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Manufacture and properties of fluoride cement

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Manufacture and properties of fluoride cement

by

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A thesis submitted to the graduate faculty
in partial fulfilment of the requirements for the degree of
MASTER OF SCIENCE

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LIST OF ABBREVIATIONS

The following abbreviations, common in literature dealing with the chemistry of cement and concrete, are used throughout this document:

AF _m	aluminium ferrite phases, Al _x Fe _y
C ₃ S	tricalcium silicate, Ca ₃ SiO ₅ ;
C ₂ S	dicalcium silicate, Ca ₂ SiO ₄ ;
CA	tricalcium aluminate, Ca ₃ Al ₂ O ₃ ;
C ₄ AF	tetracalcium aluminoferrite, Ca ₂ (Al,Fe)O ₅ ;
CH	calcium hydroxide, Ca(OH) ₂ ; and
C-S-H	calcium silicate hydrate, a material of variable composition

Also, the following abbreviations have been used

FC	fluoride cement;
OPC	ordinary Portland cement;
ISO	International Organisation for Standardisation;
ASTM	American Society for Testing and Materials;
BS	British Standard; and
MBS	Malawi Bureau of Standards.

ABSTRACT

This research work aimed at characterising composition, hydration and physical properties of fluoride cement, by studying samples of the cement obtained from Malawi, and comparing them to ordinary Portland cement. By confirming the suitable characteristics of fluoride cement through this work, the results of the research work provide a good basis for the wider adoption of fluoride cement as an alternative to ordinary Portland cement, especially in developing economies.

Numerous accounts have been cited regarding the production and use of fluoride cement. Since there have not been conclusive agreement as to its properties, this study was limited to the theories of successful incorporation of fluoride compounds in the manufacture of fluoride cement. Hence, the properties and characteristics reported in this study relate to the cement currently manufactured in Malawi, and, on a comparative basis only, to that manufactured in other parts of the world. Samples of the fluoride cement used in the study were obtained by synthetic manufacture of the cement using common raw materials for the manufacture of fluoride cement that is limestone, silica sand, and fluorspar.

These samples were subjected to several comparative tests used to characterise cements including examination under x-ray diffractometer, scanning electron microscopy and tests for setting time and compressive strength. Under similar laboratory conditions, it was possible to prove that fluoride cement hardens more rapidly than ordinary Portland cement. Also observed during the experimental work is that fluoride cement develops higher compressive strengths than ordinary Portland cement. The hardening and setting

times are significantly different between the two cements. Also the nature of the hydration products, that is the microstructural development is significantly different in the two cements.

The differences brought about between the two cements are because of the presence of fluorine during the clinkering process. It was observed in the laboratory simulated production of fluoride cement, that the clinkering temperature is much lower (around 1 170 °C) compared to that for the production of ordinary Portland cement. The other observed differences were attributed to the different mineralogical composition as a result of fluoride incorporation into the cement. While fluorine content is very minimal in fluoride cement, not more than 2 %, the resulting cementitious products are altered significantly as was observed from the study.

Part of the experimental results has been used as reference material in the preparation of a draft Malawi Standard on fluoride cement. This draft standard will be submitted to the Malawi Bureau of Standards for further processing before it can be officially endorsed as a Malawi Standard.

CHAPTER 1. INTRODUCTION

1.1 Background

Acceptability of novel materials is very important in developing economies, particularly when the cost of the material is significant. Returns on investments on technologies to produce these materials would help boost and hopefully sustain the economies of such countries. Malawi is one of the countries where cheap alternative building materials would go a long way in assisting the many poor in providing themselves with affordable and durable housing. However, a survey of the housing population shows that the majority of Malawians live in semi-permanent housing. Primarily, this is a result of the high cost of building materials such as Portland cement. The cost of housing can be divided into several components: the foundation, the superstructure, the roof and the fixtures. In order to erect a permanent house, a builder would require the use materials that have been "institutionalised" as suitable and durable. There are a variety of materials that could be used for this purpose. For cementitious materials, cement is the most effective on the list of permanent and durable materials. Although the cost of cement may vary from place to place, in many developing economies it is one of the most expensive of the building materials.

Over the years, it has now become acceptable both to the engineers and the homebuilders, that Portland cement is the only material that is to be used in the erection of permanent housing. Even though Portland cement seems to be a ubiquitous material, its usage seems to be restrictive to many homebuilders. This state of affairs, also perpetuated by statutory instruments, creates a vicious circle to the economical and

unprivileged poor who cannot afford to acquire Portland cement required for the construction work. In Malawi, the Government has instituted a number of programmes that would help alleviate this problem and improve on the housing conditions for its people. While these programmes are multisectoral and multisponsored, issues related to housing and human settlement are on the priority list. Under the same programmes, a number of research projects on specific building materials were also identified. Among these materials include fluoride cement, a material hardly known in the construction industry and that, if scientific and technical information is made available to the local engineers and contractors, would enable most Malawians afford decent and permanent housing.

The success of the technology need not be confined to Malawi or just one country. In a world where housing is one of the basic human needs, and the most expensive venture in a family, affordable materials will assist in the housing delivery system.

In light of this, fluoride cement was selected from among the list of materials readily available to construction industry in Malawi. Also some of the reports on fluoride cement that it can be manufactured at a cheaper rate compared to ordinary Portland cement influenced the decision to study this material in detail. The information and data collected from the study will thus assimilate the use of fluoride cement, particularly as a low-cost building material. It will also open up the possibility of future studies on the material.

1.2 Problem statement

Fluoride cement is currently being manufactured in very few countries in the world, namely Indonesia, Spain and Malawi. As a result very little information is available or known about its properties in comparison to ordinary Portland cement. At present, most of the little information available is based on research work that was conducted more than a decade ago. This information has been on the most part very conflicting as to the true behaviour and properties of fluoride cement. While some reports indicate that fluoride compounds reduce the strength of cement, other report that in addition to lowering the temperature, there is a positive gain in the strength of the cement. Even the manufacturing process has come under fire in some of the reports, thus halting any possibilities of improving on the manufacturing process.

Consequently the characteristic hydration and strength developing properties of fluoride cement have not been studied in detail. As is the case for many other new materials, lack of substantive and conclusive technical information hampers its widespread production, use and acceptance. Bearing in mind the importance of providing housing to people, among other things, the non-existence of tools, such as standards, for promoting the awareness of this material to the general public also becomes another problem on its own.

1.3 Research objectives and purpose

The objectives of the research study are:

- a) The determination of the mineralogical composition of anhydrous fluoride cement;

- b) The determination of the hydration properties of fluoride cement with respect to the hardening properties particularly the consistency, initial setting time and final setting time;
- c) To establish the strength developing characteristics of fluoride cement at particular ages of curing and the corresponding products of hydration;
- d) To compare the various properties of fluoride cement with those of ordinary Portland cement; and
- e) To prepare a draft Malawi Standard on fluoride cement based on the data compiled from the study.

There are several reasons why the above study was carried out. Establishing the mineralogical composition of the cement enables proper classification of the cement. By bringing to light the hydration characteristics of fluoride cement, effective utilisation of this low-cost material is made possible in the building industry.

Also it allows scientists to study the effects of the environment and other substances on the cement. By establishing an affirmative background on the nature of fluoride cement, it is possible to promote a higher awareness and utilisation of the material. Using the information gathered from the study, the cement may be publicised and hence increase the awareness of the scientist and the public at large, on efficient utilisation.

1.4 Proposed solution

This study involved preparation of fluoride cement in the laboratory using raw materials essentially used by companies involved in the manufacture of the same. Later

during the study, samples of fluoride cements were hydrated and then studied with the aid of x-ray diffractometry and fluorometry, and also scanning electron microscopy. These examinations enabled the characterisation of the fluoride cement. The corresponding physical characteristics for the various samples including setting times, consistency and compressive strengths were also studied.

Some reports indicate that fluoride cement achieves higher compressive strength values compared to those of ordinary Portland cement at same age. The only logical explanations to this phenomenon can be attributed to the properties and characteristics of the mineralogical composition of fluoride cement, and the phases (compounds) formed during hydration. In light of the above, this research work studied properties and characteristics of both unhydrated and hydrated samples of fluoride cement, with the view to establish its hydration and strength developing characteristics. Comparison of fluoride cement properties to those of ordinary Portland cement (Type I as per American Society of Testing and Materials) helped in establishing the possible uses of the former in construction work.

From the above results, a draft Malawi Standard has been prepared for endorsement by the relevant Technical Committee of the Malawi Bureau of Standards, and subsequent use by the various industries and construction organisations.

1.5 Constraints

It was not realised until the project was started that fluoride cement was temporarily unavailable on commercial basis from the Malawi factory. It was hoped that the manufacturer will resume production by December 1991. Consequently, the

manufacturer proposed use of laboratory samples instead of the commercially manufactured cement. Production of laboratory samples of fluoride cement was in small quantities owing to the equipment capacities and capabilities. For the purpose of the studies, the amount required was originally around 200 kg, but only about 10 kg were obtained, which was barely sufficient for the proposed study. For this reason, many of the properties tested were not replicated to provide sufficient data on their statistical variation and standard deviation. It can be assumed therefore that for some of the properties including soundness, fineness and optimum gypsum content, these are only indicative of the potential values.

The other option considered was to use regulated set cement which was being manufactured by a company known as Holnam Incorporated in Saratoga, Arkansas, but due to unavoidable circumstances, the company suspended production of the cement. It was the only company in the United States of America producing regulated set cement.

CHAPTER 2. LITERATURE REVIEW

2.1 The manufacture of Portland cement

Portland cement has been named after the early product which when set is said to have resembled in colour a famous building stone in Isle of Portland, England. The first commercial Portland cement was produced in the late eighteenth century^[1]. Since then there has been a lot of improvement on the techniques of producing the cement.

Chemists and material engineers alike have studied the various means by which the raw materials for the production of cement interact with each other in the kiln to produce what are now the various types of cement. Almost all of today's cement is produced in rotary kilns where strict quality control measures are undertaken.

Portland cement is manufactured from a variety of raw materials consisting of calcareous and argillaceous nature. Those materials containing predominantly lime are classified as calcareous. Those materials containing predominantly silica or alumina are classified as argillaceous. Generally, the composition of the raw mixture for the production of Portland cement would be as shown in Table 1^[1,2]. The presence of other minor compounds alters the characteristics of the cement significantly, hence leading to or allowing for the formulation of other types of cements.

Table 1. Raw materials proportioning for the manufacture of ordinary Portland cement

Material	Percentage
Limestone (Lime)	65
Sand (Silica)	20
Clay or shale (Alumina & ferric oxide)	10
Minor compounds	5

The required combination of the materials aforementioned, is usually obtained by mixing limestone, chalk or marl with clay or shale or other argillaceous materials.

Cement rock, which contains all the ingredients in nearly proper proportions, may be used, adding limestone or argillaceous material as may be required to achieve the proportions of the materials. Another method of producing Portland cement is to add blast furnace slag of low magnesia content to limestone^[3]. The presence of other minor compounds alters the characteristics of the cement significantly, hence leading to the formulation of other types of cements.

There exists two production processes, wet process and dry process, for the manufacture of Portland cement. Both require the raw materials to be thoroughly ground and intimately mixed. In the wet process, the mixing and grinding is done in water. In the dry process, the raw materials are mixed and ground in a dry condition. Each of these two production methods has its own merits and demerits. The American Society for Testing and Materials (ASTM) has defined Portland cement as a material obtained from clinkering the above-mentioned materials, and then pulverising them together with 3 % to 4 % of gypsum to a fine powder. While the quality and quantity of the raw materials is important, the dynamics of what goes on in the kiln is of equal interest. For all analytical purposes, the base materials are considered to be free of impurities.

To facilitate the analysis of the clinkering process, phase diagrams like the one shown in Figure 1 are used. From the diagram, it can be seen that the limitations within which a good cement can be produced are very narrow. Apart from ensuring that the proportioning of the materials is correct, the kiln conditions must be kept at optimum, otherwise an inferior quality cement may result. The kiln temperatures must be

maintained at around 1 300 °C to 1 450 °C for sufficient time to allow the reactions to come to completion. If the materials are removed too soon, then the amount of free lime may be as high 6 %, which is not desirable for the cement.

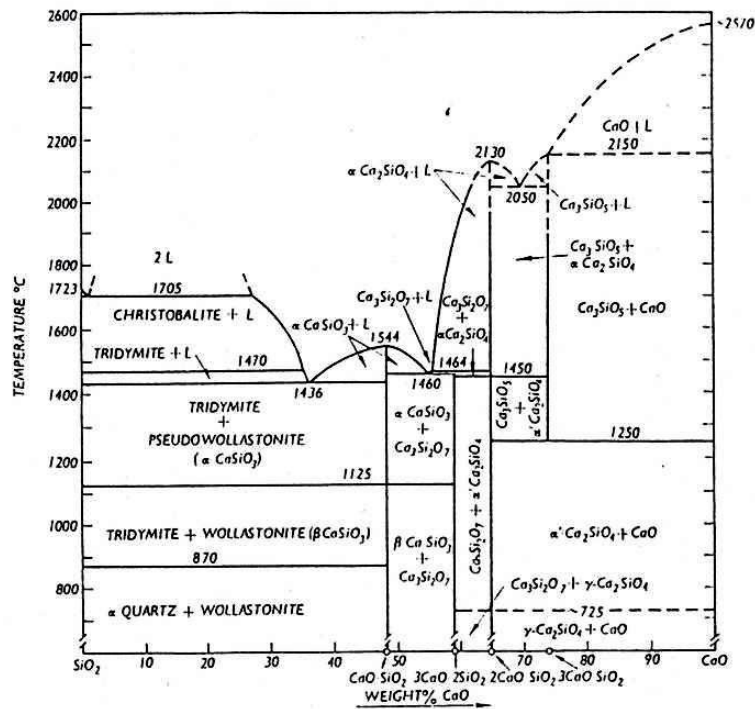


Figure 1. Phase diagram for the CaO-SiO₂-Al₂O₃ system^[2]

Although cement burning technology has been around for almost a century, new ways of improving the technology are still being investigated. Depending on specific needs of a country, several issues are being explored. Areas receiving greatest attention include improvements on the quality of the product, decreasing the variability of the clinker, improvements on the kiln operating conditions, reduction on environmental pollution and reduction on energy requirements. The last two concerns listed above led to the exploration of manufacturing of other types of cements such as fluoride cement.

2.2 The manufacture of regulated set cement

Regulated set (RegSet) cement^[4], also abbreviated as RSPC (Regulated Set Portland Cement)^[5], like fluoride cement is another type of a modified Portland cement. The modification is achieved with the addition of any halogens to the raw materials, fluorine being the most popular. This cement is commercially available on the market, but very few manufacturers are producing it. Currently only one producer of RegSet cement has been registered in the United States of America^[6].

Regulated set cement is manufactured by the addition of 5 % to 30 % of fluoroaluminate compound^[4]. The fluoroaluminate is either added to and interground with the clinker or mixed intimately to fresh Portland cement. The fluoroaluminate compound added to the clinker is basically used as a fluxing agent to facilitate clinkering of the raw materials. This compound effectively alters the phase compositions of the clinker and the cement formed. Tricalcium aluminate, which is one of the compounds in Portland cement is not formed and is replaced by another aluminate compound. The aluminate phase formed in the clinker is of the formula $C_{11}A_7.CaF_2$ ^[4], which replaces the normal aluminate phase, C_3A formed in normal Portland cement.

The presence of sulphates at no more than 5 % concentration in the raw materials during the firing improves the early strength of the cement. Regulated set cement has found many uses in the field of construction where rapid strengths are required at very early ages. However it does not meet the rate of strength development of aluminous cement^[5].

