OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.

DISCLAIMER

This document has been produced without formal United Nations editing. The designations employed and the presentation of the material in this document do not imply the expression of any opinion whatsoever on the part of the Secretariat of the United Nations Industrial Development Organization (UNIDO) concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries, or its economic system or degree of development. Designations such as "developed", "industrialized" and "developing" are intended for statistical convenience and do not necessarily express a judgment about the stage reached by a particular country or area in the development process. Mention of firm names or commercial products does not constitute an endorsement by UNIDO.

FAIR USE POLICY

Any part of this publication may be quoted and referenced for educational and research purposes without additional permission from UNIDO. However, those who make use of quoting and referencing this publication are requested to follow the Fair Use Policy of giving due credit to UNIDO.

CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org
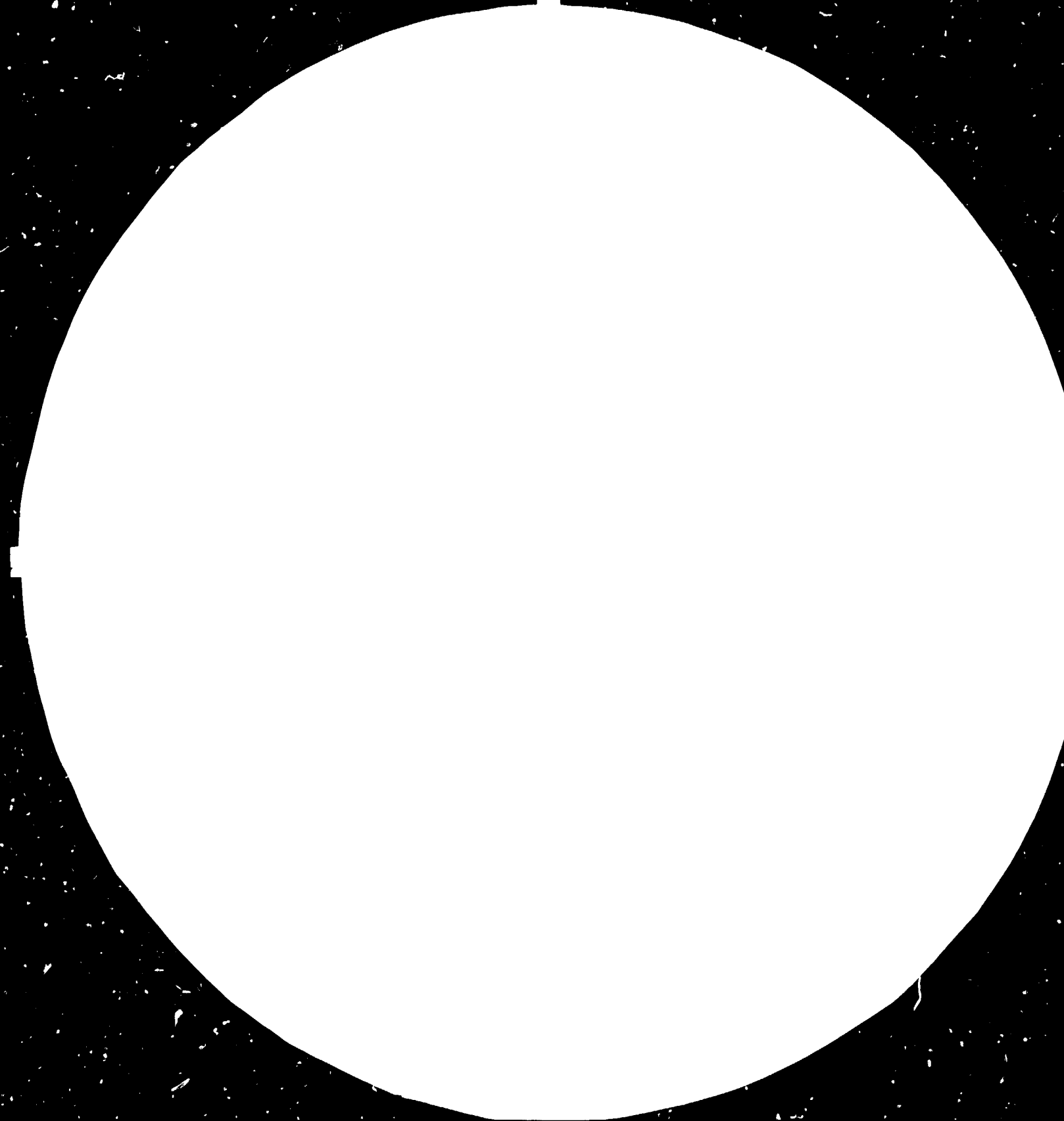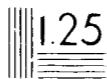
1.0

1.1

1.25   1.4   1.6

2.0

1.8

13183

ASSISTANCE TO THE LIBYAN CEMENT FACTORY, BENGHAZI

TF/LIB/75/002

LIBYAN ARAB JAMAHIRIYA

Libya.

Mission report: Formation of cement lumps and accretions
in cement silos

Prepared for the authorities of the Libyan Arab Jamahiriya
by the United Nations Industrial Development Organization

Based on the work of A.R. Marei, project co-ordinator

The monetary unit in the Libyan Arab Jamahiriya is the Libyan dinar (LD). During the period covered by the report, the value of the Libyan dinar in relation to the United States dollar was $US 1 = LD 0.296.

The following exchange rates are used in the conversion of country currencies to United States dollars:

Country	Currency	Exchange rate per US dollar in 1980
Federal Republic of Germany	mark (DM)	3.80
Switzerland	franc (SwF)	1.6655

A full stop (.) is used to indicate decimals.

A comma (,) is used to distinguish thousands and millions.

The following forms have been used in tables:

Three dots (...) indicate that data are not available or are not separately reported.

A dash (-) indicates that the amount is nil or negligible.

A blank indicates that the item is not applicable.

The following abbreviations of organizations are used in this report:

ASTM	American Society for Testing and Materials
HMC	Holderbank Management and Consultancy
KHD	Kloeckner Humboldt Deutz, Industrieanlagen AG
LCC	Libyan Cement Company

The following technical abbreviations are used in this report:

BS	British standard
C_2S	dicalcium silicate
C_3S	tricalcium silicate
C_3A	tricalcium aluminate
C_4AF	tetracalcium aluminoferrite
DTA	differential thermal analysis
LOI	loss on ignition

Mention of firm names and commercial products does not imply the endorsement of the United Nations Industrial Development Organization (UNIDO).

Material in this publication may be freely quoted or reprinted, but acknowledgement is requested, together with a copy of the publication containing the quotation or reprint.

ABSTRACT

This study forms part of the project, "Assistance to the Libyan Cement Factory, Benghazi" (TF/LIB/75/002) which is being carried out for the authorities of the Libyan Arab Jamahiriya by the United Nations Industrial Development Organization (UNIDO) under a trust-fund agreement. This project has been operating since 1976 and is designed to give direct technical assistance to the cement industry. The author of this study took over as co-ordinator of the UNIDO technical-assistance project in May 1980 and, apart from assisting with the day-to-day operational problems of the Libyan Cement Company (LCC), has also been involved in tackling various long-term problems affecting cement production.

One of these problems has been the formation of cement lumps and the aggregation of hardened cement on the walls and the discharge outlets of the storage silos in the Hawari Cement Plant. This causes serious problems in the packing section when trying to bag the cement and when loading it into bulk tankers. The storage capacity of the cement silos is also reduced.

The contractors who supplied the plant were asked to make proposals for overcoming these difficulties and the co-ordinator was also asked to investigate every aspect of the problem.

In this report, the co-ordinator comments on the proposals made by the contractors and reviews the various factors, chemical, physical and mechanical, which contribute to the problem. The results of both large-scale and laboratory tests are described and recommendations made for various ways in which the problem might be tackled.

CONTENTS

Tables

INTRODUCTION

This study forms part of the project, "Assistance to the Libyan Cement Factory, Benghazi" (TF/LIB/75/002) which is being carried out for the authorities of the Libyan Arab Jamahiriya by the United Nations Industrial Development Organization (UNIDO) under a trust-fund agreement. This project has been operating since 1976 and is designed to give direct technical assistance to the cement industry. The author of this study took over as co-ordinator of the UNIDO technical-assistance project in May 1980 and, apart from assisting with the day-to-day operational problems of the Libyan Cement Company (LCC), has also been involved in tackling various long-term problems affecting cement production.

