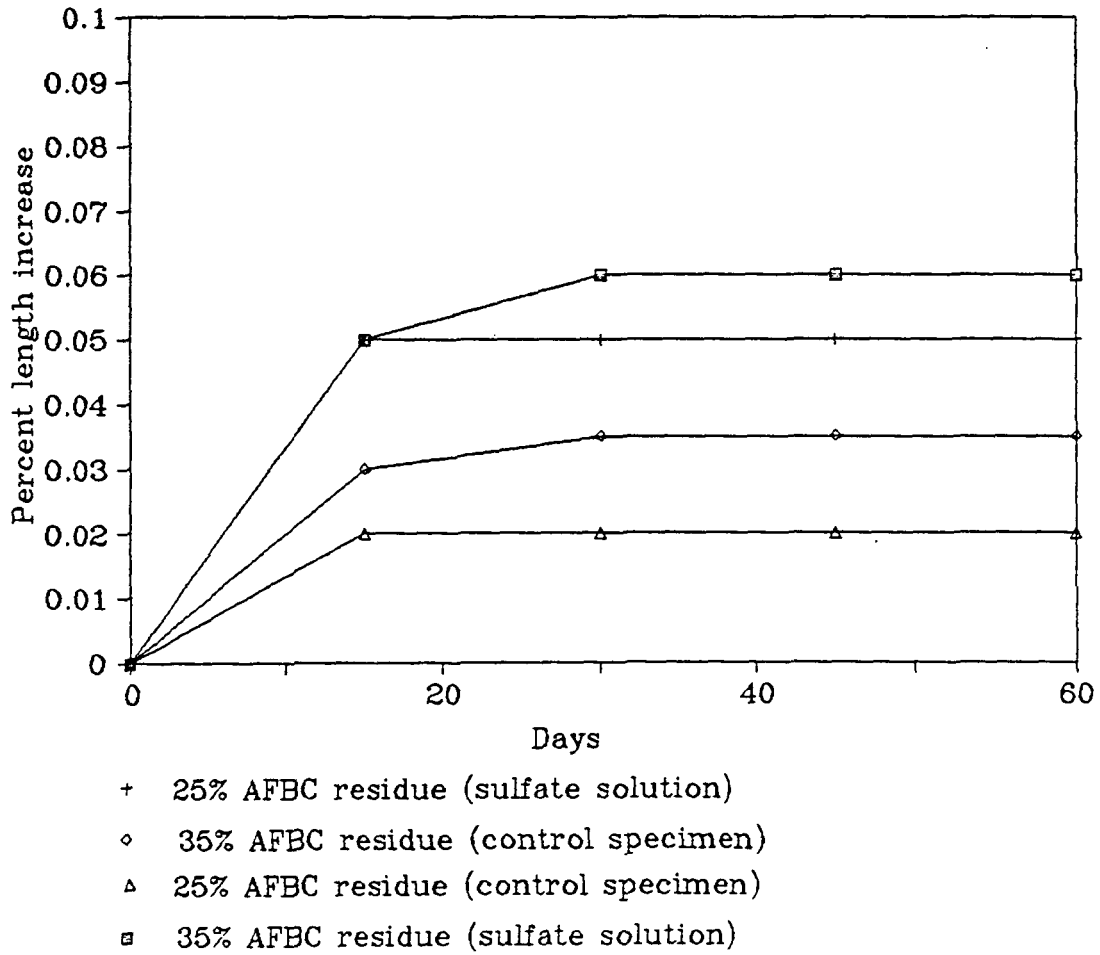


Figure 4-26: Resistance to sulphate attack of hydrated mixture of Ottumwa fly ash and AFBC residue

concentration of contaminants determined from the TCLP test should not be greater than 100 times the maximum allowable limit specified in National Primary Drinking Water Standards, for the material to be classified as non-hazardous.

Results and analysis Composition of leachate obtained from the TCLP test on agglomerates of Ottumwa fly ash and AFBC residue having 35 % AFBC residue cured for 28 days is shown below in Table 4-9. The maximum allowable limits of relevant elements as required by National Drinking Water Standards is also shown in Table 4-9.

**Table 4-9: Results of the TCLP test on agglomerates of 65% Ottumwa fly ash and 35% AFBC residue.**

ELEMENT	AMOUNT PRESENT	IN PPB
	ALLOWABLE LIMITS	TCLP EXTRACT
AG	100	1
AS	500	12
BA	1000	200
CA	-	2100
CD	1000	< 5
CR	1000	59
FE	-	< 10
PB	2000	< 20
SE	500	52
HG	100	< 0.1

The amounts of all elements are seen to be well below allowable limits and the agglomerates would thus be considered safe for use in highway base and sub-base systems based on these criteria. High amounts of calcium are observed in the leachate. This has probably originated from the readily soluble gypsum present in the agglomerates.

### Road Base Mixture

From the above experiments it was concluded that the agglomerates of Ottumwa fly ash and AFBC residue, having 35 % AFBC residue were potentially best suited for use in highway-base and sub-base systems and also maximized the use of AFBC residue. Following this evaluation, research was initiated to prepare actual road-base mixture using these agglomerates.

As a first step the bulk specific gravity and the absorption of coarse agglomerates at the above optimum proportion were determined. This was done using the procedure specified in ASTM C127-88 for determination of absorption of coarse aggregates. The fraction of the agglomerates retained on sieve sizes 3/4" and 5/8" and cured for 90 days were used for this test.

The bulk specific gravity and the absorption of the agglomerates having 35% AFBC residue and cured for 90 days as determined by the procedure specified by ASTM C127-88 are 1.70 and 16.0 % respectively. The absorption values are considered to be significant and the net effect of this will be to increase the water content of the road base mixture.

The agglomerate gradation used for the trial road-base mixture was as specified by IDOT for aggregates for a standard cement treated granular base. Twenty percent of cementing material by weight of agglomerates was used. In this case the cementing material used was the mixture of 65% Ottumwa fly ash and 35 % AFBC residue to

maximize the utilization of AFBC residue. Three road base mixtures with water contents of 10 %, 12 % and 14 % were prepared. Water contents of more than 14 % resulted in a flowable mix of very high workability, which could not be compacted. The mixtures were compacted into standard proctor sized specimens using ASTM D698 standard proctor procedure. The proctor sized specimens were then weighed. Knowing the volume of the proctor mold, the density of the proctor specimen could be calculated. The variation in density of the road base mixture with water content was determined. The compressive strength of the proctor specimen having optimum density and water content was determined.

The variation of wet density of the road base mixture with water content is shown on Figure 4-27. Above a water content of 14% the road-base mixture becomes very flowable. Figure 4-27 shows that the road base mixture composed of agglomerates and cementing mixture of AFBC residue and Ottumwa fly ash exhibits maximum density at a water content of 14%. The standard proctor specimens of the road base mixture exhibits very high crushing strengths on the order of 1225 psi. This strength is much higher than the 500 psi crushing strength normally specified for materials to be used in road base mixtures. The failure is seen to occur distinctly along the aggregate-paste interface.



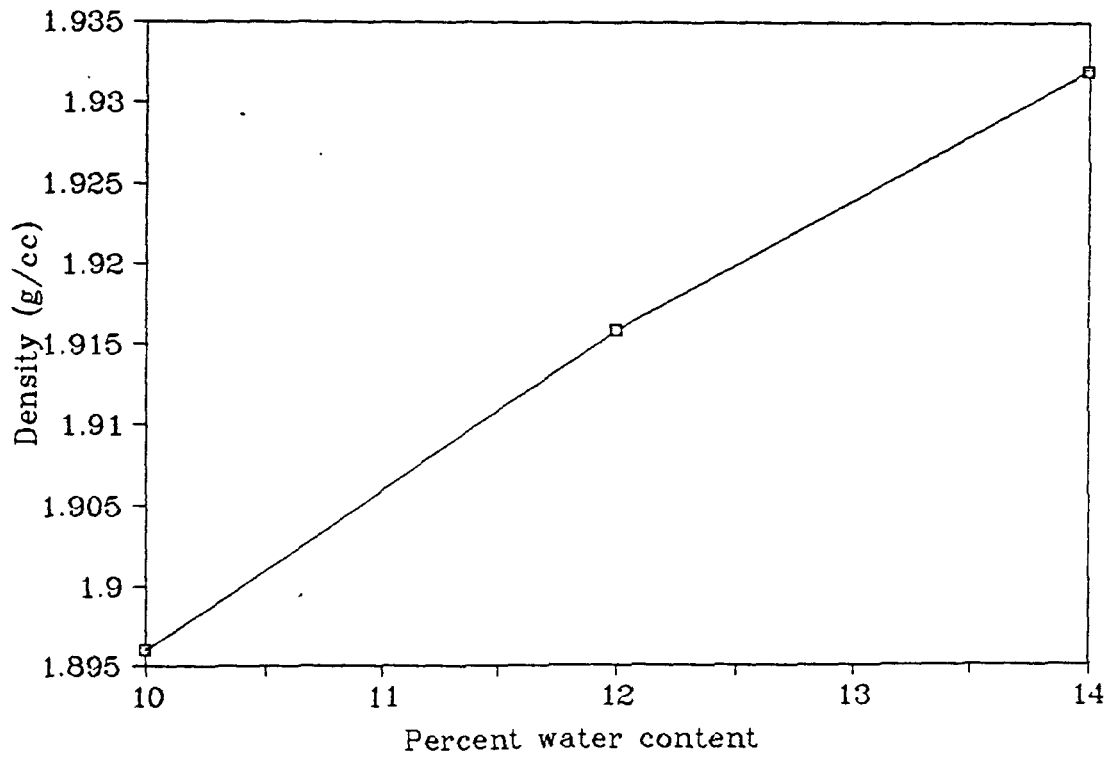


Figure 4-25. Standard proctor test on road-base mixture

## V. CONCLUSION

- The hydrated mixtures of Ottumwa fly ash and AFBC residue containing 20 % to 45 % AFBC residue exhibit very high strengths approaching 4000 psi at 28 days.