2.3 The manufacture of fluoride cement

The manufacture of commercial fluoride cement started as recently as 1979, although experimenters such as A S Holland is reported to have made a suggestion as far back as the year 1911^[1]. The production of fluoride cement in Malawi started in the late 1980s. To date, the production is still undergoing improvements particularly with respect to kiln and clinkering dynamics. Investigations carried out on the local raw materials indicated the possibility of using the available resources in the manufacturing process^[7]. Table 2 shows the required proportioning of the raw materials generally used in fluoride cement manufacturing.

Table 2. Raw materials proportioning for the manufacture of fluoride cement

Materials	Percentage
Limestone, CaCO ₃	78
Shale, SiO ₂ , Al ₂ O ₃ , Fe ₂ O ₃	20
Fluorspar, CaF ₂	2

Fluoride cement manufacture basically is similar to the manufacture of Portland cement. The same calcareous and argillaceous materials are the basic components. The only difference is the addition of mineralisers and the clinkering temperature. The effects of adding the extra Ca⁺ from the fluorspar have to be taken into consideration when maintaining the optimum ratio of CaO to SiO₂, which lies between 2.5 and 3.0.

After obtaining the right proportion of the raw materials, they are then brought to the sintering temperature of around 1 200 °C in a rotary kiln. The materials are kept in the kiln for about an hour and then allowed to cool rapidly. The clinker that is formed

later is interground to a fine powder with the addition of 2 percent gypsum. Figure 2 illustrates the phases during the formation of fluoride cement.

The clinkering process results in the formation of several compounds, some of which are intermediate. When fluoride compounds are used, they include calcium chondrodite, $(C_2S)_2.CaF_2$, and silico-fluorides with their compositions given as $(C_3S)_3.CaF_2$, $11CaO.4SiO_2.CaF_2$ or $19CaO.7SiO_2.2CaF_2$ ^[5]. However, the presence of compounds such as $CaSO_4$ could cause the formation of fluor-ellestadite, $3C_2S.3CaSO_4.CaF_2$, or silico-sulphate, $2C_2S.CaSO_4$.

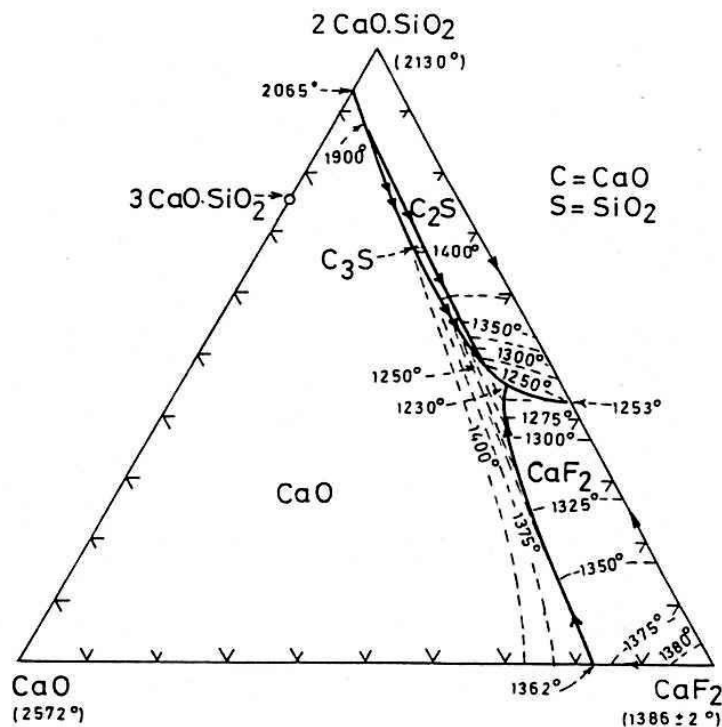


Figure 2. Phase diagram of the $2CaO.SiO_2$ - CaO - CaF_2 system^[8]

A promising thing about fluoride cement is its low energy requirement during production. For many developing nations, the considerable energy savings would contribute toward making the product available at very economic rate. A manufacturing

firm known by the name of Fluoride Cement Company situated in Balaka, Malawi has embarked on the project of manufacturing and promoting use of this cement in Malawi. This undertaking will be more efficient and effective if technical information of the cement is made available to all concerned with building materials^[3,9].

2.4 Use of mineralisers in cement making

Studies on the general use of mineralisers in the manufacture of Portland cement have been reported as early as 1882^[8,10]. These early literature advocated the utilisation of mineralisers during clinker formation, as a means of aiding and accelerating the kinetics of reactions^[8]. Mineralisers are important in phase equilibria, role of intermediate compounds, clinker liquid and kinetic studies. The importance is relevant to the formation of cementitious compounds such as C_3S ^[11]. Attaining the right temperature and holding it for the required amount of time are crucial factors in governing the quality of burning and fuel efficiency. With the lowering of the temperature of liquid formation, it is important that it should be achieved with the minimum quantity of melt phase^[8]. The importance is related to the grindability of the resulting clinker and the energy required for grinding the clinker. The more the melt phase present the harder it is to grind the resulting clinker.

From review of literature, it has been reported as early as four decades ago that some studies had been carried out on the use of and effects of fluorides and fluoride containing materials in the manufacture of Portland cement^[1,10,11]. The studies were on natural occurring mineral deposits and fluoride wastes from industrial processes. These compounds were added to the raw materials mixes as fluxes or mineralisers to aid in the

burning of cement. Occasionally they occurred sporadically as impurities in the limestone component. Compounds studied include magnesium fluosilicate, $MgSiF_6$, cryolite, Na_3AlF_6 , and fluorspar, CaF_2 . The list is not exhaustive but the most common mineralisers are listed in Table 3. Eitel reported on the successes as well as the limitations of the presence of fluorine in the clinkering process^[1,11]. The effects of fluorine on the clinker were also documented by other researchers, but mainly reported were the negative effects rather than the positive effects.

Table 3. Compounds that are commonly used as mineralisers in the manufacture of cements

Material	Quantity, %	Effects
Fluorspar	3.4	Reduces liquidus temperature, free CaO, beta-C ₂ S; increases gamma-C ₂ S
Cryolite	30.0	Like fluorspar, but more effective
Calcium aluminofluorite	-	No information available
Magnesium fluosilicate	10	Most effective in reducing free CaO
Calcium phosphate	10	Increases free CaO; no effect on C ₂ S inversion

The negative effects that surfaced in the early use of fluoride bearing compounds include the formation of non-cementitious compounds in the clinker^[8,10]. The principal drawbacks were the decomposition of C₃S at a temperature of 1 250 °C, and the inversion of beta-C₂S into gamma-C₂S. The formation of these non stable compounds which tend to decompose below equilibrium temperatures have been reported^[10] in several reports. These compounds have the tendency of lowering the strength of the cement upon

hydration, or do not effectively contribute to the strength development process. Recent studies however have reported on the successful synthesis of Ca_3SiO_5 solid solutions containing fluorine and aluminium, and thus the name "Alfluoral route" in the manufacture of fluoride cement^[7,12].

Also reported in some literature is the formation of modified calcium silicate and calcium aluminate compounds. A compound having the composition $3\text{CaO}.3\text{Al}_2\text{O}_3.\text{CaF}_2$ has been identified as being present and having cementitious properties^[10]. Another dominant compound, $(3\text{CaO}.\text{SiO}_2)_3.\text{CaF}_2$ is known to be present when the clinker is fired in the presence of calcium fluoride^[10]. These compounds have been reported as having positive influence on the strength of the cement. The occurrence of these compounds is however dependent on the composition of the raw meal and temperature of the clinker and the cooling rate. They may at times occur as part of interstitial phase, such as fluor-ellestadite with the general formula $3\text{C}_3.3\text{CaSO}_4.\text{CaF}_2$ ^[13], or on the coatings of some cement kilns.

In all the cases reported in literature, there is a concordance on the fact that the liquidus temperature of the phase system containing the cement making compounds is reduced. At CaF_2 concentration of 5 % the liquidus temperature is reduced by 50 °C to 70 °C and by 100 °C to 120 °C when the CaF_2 concentration is 10 %. More recent documentation^[7] report the temperature may be reduced by 200 °C at CaF_2 concentration of only 2 %. Further reduction in the liquidus temperature is also possible at higher concentrations of up to 30 % CaF_2 . However, the resulting clinker will be affected in terms of its mineralogical composition and hence the compressive strengths that can be

achieved. Also, the resulting clinker relates more to RegSet cement which has a very high content of fluoride.

Production problems have also been reported. The escape of fluorine from the mixes during the firing process causes deterioration of the kiln linings. It has been reported that the kiln refractory layers and flues have been etched and attacked by fluorine emissions. However, some researchers have reported the successful incorporation of up to 85 % of the fluorine in the clinker, following a well controlled firing process. It is therefore important to control the temperature in the kiln in order to prevent the release of fluorine, which could also be a concern in air quality and pollution control.

2.5 Highlights on ordinary Portland cement properties

2.5.1 Composition

Raw materials for the manufacture of Portland cement basically consist of lime, silica, alumina and iron oxide. During the clinkering process in the kiln, these compounds interact to form more complex products. It is assumed that an equilibrium state is arrived at when the products finally cool down. From this assumed state of equilibrium, the products forming the compound composition of Portland cement have been calculated^[1,2,5]. The quantities are based on the oxide composition of the clinker, ignoring the presence of minor compounds.

The calculated values for the composition of Portland cement are based on Bogue equations^[1]. Four compounds are usually regarded^[1] as the major constituents of Portland cement. Table 4 shows the compounds names, their oxide composition and their

abbreviated symbols. It should be noted that in reality, these compounds do not exist in pure state, but contain impurities from minor constituents in solid solutions.

Minor compounds found in Portland cement usually amount to not more than a few percent. However these are minor in terms of their quantities but not their importance. Their effect may vary from reducing the strength of the cement, altering the basic properties of the cement to forming harmful products when hydrated in a concrete mix.

Table 4. Compound composition of Portland cement

Name of compound	Oxide composition	Abbreviation
Tricalcium silicate	$3\text{CaO}.\text{SiO}_2$	C_3S
Dicalcium silicate	$2\text{CaO}.\text{SiO}_2$	C_2S
Tricalcium aluminate	$3\text{CaO}.\text{Al}_2\text{O}_3$	C_3A
Tetracalcium aluminoferrite	$4\text{CaO}.\text{Al}_2\text{O}_3.\text{Fe}_2\text{O}_3$	C_4AF
Free lime	CaO	C

The possibility of the main compounds existing in solid solutions with other minor constituents, led to the development of cements of other characteristics. The required chemical and physical characteristics of the final cement can be obtained by varying the compositions of the raw materials. The various compositions of the cements determine the types and characteristics of the cement.

This enables cement chemists to formulate cements of different types for different applications. Different countries have different types and designation for the cements. These include ordinary Portland cement, rapid hardening cement, low heat cement, high alumina cement and sulphate resisting cement. Also special cements such as white

Portland cement and modified cements have been formulated and are being manufactured. Fluoride cement falls under the category of modified cements.

2.5.2 Setting times

The phenomenon commonly described as setting is the chemical transformation of cement components when mixed with water^[5]. In very broad terms, setting is the process resulting in the formation of a rigid and stiffened paste from a workable plastic cement paste. During this transformation a rapid formation of crystalline products is observed, together with a mutual coagulation of the components^[2]. For practical purposes it is distinguished from hardening, whereby the cement is said to gain strength.

Two stages of setting have been commonly agreed upon to describe the hardening process in a cement paste. These are arbitrary and empirical values, indicative of the progress of hardening, as set by various standards^[2,5], for example Malawi Standard MBS 29, British Standard BS 12 and American Society for Testing and Materials ASTM 150. There are two other forms of setting of cement, false set and flash set. The former describes the abnormal premature stiffening of cement within a few minutes of mixing with water. The latter is the rapid and violent reaction of C_3A with water leading to immediate stiffening of the paste.

The first one is initial setting, believed to be caused by the hydration and crystallisation of calcium aluminate. Neat C_3S also exhibits an initial set when mixed with water. The second stage is termed final set, caused by the beginning of the decomposition of tricalcium silicate^[1]. Initial set in ordinary Portland cement is said to take place between 30 minutes and 45 minutes, while final set takes place between 375

minutes and 600 minutes. Table 5 shows the allowable setting times for ordinary Portland cement, as prescribed in ASTM C 150^[14].

When ordinary Portland cement clinker is ground to a fine powder without the addition of set retarders such as gypsum, its setting takes place very rapidly. The practice has thus been to add 2 % to 3 % of gypsum and intergrind it with the clinker. The addition of these retarders in optimum quantities, gives the cement a reasonably long working life to allow for proper placing.

Table 5. Setting times for ordinary Portland cement

Characteristic	Setting time
Initial setting	45 minutes, min
Final setting	10 hours, max

2.5.3 Compressive strength

One of the most important physical characteristics of cement is its compressive strength. This is the most required property in terms of its structural requirements. The compressive strength of cement mortar or concrete is dependent on the cohesion of the cement paste, its adhesion to aggregate particles and to a certain extent the strength of the aggregate.

There are two classical theories on gain of strength in cement. Le Chatelier in 1882, and later supported by others, established that when cement is hydrated the products of hydration precipitate from the supersaturated solution of calcium hydroxide and concentrations of calcium silicate hydrates. The other theory is centred on the formation of a gelatinous mass from the initial colloidal system of crystalline aluminates.

The actual source of the strength of the system comes from the physical attraction (van der Waal's forces) between solid surfaces^[1,15]. The other part of the strength is brought about by the chemical forces between the gel particles. Both of these contribute to the considerable strength of the hardened paste. Table 6 shows some typical values of the compressive strength of ordinary Portland cement pastes.

Table 6. Compressive strength of ordinary Portland cement paste

Age, days	Compressive strength, MPa
3	76
7	120
14	131
28	175

2.5.4 Hydration properties and products

Several studies have been conducted with the view to understand the nature of the hydration properties of ordinary Portland cement. The nature of hydration is directly related to the mineralogical composition of the cement. Although the hydraulic properties have been established the exact nature of the mechanism leading to hardening are still not very clear. It is well known that the setting and hardening of cement is the result of a series of simultaneous and consecutive reactions between the water and the mineral components^[10]. The reactions are partly hydration and partly hydrolysis. It has been established that the addition of water results in the reduction of size of cement particles. Crystallisation takes place and as these precipitate from the solution a colloidal material is formed. With time the hydration products form a fine textured solid - gel^[2,16]. The hydration process is exothermic. It has been observed that during the first 24 hours,

selective hydration takes place, and that the process starts from the surface of the particles. Because of this the fineness of the cement affects the hydration process.

In the presence of water, the silicate and aluminate compounds in the cement form products of hydration which harden with time. The compounds C_3S and C_2S are primarily responsible for the strength of the cement. Upon hydration of the silicates, the compound with the formula $C_3S_2H_3$ is formed by ion diffusion rate through the hydrate film. A tricalcium aluminate hydrate, C_3AH_6 , is formed from the hydration of C_3A . It is common practice to designate the combined silicate hydration products as C-S-H. Also formed during the hydration is calcium hydroxide, $Ca(OH)_2$.

2.5.5 Microstructure of hydrated cement

Normal hardened Portland cement paste is a heterogeneous and porous material. Most of the products of hydration appear as an amorphous C-S-H gel which takes a variety of morphologies such as spiny crystalline ettringite and hexagonal tabular plates $Ca(OH)_2$ and AF_m phases. The pores are basically empty spaces left behind by the evaporating water or water used up in the hydration process, or simple air bubbles. Other spaces are present in the form of microcracks originating from the reaction products and mechanical effects.