The Libyan Cement Company has two cement plants, Benghazi (with three production lines) and Hawari (with two production lines). The Hawari Cement Plant was supplied under a turnkey contract between the General National Organization for Industrialization (GNOI) and a consortium of two contractors from the Federal Republic of Germany, Kloeckner Humboldt Deutz Industrieanlagen AG (KHD) and Bilfinger and Berger AG (B & B). The contract was signed in 1975 and the plant provisionally taken over in 1978. Since the start of its operations, serious troubles have occurred in the packing section caused by the formation of cement lumps and clogging of the storage silos. A coating of cement is usually formed on the internal walls of the LCC cement silos and also on the cement discharge exits causing difficulty and operational failure when filling cement into bulk tankers or in the bagging section. The storage capacity of the silos is also reduced as it has proved inadvisable to store cement for a long time or to keep the cement silos full all the time.

The contractors, KHD, were asked to investigate this problem and to make practical suggestions for eliminating the difficulties. They submitted four reports to the LCC on 6 March 1978, 16 August 1978, 4 December 1978 and 11 May 1979. In May 1980, a meeting was held with A.M. El-Gheriani, Secretary of the People's Committee and General Manager of LCC, and A.M. Afify, the previous project co-ordinator, at which the problem was discussed. The present project co-ordinator was asked to pursue the matter further and to advise on the recommendations made by KHD.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

1.   The flowability of LCC cement is very poor. Good results have been achieved elsewhere by partially replacing gypsum by limestone as an additive. However, operational tests on plant production using different proportions of limestone did not give any clear results or bring about a distinct improvement in cement flowability.

2.   The limestone and marl used in the LCC raw mixes was found to produce a high tricalcium aluminate (C_3A) content and a low tetracalcium aluminoferrite (C_4AF) content in the clinker which makes it moisture-sensitive and encourages hydration in the silos leading to lump formation.

3.   During cement grinding, most of the mechanical energy supplied to the mill is transformed into heat as a result of elastic deformation within the particles. The temperature of the material in the mill increases as comminution proceeds. The clinker temperature of $100°C$ on entry into the cement mill may rise above $150°C$. During the storage period in the silos, which may last from a few hours to several months, the cement remains for some time at a temperature within $10-20°C$ of the exit temperature from the cement mill (i.e. $90-100°C$). As a result the gypsum is partially dehydrated to form hemihydrate. The liberated moisture will travel to the colder walls and will affect the cement grains by reacting with the clinker phases, especially the aluminates, to form crystals of ettringite and syngenite which leads to lump formation.

4.   The thick coating of powdered cement on the grinding media in the cement mill was found to decrease the mill efficiency, raise energy consumption and reduce the flowability of cement after grinding.

5.   Various features of the design of the cement silos were found to be contributory factors in the formation of lumps:

   (a) The air slides are too far apart, allowing static cement to accumulate between them and harden;

   (b) The compressed air which is injected has to be kept free of water condensation;

   (c) There is a dead space between the two discharge outlets in which cement accumulates and undergoes the chemical reaction described above during the storage period. A proposal was considered for erecting a cone-shaped structure inside the silo bottom which would eliminate the dead space and allow the cement to flow easily over the cone to eight evenly-distributed outlet points. It was concluded, however, that as the problem of lump formation was primarily a chemical one, the installation of the cone structure was not likely to provide a complete solution;

   (d) To prevent cement adhering to the silo walls and hardening into aggregations, it was proposed to paint the inside of the silo walls with a non-stick coating. However, it was decided that this could only be done successfully at the beginning before the silo is filled and would not in any case affect the chemical reaction which causes the lumps.

6.   Laboratory tests on using limestone as an additive confirmed the results of the large-scale operational tests that this does not bring about a significant improvement. However, encouraging results in terms of fineness, flowability and compressive strength, were achieved in laboratory tests using limestone associated with pure gypsum, ethylene glycol and commercial additives (HEA).

Recommendations

1.   Grinding aids should be used to reduce the cement coating on the grinding balls and cylpebs in the cement mill to improve the efficiency of the mill and the flowability of the ground cement.

2.   The chemical problem should be tackled by adding a ferriferous third component such as pyrite ash to the raw mix in a proportion of between 1.0 and 1.36%. This will increase the C_4AF content and reduce the value of C_3A to a maximum of 10% which will help prevent the formation of lumps in the silos.

3.   The temperature of the cement produced should be kept as low as possible. This can be achieved by:

    (a) Only using for grinding clinker which has been stored and cooled for at least a week;

    (b) Feeding the ground cement into cooling tanks.

4.   The amount of moisture available to the cement should be kept as low as possible. Water injection into the cement mills should be avoided to prevent the adsorption of any droplets on the cement grains and to eliminate the 15% of water vapour which actually reaches the cement silos. The compressed air injected into the silos should be freed from water condensation by installing water traps before the silos or by passing the compressed air through big tanks equipped with taps at the bottom through which the condensed water is continually expelled.

5.   In the silos themselves, it would be possible to enlarge the air slides to minimize the dead space between them. Regular cleaning of the silos every six months will help prevent the accumulation of hardened cement.

6.   Trials should be carried out in the regular LCC production using some of the additives which showed promising results in the laboratory tests. An Italian company has agreed to carry out these trials.

I. BACKGROUND TO THE PROBLEM

A. The setting time of cement

The setting time of Portland cement is the time which elapses after mixing the cement with water before the paste will resist a certain fixed pressure.

There are some factors which influence the setting time of cement. These factors can be stated as follows:

(a) The greater the proportion of alumina and ferric oxide in cement the more rapid is the initial set;

(b) Fineness of cement has a great influence on the setting time, i.e. fine cement sets quicker than the same type of cement ground more coarsely;

(c) Calcium sulphate (gypsum) contaminated with coal or heavy oil has a remarkable effect in retarding the setting time;

(d) In addition to calcium sulphate, there are some salts that cause retardation while other groups of salts have an accelerating effect on the setting when large amounts are added to cement. The effect produced by adding these salts varies according to the degree to which the setting time is already retarded by gypsum;

(e) Sugar has a very marked effect as a 1% solution completely inhibits real setting and hardening.

The use of some agents to control the setting of cement was seen to be necessary and the addition of gypsum during grinding of the clinker became general. The amount of gypsum added to the clinker corresponds to about 1-3% sulphur trioxide (SO_3) and is limited by the specification requirements, which in all countries only permit the presence of a certain proportion of gypsum in the finished cement.

The presence of free lime in clinker assists in the retardation of setting. Although plaster of paris ($CaSO_4 . H_2O$) in small quantities retards the setting of cement more vigorously than gypsum, the addition of larger quantities (more than 4%) renders the cement quick-setting again (less than 30 minutes).

Mixtures of gypsum and anhydrite in roughly equal proportion are sometimes used as a means of overcoming problems of false set. False set is attributed to the dehydration of gypsum caused by the high temperatures reached in grinding the cement clinker and its recrystallization. On occasion, temperatures may exceed 150°C.

There are some factors which influence the susceptibility of clinker to develop a false set:

(a) The presence of free lime assists the dehydration of the gypsum ore;

(b) Carbonation of alkalies in the cement during storage has also been suggested as a cause, but this is more likely to produce a flash set than a false set.

B. Effect of storage on cement properties

Cement stored in sealed containers at ordinary temperatures does not usually change even over long periods, but at high temperatures some change is produced for, although the cement appears normal, it may rapidly develop a flash set if subsequently exposed to air. Trouble with rapid setting is occasionally experienced with cements shipped from temperate to tropical climates. Development of a flash set also occasionally occurs in cement stored in bulk. The high temperatures produced during grinding probably persist for a considerable period of time in cement stored in silos, but the particular conditions which can lead to rapid setting and the corresponding changes occurring in the cement are far from clear.

Takemot (1959) studied the dehydration of gypsum when ground with clinker in a laboratory mill at different temperatures, using the thermal analysis method. The results showed that hemihydrate was formed at 85°C after 40 minutes grinding and soluble anhydrite was formed at 130°C after grinding the mixture for up to 80 minutes. Due to the formation of hemihydrate, water leaves the clinker-gypsum mixture. This water, where more than 4% of hemihydrate is present, leads to later hydration of the cement in the storage silos.

During grinding and storage, cement may come in contact with water vapour formed as a result of:

(a) Spraying water into the cement mill during grinding;

(b) Dehydration of the gypsum at high temperatures;

(c) Water accompanying the compressed air.

The cement can react chemically with the water vapour and undergo solidification which creates lumps and aggregations. These solidified lumps are due to the formation of acicular syngenite ($K_2SO_4.CaSO_4.H_2O$) or ettringite ($3CaO.Al_2O_3.3CaSO_4.32 H_2O$) and may cause slower setting and reduced strength in the concrete, though rapid setting may occur as a result of secondary formation of gypsum if the cement contains substantial amounts of hemihydrate.

The dehydration of gypsum takes place at different rates at various storage temperatures. Dehydration evidently occurs more rapidly and the demonstrable residual gypsum content is lower when the clinker contains more tricalcium aluminate (C_3A) and when the amounts of alkali combined in the C_3A are greater.