- Low water contents and small particle sizes lead to higher strengths. Curing at higher temperatures increase rate of strength development, however the ultimate strength development is the same.

- Advanced techniques including X-ray diffraction, SEM, TGA and mercury porosimetry were used to analyze this binder system and to determine the cause of the optimum strength range. Although pore volume was seen to increase with the percentage of AFBC residue in the mixture, this did not appear to account for the high strength differences.

- Chemical reactions resulting in formation of certain strength giving compounds are responsible for the high strengths. Ettringite is the dominating phase in the mixtures with high strengths and all evidence points to ettringite being the phase imparting strengths. Ettringite is formed from the reactions between Ottumwa fly ash, and the CaO, CaSO<sub>4</sub> components in the AFBC residue. Substitution of sulfate ions in ettringite by silicate and/or carbonate ions is believed to be the reason for high strength development. However, further research is necessary to verify this hypothesis.

- Agglomerates of the mixture were prepared. The agglomerates were analyzed in a scanning electron microscope along their cross-section to evaluate the binding mechanism. The gypsum crystals appear to play a major role in encapsulating the

mixture into agglomerates.

•The agglomerates were evaluated for their durability and suitability for use in highway base and sub-base systems. The agglomerates prepared from Ottumwa fly ash and AFBC residue are very strong and resistant to abrasion. When compared to limestone aggregates, the agglomerates having 35 % AFBC residue have a high resistance to freeze-thaw action and volume expansions are also within limits. The TCLP test conducted to evaluate the leachate from these agglomerates did not indicate the presence of any hazardous element above the limit specified by drinking water standards.

•The road base mixture prepared with these agglomerates and fly ash/AFBC residue binder exhibit high strengths approaching 1225 psi and thus show high potential for use in highway base and sub-base systems.

## RECOMMENDATIONS FOR FIELD TRIAL

The above results indicate that there is a high potential for use of the agglomerates containing 35% AFBC residue and Ottumwa fly ash along with a cementing mixture of the same proportion in highway bases. However, this road-base mixture has to be tested in a small scale field application before any large scale applications are attempted.

The following recommendations are suggested for field trial applications;

- 1) The proportion of 35% AFBC residue and 65% Ottumwa fly ash is suggested for use in highway bases in the form of agglomerates and cementing mixture. A target water content of 20% by weight of dry AFBC residue and Ottumwa fly ash should be used for agglomerating this mixture. This water content should impart high strengths to the agglomerates and should result in a maximum particle size conforming to that specified by IDOT for a cement treated granular base. To prepare the particle size gradation as required by IDOT, agglomerates of different sizes will have to be screened as the agglomeration process will not yield the required graded agglomerates directly. The agglomeration process will not yield the fines ( < sieve # 16) required in the particle size gradation and the raw unhydrated mixture of 35% AFBC residue and 65% Ottumwa fly ash will be used for this purpose.
- 2) A large field sized pan agglomerator will be required to meet the large quantities of agglomerates required for field applications.
- 3) The operating variables for the field sized agglomerator should be determined by a trial and error process at a water content of approximately 20%.

- 4) Heat will be liberated during the agglomeration process due to the exothermic hydration reaction of the lime and gypsum components of the mixture. However, this heat is not expected to cause any detrimental problems.
- 5) The agglomerates ready for removal from the agglomerator should be subjected to a charge of dry feed material. This will result in coating of the agglomerates with a dry layer and will prevent them from sticking to each other during the stockpiling process.
- 6) The rate of strength gain in the mixture was seen to be high at 28 days at 21°C. Rate of strength gain was seen to be negligible after 60 days. For best results the agglomerates and cementing mixture must be allowed to cure for at least 28 days during periods of warm weather. Use of these agglomerates and mixture should be avoided in winter due to low strength development at low temperatures. Agglomerates prepared in winter may also be susceptible to freeze-thaw degradation.
- 7) The agglomerates and cementing mixture should not be used where sulfate attack on adjoining structures might be a consideration, as the mixture is high in sulfate content.
- 8) The agglomerates should not be used in marine applications or where a high water table is present, due to the solubility of the gypsum in the mixture.
- 9) The road-base mixture should be prepared using the gradation as specified in IDOT specifications for a cement treated granular base. The cementing mixture should make up 20% by weight of the total road-base mixture. A water content of about 14% by weight of total raw mixture including agglomerates, will be used in preparing the road-base mixture which will result in adequate workability and optimum compaction moisture content.