The bulk of the solid phases present in the hydrated paste are C-S-H (~ 70 %), CH (~ 20 %) and the rest composed of sulfoaluminates and minor constituents^[17]. Also present in the solid matrix are dissolutions from the clinker products. The microstructure of these compounds depend on the concentration of the other minerals in the matrix.

When the proportion of $Ca(OH)_2$ is less in the matrix, and more $CaSO_4$ is present, then

the structure takes the form of tabular crystals. Needle-like structures are formed when the ratio of CaSO_4 to free CaO is around 2:1

2.6 Highlights on fluoride cement properties

2.6.1 Composition

As learned in the previous sections, the same raw materials for the manufacture of Portland cement are used in fluoride cement manufacture, namely consisting of lime, silica, alumina and iron oxide. Their interaction with fluoride during the sintering process in the kiln, causes the modification of the normal compounds formed in Portland cement.

Studies on fluoride cement have suggested the formation of several compounds, some of which are intermediate. They include silico-fluorides with their compositions given as $(\text{C}_3\text{S})_3.\text{CaF}_2$, $11\text{CaO}.4\text{SiO}_2.\text{CaF}_2$ or $19\text{CaO}.7\text{SiO}_2.2\text{CaF}_2$, or calcium chondrodite, $(\text{C}_2\text{S})_2.\text{CaF}_2$ ^[1,4,7,10]. The existence of the normal cement compounds, that is, tricalcium silicate, dicalcium silicate, calcium aluminate and tetracalcium aluminate has also been reported. However, F P Glasser states that these have modified crystal structures^[7]. The phase $11\text{CaO}.7\text{Al}_2\text{O}_3.\text{CaF}_2$ is also reported as being present. The presence of sulphates such as calcium sulphate causes the formation of fluor-ellestadite, $3\text{C}_2\text{S}.3\text{CaSO}_4.\text{CaF}_2$, or silico-sulphate, $2\text{C}_2\text{S}.\text{CaSO}_4$.

Table 7 shows the probable composition of fluoride cement, as there still exists some compounds whose exact chemical formulae are not known. Again, the quantities are based on the oxide composition of the clinker, ignoring the presence of minor compounds.

2.6.2 Setting times

Like in all other cements setting is an important property in terms of the workability of the cement. Again gypsum may be interground with the clinker in order to regulate the setting time of the cement^[2]. Table 8 shows the range of the setting times.

Table 7. Major compound composition of fluoride cement^[5,8,10]

Name of compound	Oxide composition	Abbreviation
Silico-fluorides	11CaO.4SiO ₂ .CaF ₂	C ₁₁ S ₄ .CaF ₂
	19CaO.7SiO ₂ .2CaF ₂	C ₁₉ S ₇ .2CaF ₂
	(3CaO.SiO ₂) ₃ .CaF ₂	(C ₃ S) ₃ .CaF ₂
Calcium chondrodite	(2CaO.SiO ₂) ₂ .CaF ₂	(C ₂ S) ₂ .CaF ₂
Fluor-ellestadite	3(2CaO.SiO ₂).3CaSO ₄ .CaF ₂	3C ₂ S.3CaSO ₄ .CaF ₂
	11CaO.7Al ₂ O ₃ .CaF ₂	C ₁₁ A ₇ .CaF ₂
Tricalcium silicate	3CaO.SiO ₂	C ₃ S
Dicalcium silicate	2CaO.SiO ₂	C ₂ S
Tricalcium aluminate	3CaO.Al ₂ O ₃	C ₃ A
Tetracalcium aluminoferrite	4CaO.Al ₂ O ₃ .Fe ₂ O ₃	C ₄ AF
Free lime	CaO	C

Table 8. Setting times of fluoride cement^[7]

Characteristic	Setting time, minutes
Initial setting	30 min
Final setting	60 min

2.6.3 Compressive strength

Studies on compressive strength have been conducted on neat synthetic compounds found in fluoride cement. Shame^[7] reports the compressive strength of synthetic preparations of C₃S obtained in the presence of fluor-aluminate and then mixed

with 2.5 % gypsum, as 147 MPa at 28 days. The range of the strengths obtained are as shown in Table 9.

Table 9. Compressive strength of fluoride cement^[7]

Age, days	Compressive strength, MPa
1	114
3	148
7	154
28	147

2.6.4 Hydration properties and products

Studies of the hydration properties conducted on phase pure alites made in the presence of fluoride cement show some variance from the normal hydration of alites found in ordinary Portland cement. The most notable one is the rapid hydration indicating a shift in the phase structure and reactivity. It has thus been suggested that the resulting alite phase is rhombohedral^[9]. The hydration process is exothermic. The fineness of the cement is important in the hydration process, commencing from the surface of the cement particles and progressing toward the centre of the particles. The products of hydration are quiet similar to those ordinary Portland cement, although they may tend to be denser as in regulated set cement^[18]. It has thus been implied that the nature of the mechanisms leading to hardening are also similar to those of Portland cement^[11,18,19].

In this regard, in the presence of water, the silicate and aluminate compounds form crystalline products of hydration. As these precipitate from the pasty solution a colloidal material is formed which hardens with time. The fluorosilicate compounds are

primarily responsible for the strength of the cement. Upon hydration of these silicates, the compound with the formula $\text{Ca}_3\text{Si}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ is formed. An aluminate hydrate, $6(\text{Ca}_3\text{Al}_2\text{O}_6 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O})$ plus $2\text{Al}(\text{OH})_2\text{F}^-$, is formed from the hydration of $\text{C}_{11}\text{A}_7\text{CaF}_2$, which has a lower rate of hydration compared to the silicofluoride. Also formed during the hydration is calcium hydroxide, $\text{Ca}(\text{OH})_2$ and a product containing the gypsum component $\text{Ca}_3\text{Al}_2\text{O}_6 \cdot \text{CaSO}_4 \cdot 32\text{H}_2\text{O}$.

Table 10. Comparison of ordinary Portland cement and fluoride cement

Comparison area	Ordinary Portland Cement	Fluoride Cement
Raw materials used for cement production	Limestone, chalk or marl with clay or shale or other argillaceous materials	Limestone, chalk or marl with clay or shale or other argillaceous materials plus fluorspar
Production process	Sintering of pulverised mix at 1350 – 1450 °C followed by rapid cooling	Sintering of pulverised mix at 1200 – 1270 °C followed by rapid cooling
Chemical composition of cement	Monoclinic alite, belite, and calcium aluminoferrite	Alite, belite, calcium, fluoroaluminate, and ferrite
Setting behaviour (IS/FS, min)	Initial setting = 30 – 45 min Final setting = 375 – 600 min	Initial setting = 5 – 10 min Final setting = 10 – 20 min
Major hydration products	Calcium silicate hydrate, Ettringite, Calcium hydroxide, Monosulfate hydrate	Ettringite, Calcium silicate hydrate, Calcium hydroxide, Monosulfate hydrate
Compressive strength (MPa)	1 day = - 3 day = 76 7 day = 120 28 day = 175	1 day = 15.6 3 day = 114 7 day = 148 28 day = 147

The nature of hydration is directly related to the mineralogical composition of the cement. The products appear to vary not only with the composition of the constituent raw materials but also with time and compound composition of the anhydrous cement.

Shame reports on improved hydraulic properties of laboratory synthesised materials. . have been established the exact nature of the mechanism leading to hardening are still not very clear. It is well known that the setting and hardening of cement is the result of a series of simultaneous and consecutive reactions between the water and the mineral components^[10]. The reactions are partly hydration and partly hydrolysis. It has been established that the addition of water results in the reduction of size of cement particles. Crystallisation takes place and as these precipitate from the solution a colloidal material is formed. With time the hydration products form a fine textured solid - gel^[12]. The hydration process is exothermic. It has been observed that during the first 24 hours, selective hydration takes place, and that the process starts from the surface of the particles. Because of this the fineness of the cement affects the hydration process.

2.6.5 Microstructure of hydrated fluoride cement

A normal hardened Portland cement paste is a heterogeneous and porous material. In the case of hardened fluoride cement, the phases present are in the form of crystalline C-H-S and also some C-H compounds, and quite similar to hardened Portland cement. Most of the products of hydration appear as an amorphous C-S-H gel. Spiny crystalline ettringite and hexagonal tabular plates of monosulphate hydrate and Ca(OH)_2 , and AF_m phases are some of the major phases that have been identified as present. As in Portland cement, the microstructure of these compounds depend on the concentration and presence of the other minerals in the matrix. The main reason for this is the complementary reactions that may or may not occur depending on the prevailing conditions. However

the microstructure of the hardened paste is much denser than that of ordinary Portland cement.

When the proportion of Ca(OH)_2 is less in the solution, and more CaSO_4 is present, then the structure takes the form of tabular and hexagonal crystals. Needle-like structures of ettringite will appear when sufficient Ca(OH)_2 is present, and then disappear (actually, converted to monosulphate hydrate) with the shortage of CaSO_4 .

CHAPTER 3. EXPERIMENTAL APPROACH

The experimental stage of this study was divided into two parts. The initial part was to prepare fluoride cement in the laboratory, which would be as close as possible, in terms of its properties, to commercially manufactured cement. The absence of commercial fluoride cement on the market necessitated the need to prepare laboratory samples of the cement. To do this, raw materials were collected from suitable sites in Malawi and fluoride cement production in the laboratory was carried out. The second part of the study centred on characterising the properties of this cement and comparing them with those of ordinary Portland cement. ASTM Type I Portland cement was chosen as a basis for comparison, as this is the type most commonly used in Malawi.

3.1 Laboratory production of fluoride cement

3.1.1 Raw materials selection, sampling and proportioning

As reported earlier on the constraints on materials, it was necessary to produce fluoride cement in the laboratory in the place of commercial fluoride cement. Selection of materials for this part of the investigation was based on the "Alfluoral route" in the formation of tricalcium silicate (C_3S)^[7]. This is the commercially preferred method in the preparation of fluoride cement in Malawi. To reduce the effect of contaminants on the cement, it was very important to use high purity raw materials. The raw materials included limestone, shale and calcium fluoride. Two sets of samples, each composed of five individual samples of the limestone used in the manufacture of the fluoride cement, were collected for screening purposes and selection. For argillaceous material, shale and

silica glass were used. Chemical grade calcium fluoride was substituted for fluorspar, the natural form of the mineral.

One set of the samples of the limestone plus the shale were collected from an area called Changalume in Malawi, rich in limestone deposits and other cement making minerals. The other set of raw materials was collected from an area called Balaka. Based on the results of the preliminary testing, it was decided that high-calcium calcitic limestone as the source of CaO from Balaka area, silica glass for SiO₂, obtained from broken window panes and chemical grade calcium fluoride (CaF₂) be used for the study. The silica glass, with its high content of sodium, was at a later stage during the study substituted with silica sand.

3.1.2 Raw materials testing

Preliminary testing of raw materials was part of the first stage of the study. Testing was carried out on the limestone and the shale to determine the content of CaO for each and also their quality and purity. The values obtain were also used for proportioning the raw materials for the fluoride cement mix proportion. Table 11 shows the preliminary results of wet chemistry analysis of the raw materials. The results are based on the average of five composite samples collected from each of the quarries at Changalume and Balaka.

Table 12 shows the oxide composition of the best choice of the materials using x-ray fluorescence analysis. For the type of limestone selected for the project, the total carbonate content was 95.0 % by mass. For the shale the total carbonate content was

below analytically detectable limits. The SiO₂ content of the shale was considerably high enough for cement manufacture.

Table 11. Quality of raw materials

Compound	Source	Quality, %
CaO	Balaka limestone	95.0 % total CO ₃
CaO	Changalume limestone	84.5 % total CO ₃
SiO ₂	Silica glass (ground)	78.0 % SiO ₂
SiO ₂	Shale	below 0.5 % SiO ₂
CaF ₂	Chemical grade	99.9 % pure

Table 12. Oxide composition of FC raw materials (adjusted for loss on ignition)

Oxide	Limestone	Shale	Silica glass
CaO	53.87	0.03	9.48
SiO ₂	2.75	57.59	72.87
MgO	1.95	0.09	3.99
Al ₂ O ₃	0.10	18.41	0.10
Fe ₂ O ₃	0.12	11.88	0.36
Na ₂ O	0.06	0.22	12.36
K ₂ O	0.05	0.36	0.07
TiO ₂	0.02	2.72	0.04
SO ₃	0.14	0.02	0.10
LOI	40.5	7.72	0.59

3.1.3 Proportioning and preparation

All the materials were carefully sorted and then ground in agate rotary ball mills to a fine powder passing through 150 μm sieve. In actual manufacturing practice the recommended fineness is materials passing 75 μm sieve. Thereafter the raw materials

were thoroughly mixed in fixed proportions by weight as established and recommended by previous studies^[7] on the manufacture of fluoride cement.

It is a known fact that the firing conditions in the kiln are never the same during any two production runs^[2]. Coupled to this is the realisation that the raw materials also exhibit some inherent variation in their composition. While it was imperative to achieve homogeneity in the mixes, some degree of freedom had to be allowed for. For this reason it was decided to have more than one mix proportion for cement production. The eight ratios used in the various mixes are given in Table 13 below:

Table 13. Mix ratios for fluoride cement raw meal

Sample number	Ratio of $\text{CaCO}_3:\text{SiO}_2$	% mass of CaF_2
1	4.0:1	1.0
2	3.4:1	1.0
3	3.0:1	1.0
4	2.8:1	1.0
5	2.7:1	1.0
6	4.0:1	2.0
7	2.4:1	2.0
8	2.4:1	0.0

3.1.4 Firing and quality control

Using platinum and nickel boats all the mixes were fired at 1 150 °C in muffle furnaces in air for 1 hour and then allowed to cool, after which they were again crushed into powder form before firing for a second time for another 1 hour, also at 1 150 °C.

Other samples, placed in silica crucibles, were fired in gas fired furnaces initially at 1 350 °C, so as to observe the temperature at which the materials form a liquid. During the

subsequent firings when the right composition was established, the temperature was adjusted to 1 150 °C. Upon cooling, the clinker was then ground in the ball mills to a fine powder passing the 75 µm sieve. This fineness was achieved on dry materials and running the mills for 12 hours. At this point anhydrous calcium sulphate (gypsum) was added to the clinker.

Since the addition of calcium fluoride as a mineraliser lowers the clinkering temperature from around 1 450 °C to 1 100 °C^[7,8,10], accordingly then the samples were clinkered at 1 150 °C. Higher temperatures than this would result in volatilisation of fluorine, and hence alter the formation pattern for C₃S. Also to avoid the problems that have been reported^[8] that the main production problem in the manufacture of fluoride cement is the destruction of the refractory layers in the kilns by the fluorine vapours^[19]. Hence the firing times and temperatures were strictly controlled to avoid damaging the furnaces.

3.2 Determination of properties of fluoride cement

3.2.1 General

Testing of the samples was conducted on all the samples that were prepared using standard test methods as established by Malawi Standards, ASTM or British Standards. Also test procedures for the x-ray diffraction (XRD), x-ray fluorometry (XRF), scanning electron microscopy (SEM) and energy dispersive x-ray (EDX) analyses of specimens were conducted according to equipment manufacturer's instructions. All physical tests were conducted on equipment used for testing cement and cement products, and meeting the ASTM requirements.