The water liberated from the gypsum diffuses as vapour into the colder areas of the silo where it reacts with the stored cement. The water content of the cement rises from about 1% at the centre of the silo to 5-10% by weight near the silo wall. In consequence, solidification of cement occurs, starting at the wall and progressing towards the centre. The cause of such solidification is the build up of a rigid structure of tabular calcium aluminate hydrate and acicular syngenite and ettringite which are formed by the reaction of C_3A, alkali sulphate and calcium sulphate with water.

C.   Previous research on the substitution of limestone for gypsum

As will be seen from the foregoing, one possible solution to the formation of lumps in storage silos would be partially to replace some of the gypsum by other cement ingredients. The co-ordinator had already, as part of his Ph.d work, made a study of the effect of replacing varying proportions of gypsum during grinding by other materials such as limestone or clay. His findings were supported by a paper appearing in the magazine, Rock Products, in February 1977 entitled, "Limestone substitutes for gypsum as a cement ingredient". The research carried out was very thorough and the results can be reliably taken as a basis for conducting practical tests on the effect of such substitution in LCC cement plants. The findings of this paper are summarized here.

Samples of clinker were taken from eight plants using their typical limestone and gypsum. These materials were then ground separately to different finenesses (clinker 3,300 cm^2/g, limestone and gypsum 4,000 cm^2/g). Care was taken to avoid exposure of the pastes to atmospheric carbon dioxide (CO_2). The pastes were allowed to hydrate for 1, 3, 7, 14, 28 and 60 days in sealed vials. Subsequently, production trials were carried out in a cement plant.

From the results of all the experiments and the plant production trial of substituting limestone for gypsum in cement production, it was concluded that:

(a) In the laboratory grinds with partial substitution of limestone for gypsum, a definite reaction between limestone and clinker does take place. The reaction product is a calcium carboaluminate (CCA) which may form in a mechanism similar to that of calcium sulphoaluminate (CSA);

(b) Physical properties of the cement such as autoclave expansion and setting time can be maintained at acceptable values with the correct ratio of limestone to gypsum for a given clinker;

(c) Mortar strength at constant water content is generally reduced but concrete strength, although lower at early stages, generally compared favourably with the straight gypsum product;

(d) Materials obtained by actual plant experimental grinds generally show an acceptable performance in all areas except very early strength;

(e) No operational problems were encountered during this plant evaluation;

(f) Partial substitution of limestone for gypsum reduces false-set properties dramatically in a severe false-setting system.

Although more work needs to be done before definite conclusions can be reached, the results of work thus far indicate that partial substitution of limestone for gypsum can be a positive factor not only in cement performance but in cement plant profitability as well. Of key interest was the fact that the substitute for gypsum was not some highly-complex additive but was the commonly-used and available limestone, whose cost was about 30% of the cost of gypsum. A further factor was that, with the increased use of coal as a

primary fuel, the sulphur trioxide (SO_3) content of clinker has increased and will probably continue to increase. If the SO_3 content in the clinker was high enough, one would be able to avoid the addition of 5-7% gypsum and depend on the clinker SO_3 to control the immediate setting characteristics and then use limestone as a set-controlling agent after the initial reaction between the clinker SO_3 and C_3A had taken place. These were sufficiently large potential benefits to obtain approval to proceed with the project.

D. Preliminary work carried out by KHD

As mentioned earlier, the contractors, KHD, were asked to investigate the problem of cement lumps in the silos and to make practical suggestions for dealing with this problem. They were sent various samples of the cement produced to analyse in their laboratories.

The first batch of cement samples, received on 1 January 1978, consisted of:

A1 - from behind cement mill III (not characterized by the formation

of lumps)

A2 - lumps from cement silo III

A3 - gypsum rock

Another set of cement samples, received on 4 July 1978, consisted of:

B1 - from silo II (containing lumps less than 1 mm)

B2 - from silo II (containing lumps 1 mm +)

B3 - from silo III (lumps less than 1 mm)

B4 - from silo III (lumps 1 mm +)

B5 - from silo IV (lumps less than 1 mm)

B6 - from silo IV (lumps 1 mm +)

B7 - from behind cement mill

A third group of samples were received on 20 and 28 November 1978 for further investigation and testing:

C1 - from behind cement mill (silo IV)

C2 - ⎫
C3 - ⎬ residual (undischarged) cement (silo IV)

C4 - ⎫
C5 - ⎬ "flowing" cement (silo IV)

The C samples derive from a test programme that was carried out in cement silo IV. After complete emptying of the silo, cement was filled in up to a height of about 10 metres. The temperature of cement entering the silo did not exceed 110°C and the water injection system of the cement mill was out of operation.

At the end of March 1979, two further cement samples were handed over to KHD:

D1 - from behind cement mill (temperature 115°C, no water injection)

D2 - from behind silo V

These samples were examined physically, chemically, technically and mineralogically and KHD submitted four reports on the different batches. The chemical analysis of cement samples A, B and D are shown in table 1.

Samples C1, C2, C3, C4 and C5 were subjected to a chemical test for ignition loss and SO_3 content. The results were as follows:

	(Percentage by weight)				
	C1	C2	C3	C4	C5
LOI	1.45	1.56	1.53	1.33	1.37
SO_3	2.83	1.98	2.86	2.84	2.47

In general, the four reports on the chemical composition of the cement samples show the following:

(a) The high loss on ignition of the lumpy cement is striking, especially in samples A1 and A2. This reveals without doubt that lumps are formed as a result of excess moisture;

(b) There are noticeable differences in the lime standard which reflect variations in the alite (C_3S) reduction and belite (C_2S) content accompanied by a slight lowering of the alumina modulus;

(c) The calculated C_3A content of the cement samples ranges from 10-11.8% by weight;

(d) This cement is rich in alkali, which suggests a high C_3A sensitivity;

(e) The sulphate content of samples B and C could be lowered (to some 1.8-2.5% SO_3 by weight) by reducing the quantity of gypsum added to clinker during grinding in view of the C_3A contents given (see table I).

The results of the chemical analyses alone do not allow decisive conclusions as to the reason for lump formation. Therefore, KHD determined the phase composition of some samples radiographically.

In these tests, aluminate (alkali aluminate and aluminate ferrite) has been found to be 12.2% and 14.6% by weight in cement and cement lumps respectively (samples A1 and A2).

Syngenite has not been definitely proved to exist in the samples. The differential thermal analysis (DTA) showed that there is no doubt about the existence of ettringite in the samples from silo III. In the samples from silo IV, the presence of ettringite and syngenite could not be definitely proven.

Table 1.   Chemical composition of test samples A, B and D
(Percentage by weight)

Components	Samples [a/]										
	A1	A2	B1	B2	B3	B4	B5	B6	B7	D1	D2
LOI	0.89	3.91	2.13	2.41	1.86	1.91	2.12	2.39	1.36	2.17	1.67
SiO_2	21.81	21.56	21.14	20.86	21.34	21.24	21.43	21.?6	21.46	22.30	22.90
Al_2O_3	5.3?	5.28	5.03	5.00	5.19	5.15	5.29	5.20	5.40	5.08	5.09
Fe_2O_3	2.02	1.97	1.91	1.89	1.94	1.96	2.06	2.06	2.09	2.19	2.22
TiO_2	0.34	0.33	0.42	0.31	0.32	0.32	0.33	0.33	0.33	0.31	0.32
CaO	63.32	60.45	63.04	62.81	63.05	62.93	62.96	62.44	63.21	61.00	60.90
MgO	2.71	2.42	2.71	2.87	2.66	2.83	2.40	2.65	2.57	2.52	2.57
SO_3	1.99	2.58	2.87	2.98	2.36	2.76	2.54	2.53	2.53	3.16	3.08
K_2O	0.93	0.92	0.88	0.88	0.87	0.90	0.92	0.91	0.87	0.94	0.98
Total	99.33	99.42	100.03	100.01	100.11	99.97	99.85	99.76	99.81	99.70	99.73
Lime saturation (%)	92.?	86.4	92.00	92.70	90.90	91.40	89.90	90.60	90.60	84.2	82.1
Silicate modulus	2.9?	2.97	3.06	3.03	2.99	2.98	2.92	2.93	2.86	3.07	3.13
Silica modulus	...	...	4.30	4.17	4.11	4.12	4.05	4.09	3.96	4.45	4.50
Alumina modulus	2.63	2.68	2.63	2.65	2.66	2.63	2.57	2.54	2.58	2.52	2.59
Clinker phases:											
C_3S	47.7	30.5	41.30	42.40	48.60	49.70	46.00	47.60	47.80	32.0	27.7
C_2S	28.9	34.3	21.90	20.30	24.60	23.30	26.70	25.10	25.40	39.3	44.8
C_3A	10.7	10.7	10.10	10.10	10.50	10.30	10.50	10.30	10.80	9.8	9.7
C_4AF	6.2	6.0	5.80	5.80	5.90	6.00	6.20	6.20	6.40	6.7	6.8

Note: It is assumed that the Na_2O content will equal approximately 0.3% by weight and the alkali content has to be increased by this percentage.

a/   For origin and nature of samples, see text.