## ACKNOWLEDGEMENTS

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APPENDIX

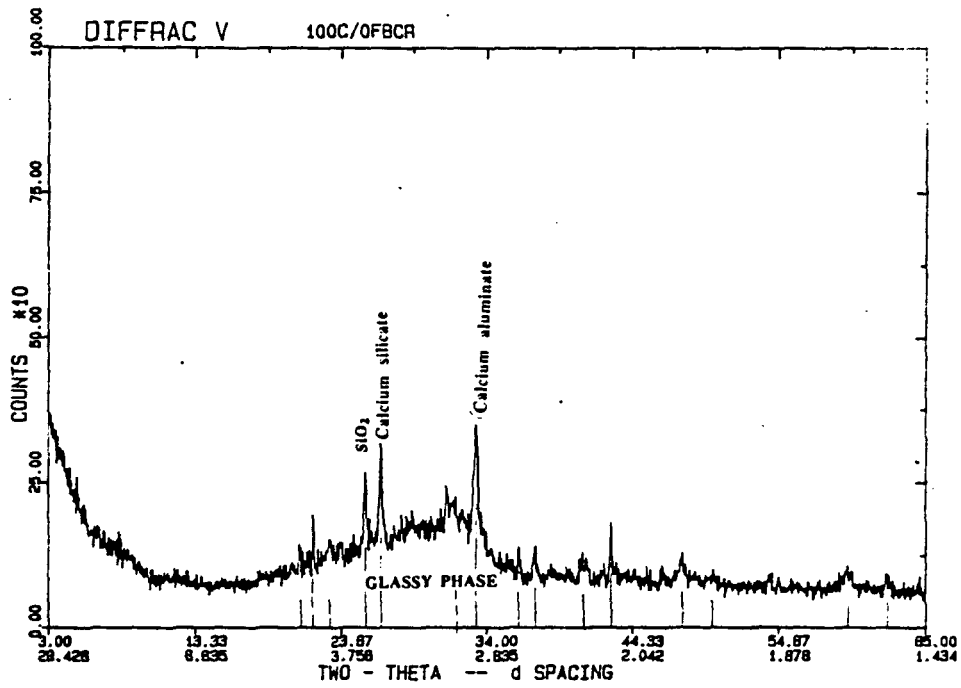


Figure A-1a: Typical X-ray diffractogram of raw Ottumwa fly ash

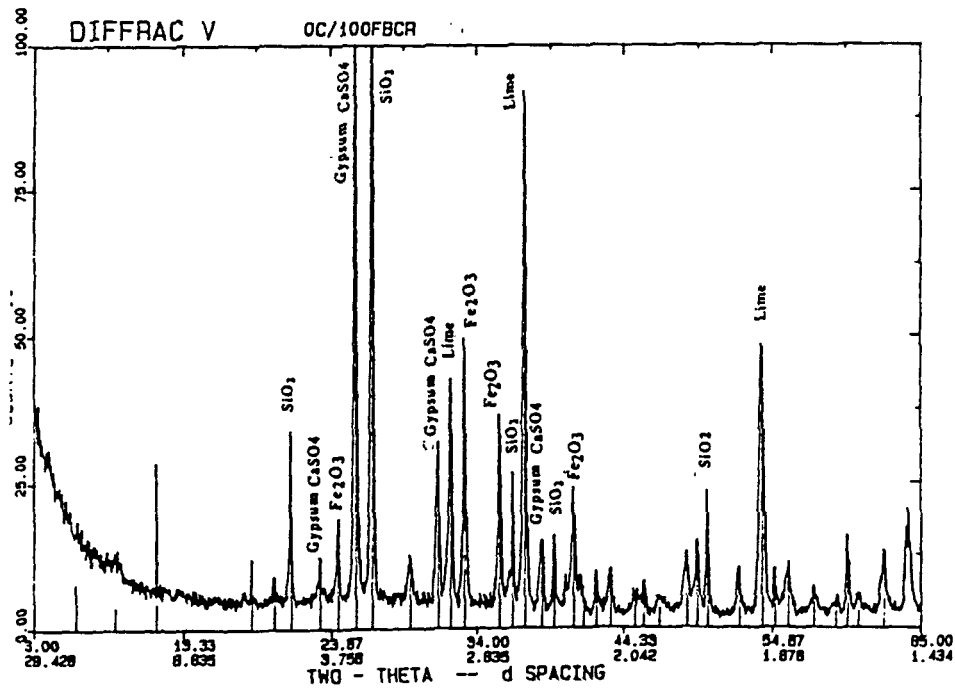


Figure A-1b: Typical X-ray diffractogram of raw AFBC residue

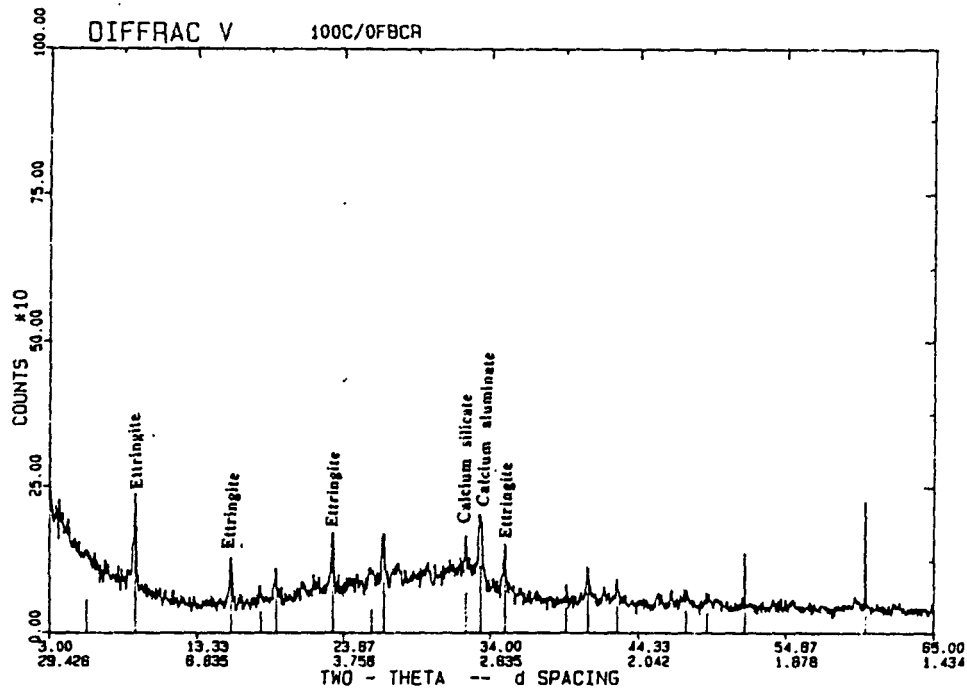


Figure A-2a: Typical X-ray diffractogram of hydrated Ottumwa fly ash

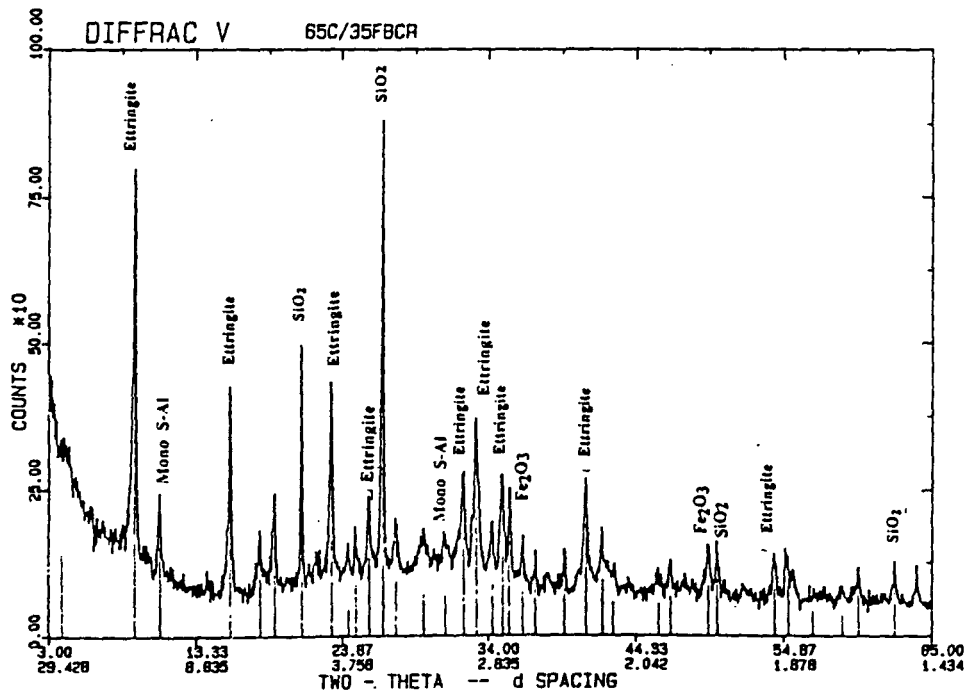


Figure A-2b: Typical X-ray diffractogram of hydrated mixture of 65% Ottumwa fly ash and 35% AFBC residue

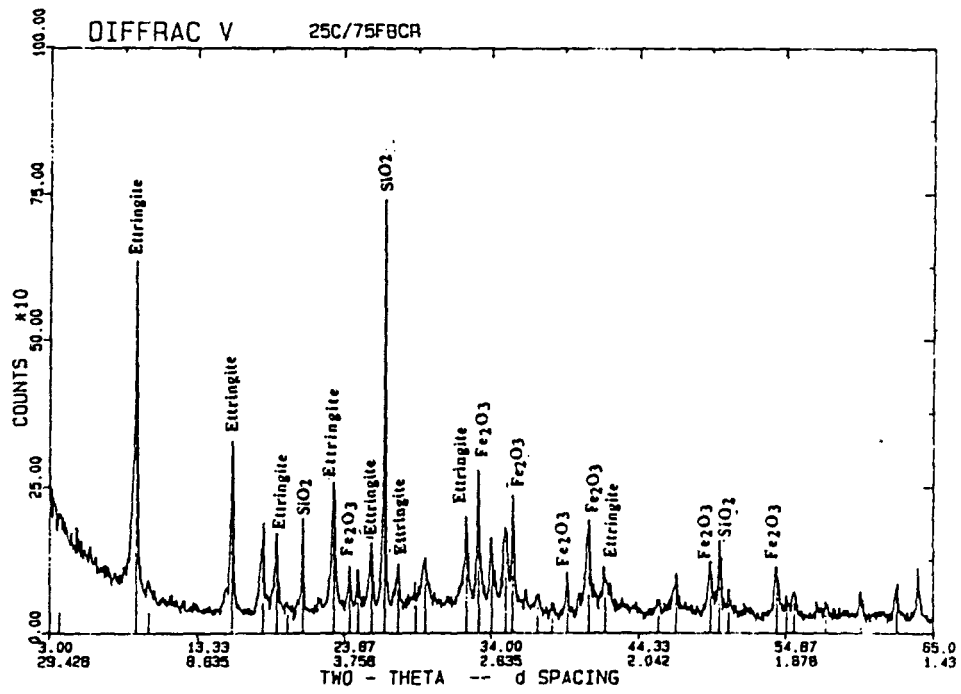


Figure A-2c: Typical X-ray diffractogram of hydrated mixture of 25% Ottumwa fly ash and 75% AFBC residue