3.2.2 Chemical and mineralogical composition

The samples of fluoride cement were then chemically analyzed for their oxides content in accordance with the British Standard^[20] for chemical analysis of ordinary Portland cement. This is a classical approach for use with the Bogue equation in the determination of the compounds (tricalcium silicate, dicalcium silicate, tricalcium aluminate and tetracalcium aluminoferrite) formed in the cement. In addition to the wet chemistry analysis, x-ray analysis and SEM/EDXA analyses were carried out. For x-ray diffraction a Siemens PDP 500/LC 500 with $2\tilde{O}$ Cu K_a operating at 40 kV and 20 mA was used, while a Siemens LC 200 X-ray Fluorescence Equipment was used for oxide and mineralogical composition. The two were complemented with the Scanning Electron Microscope (JEOL JSM 840A) for elemental composition.

3.2.3 Hydration reactions and products

Determination of hydration products was conducted on the test specimens used for compressive strength determination. Examinations were done on the hardened paste after being aged for 1, 3, 7, 14 and 28 days, and also after 3 months. Identification of the compounds present was achieved using the XRD technique with the help of computerised search and match on standardised materials database, as maintained by the American National Bureau of Standards. Examination revealed the presence of several compounds formed during the hydration process. Most of the compounds identified in the paste were silicate hydrates, some with complex chemical formulae. Their probable chemical formulae was presented by the micro powder diffractory standards. A portion of the specimens were also analyzed using SEM and EDX analysis. The specimens for

microscopic examination were scrutinised for the morphological features and also for improving results from the XRD tests.

3.2.4 Setting times

The times of setting for the cement were determined in accordance with ASTM C 191 by the Vicat apparatus^[21]. The test specimens were mixed and prepared as for normal consistency tests. The test was conducted on two batches, one from laboratory made fluoride cement and the other from commercially made cement. Three specimens each were made for the laboratory made cement and the commercial batch. The interval between each penetration measurement was 10 minutes, to allow for any uncertainties on the setting times of the cement.

3.2.5 Microstructural development and hardening

The microstructure of hydrated fluoride cement was analyzed with the aid of scanning electron microscope and x-ray powder diffraction. The fluoride cement was hydrated and then observed at various stages of hydration namely 1, 3, 7, 14, 28 and 90 days. The specimens were collected and prepared from fragments of specimens used in the compression strength tests.

3.2.6 Strength development

Strength development was measured by observing the compressive strength of the hardened pastes at specific intervals as required by ASTM C 191. Three specimens were prepared and the results were correlated to the microstructural development. The specimens were then subjected to compressive force until failure occurred. The force

measured was then recorded as the compressive strength of the paste at the particular age of hardening.

CHAPTER 4. RESULTS AND DISCUSSIONS

The results that have been discussed in this study relate to those that were of relevance to the study objectives. Most of the discussions dwell on the properties of fluoride cement, as these are the ones that have not been extensively researched. Properties of ordinary Portland cement reported and discussed have been limited to those that could be compared to fluoride cement.

4.1 Raw materials for cement production

Raw materials used in the production of fluoride cement are essentially the ones used in the manufacture of ordinary Portland cement. The addition of fluorspar (natural form of calcium fluoride) acts as a mineraliser and reduces the clinkering temperature and thus acts as energy saver. To ensure the consistency of the cement quality, it is essential that the quality of the raw materials also be consistent and of high purity. This allows for the variations in the firing process and kiln dynamics.

Availability of good quality raw materials in most developing countries is not a major drawback. This makes it advantageous towards the manufacture and use of low-cost cement. Malawi with an abundant supply of good quality raw materials should seriously look into the production of such cement.

4.2 Production of fluoride cement

The greatest challenge in the production of fluoride cement, as for any other cement is to achieve materials that are uniformly clinkered at the right temperature. In the laboratory the raw materials had to be fired twice with some regrinding between each

firing. In actual factory production the raw materials have to be fired in adequate supply of oxygen and at well controlled temperatures to avoid the volatilisation of the fluorine. The cooling of clinker is required to be as rapid as possible in order to avoid destabilisation and decomposition of the cementitious compounds formed in the clinkering process.

It was observed during the laboratory production of the cement that the clinker had to be cooled rapidly to obtain a correct balance of glassy and crystalline materials. There was observed a powdery material and glassy phase in the clinker. Attempts to temper the glassy phase so as to produce a powdery material did not go very well. However given the right conditions it is possible to reverse the morphology of the glassy phase into a powdery crystalline material.

The use of mineralisers has long been of interest due to the low energy requirements. However the resulting clinker has been handicapped by lack of fundamental knowledge of their mode of action, and the complexity of the system and that introduced by the minor constituents

4.3 Test results

4.3.1 Chemical analysis

Laboratory results on the chemical analysis of oxides indicate a slight variation in cement composition compared to ordinary Portland cement. Cementitious compounds were also determined according to Bogue calculations. However it has been established that the Bogue equation is only an approximation and indication^[10,22] of the compounds formed and may not be very accurate. From these results, sample number three came

close to the expected composition of fluoride cement made from high purity CaCO_3 , SiO_2 and CaF_2 . Sample number six made from commercial grade raw materials for fluoride cement production showed there was a high content of Fe_2O_3 and Al_2O_3 , which required some adjusting.

For accurate quantitative determination of the compounds, other means such as Qualitative X-ray Diffraction Analysis (QXDA) were employed. More samples of the cement shall be prepared since there was an imbalance of the compounds and unburnt materials (lime) that were not readily detectable under wet chemical analysis. Mix ratios that were of interest were for samples number 3 and number 6 (representing commercial grade materials) Sample number 6 was obtained directly from Malawi from the manufacturer's factory, and all results presented in this study relate to this material.

Table 14 shows the values of the analysis on the oxides whereas Table 15 shows the compounds composition according to standard Bogue methods of calculation. In the hydration of normal ordinary Portland cement the cementitious compounds have been studied in detail. This has led to a greater degree of understanding the hydration behaviour of ordinary Portland cement, even with the numerous perplexing phenomena.

Table 14. Oxide composition of fluoride cement samples (percentage by weight)

Sample nr	CaO	SiO ₂	SO ₃	Al ₂ O ₃	Fe ₂ O ₃	Free CaO
1	66.80	22.40	0.65	0.87	0.61	5.25
2	64.29	24.52	0.88	0.93	0.54	4.35
3	61.50	26.67	2.23	1.04	0.58	3.63
4	65.64	28.58	2.78	0.80	0.56	5.04
5	63.62	28.17	3.64	1.10	0.57	3.82
6	66.34	19.59	0.27	6.70	3.83	3.54

The raw fluoride cement was also analysed using powder XRD technique. The results from this analysis are shown in Figure 3. There is a substantial amount of crystallinity in the raw fluoride cement. The main compounds identified in the phases include silico-fluorides and dicalcium silicates. Also ferro-aluminate phases are present in the cement, bearing a resemblance to ordinary Portland cement, and a myriad of minor compounds that could result from the interaction within the complex phase system.

Table 15. Mineralogical composition of fluoride cement samples (percent by weight)

Sample nr	C ₃ S	C ₂ S	C ₄ AF	C ₃ A
1	73.57	8.73	1.27	1.85
2	50.60	32.14	1.55	1.64
3	25.04	57.58	1.77	1.76
4	15.46	70.26	1.70	1.16
5	10.71	72.71	1.96	1.74
6	56.36	13.66	11.26	11.64

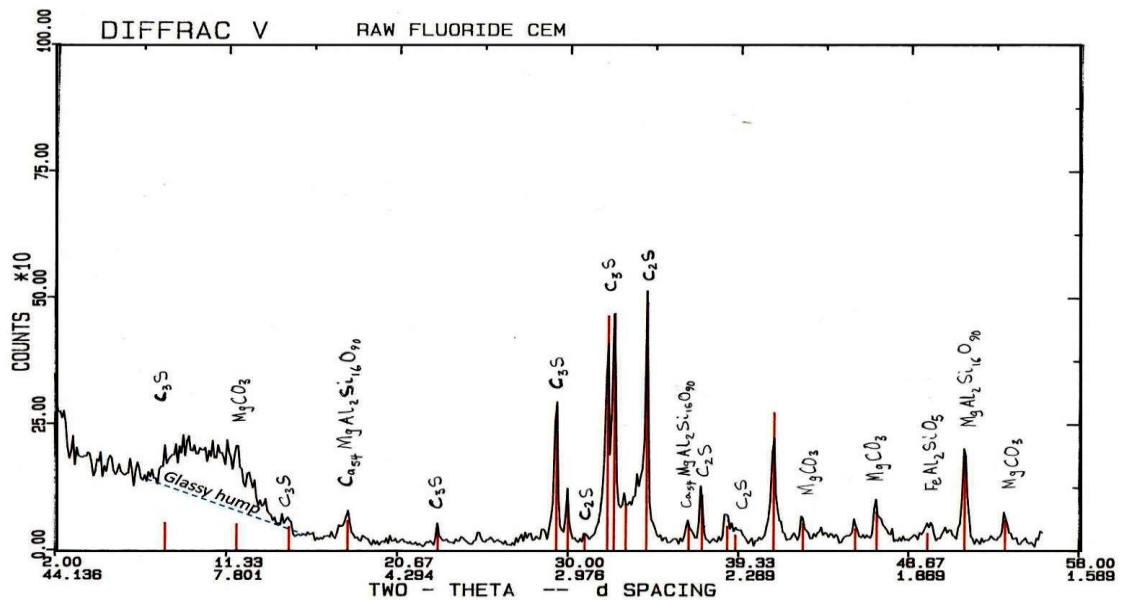


Figure 3. XRD diffractogram of raw fluoride cement

4.3.2 Consistency tests

Results from normal consistency tests show that the amount of water required is 25.38 % of the weight of dry fluoride cement. For OPC Type I, the normal consistency was 26.15 %. These values were obtained from three test specimens each consisting of 650 g of cement and the correct amount of water to achieve the required penetrations in 30 seconds.

4.3.3 Setting times tests

The tests were carried out on both ordinary Portland cement and fluoride cement, after establishing the required normal consistency. The results of the tests for ordinary Portland cement are given in Table 16. For Type I Portland cement, the initial setting time varied from 35 minutes to about 45 minutes. The final setting time was measured to be between 523 minutes and 576 minutes. This is in agreement with the requirements set by ASTM C 150.

Table 16. Setting times of ordinary Portland cement based on laboratory data

Characteristic	Setting times, minutes			
	Observed			Mean
Initial setting	41	43	42	42
Final setting	523	576	544	547

As for fluoride cement, the results are given in Table 17, showing the initial setting times and the corresponding final setting times. The initial setting time was observed to lie between 65 minutes and 87 minutes. The final setting time was measured to be between 545 minutes and 580 minutes. This revelation means that fluoride cement

sets at a slower rate than ordinary Portland cement Type I. Apparently, less gypsum would therefore be required in the cement.

4.3.4 Compression strength tests

Strength tests were conducted on hardened fluoride cement paste and also on hardened ordinary Portland cement Type I paste for comparison purposes. The results are shown in Table 18. Figure 4 gives a graphical presentation of the data. Three specimens were tested, and the averages of the three results at each testing age were calculated.

Table 17. Setting times of fluoride cement

Characteristic	Setting times, minutes			
	Observed			Mean
Initial setting:				
laboratory cement	65	73	87	75
commercial cement	83	91	92	87
Final setting:				
laboratory cement	545	565	580	563
commercial cement	605	635	705	648

Table 18. Compressive strength of ordinary Portland cement

Age, days	Compressive strength, MPa	
	OPC	FC
3	76	120
7	120	135
14	131	133
28	175	160

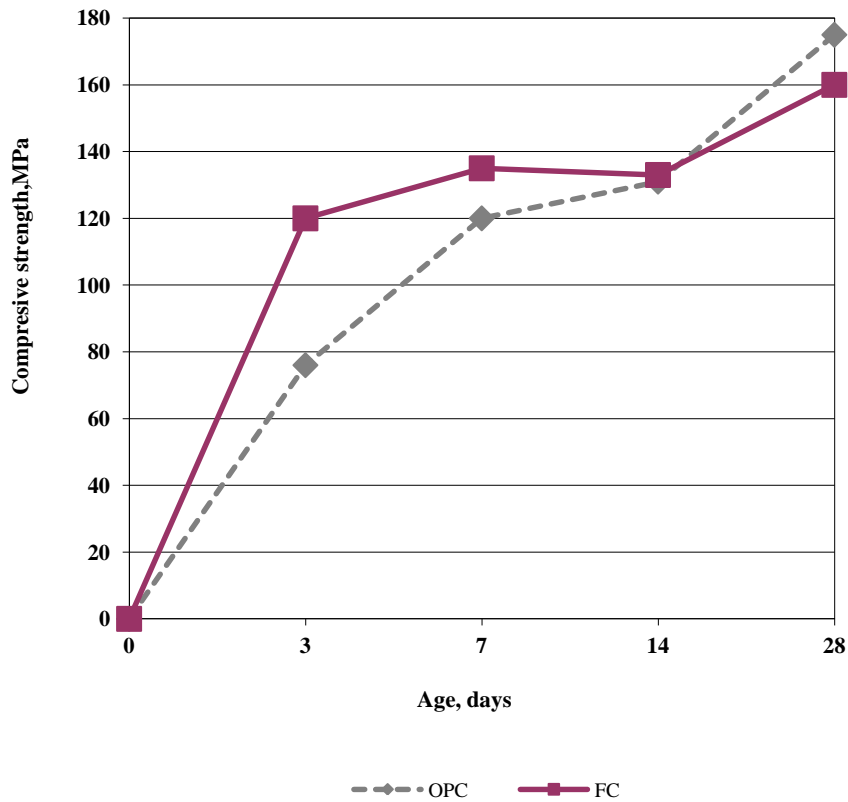


Figure 4. Compressive strength of fluoride and ordinary Portland cements, as a function of age

4.3.5 XRD analysis

Raw materials were analyzed using XRD powder technique in order to identify the major and minor compounds present in the materials. Test specimens from each of the six samples of fluoride cement were then subjected to XRD analysis. Based on the selection made for the sample with best compositional requirements, test specimens for compressive strength determination were made. From these specimens, XRD samples were prepared from the fractured pieces after conducting the compression strength tests.

Results of the analyses at various stages during the hydration of the cement are shown in Figures 5 to 8. The powder XRD patterns show an unmistakable increase in the

crystallinity as well as the glassy phase of the paste. There are various peaks appearing in the hydrated cement as compared to those revealed in the raw fluoride cement, and there is a incontestable tendency for their increase as the cement ages.