The maximum gypsum content for the freshly ground cement was compared with that of cement stored in the silos and it was noticed that the silo cement samples contained less gypsum. In the sample from silo II, gypsum was not detected at all. The x-ray tests revealed that all samples contain small amounts of hemihydrate ($CaSO_4. H_2O$) in addition to gypsum ($CaSO_4.2H_2O$).

Fineness tests on samples D1 and D2 gave the following results:

	D1	D2
Specific surface (cm^2/g)	3,200	2,960
Residue on an 0.09 mm screen (% by weight)	3.7	8.6

Findings

The four KHD reports produced the following findings.

1. Apart from gypsum, hemihydrate has been found in all the cement samples investigated. This can be attributed to the fact that excess cement temperature in the cement mill has caused partial dehydration of gypsum to hemihydrate. The moisture thus liberated reacts with the clinker phases, above all the aluminate and especially the alkali aluminate, which is sensitive to moisture, to form needle-shaped ettringite and syngenite, which in turn leads to the formation of lumps and aggregations. Since, in addition to hemihydrate, a high loss on ignition was found in some samples and to a certain extent in all the samples, it is not clear to what extent gypsum dehydration continues in the silo.

2. The cement produced by LCC has very poor flow properties. It has not been clarified whether the poor flow properties result from the formation of lu or whether the chemical composition of the cement adversely affects the cement's flow properties independently.

Recommendations

The reports stated that, basically, there are two possible ways to eliminate lump formation in LCC cement silos.

1. Avoiding chemical reactions that may result in the formation of lumps by some or all of the following measures:

(a) Lowering the alkali content;

(b) Lowering the aluminate content by adding iron ore to the raw mixture;

(c) Reducing the loss on ignition of the cement by adding less gypsum, by raising the mill temperature, by replacing the gypsum by anhydrite, or by proper adjustment of the water-injection system;

(d) Bonding the alkalies by sulphate up to 70% in the raw mix to decrease the alkali included in the aluminate which would therefore become less sensitive.

2. Improving the flow properties by some or all of the following:

(a) Using grinding aids in cement grinding;

(b) Using additives (e.g. limestone) during cement grinding;

(c) Substituting the gypsum rock either partly or completely by anhydrite $(CaSO_4)$ to avoid dehydration of gypsum.

In April 1980, KHD proposed that operational tests should be carried out in the LCC plants over a period of two months to determine the effect on cement flowability of the addition of limestone. They proposed to send an expert for the test period to supervise and co-ordinate the test procedure with LCC personnel.

E. Other considerations

Grinding aids

During daily visits to the cement mills, it was observed that the grinding balls and cylpebs discharged from cement mill II in the Hawari Cement Plant were completely coated with a thick layer of finely ground cement particles, sometimes two millimetres thick. This coating may be attributed to static electricity, adsorption or to mechanical packing. The presence of this thick coating leads to increased energy costs and decreases the efficiency of the air separators and the flowability of the cement after grinding. It was also observed that coating of grinding balls or cylpebs was found throughout the discharged grinding media. It was suggested that the use of suitable grinding aids added to the clinker before the mill would help solve this problem and might improve the flowability of the cement.

Heat generation

Overcoming heat generation during grinding can be approached by spraying water along the longitudinal mill axis or by injecting water into the mill, which is not to be recommended as this process might have a negative influence on the cement produced. Cooling of the cement can also be done by introducing the discharged ground cement into special tanks equipped with an internal water-pipe cell system. The only disadvantage of using such a system is the likely formation of cement lumps around the water-cooling pipe cell.

Silo design

The flowability of cement is also affected by the design of the cement silo. This should be such as to allow the cement to flow easily inside the silo and to be discharged without serious problems. The silo design must take into account the high alkali and C_3A content of the clinker produced at LCC. A study of the LCC silos showed that factors contributing to lump formation were:

(a) The designed distance between the air slides at the bottom of the cement silos is obviously not correct;

(b) The dead space between the cement discharge outlets and the silo wall leads to the presence of quantities of dead cement which, within the required storage period, undergo chemical reactions leading to lump formation.

A proposal was made by IBAU, Hamburg, that they should install a cone-shaped structure inside the silo to minimize the dead space between the discharge outlets and the silo wall.

Another proposal was made by Holderbank Management Consultancy (HMC) for painting the inside walls of the silos with a non-stick coating.

F. Summary

As can be seen from the foregoing sections, the formation of cement lumps can be due to a combination of various factors. These factors can be related to the specific properties of the LCC-produced cement, either in chemical or physical terms, or to the design of the cement silos or to a combination of both.

As it is not clear which specific factor has the greatest influence on creating lump formations inside the LCC cement silos, it was decided to tackle the problem in several different ways as follows:

(a) To accept the KHD proposal to carry out operational tests on the partial substitution of gypsum by limestone;

(b) To study the different types of grinding aids which could be added to the clinker;

(c) To consider the addition of iron oxides to the raw mix;

(d) To study the problem of heat generation during grinding in the cement mills;

(e) To investigate further the HMC proposal for painting the inside walls of the silo and the IBAU proposal to install a cone-shaped structure inside the silo;

(f) To carry out tests in the LCC laboratories on the effect of various additives on the flowability of cement.

All these approaches to the problem are described in the following chapter.

II. APPROACHES TO A SOLUTION

A. Operational tests on using limestone additives to improve the flowability of cement

The preliminary work carried out by KHD led them to propose that operational tests should be carried out in the Hawari Plant on the effect of using limestone additives to improve cement flowability. This proposal was accepted and KHD asked the firm, ZEMLABOR, to make a technician available to carry out these tests. T. Brunnert was assigned to this job and arrived in Benghazi on 22 August 1980.

Discussions between T. Brunnert, A. Fathi (LCC Works Manager), S. Mohamed (LCC Head of Laboratory) and the co-ordinator on the programme for the tests came to an agreement on the following points:

(a) That the SO_3 content of the cement produced should be fixed to certain limits;

(b) That a low percentage of limestone should be added to the gypsum at first and its percentage gradually increased (as shown in table 2);

(c) That the cements produced must meet the standard specification, BS 12/195, for ordinary Portland cement which is applicable in the Libyan Arab Jamahiriya;

(d) That individual samples would be tested every hour and would later be combined and subjected to testing by ZEMLABOR.

Table 2. Test grinding operations

Grinding operation number	Date	Limestone addition (% by weight)	SO_3 (% by weight)
1	28 August 1980	2	3.0
2 (1)	4/5 September 1980	2	2.2
2 (2)	7 September 1980	2	2.0-2.2
3	21/22 September 1980	3	2.0-2.2
4	2/3 October 1980	4	2.0-2.2

An analysis was also made by ZEMLABOR of the constituents of raw materials used in LCC cement production. The following table shows the chemical composition of representative samples of the Portland cement clinker, gypsum ore, and limestone.

Table 3. Chemical composition of Portland cement clinker,
gypsum ore and limestone
(Percentage by weight)

Constituent	Portland cement clinker	Gypsum ore	Limestone
Loss on ignition	0.43	26.41	(43.28)
(insoluble matter)	(0.57)		
SiO_2	22.75	7.31	2.15
Al_2O_3	5.70	1.60	0.87
Fe_2O_3	2.42	0.80	0.24
MnO	0.06	-	-
CaO	63.47	36.24	93.32
MgO	3.28	-	2.52
SO_3	0.32	27.11	-
Na_2O	0.19	0.07	0.03
K_2O	0.81	0.52	0.78
Balance	0.57	-0.06	0.09
CO_2	0.21	13.84	Not determined
Lime saturation factor	88.2		
Silica ratio	2.80		
Alumina modulus	2.35		
C_3S	42.9		
C_2S	32.9		
C_3A	11.0		
C_4AF	7.4		
Free CaO	0.20		
Hydrate water	-	12.57	

T. Brunnert made the following observations on the material tests:

Portland cement clinker:

 Satisfactory quality as inspected visually.
 Mean loss on ignition is approximately 0.2% by weight.
 Lime saturation factor is approximately 90-95 (daily analyses).

Gypsum ore rock: (delivered to the plant by trucks)

 Strongly fluctuating quality.
 Approximately 75% is superfine particles.
 SO_3 content ranges between 23.0 and 30% by weight (according to
  tests made by T. Brunnert).
 Residual moisture is approximately 1.5% by weight.