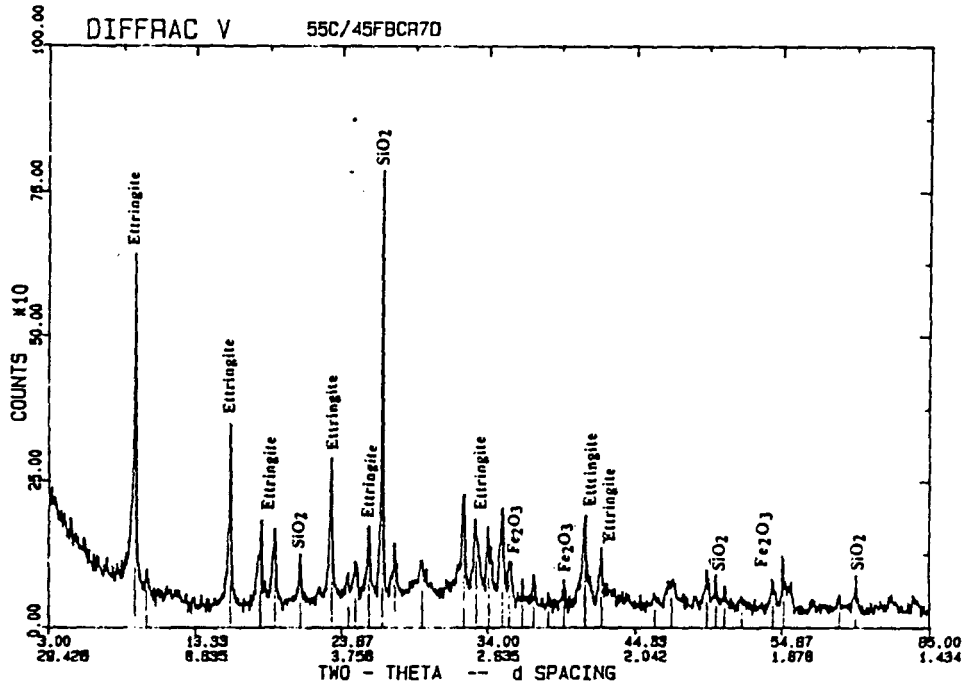


Figure A-3a: Typical X-ray diffractogram of hydrated mixture of 55% Ottumwa fly ash and 45% AFBC residue after 3 days of curing

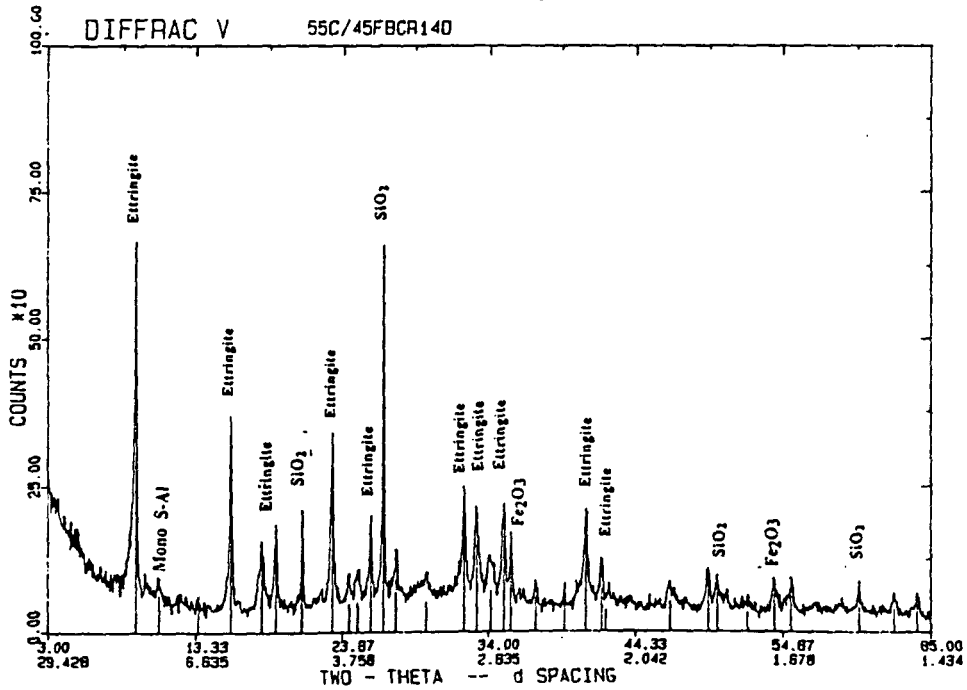


Figure A-3b: Typical X-ray diffractogram of hydrated mixture of 55% Ottumwa fly ash and 45% AFBC residue, after 28 days of curing

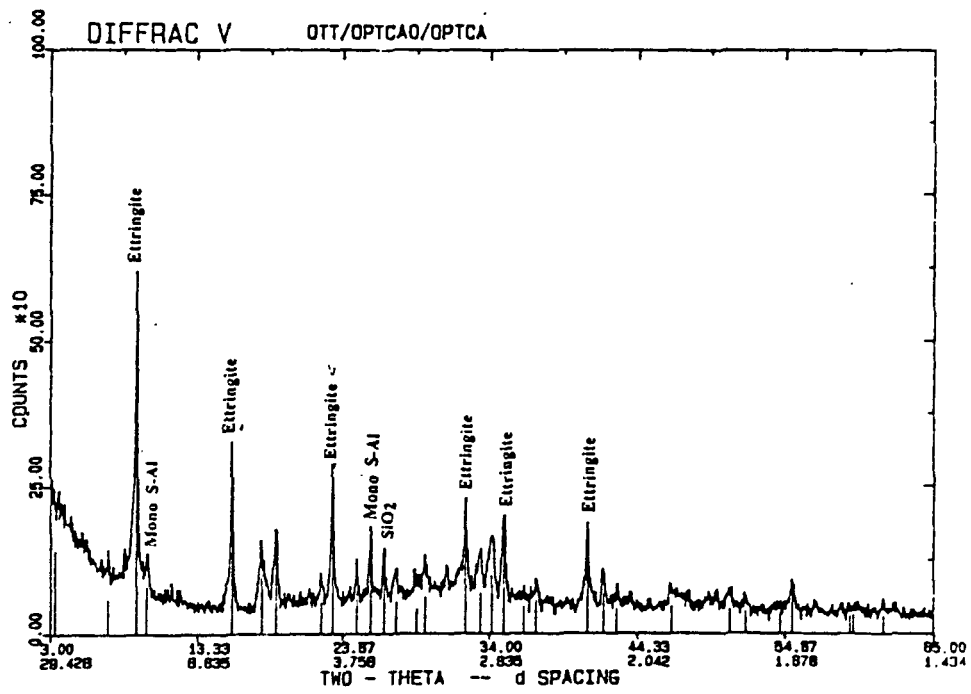


Figure A-4: Typical X-ray diffractogram of hydrated mixture of Ottumwa fly ash, CaO and gypsum