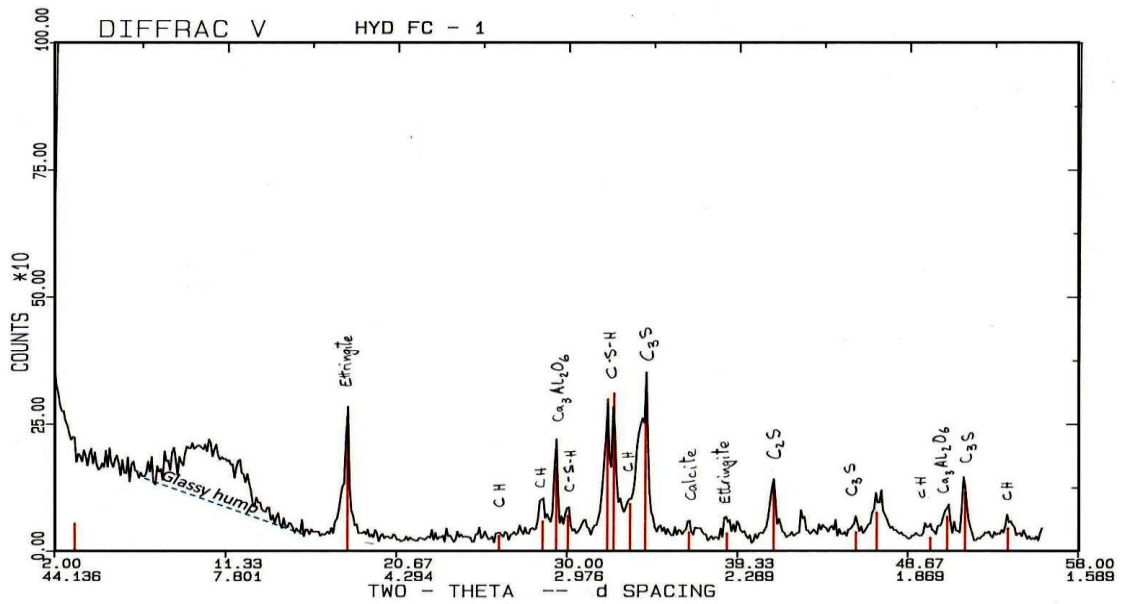


Figure 5. X-ray diffractogram of hardened fluoride cement at 1 day

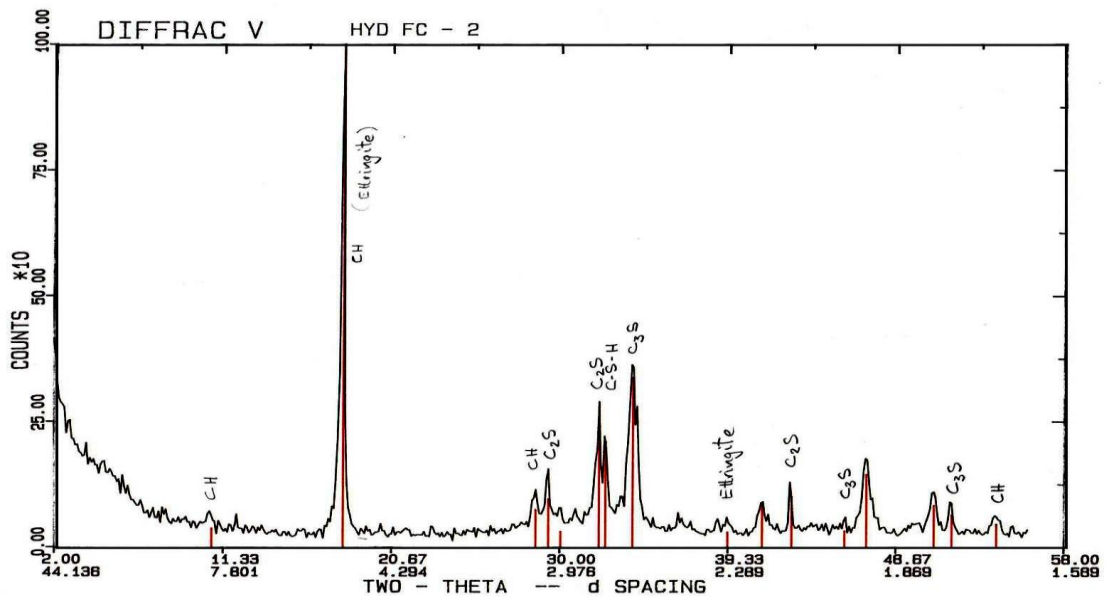


Figure 6. X-ray diffractogram of hardened fluoride cement at 3 days

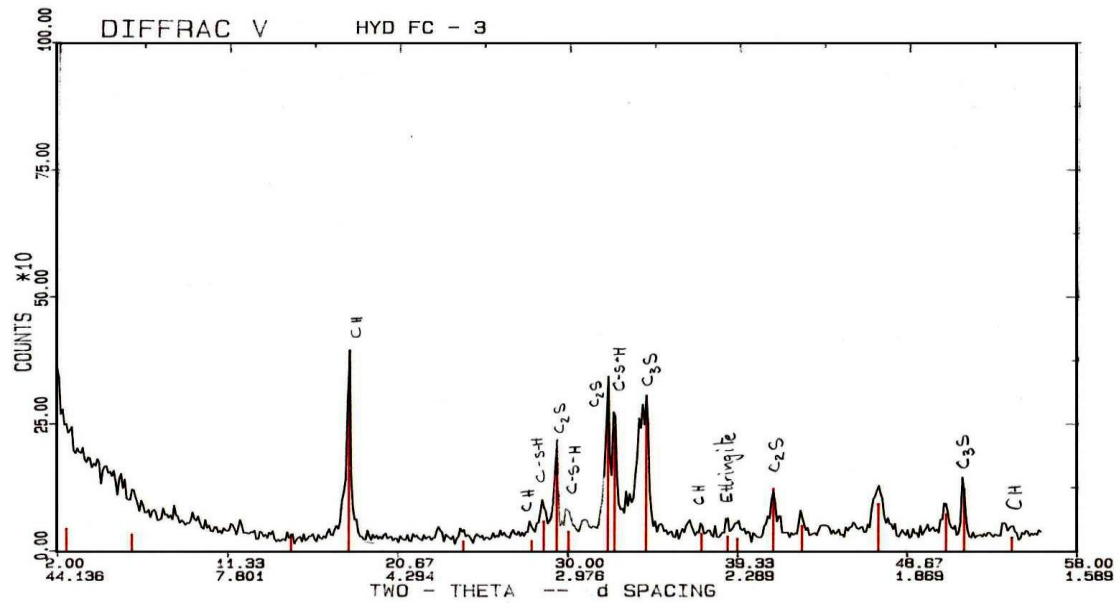


Figure 7. X-ray diffractogram of hardened fluoride cement at 7 days

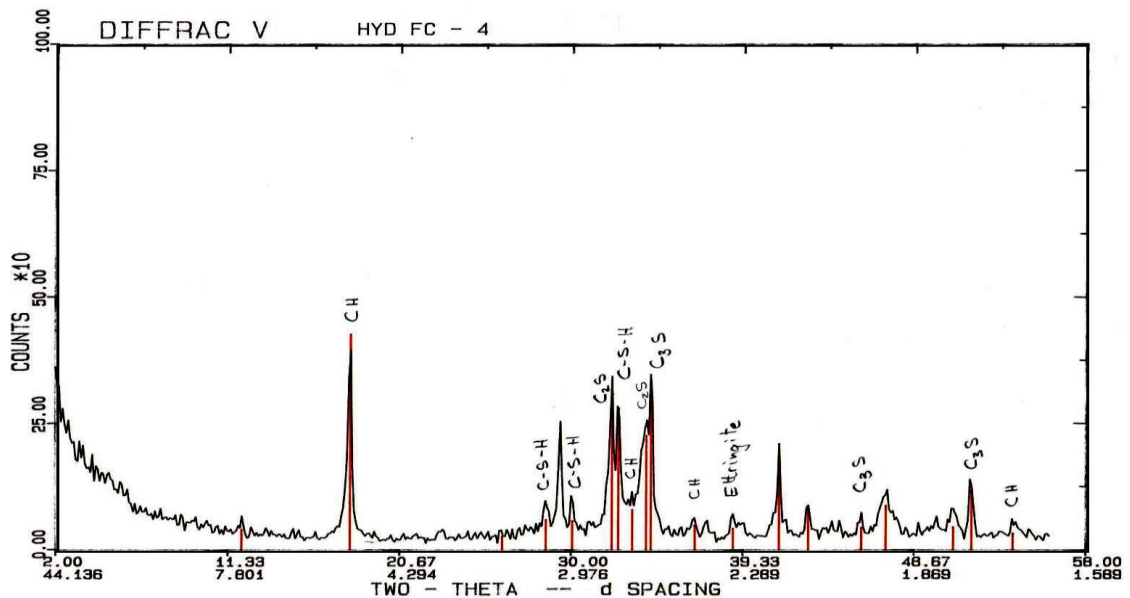


Figure 8. X-ray diffractogram of hardened fluoride cement at 28 days

The degree of crystallinity can be inferred from the intensity of the peaks, as they grow more with hydration. It can be deduced here is that the resulting hydration products are crystalline in nature. This inference is confirmed by the observations made under the

scanning electron microscope, results of which are discussed in more detail later in this study. The observed compounds formed during hydration are ettringite, monosulphate hydrate, calcium hydroxide and calcium silicate hydrates. It has been reported that in high concentrations of fluoride bearing compounds, calcium fluoroaluminate also forms in the hardened pastes^[18], although this may be particularly the case for regulated set cement.

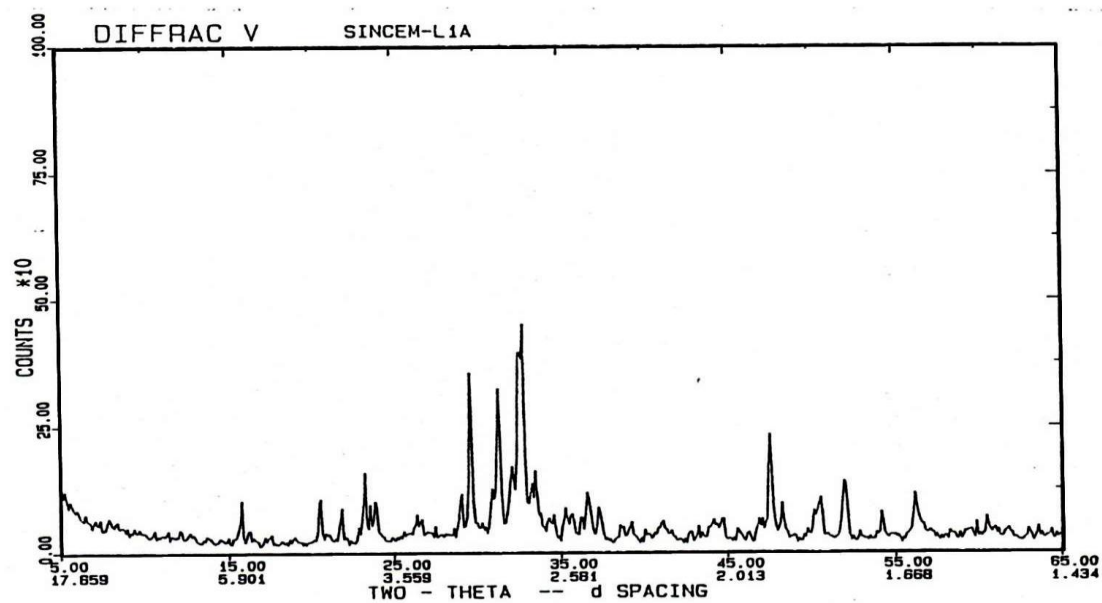


Figure 9. X-ray diffractogram of hardened fluoride cement at 3 months

4.3.6 SEM analysis

The sample of unhydrated fluoride cement mounted on the carbon stud, indicated the presence of fluorine in some of the clinker crystals. Even at low concentrations of only about 2 %, the EDXA results showed that fluoride was successfully incorporated in the clinker matrix. The particles analysed, shown in Figure 10, reveal that other elements present in the particle include calcium, silicon, oxygen, possibly indicating the existence of a silicofluoride compound. Not all particles in the fluoride cement incorporated

fluorine in the matrix. Figure 11 and 12 show the typical EDXA spectra of the clinker particles. The EDXA results of the majority of the particles have calcium and oxygen as their main elemental composition, with fluorine barely detectable under the examination.

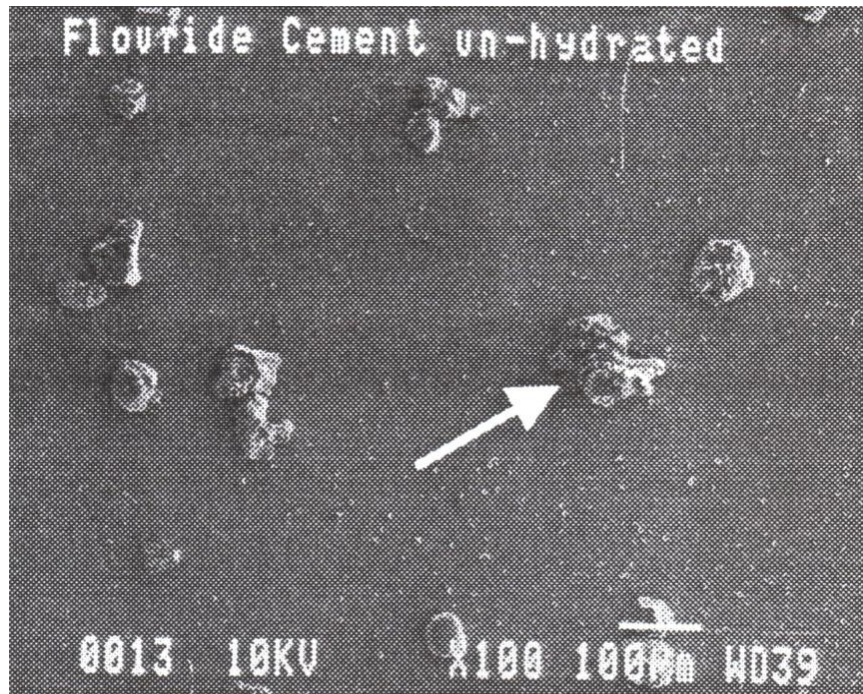


Figure 10. Scanning electron micrograph of anhydrous fluoride cement powder

SEM studies of normal hardened Portland cement paste exhibit it as a heterogeneous and porous material. The SEM analysis reveals a high degree of similarity in the morphology of fluoride cement to Portland cement. Most of the products of hydration appear as an amorphous C-S-H gel. Figures 13 to 16 exhibit the similarity of the features on a large scale. This similarity is also evident between the samples at various hardening ages. This lack of significant difference in the microstructure could explain the reason why fluoride cement achieves higher strengths even at early age.