The test samples of ground cement taken on the dates shown in table 2 were subjected to various testing procedures. Their chemical composition is given below in table 4. Table 5 shows the grinding fineness of the samples tested and table 6 the results of tests in accordance with the standard specification, BS 12/58.

Table 4. Chemical composition of the sample Portland cements tested
(Percentage by weight)

| Constituent | Cement sample | | | | | |
	0[a/]	1	2(1)	2(2)	3	4
Loss on ignition	(1.95)	(3.62)	(2.37)	(2.62)	(2.96)	(3.32)
(Insoluble matter)	(0.67)	(0.65)	(0.44)	(0.32)	(0.36)	(0.30)
SiO_2	21.82	20.91	20.90	20.76	21.26	21.36
Al_2O_3	5.42	5.17	5.40	5.30	5.50	5.53
Fe_2O_3	2.29	2.20	2.27	2.23	2.25	2.28
MnO	0.05	0.05	0.05	0.05	0.05	0.05
CaO	63.97	64.90	64.23	64.33	64.05	64.13
MgO	3.54	3.09	3.32	3.18	3.38	3.70
SO_3	1.50	2.07	2.18	2.32	2.15	1.69
Na_2O	0.17	0.16	0.14	0.15	0.23	0.25
K_2O	0.75	0.73	0.74	0.73	0.74	0.73
Balance	0.49	0.72	0.77	0.95	0.39	0.28
CO_2	1.34	2.67	1.74	1.91	2.22	2.81
Lime saturation	91.2	96.0	94.5	95.3	92.7	92.8
Silica ratio	2.83	2.84	2.73	2.76	2.74	2.74
Alumina modulus	2.37	2.35	2.39	2.37	2.45	2.43
C_3S	50.7	61.5	56.3	58.7	52.9	53.5
C_2S	24.3	13.6	17.1	15.2	21.1	20.9
C_3A	10.5	10.0	10.5	10.3	10.8	10.8
C_4AF	7.0	6.7	6.9	6.8	6.8	6.9

a/ Comparative sample of cement without limestone additive.

Determination of the grinding fineness

Specific surface according to Blaine tests:

Table 5. Blaine values
(cm^2/g)

Cement sample tested	Specific surface
0[a/]	2 730
1	3 050
2(1)	2 780
2(2)	2 890
3	3 060
4	2 820

a/ Comparative sample of cement without limestone additive

Tests for standard specification requirements

Table 6. Results according to BS 12/58

Factor	Cement sample					
tested	0[a/]	1	2(1)	2(2)	3	4
Volume stability						
(Le Chatelier test)						
(mm)00	1.5	1.5	1.0	1.0	2.0	1.0
Setting						
Beginning (h)	2.30	2.20	2.20	2.20	2.20	2.40
End (h)	3.30	3.40	3.40	3.30	3.30	3.50
Compressive strength (lbf/in^2)[b/]						
After 3 days	3 356	3 877	3 745	4 465	3 678	3 394
After 7 days	4 370	5 480	5 280	5 555	5 385	4 787

a/ Comparative sample of cement without limestone additive.

b/ 1 lbf/in^2 = 6.895 kPa.

Compressive strength

Increase in compressive strength can be represented in comparison to grinding 0 (comparative sample) as shown in table 7.

Table 7. Relative compressive strength
(Grinding 0 = 100%)

Compressive strength	Cement sample					
	0	1	2(1)	2(2)	3	4
After 3 days	100	115.5	111.6	133.0	109.6	101.1
After 7 days	100	125.4	120.8	127.1	123.2	109.5

Determination of flow properties

The flowability tests on the cement samples were carried out by ZEMLABOR according to the Imse method (published in journal ZKG 25 (1972) p.147).

ZEMLABOR used a steel plate instead of a glass plate as specified in the ariticle mentioned above. Sieves of mesh widths 0.20, 0.50, 0.63 and 1.0 mm were used. Each experiment was carried out twice and the results are shown in table 8 as the average value of both trials.

Table 8. Flow property of samples
(Percentage by weight through the screen)

Sieve-mesh width (mm)	Cement sample					
	0	1	2(1)	2(2)	3	4
1.0	100.0	100.0	100.0	100.0	100.0	100.0
0.63	94.5	76.0	80.0	85.5	86.7	83.5
0.50	71.5	62.5	67.5	69.0	74.8	72.0
0.20	14.0	13.0	15.0	14.5	14.2	14.2

Conclusions from the tests on using limestone as an additive

1. The addition of limestone (especially in the amount of 2%) to clinker
during cement grinding leads to an increase in compressive strength. This
fact was already well known from previous research and the result was to be
expected.

2. Impure gypsum is used as an additive in LCC during clinker grinding. The
relatively-high percentage of gypsum impurity (mainly limestone and marl)
influences the percentage of limestone to be added. Consequently, the
percentage of impurity of limestone contaminated with gypsum ore can influence
the grindability and flowability of the cement to a great extent and thus the
effect of the additive is not so obvious or distinct. Laboratory tests will
be needed to assess the effect of adding limestone to impure and pure gypsum
respectively.

3. It is clear from the results shown that the effect of adding limestone to
gypsum during grinding with clinker is very difficult to assess and does not
appear to be significant. The operational tests in the LCC on the effects of
the addition of limestone to improve the flowability of cement did not reveal
significant improvements, although these had been achieved by some other
plants using limestone additives, as mentioned previously.

B. Using grinding aids

The factors contributing to a cement coating on the grinding balls and
cylpebs of a cement mill are:

(a) Ball coating increases with elevated temperatures;

(b) When gypsum is ground with clinker, gypsum dehydrates which causes
ball coating;

(c) Stored clinker has a tendency to cause ball coating more than
fresh-burned clinker. However, stored clinker is ground more easily than
fresh clinker. This can be due to the slaking of free lime which helps in
weakening the structure of clinker, apparently because of expansion of the
free lime as it hydrates during storage;

(d) A rougher ball surface accumulates coating while smooth surface balls do not cause accumulation of finely ground cement;

(e) The presence of non-burned clinker. The coating of the grinding media with finely-ground cement increases with the decrease of the clinker litre weight (the weight of a litre volume) and coating is reduced to a minimum by increasing the clinker litre weight;

(f) Absence of hard material. Hard materials like sand act as an abrasive agent to eliminate the accumulation of finely-ground cement on the surface of the grinding balls and cylpebs;

(g) Using open-circuit mills. In closed-circuit mills, fine particles have to be eliminated instantaneously and transported to the separators, whereas in open-circuit mills the fine particles pass with the coarse ones through the mill compartments. These particles, under the action of ball knockings, accumulate together on the surface of the grinding media to create a cushion-like coating.

The presence of this thick coating makes it necessary to use grinding aids. These grinding aids are materials able to enter the micro-cracks of the solids and, because of the highly reactive surfaces produced in braking, these materials move with velocities akin to the velocities of the crack propagations and provide a barrier to the dissipation of energy. Rehbinder, Schreiner and Zhigach suggested that the effect was that of the additive filling the cracks during stress relief and preventing them sealing up during the comminution process. The grinding aids thus prevent ball coating and disperse the ground material. The majority of the grinding aids can be strongly adsorbed by the ground particles, so that surface energy requirements are satisfied and no bonds remain to attract other particles and cause agglomeration. These materials increase mill efficiency beside reducing power costs, thus paying their way. They increase the efficiency of the air separators by dispersing the particles so that the smaller ones are not carried along by the larger. There is a decrease in volume of the circulating load as a result of more finess being released as finished product. The grinding aids improve the cement flowability after grinding. It is therefore proposed to use such grinding aids in the Hawari cement mills.

C. Addition of iron oxides to the raw mix

The alumina and ferric-oxide contents in a cement need to be considered together since, although they are by no means equivalent to one another, their effects are closely interconnected. Cements with a high total alumina and ferric-oxide content are easily clinkered and, unless carefully burnt, tend to cause ring formation in the kiln. In this respect, the two oxides act somewhat similarly, but in most respects they cannot be treated as similar. They form the compounds C_3A and C_4AF. The relative proportion of these two compounds depends on the ratio of alumina to ferric oxide present. Increase of alumina with no change or with a reduction in the ferric-oxide content hastens the setting time of a cement and a point is eventually reached at which it becomes impossible to control the setting time adequately. The substitution of ferric oxide for alumina, or an increase in ferric oxide content, reduces the proportion of C_3A and increases that of C_4AF in the cement. The latter has less rapid setting properties and hence if the iron-oxide content is raised along with the alumina, an increased alumina and ferric-oxide content can be carried without setting troubles arising.