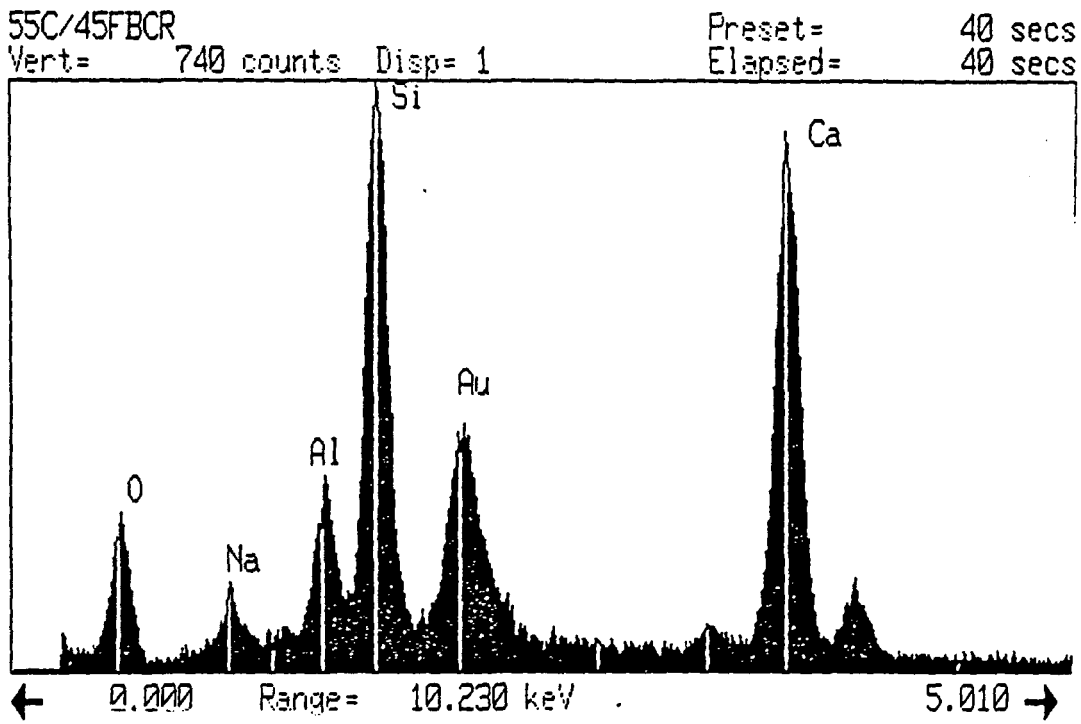


Figure A-5a: Typical element analysis (energy dispersive) of matrix

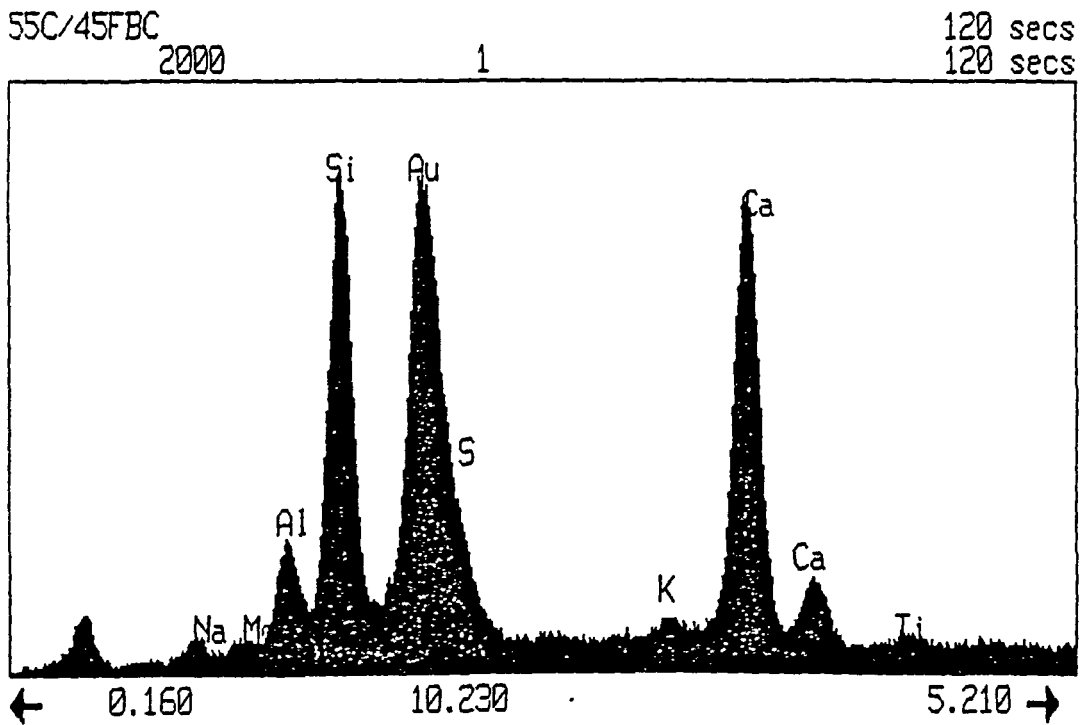


Figure A-5b: Typical element analysis (energy dispersive) of ettringite



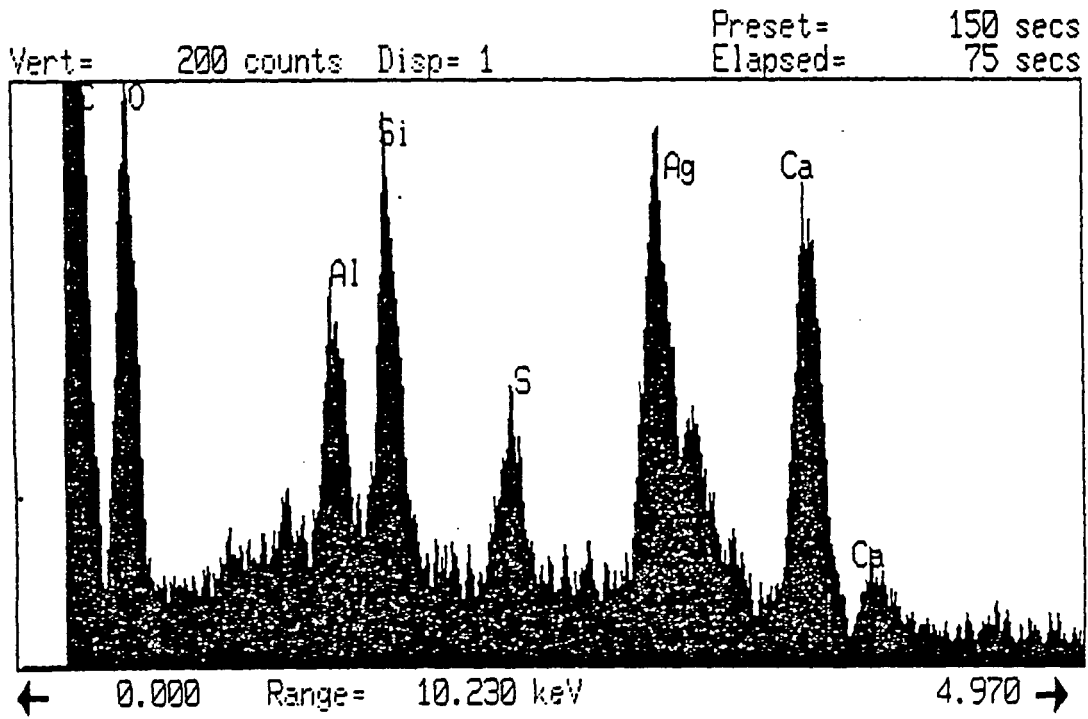


Figure A-5c: Typical element analysis (energy dispersive) of single ettringite crystal at edge of the sample

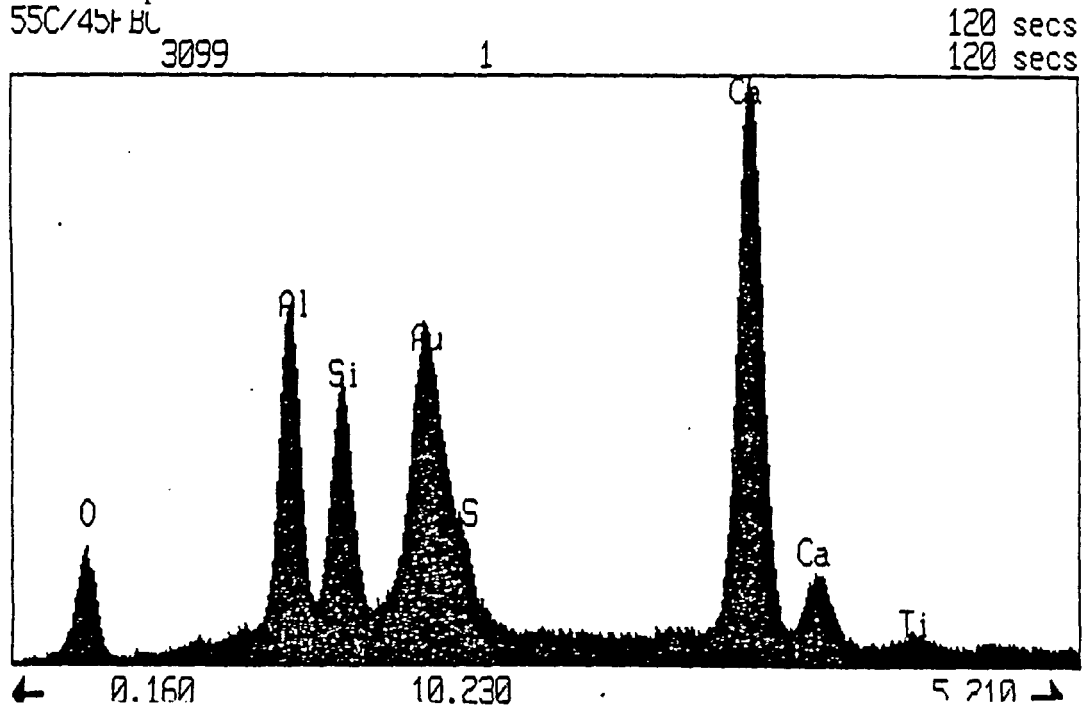


Figure A-5d: Typical element analysis (energy dispersive) of platy crystals of mono sulfo-aluminate

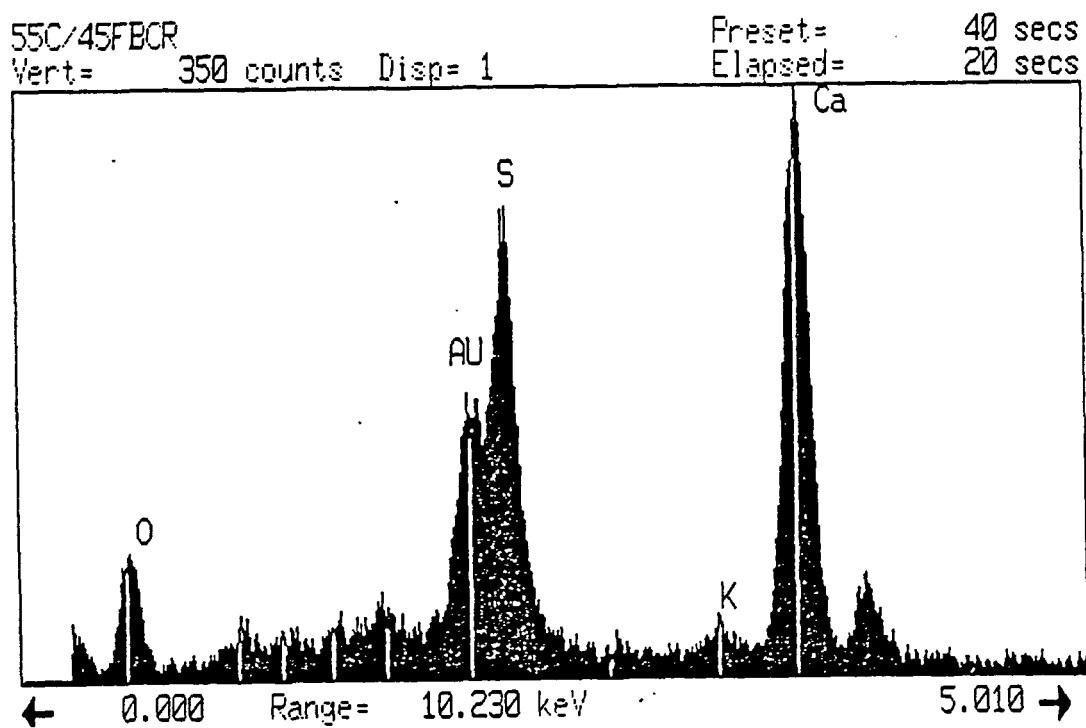


Figure A-5e: Typical element analysis (energy dispersive) on thick plates of gypsum