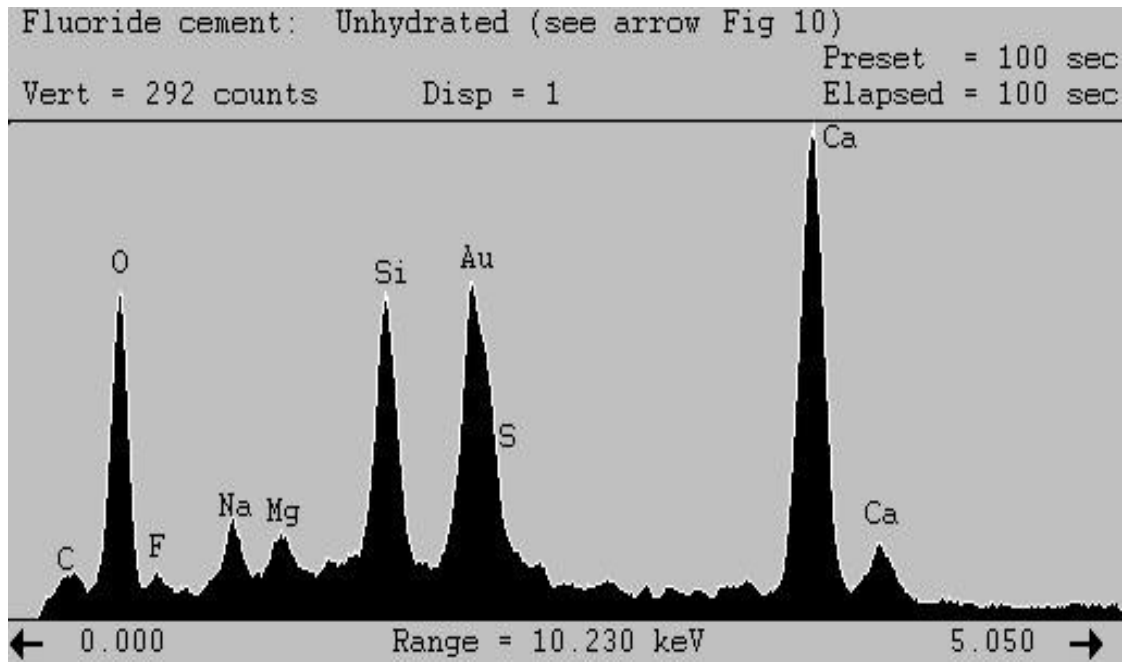


Figure 11. EDXA spectrum of anhydrous fluoride cement particle (see arrow in Figure 10)

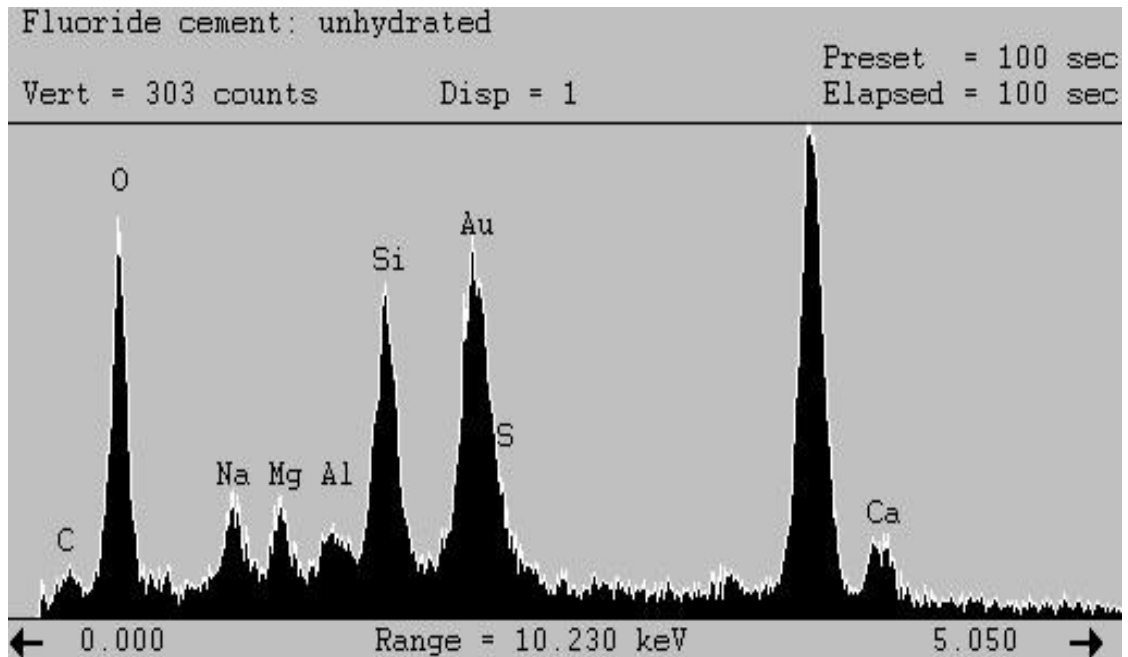


Figure 12. EDXA spectrum of anhydrous fluoride cement particles (typical)

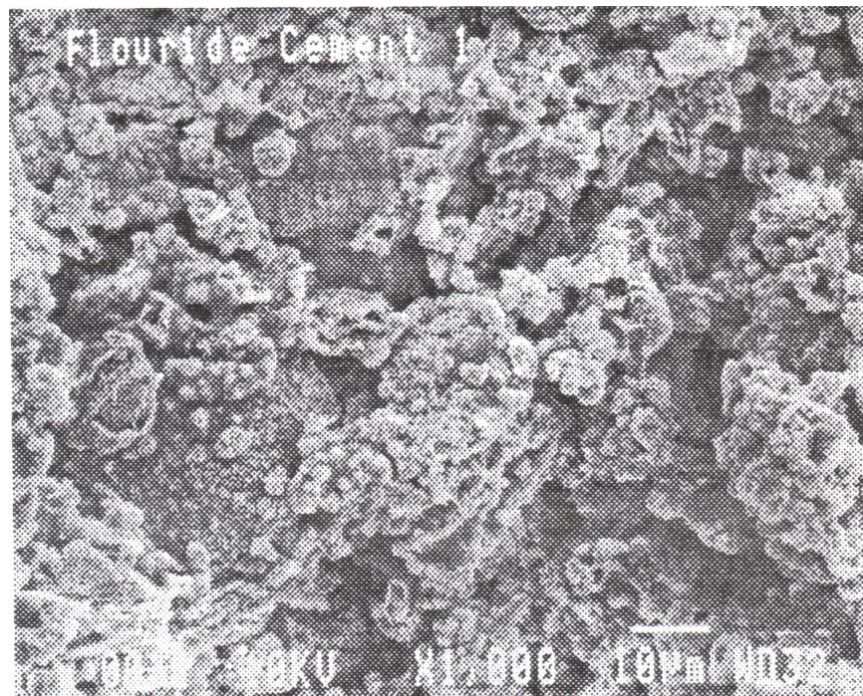


Figure 13. Scanning electron micrograph of hydrated fluoride cement - overview (age - 1 day)

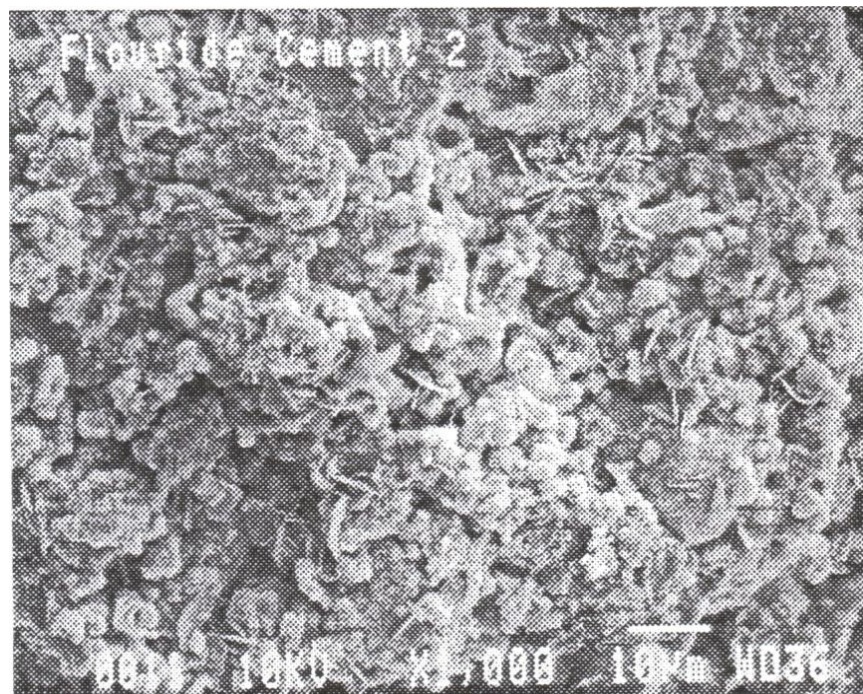


Figure 14. Scanning electron micrograph of hydrated fluoride cement - overview (age - 3 days)

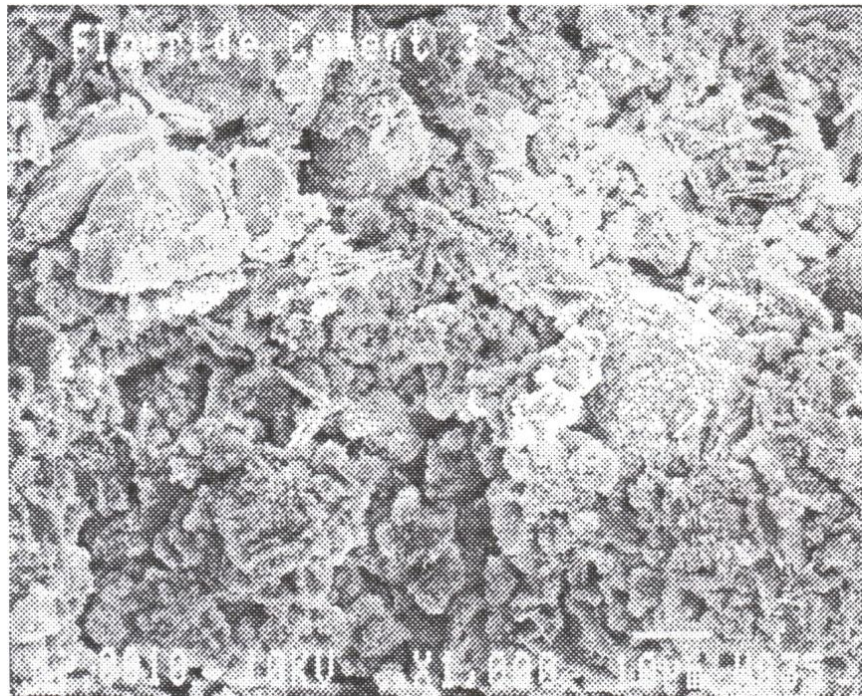


Figure 15. Scanning electron micrograph of hydrated fluoride cement - overview (age - 7 days)

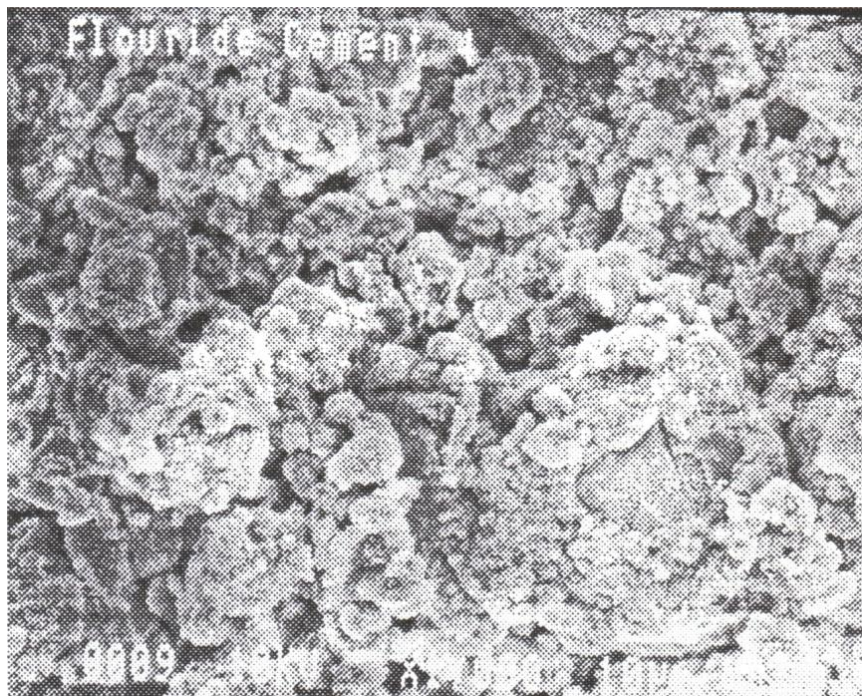


Figure 16. Scanning electron micrograph of hydrated fluoride cement - overview (age - 28 days)

On a smaller scale however, several microstructures were observed on the SEM of the broken surface of hardened fluoride cement. Figures 17 to 28 show the SEM micrographs and the respective EDXA spectra at various stages of hardening of the fluoride cement. All the SEM micrographs of the hardened paste disclose some crystalline structures as well as amorphous material surrounding or attached to the crystals. Observed include spiny crystalline ettringite (Figures 17, 23, and 26), hexagonal tabular $\text{Ca}(\text{OH})_2$ plates (Figures 24), and rosettes of aluminate phases (Figure 21 and 23) and AF_m phases. Also some unmistakable flat crystals manifest with their probable composition being hydrates of aluminium silicates (Figure 21). The microstructures are less defined than in Portland cement.

The platy hexagonal crystal structures that were observed in the early stages of hardening are basically calcium hydroxide crystals. At the early stages of hydration, 1 day to 3 days, the presence of these $\text{Ca}(\text{OH})_2$ crystals appears to be more pronounced (Figure 24). As the paste aged, more and more tiny needle-like and spiny structures are observed, growing on the surface of the plates and forming a close knit and intertwined structure (Figures 26, 27 and 28). EDX analysis show the amorphous matter is made up of calcium silicate hydrates with likely inclusions of calcium aluminate hydrates (Figure 23). The well defined crystalline matter in spiny shape is mainly ettringite, which in Portland cement is sometimes under the right conditions, transformed into monosulphoaluminate crystals at later stages of hardening. This was not so evident in the hardened fluoride paste.

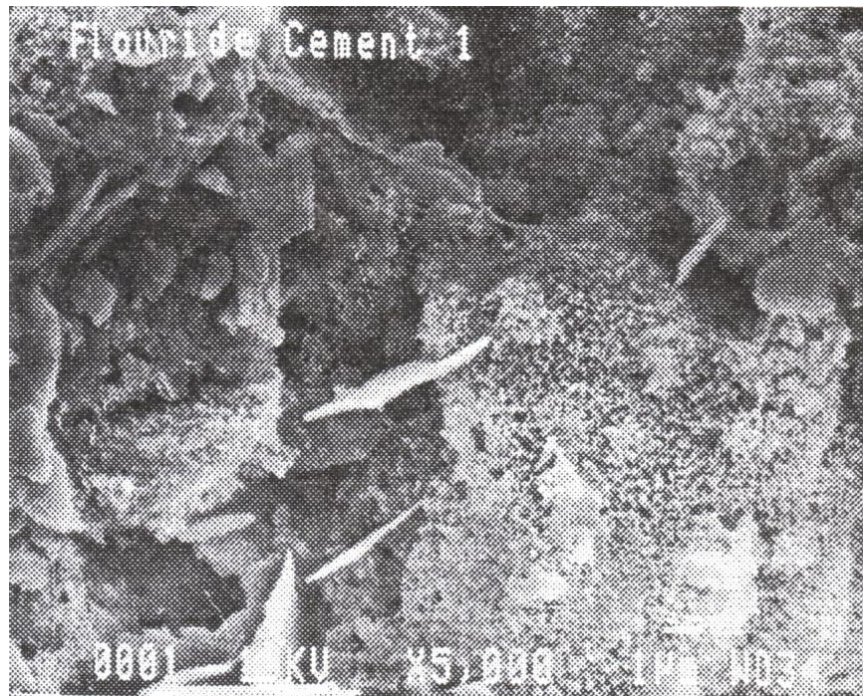


Figure 17. Scanning electron micrograph of hydrated fluoride cement showing ettringite crystals (age - 1 day)