Synthetic studies of the influence of gypsum content have shown that there is an optimum content which produces the highest strengths and the lowest drying shrinkage. This amount varies with the contents of alkalies and tricalcium aluminate in the cement. For a content of C_3A below 6%, it is as low as 2% SO_3 for low-alkali contents (below 0.5%), increasing to 3-4% SO_3 as the alkali content rises to 1% or more. With higher C_3A contents, e.g. 10% or more, the optimum percentage of SO_3 is about 2.5 - 3% and 3.5 - 4% with cements of low- and high-alkali contents respectively. With additions in excess of these optimum values, a tendency to slow expansion in water appeared, indicating a continuing delayed reaction with the alumina compounds.

To study the trend in the tricalcium aluminate content of the clinker produced with the raw materials available to the Libyan Cement Company, the co-ordinator turned back to the consultant's report on the raw-material basis and the plant site (HMC report no. ED 67/6075/E, section C).

In the report, the results are given of a complete analysis of the limestone and red clays available to the LCC from the area south of Wadi Al Qattarah (about 13 kilometres south of Benghazi city) and it is stated that an ordinary Portland cement of the ASTM Type I ("for use in general concrete construction") may be obtained from a calculated raw mix using these two components. However, it is clear from the calculated raw-mix results shown in table 9 that the C_3A content of the clinker would range between 10.67% and 13.36%. These percentages accord with the amount of C_3A content in the clinker actually produced in the LCC production lines as shown in table 10 and they can be considered as fairly high, taking into consideration the presence of high percentages of alkalies which makes the clinker very sensitive to any moisture content. The clinker alkali content ranges from 1.34-1.55.

For these reasons it was suggested that a ferriferous material such as pyrite ash should be added to the raw mixes as a third component to decrease the C_3A and increase the C_4AF content of the clinker.

The chemical composition of the pyrite ash used for the calculations of the raw mixes was:

	Percentage
Loss on ignition	3.4
SiO_2	5.25
Al_2O_3	5.95
Fe_2O_3	82.26
CaO	1.96
MgO	0.45
SO_3	2.51
K_2O	0.32
Na_2O	0.07
	102.17

Table 11 shows the calculations of three-component raw mixes. By using pyrite ash as a third component in the raw mixes in a proportion of from 1.4% - 2.4%, it will be possible to manufacture a cement which will satisfy the ASTM specifications for a type II cement ("for use in general concrete construction exposed to moderate sulphate action or where moderate heat of hydration is required"). The addition of pyrite reduced the silica ratio from an average value of about 2.6 to about 2.0, the alumina ratio falling as well.

Table 9. Chemical and mineralogical composition of raw mixes
calculated with two components from the Benghazi area
(Calculated to 50% C_3S)

Component		Raw-mix number												
		1	2	3	4	5	6	7	8	9	10	11	12	13
Limestone designation		Z-A	Z-4	Z-5	Z-5	Z-5	Z-31	Z-31	Z-11	Z-28	Z-28	Z-31	Z-28	Z-11
mixing ratio (%)		66.08	70.66	71.95	67.84	61.54	54.82	58.69	57.20	62.61	64.32	60.47	74.73	56.06
Red clay designation		Z-4	Z-5	Z-5	Z-4	Z-11	Z-4	Z-11	Z-11	Z-11	Z-16	Z-16	Z-28	Z-11
mixing ratio (%)		33.92	29.34	28.05	32.54	38.46	35.18	41.31	42.80	37.39	35.68	39.53	25.63	43.94
Calculated	SiO_2	23.01	22.13	21.88	22.69	22.21	22.72	22.19	21.89	22.18	22.53	22.56	22.19	22.53
chemical	Al_2O_3	5.50	6.29	6.27	5.54	6.09	5.64	6.26	6.56	6.34	5.95	5.82	6.36	5.81
composition	Fe_2O_3	2.30	2.48	2.53	2.35	2.42	2.23	2.34	2.37	2.37	2.34	2.33	2.33	2.21
of the	CaO	65.09	64.81	64.35	64.61	64.66	64.82	64.84	64.83	65.04	64.99	64.08	65.05	64.74
clinker	MgO	2.08	2.50	2.56	2.56	2.50	3.25	3.14	3.19	2.90	3.06	3.31	2.93	3.38
(%)	K_2O	1.02	1.12	1.08	1.00	1.03	1.05	1.08	1.04	0.98	1.01	1.08	1.0	1.01
	Na_2O	0.25	0.43	0.34	0.36	0.37	0.42	0.44	0.44	0.36	0.33	0.36	0.36	0.11
	SO_3	0.15	0.15	0.88	0.84	0.78	0.19	0.17	0.17	0.16	0.16	0.19	0.14	0.14
Total		99.40	99.91	99.89	99.95	100.06	100.32	100.46	100.49	100.33	100.37	100.44	100.37	100.23
Moduli	$\dfrac{Al_2O_3}{Fe_2O_3}$	2.39	2.53	2.45	2.36	2.51	2.53	2.67	2.77	2.68	2.54	2.50	2.73	2.63
	$\dfrac{SiO_2}{R_2O_3}$	2.95	2.52	2.49	2.88	2.61	2.89	2.58	2.45	2.54	2.71	2.77	2.56	2.81
Lime saturation factor (%)		89.88	91.29	91.54	90.24	91.13	90.37	91.27	91.87	91.45	90.74	90.58	91.44	90.70
Potential	C_3S	49.63	49.64	49.73	49.77	49.84	49.90	49.96	49.88	50.00	49.80	49.76	49.89	49.90
mineralo-	C_2S	28.60	26.08	25.29	27.57	26.15	27.56	26.20	25.19	25.93	27.09	27.21	26.06	27.01
gical	C_3A	10.67	12.46	12.33	10.69	12.04	11.17	12.62	13.36	12.78	11.80	11.45	12.90	11.65
composition of the clinker	C_4AF	6.99	7.54	7.69	7.14	7.36	6.78	7.11	7.20	7.20	7.11	7.08	7.08	6.72

Table 10. Chemical and mineralogical analysis of LCC clinker
produced in April 1980
(Percentage)

Component	Samples taken from daily production (34 times in the month)																
LOI	0.62	0.76	0.60	0.70	0.62	0.62	0.60	0.65	0.70	0.65	0.64	0.75	0.63	0.64	0.65	0.70	0.52
SiO_2	21.53	21.04	20.92	21.50	21.55	21.92	21.68	20.62	20.87	21.00	20.44	21.00	21.34	21.06	21.69	20.98	21.40
Al_2O_3	6.52	5.93	6.47	6.50	6.59	6.64	6.39	6.56	6.35	6.52	6.53	6.39	6.44	6.56	6.60	6.60	6.31
Fe_2O_3	2.36	2.32	2.28	2.40	2.36	2.36	2.36	2.32	2.40	2.36	2.32	2.34	2.36	2.32	2.28	2.28	2.32
CaO	63.48	64.03	64.58	64.58	64.03	64.03	64.03	64.03	64.03	64.03	64.03	64.48	64.03	64.68	64.03	64.58	64.03
MgO	2.70	2.70	2.70	2.60	2.60	2.80	2.80	2.80	2.60	2.60	2.60	3.10	2.60	2.60	2.60	2.60	2.60
SO_3	0.53	0.55	0.54	0.38	0.38	0.53	0.46	0.49	0.54	0.58	0.56	0.69	0.62	0.45	0.56	0.53	0.51
Na_2O	0.45	0.56	....a/	....	....	....	....	....	....	....	....	....	....	0.54	0.54	0.30	0.30
K_2O	0.98	0.98	....	....	....	....	....	....	....	....	....	....	....	1.80	1.80	0.90	0.90
Free lime	2.24	2.13	3.36	2.24	2.24	1.18	1.06	2.58	1.68	1.40	2.07	1.75	2.35	7.96	2.02	2.80	2.24
Total	101.41	101.00	101.45	100.90	100.37	100.08	99.38	101.05	99.17	99.14	99.19	99.54	100.37	102.51	102.77	102.27	101.53
LSF	91	95	95	93	92	90	92	92	95	94	97	93	93	94	91	95	93
SM	2.42	2.55	2.39	2.42	2.41	2.44	2.48	2.43	2.35	2.36	2.31	2.43	2.43	2.37	2.44	2.36	2.48
AM	2.76	2.56	2.84	2.71	2.79	2.81	2.71	2.83	2.65	2.76	2.81	2.85	2.73	2.83	2.89	2.89	2.72
C_3S	47.04	57.27	56.66	51.87	48.65	45.48	49.08	48.39	55.47	53.33	59.82	52.16	51.31	54.70	47.63	55.28	51.83
C_2S	24.80	15.20	15.34	20.86	23.58	27.18	25.61	23.99	16.15	18.24	11.42	19.17	20.84	17.16	24.80	16.62	20.59
C_3A	13.59	12.07	13.59	13.47	13.78	13.92	13.24	13.77	13.07	13.59	13.69	13.45	13.38	13.77	13.94	13.94	13.09
C_4AF	7.17	7.05	6.93	7.30	7.17	7.17	7.17	7.05	7.30	7.17	7.05	6.81	7.17	7.05	6.93	6.93	7.05