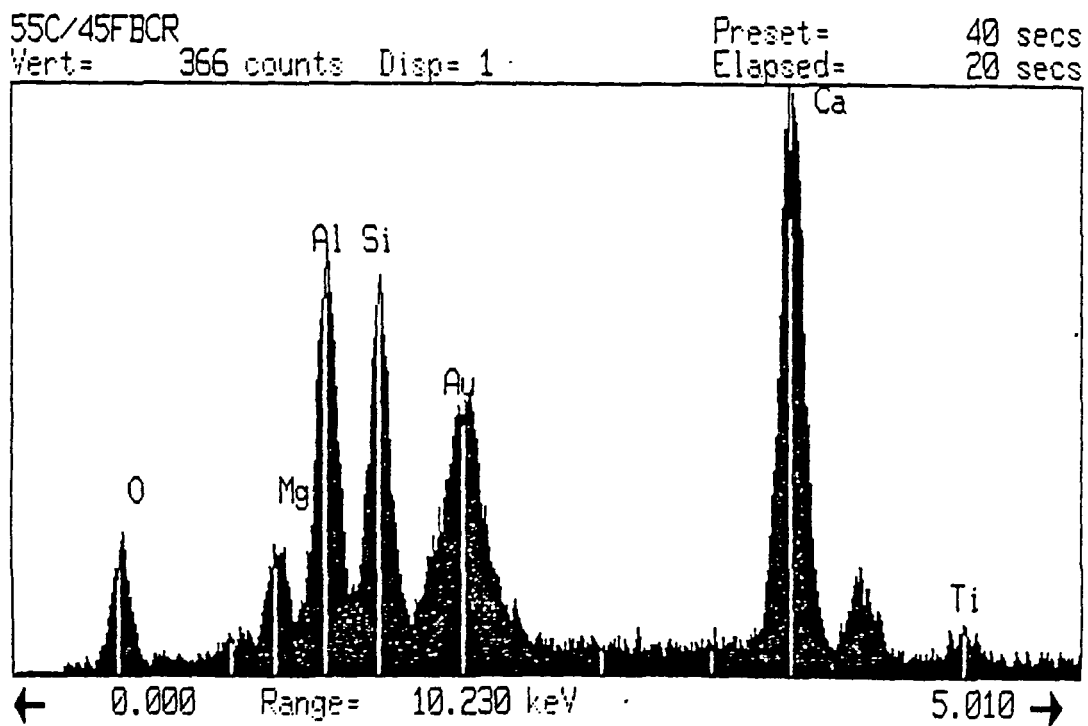
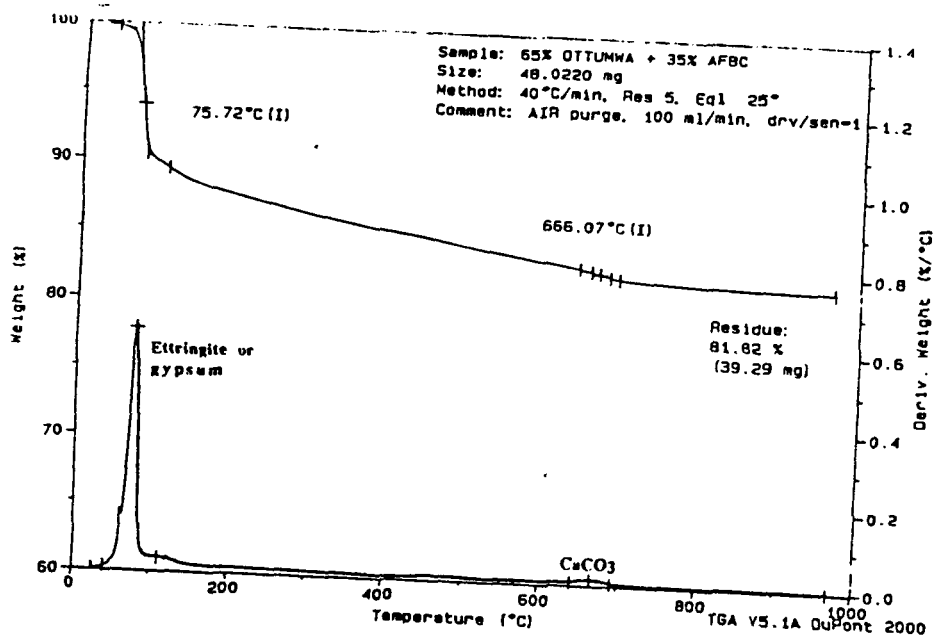
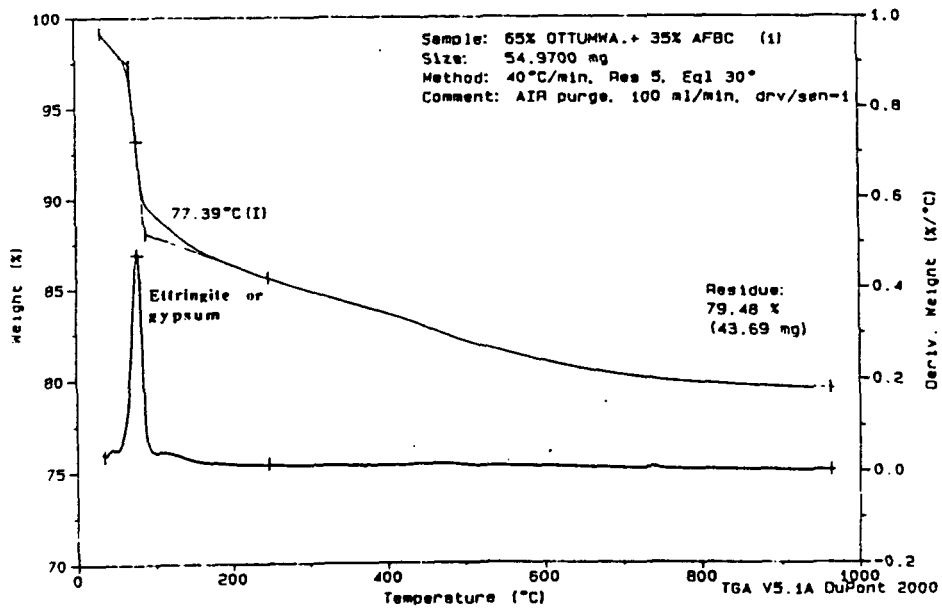


Figure A-5f: Typical element analysis (energy dispersive) on massive matrix structure

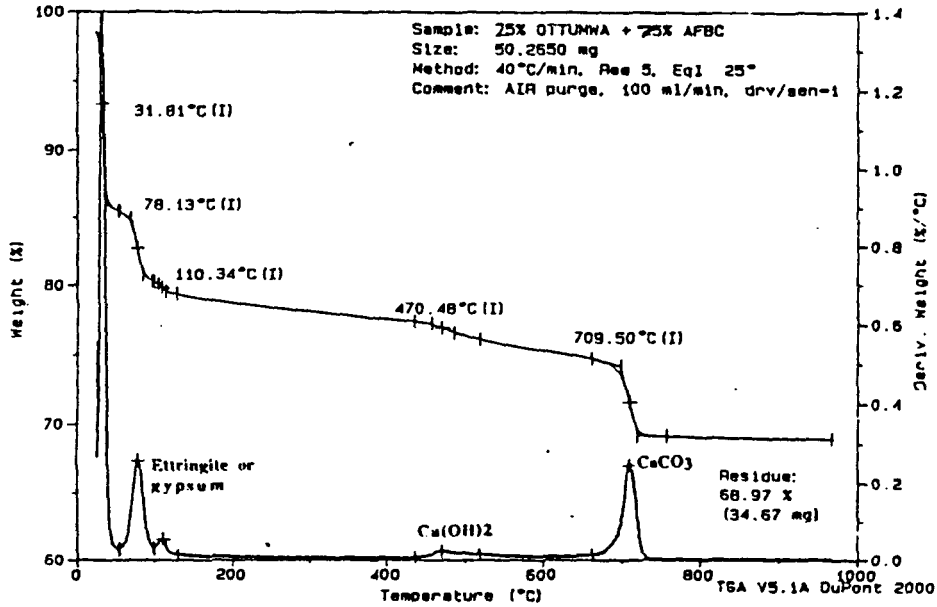


(a)