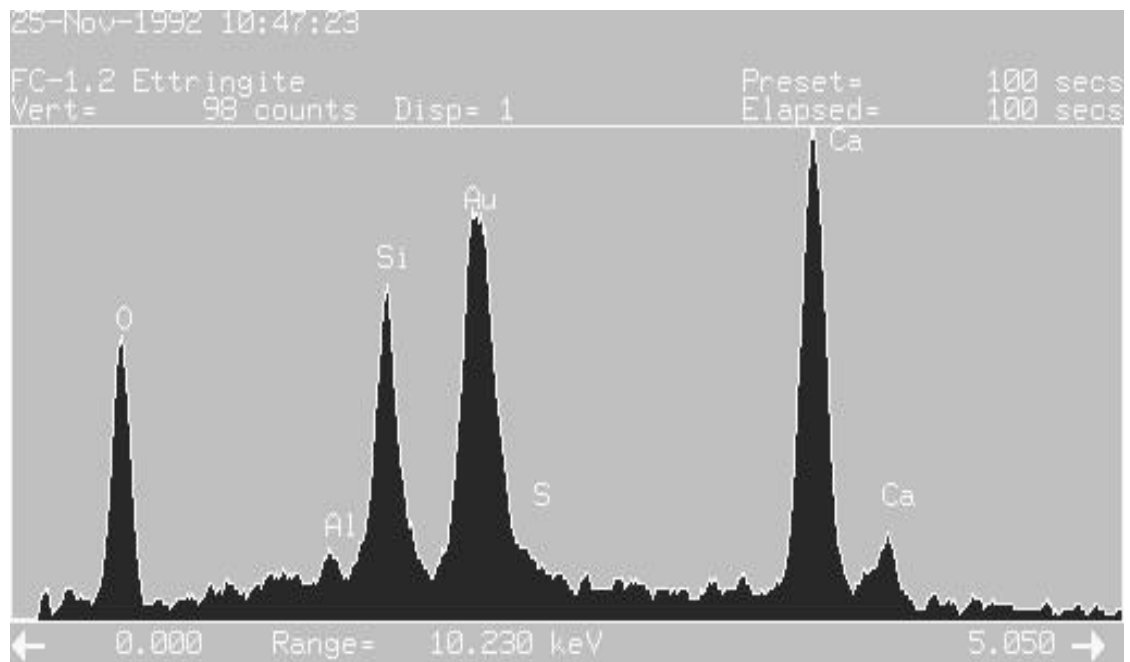


Figure 18. EDXA spectrum of ettringite crystals in hydrated fluoride cement (age - 1 day)

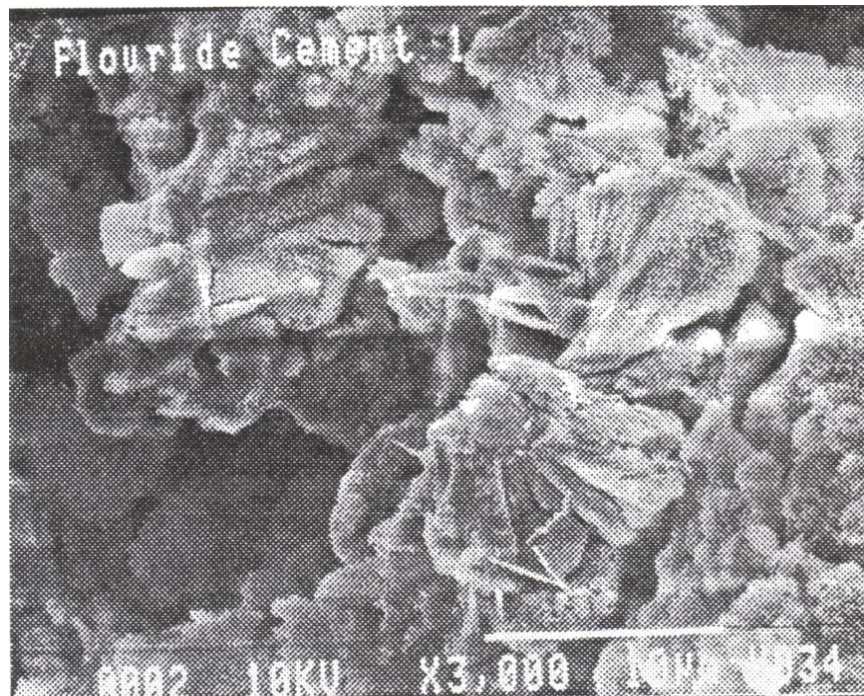


Figure 19. Scanning electron micrograph of hydrated fluoride cement showing hydroxide crystals (age - 1 day)

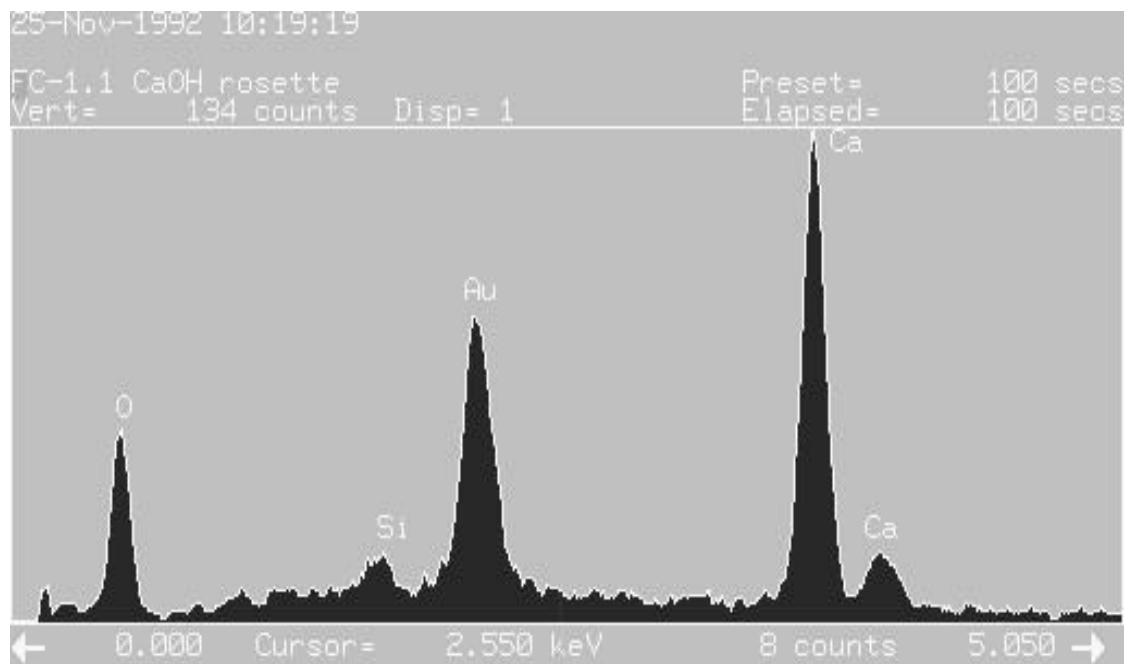


Figure 20. EDXA spectrum of hydroxide crystals in hydrated fluoride cement (age - 1 day)

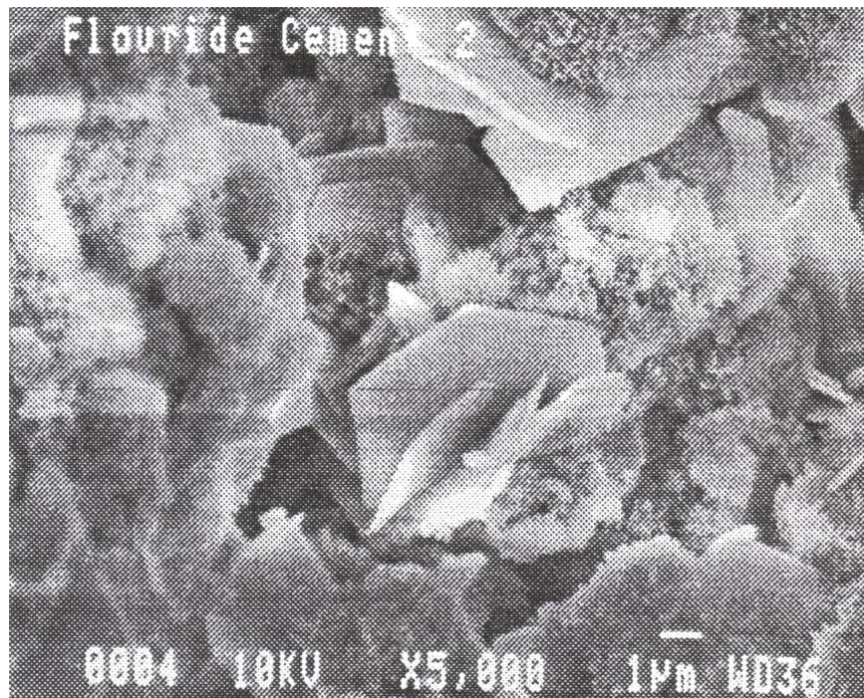


Figure 21. Scanning electron micrograph showing rosette crystals in hydrated fluoride cement (age - 3 days)

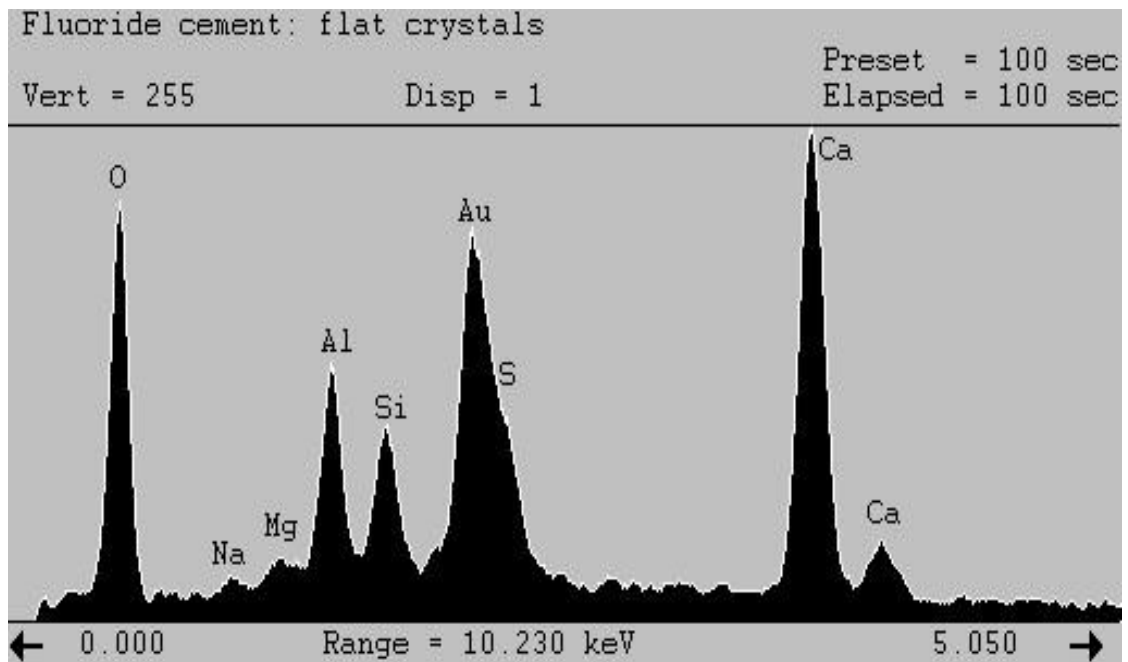


Figure 22. EDXA spectrum of rosette crystals in hydrated fluoride cement (age - 3 day)

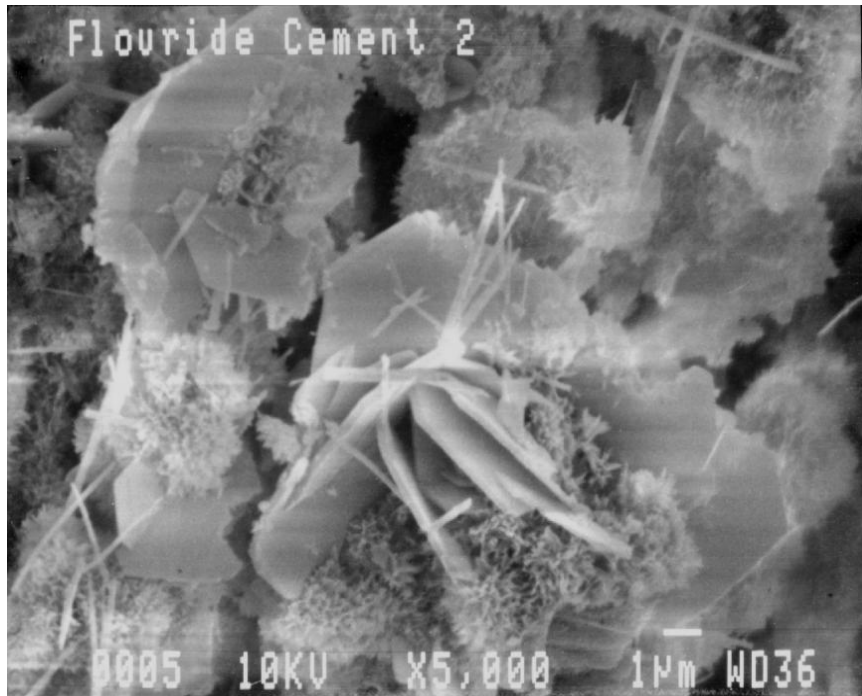


Figure 23. Scanning electron micrograph of hydrated fluoride cement (age - 3 days)

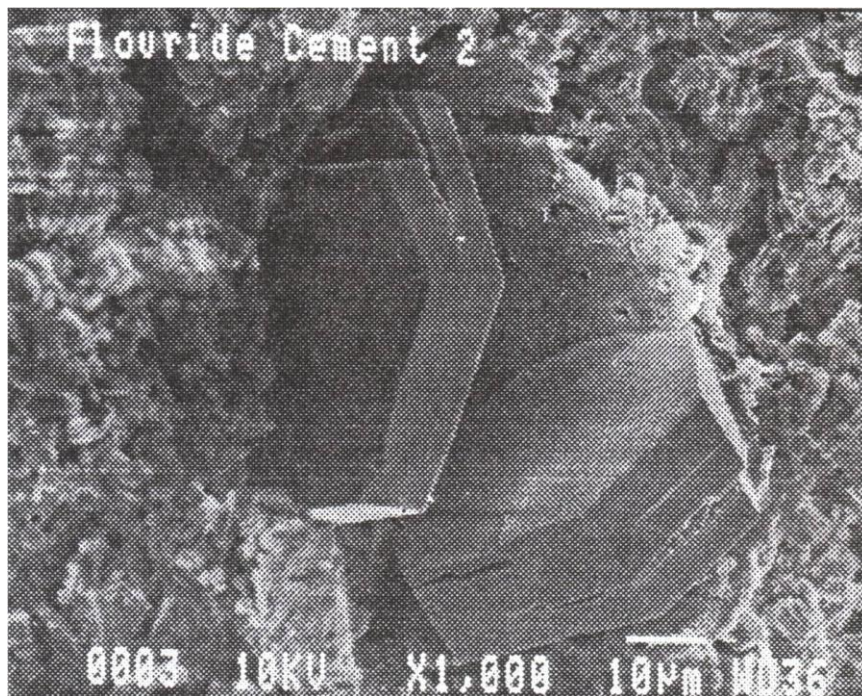


Figure 24. Scanning electron micrograph of hydrated fluoride cement showing hexagonal crystals (age - 3 days)

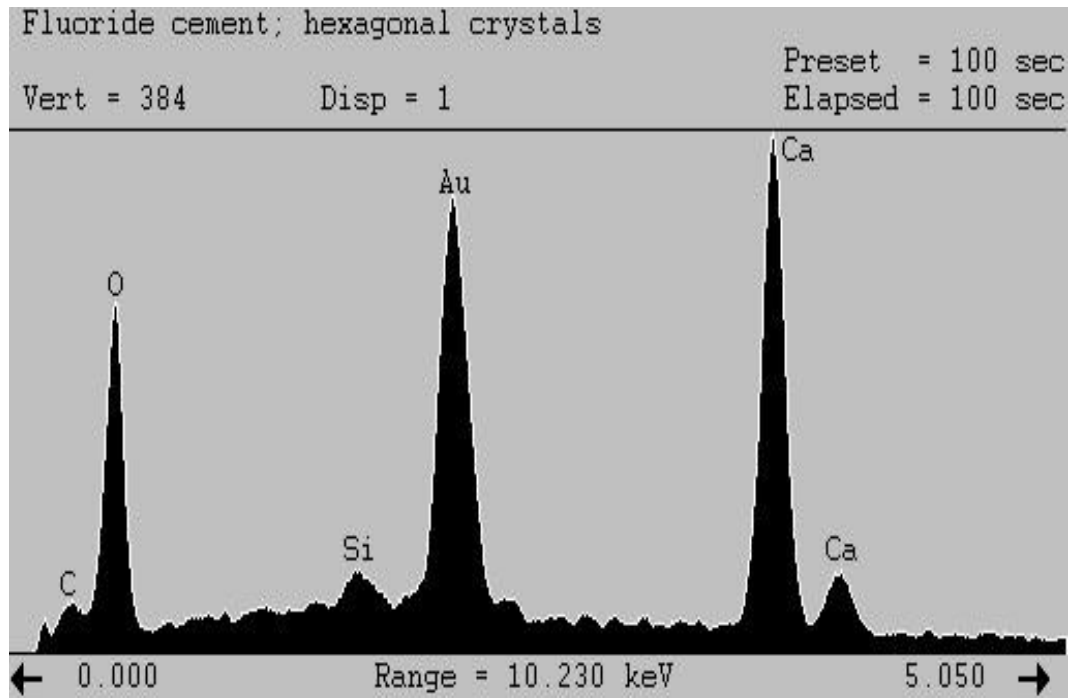


Figure 25. EDXA spectrum of hexagonal crystals in hydrated fluoride cement (age - 3 days)