Table 10 (continued)

LOI	0.45	0.35	0.37	0.73	0.99	0.51	0.61	0.56	0.51	0.50	0.30	0.52	....	....	....	....	
SiO$_2$	22.60	22.58	22.70	23.85	22.95	23.40	23.04	23.22	23.26	23.20	23.08	23.45	23.4	23.35	22.85	23.40	23.30
Al$_2$O$_3$	6.92	6.45	6.00	5.90	6.35	6.00	6.14	6.55	6.00	6.67	6.81	6.32	6.58	6.27	5.28	6.36	6.36
Fe$_2$O$_3$	2.40	2.40	2.40	2.40	2.40	2.40	2.36	2.40	2.40	2.28	2.32	2.28	2.40	2.36	2.40	2.44	2.40
CaO	62.37	62.66	64.03	62.38	63.76	64.03	64.03	64.58	64.03	64.80	64.03	64.80	64.58	64.58	64.58	63.48	64.58
MgO	2.00	2.20	2.00	2.60	2.40	2.20	2.20	2.00	2.20	2.20	2.20	1.20	2.00	2.00	2.00	2.40	2.00
SO$_3$	0.19	0.62	....	0.38	0.56	0.28	0.63	0.45	0.35	0.42	0.38	0.49	0.42	0.41	0.40	0.37	0.39
Na$_2$O	....	....	....	....	....	....	....	....	....	....	....	....	0.50	0.60	0.74	0.45	0.60
K$_2$O	....	....	....	....	....	....	....	....	....	....	....	....	1.80	1.71	1.89	1.79	1.89
Free Lime	1.12	1.10	0.95	0.73	....	1.09	1.68	1.12	1.09	1.09	1.68	1.12	0.95	1.68	1.06	1.01	1.56
Total	98.05	98.36	98.45	98.97	99.41	99.91	100.69	100.88	99.89	101.16	100.80	100.18	102.66	102.96	101.20	101.70	103.08
LSF	85	85	88	82	87	86	87	87	86	86	86	86	89	88	90	85	87
SM	2.72	2.55	2.70	2.88	2.62	2.79	2.73	2.73	2.72	2.59	2.52	2.73	2.59	2.70	2.98	2.66	2.66
AM	2.88	2.68	2.50	2.45	2.65	2.50	2.59	2.73	2.50	2.92	2.94	2.77	2.74	2.65	2.20	2.61	2.62
C$_3$S	33.31	36.10	43.96	42.25	38.78	38.88	35.91	38.44	39.79	35.65	35.51	36.34	36.64	38.50	50.27	33.85	39.18
C$_2$S	21.10	36.60	30.65	45.76	35.45	36.88	35.18	36.59	35.62	34.12	38.52	39.01	38.81	33.13	26.06	40.78	36.22
C$_3$A	14.60	13.33	12.12	11.85	13.07	12.12	12.51	13.61	12.12	14.73	13.45	13.18	13.76	12.92	10.18	13.02	12.20
C$_4$AF	7.30	7.29	7.35	7.30	7.30	7.30	7.17	7.30	7.30	6.93	7.05	6.93	7.29	7.17	7.30	7.42	7.30

a/ .... data not calculated.

LOI - loss on ignition
LSF - lime saturation factor
SM - silica modulus
AM - alumina modulus

Table 11. Chemical and mineralogical composition of raw mixes calculated with three components
(Calculated to 50% C_3S and 8% of C_3A) Pyrite ash = CA Mat. No. 5244 "Attisholz"

Component		1A	2A	3A	4A	5A	6A	7A	8A	9A	10A	11A	12A	13A
							Raw mix number							
Limestone designation		Z-4	Z-4	Z-5	Z-5	Z-5	Z-31	Z-31	Z-11	Z-28	Z-28	Z-31	Z-28	Z-11
mixing ratio (%)		64.25	70.16	71.41	65.64	61.48	62.94	58.67	57.18	62.59	64.24	60.39	73.66	56.14
Red Clay designation		Z-4	Z-5	Z-5	Z-4	Z-11	Z-4	Z-11	Z-11	Z-11	Z-16	Z-16	Z-28	Z-11
mixing ratio (%)		34.34	27.85	26.63	32.96	36.70	35.44	39.28	40.42	35.27	34.07	38.07	24.18	42.23
Pyrite Ash mixing ratio (%)		1.41	1.99	1.96	1.40	1.81	1.62	2.05	2.40	2.14	1.69	1.54	2.16	1.63
Calculated chemical composition of the clinker	SiO_2	21.48	21.15	20.91	21.25	21.27	21.06	21.10	20.62	21.06	21.60	21.71	21.06	21.65
	Al_2O_3	5.63	6.14	6.13	5.64	5.96	5.76	6.10	6.38	6.19	5.84	5.70	6.19	5.72
	Fe_2O_3	4.10	4.90	4.88	4.11	4.62	4.30	4.83	5.27	4.97	4.42	4.21	4.97	4.23
	CaO	63.25	63.66	63.19	62.74	63.49	62.64	63.46	63.19	63.59	63.83	63.71	63.59	63.65
	MgO	2.46	2.44	2.49	2.51	2.45	3.17	3.06	3.11	2.83	2.99	3.24	2.86	3.32
	K_2O	1.04	1.08	1.04	1.01	0.98	1.06	1.03	1.00	0.97	1.00	1.05	0.97	1.00
	Na_2O	0.37	0.36	0.33	0.35	0.39	0.39	0.42	0.42	0.37	0.32	0.36	0.35	0.40
	SO_3	<0.15	<0.15	<0.87	<0.76	<0.78	<0.12	<0.17	<0.17	<0.16	<0.14	<0.19	<0.14	<0.14
Total		98.38	99.88	99.84	98.37	99.94	98.90	100.17	100.16	100.14	100.14	100.17	100.13	100.11
Moduli	$\dfrac{SiO_2}{R_2O_3}$	2.21	1.91	1.90	2.17	2.01	2.09	1.93	1.77	1.89	2.10	2.19	1.88	2.18
	$\dfrac{Al_2O_3}{Fe_2O_3}$	1.37	1.25	1.26	1.37	1.29	1.34	1.26	1.21	1.24	1.32	1.35	1.25	1.35

Table 11 (continued)

Lime saturation factor (%)		90.92	91.38	92.62	91.15	91.22	91.37	91.43	91.99	91.50	90.87	90.70	91.49	90.78
Potential	C_3S	50.05	50.05	50.05	50.05	50.05	50.05	50.05	50.05	50.05	50.05	50.05	50.05	50.05
mineralogical	C_2S	23.86	22.92	22.24	23.19	23.26	22.64	22.75	21.39	22.64	24.19	24.53	22.65	24.34
composition	C_3A	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
of the clinker	C_4AF	12.46	14.90	14.82	12.50	14.04	13.06	14.68	16.03	15.12	13.45	12.80	15.11	12.87

If pyrite ash is added to the raw mixes in a proportion of between 1% and a maximum of 1.36%, this will increase the value of the C_4AF and decrease the value of C_3A to a maximum of 10% which helps in eliminating the formation of cement lumps in the cement silos to a great extent. Applied in this proportion, the quantity of pyrite ash required to produce two million tons of cement is:

$$2,000,000 \times 1.18\% = 23,600 \text{ tons per year}$$

D. Overcoming generation of heat during grinding in the cement mill

The majority of the energy input is usually converted into heat during grinding material in ball mills. The mill temperature rises to well over $100^\circ C$ and the gypsum, which is sensitive to temperature, dehydrates with partial separation of its water through crystallization and thus loses its property as a cement-setting retarding agent. It should be noted that more than 80% of the energy input can be converted into heat during grinding in the ball mill. If the clinker introduced into the mill is already at a temperature of $100^\circ C$, the temperature during grinding can rise to $180^\circ C$.

Cooling of the ball mill can be achieved through mill ventilation, mill-shell cooling by spraying water along the longitudinal mill axis to decrease the temperature of the ground cement by $30^\circ C$ at least, or by injecting water into the mill.

In this last solution, a controlled amount of water is injected inside the hottest part of the finish mill where most of it is evaporated at once. About 15% of the non-evapourated water is carried out to the storage silos. The problems that may accompany water injection arise from the dropping of such non-atomized water inside the mill. Such water droplets are adsorbed on the cement grains leading to setting, hydration and accumulation of cement aggregations. This process can have a negative influence on the produced cement. Injection of non-atomized water inside the ball mill can result from the clogging of the water nozzle or to an insufficient amount of compressed air pushing the water through the nozzle or to the diameter of the nozzle opening.