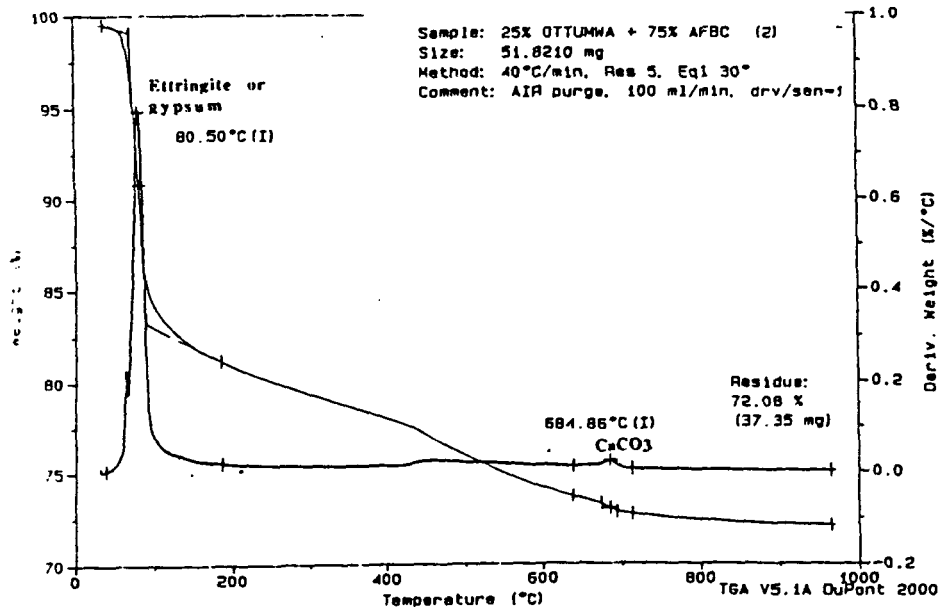


(b)

Figure A-6b: Typical TGA/DTG weight losses in hydrated mixture having 35% AFBC residue; (a) after curing for 3 days; (b) after curing for 28 days



(a)



(b)

Figure A-7: Typical TGA/DTG weight losses in hydrated mixtures having 75% AFBC residue; (a) after curing for 3 days; (b) after curing for 28 days

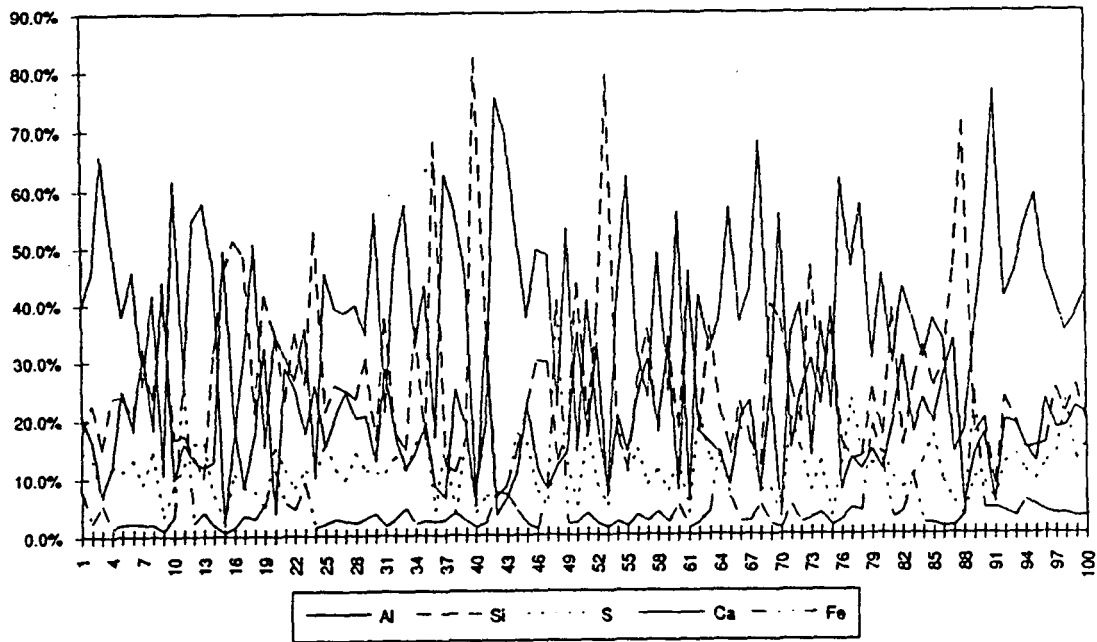


Figure A-8a: Element analysis (line scan) from center to edge of the agglomerate having 35% AFBC residue.

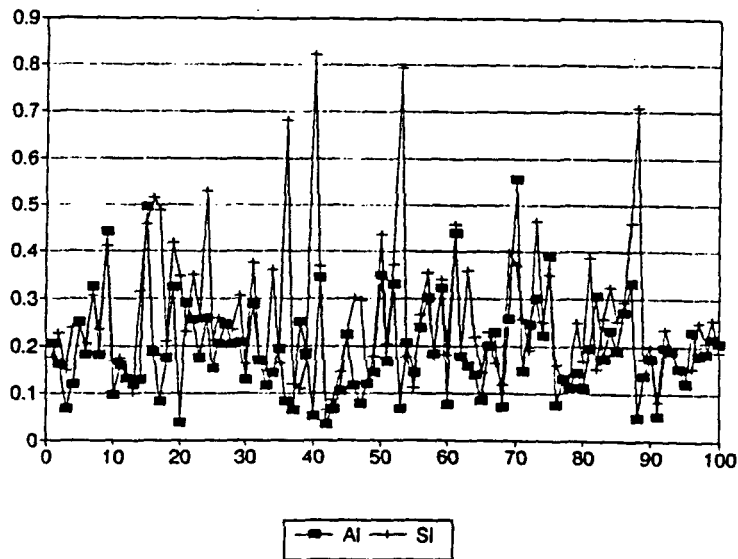


Figure A-8b: Percent counts of aluminium and silicon at 100 points from center to edge of agglomerate having 35% AFBC

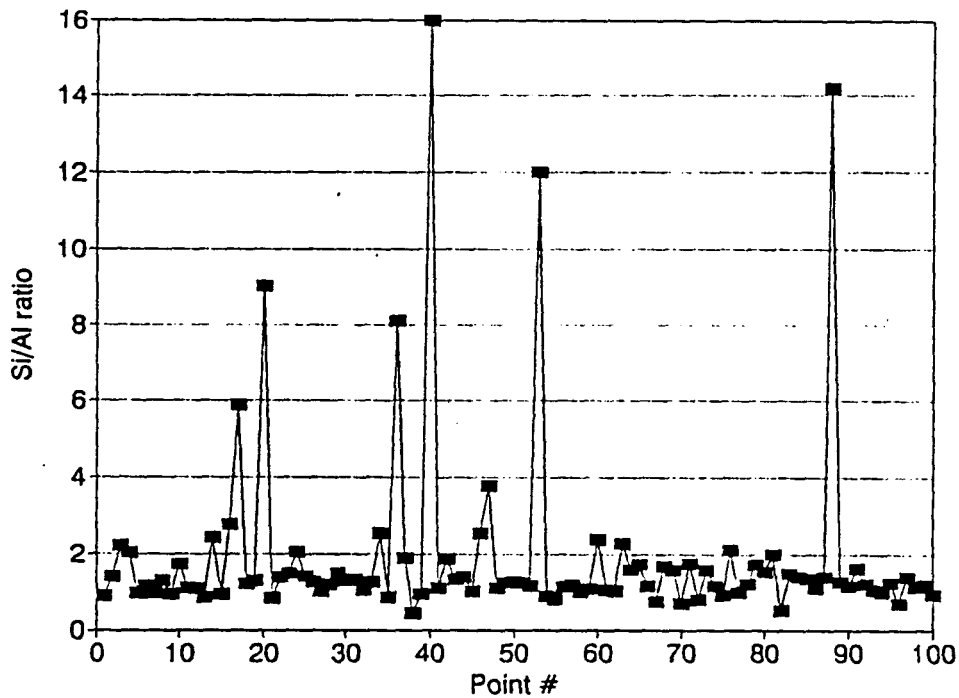


Figure A-8c: Ratio of counts of silicon to aluminium from center to edge of agglomerate having 35% AFBC residue