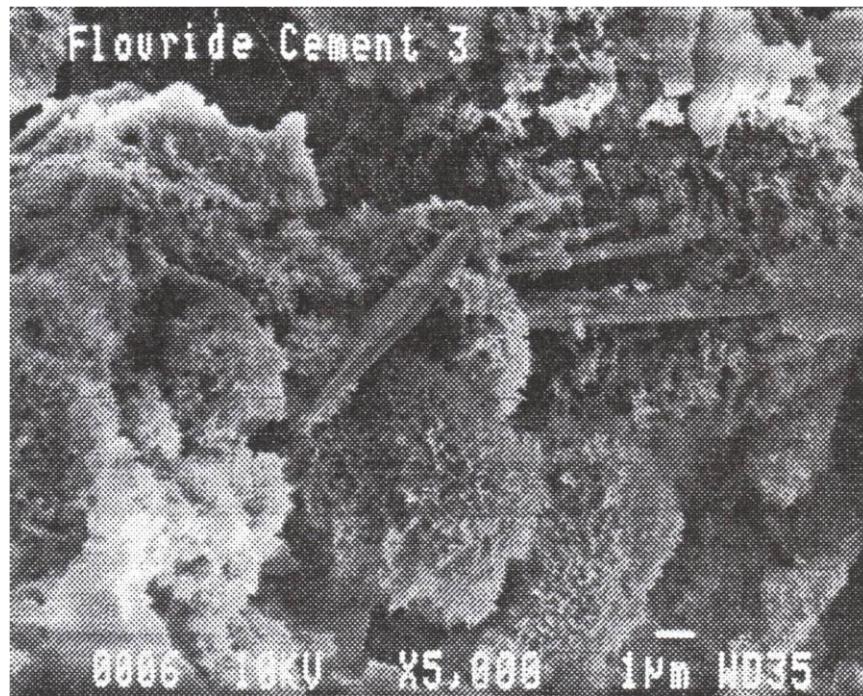


Figure 26. Scanning electron micrograph of hydrated fluoride cement (age - 7 days)

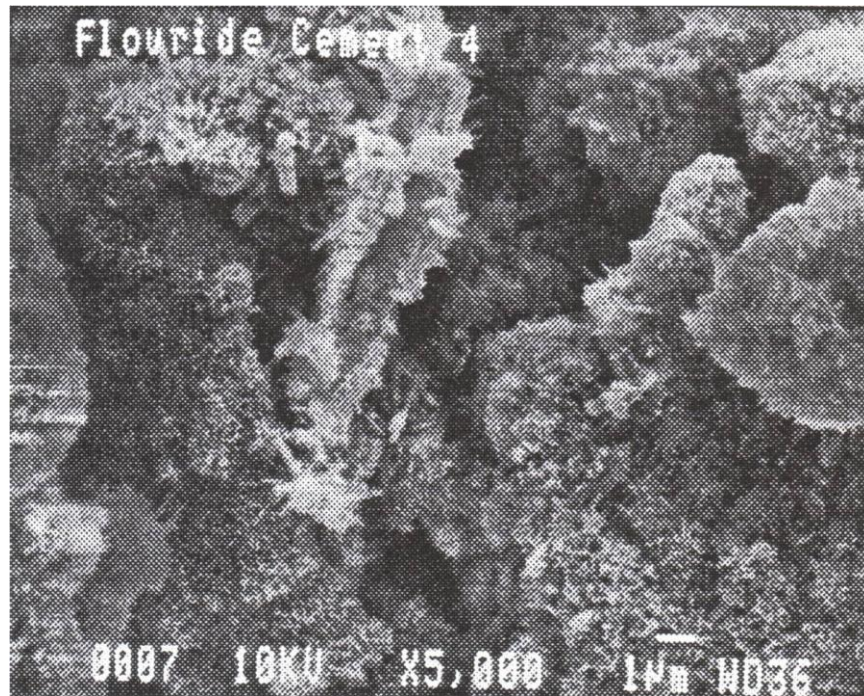


Figure 27. Scanning electron micrograph of hydrated fluoride cement (age - 28 days)

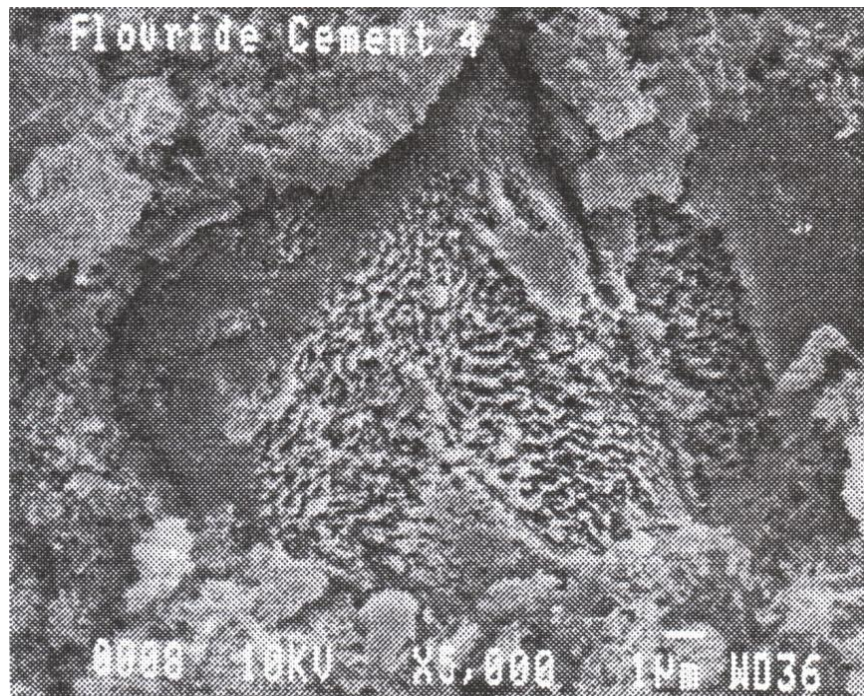


Figure 28. Scanning electron micrograph of hydrated fluoride cement (age - 3 months)

The morphological pattern on micro scale, of the hardened paste varies reasonably with the age of the cement. However on a larger scale, there does not seem much difference in the pattern. The SEM examination of the solid phases do not show a typical increase in the amount of crystallinity of the paste as it ages, but the XRD analysis reveal the slight increase by the increase in the number and intensity of the peaks observed. Use of EDXA to determine the elemental composition of the various phases in the matrix, enabled the positive identification of the probable products of hydration.

Some literatures^[23,24] have presented the formation of $C_{11}A_7CaF_2$ as one of the main phases in fluoride cement. The presence of $C_{11}A_7CaF_2$ significantly alters the outlook of the mineralogical composition of fluoride cement which was shown in table 14. The higher the concentration of this phase coupled with the high reactivity of anhydrite form of calcium sulphate contribute to the speedy formation of ettringite at an early age, giving fluoride cement a denser matrix and also the observed higher early compressive strength.

CONCLUSIONS

The following conclusions are drawn from the work carried out during the study. As part of the study, samples of fluoride cement were prepared in the laboratory using raw materials generally used in actual factory production runs. The limited size of samples so prepared was then subjected to characterisation analyses to determine the major chemical components found in the fluoride cement as well as the physical characteristics of the cement. These analyses were done on a comparative basis with that of ordinary Portland cement, to confirm the suitability of the fluoride cement as a cheaper alternative cement.

5.1 Test samples collection and preparations

An important part of any research work is that of obtaining the right samples for the work. In this respect materials were collected based on the information given by the manufacturer. The formulation of the raw mix proportion is based on studies conducted earlier by other researchers on the use mineralisers in the production of cement. This study shows that it is possible to produce fluoride cement using correct raw materials and mix proportions. Based on the quality of materials available at the cement producing sites in Malawi, it can be concluded that sample number 6 gives the optimum mix formulation for fluoride cement production.

5.2 Physicochemical characteristics

Results also show that the presence of silicofluorides imparts good hydraulic properties to fluoride cement, and thus they play a major role in distinguishing its hydration characteristics from those of ordinary Portland cement. Major compounds

present in the anhydrous fluoride cement are silicofluorides with various chemical formulae. This study was unable to positively establish the chemical formulae of some of the phases observed to be present, particularly in the anhydrous cement. The products formed and the phases present in the hydrated paste are identical except for their relative concentrations. The presence of calcium silicate hydrate, ettringite, calcium hydroxide and monosulphate hydrate was detected, as is the case in Portland cement. More ettringite is observed in hydrated Portland cement than in fluoride cement, but it could not be established whether the presence of fluorides had significant effects on the dynamics of the hydration reactions.

Also from the test results it was shown that fluoride cement has significantly early initial and final setting times in comparison to ordinary Portland cement. The values concur with other studies which place the initial and final setting times of fluoride cement at around 10 minutes and 20 minutes respectively.

The strength developing characteristics of fluoride cement are fairly comparable to those of ordinary Portland cement. However tests show that fluoride cement consistently having higher compressive strength values, particularly at early age attributed to the higher concentration of ettringite. The compressive strength of the two cements however is almost comparable at later age.

The formulation of a Malawi Standard on fluoride cement is an important step toward the utilisation of this material. The draft appended to this thesis should be finalised upon establishing the reproducibility of the results at factory or commercial level. For this reason, sufficient time and more studies should be conducted in order to

prove the properties of the manufactured fluoride cement. With a strict control on the production techniques it is possible to replicate and even improve these results.

As regards the laboratory test results, the test methods used are those established for Portland cement. As the two cements are basically made from the same compounds it can be safely concluded that for the purpose of performing Bogue calculations the results obtained were accurate enough. However the compound composition requires verification using more accurate methods.

Testing was done at competent laboratories in Malawi: at the Portland Cement Company, Geological Survey Department and at Malawi Bureau of Standards. Further testing shall be carried at Iowa State University where more conclusive results on the nature of fluoride cement shall be established.

All in all, despite the major setback on the unavailability of commercial grade fluoride cement from the manufacturer during the project, some critical tests were conducted. It is hoped that further studies may continue to provide more insights on the properties of fluoride cement.

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APPENDIX. DRAFT MALAWI STANDARD ON FLUORIDE CEMENT

This Appendix forms part of the thesis on fluoride cement. The data contained in this draft shall be reviewed by the Malawi Bureau of Standards Technical Committee responsible for formulation of standards on cementitious materials, before being adopted as a Malawi Standards by the Malawi Standards Board. Some of the parameters are yet to be determined or verified for repeatability and reproducibility, as the samples used in the preparation of this thesis were not sufficient.

0. Foreword

This Draft Malawi standard has been prepared for the purpose of promoting the use of fluoride cement in the construction industry. The standard was prepared under the supervision of Technical Committee MBS/TC 9, *Cement and lime*, and the following organisations were represented:

(List of member organisations of MBS/TC 9)

This standard shall be reviewed when necessary and/or every five years in order to keep abreast of progress. Comments are welcome and will be considered when the specification is revised.

1. Scope

This Draft Malawi Standard specifies requirements for the manufacture, composition, chemical and physical requirements,

2. References

The following documents have been referred to in this standard:

MBS 29, Ordinary and rapid hardening cement

BS 4550:Part 2, Methods of testing cement: Part 2: Chemical tests.

3. Composition and manufacture of fluoride cement

The fluoride cement shall be manufactured by intimately mixing together calcareous or other lime-bearing material with argillaceous and/or silica, alumina and iron oxide

bearing materials. The materials shall then be burnt at a clinkering temperature and the resulting clinker ground so as to produce a cement complying with this standard.

4. Chemical composition

The chemical composition of fluoride cement shall comply with the requirements of Table A1:

Table A1. Chemical requirements¹

Property	Requirement
Lime saturation factor (LSF)	(yet to be determined)
MgO content, %	5.00
SO ₃ content, %	3.00
Loss on ignition (LOI)	4.00
Insoluble residue, %	2.50

5. Physical requirements

When tested in accordance with the methods in MBS 29, fluoride cement shall comply with the relevant requirements of Table A2.

Table A2. Physical requirements

Property	Requirements	Test method ²
Fineness, m ² /kg (min)	225	
Compressive strength, MPa		
3 days	120	
28 days	160	
Setting times, minutes		
Initial (min)	85	
Final (max)	640	
Soundness		
Maximum expansion, mm	10	

¹. As determined by methods described in MBS XXX: Methods of test for chemical analysis of cements. (To be formulated).

². The methods of test will be as those prepared by the MBS for OPC testing.

6. Manufacturer's certificate

6.1 The manufacturer shall be satisfied that the cement at the time of its delivery complies with the requirements of this standard. If requested, he shall forward a certificate to this effect to the purchaser or his representative at no charge.

6.2 The certificate shall include the results of test on samples of cement relating to the material delivered. The following test information shall be provided: fineness, compressive at 3 days and 7 days, initial and final setting times and soundness.

7. Packing and marking

7.1 Cement shall be packed in multilayered bags capable of withstanding handling in the normal course of transportation.

7.2 The bags shall be marked legibly and indelibly by the following information:

7.2.1 The manufacturer's name and either trade name or trade mark or both.

7.2.2 The type of the cement, that is "fluoride cement".

7.2.3 The nett content in kilograms

7.2.4 The MBS Mark

NOTE: Use of the MBS Mark is governed by the rules and regulation of the MBS Certification Marking Scheme.

8. Sampling

8.1 All sampling shall be carried out under cover.

8.2 For cement supplied in bulk, the lot shall be sampled by taking sufficient cement to form a composite sample of at least 10 kg. Approximately equal increments of about 1 kg shall be taken randomly from at least 12 different positions and depths in the bulk container. By agreement between the vendor and purchaser a composite sample may be obtained by taking 12 increments of about 1 kg at 12 different times when loading or unloading into a transport vehicle or purchaser's silo.

8.3 For cement supplied in bags or other containers, a composite sample of at least 10 kg shall be collected. Approximately equal increments shall be taken from at least 12

bags or containers, chosen at random from the lot. Increments shall not be taken from broken bags or containers.

8.4 After sampling, the composite sample shall be thoroughly mixed and placed into a clean, dry, airtight container which shall be immediately sealed and marked for future identification.

9. Testing

All tests shall be carried out in accordance with the methods specified in the relevant clauses.

ACKNOWLEDGEMENTS

Special thanks go to the staff of Malawi Human Resources and Institutional Development Project (HRID), the Governments of Malawi and the United States of America and to my employers, the Malawi Bureau of Standards for enabling me undertake this research work.

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Thank you all.