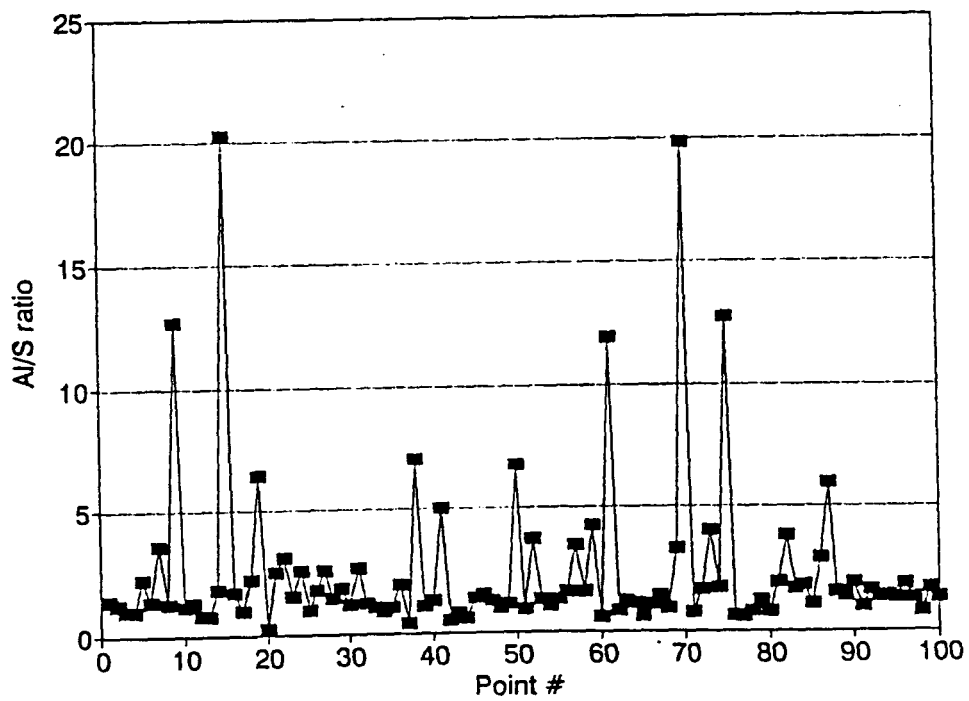


Figure A-8d: Ratio of counts of aluminium to sulphur from center to edge of agglomerate having 35% AFBC residue

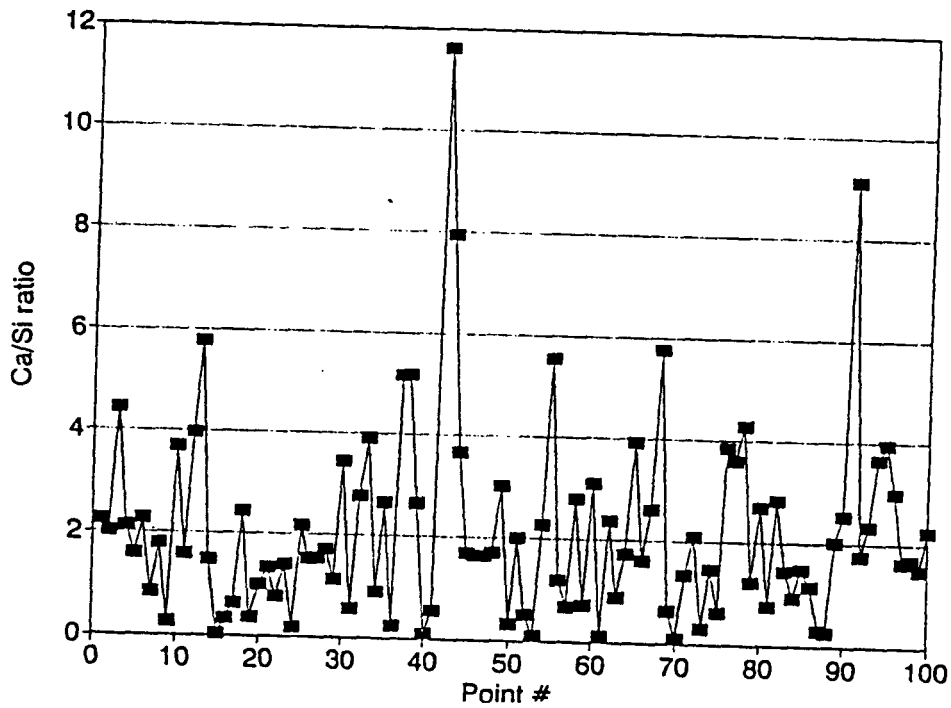


Figure A-8e: Ratio of counts of calcium to silicon from center to edge of agglomerate having 35% AFBC residue

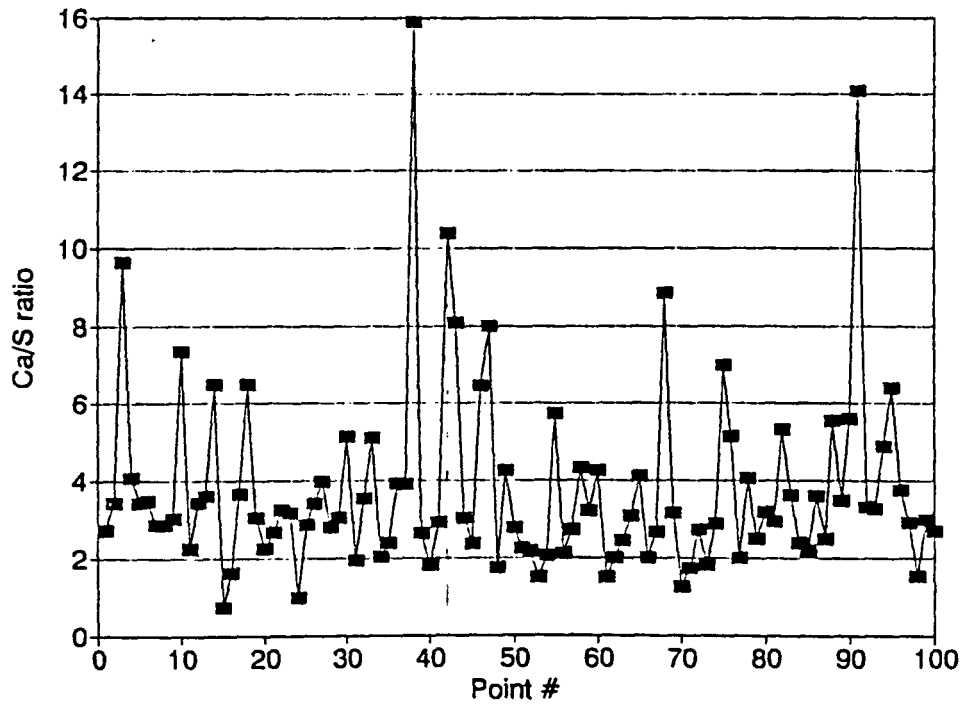


Figure A-8f: Ratio of counts of calcium to sulphur from center to edge of agglomerate having 35% AFBC residue

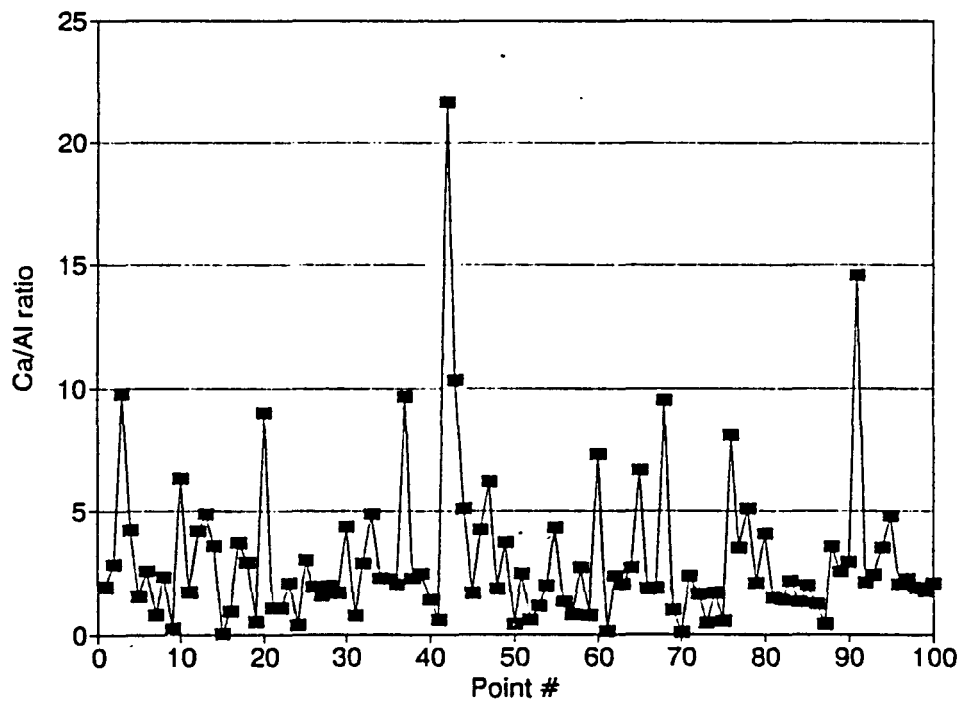


Figure A-8g: Ratio of counts of calcium to aluminium from center to edge of agglomerate having 35% AFBC residue