In some cases, cement can be cooled in the air separators or by introducing the discharged ground cement into special tanks equipped with an internal water-pipe cell system and a sloping bottom made of a porous medium through which compressed air is applied and passes to the cement to fluidize, mix and cool. The temperature of the cement coming out of these tanks is reduced to approximately $65^\circ C$ depending on the cooling water temperature and this minimizes the possibility of gypsum dehydration. The only defect of using such a system is the formation of cement lumps around the water-cooling pipe cell.

Some cement plants spray water on the clinker while it is being transported by drag chain. This process is not to be recommended as it usually creates severe problems in forming big clinker lumps during the storage period.

It is advisable to keep the temperature of the cement produced as low as possible (less than 110°C) by using the stored clinker which has been cooled. Newly-produced clinker must be stored for about one week before grinding. Water injection into the cement mills must be avoided. The possibility of introducing the ground cement into special cooling tanks, as described above, must be further investigated.

E. Cement-silo design

Many factors have to be taken into account in designing a cement silo. Of critical importance is the chemical composition of the cement which, in this case, has been shown to have a relatively high C_3A and alkali content which tends to lead more easily to the formation of lumps and aggregations.

The distance between the air slides has a pronounced effect on fluidizing and mixing the stored cement easily inside the cement silo. The smaller the distance between the slides, the greater the fluidizing action. In the Hawari cement mill, the designed distance between the air slides at the bottom of the tank is obviously too great and the air slides should possibly be widened to minimize the distance between them in order to reduce the static state of the surrounding stored cement by continuously fluidizing it.

Efficiency of the compressed-air system and its injection-fluidizing device in the cement silo is helpful for continuous fluidizing and mixing cement inside the silo. However, the injected compressed air must be free of water resulting from condensation of the water vapour. This can be done by water traps installed before the cement silo or by introducing the compressed air inside big tanks where the water is expelled continuously through a tap installed at the bottom of these air tanks.

Periodical cleaning of the inside of the cement silos on a regularly--programmed basis will avoid hardening of the cement.

The dead space between the discharge outlets and the silo wall allows the presence of a quantity of static cement which, within the required storage period, undergoes a chemical reaction leading to the dehydration of gypsum and the formation of lumps and aggregations particularly in this space. The formation of lumps in this space makes it possible for more cement to adhere and accumulate.

To minimize the dead space around the discharge openings, some silo designers prefer to install a cone-shaped structure inside the silo, covering these discharge openings. In this way, the space between the conical structure and the silo wall is kept to a minimum, avoiding any accumulation of dead cement. At the same time it would be possible to increase the number of discharge outlets from all parts of the silo bottom to avoid the cement remaining long in one place. At present the silo contains two discharge outlets. It is also possible to increase the slope of the silo bottom along and vertical to the air slides.

Painting the walls inside the silo with a special enamel coating could help to reduce the adhesion of stored cement to these walls to a minimum, though it would not avoid the lump formation caused by chemical reaction.

Proposals under the last two headings were made by IBAU HAMBURG (to install a cone-shaped structure inside the silo) and by HMC (to paint the inside silo walls with a non-stick coating). These are discussed below.

Installation of a cone-shaped base in the cement silo

The conical cement-silo base is a design of the company IBAU HAMBURG. This firm was therefore asked if they could send a specialist to discuss the problems of the LCC silos on the spot.

In June 1980, an offer and proposal were received from IBAU HAMBURG who expressed their willingness to send out two representatives to study the exact technical requirements. The proposal envisaged the following:

(a) The existing equipment and coating concrete have to be removed from the bottom of the cement silo. Then a steel cone with eight discharge openings has to be installed. The silo openings have to be prepared and the silo doors prefabricated;

(b) The designers will not offer for the steel cone itself as they assume that LCC will be able to manufacture this in its workshop. The designer will only offer the static calculations for this steel cone for about DM 15,000;

(c) Below the steel cone, the collecting hopper has to be installed on the concrete bottom. The dedusting of the silo discharge will be done through this hopper (calculated rate of 30 m^3/min).

The LCC also proposed that, while the designers' specialists were in Benghazi, it would be of great interest if they could give lectures to the LCC engineers on the most up-to-date technology in designing and manufacturing cement silos as the designers' representatives had contributed papers on this subject to the Baghdad Cement Seminar in 1980.

When the representatives of IBAU HAMBURG, W.E. Lummel and H.K. Klein-Alibenhausen, arrived in Benghazi, meetings were held with A. Fathi and the co-ordinator to discuss all aspects of the installation of a steel cone with eight discharge openings at the bottom of the LCC cement silos. A meeting was also held in the training centre between LCC engineers and the representatives who lectured on up-to-date technology in designing cement silos, concentrating on their own design (steel-cone structure in the silo base) as it is the latest design in this field and is performing successfully in many cement companies all over the world.

In the tripartite discussion meetings and at the end of the lecture, the co-ordinator brought up the following questions:

(a) Is this design likely to help LCC to completely overcome the problem of cement lumps and aggregations in its existing cement silos?

(b) As this structure and the upper parts of the cement walls are the coldest parts of the silo, it is likely that lumps and adhesions of cement particles will form not only against the upper parts of the silo inner walls but also against the steel-cone structure itself. As the main factor creating such lumps is a chemical factor, is it possible to overcome this chemical action or to decrease its influence and to what extent?

(c) What is the main action of this steel-cone structure against lump formation?

(d) What is the likelihood of all the eight discharge openings becoming clogged?

(e) What is the best way of getting rid of these lumps?

The answers which emerged to these questions during the various discussions were as follows:

(a) This cone will not influence the formation of the cement lumps inside the silo as these lumps are caused chemically;

(b) The design of the steel-cone structure is intended to decrease the dead space between the discharge points and to give cement particles accumulated in this dead space no opportunity to form lumps as the cement does not remain long enough in this place to allow a chemical reaction;

(c) The likelihood of lump formation will be concentrated on the upper parts of the inner silo walls where it is coolest;

(d) The main action of this design is a physical one depending on the following concepts;

   (i) The cone structure leads to easy sliding of the cement grains and particles against it, i.e. they do not adhere;

   (ii) Decreasing the dead space to a minimum gives no chance for the chemical reaction to continue as the cement gathered will have more opportunity to flow out;

   (iii) There are an increased number of discharging points (eight) distributed equally around the periphery of the steel-cone structure giving the cement more chance to flow out from all areas of the bottom of the cement silo which again reduces dead space;

   (iv) These openings can be equipped with a lump crusher type H and an IBAU flow-control gate to catch the lumps moving with the fresh cement towards the discharge spouts. At this bottleneck, any lumps plugging up the discharge aperture or reducing the flowability of the cement can be crushed into very small pieces so that the cement passes the aperture of the flow-control gate of the crusher without trouble;

(e) When one or more of the discharge apertures are clogged or fully blocked, the cement silo has to be completely emptied of cement through the other apertures, giving an opportunity to personnel to get inside the cement silo to clean it;

(f) The total cost of installing such a steel-cone structure inside one of the LCC cement silos would be more than DM 400,000.

It was concluded that installing such a structure at the bottom of the cement silo would not completely overcome the problem which is mainly chemical. Accordingly, the whole matter was postponed for the firm of designers to restudy the offer in the light of the facts explained to them at the tripartite meetings and lectures.

Since then, no further offer has been received from this company and it seems unlikely that this solution will be adopted.

Painting the inside walls of the silo

As mentioned earlier, the consultants, Holderbank Management and Consultancy (HMC) had proposed that the application of a non-stick coating to the inside walls of the silo would greatly reduce the adhering of stored cement to these walls.

A representative of HMC, accompanied by H. Schatzmann from SCHATZMANN AG, visited the LCC in Benghazi in July 1981 to discuss this proposal. A meeting was held between H. Schatzmann, Abu Bakr El-Sultani and the co-ordinator.

At this meeting, H. Schatzmann made the following points:

(a) Painting the inner silo walls with a special enamel paint produced by his company will prevent lump formation in cement silos as the plastic coating will act as a very smooth surface which will prevent adherence of cement particles on these inner silo walls;

(b) It is preferable that the painting be done after the erection of new cement silos. In that case, the painting can be applied to the bottom surface and up to about two meters height on the walls;

(c) For the old LCC cement silos it would be advisable to paint all the inner silo walls;

(d) Painting of one square meter (when applied in Switzerland) costs SwF 65.

The co-ordinator discussed these points and concentrated on the following problems:

(a) Painting can be applied successfully only immediately after erecting the cement silos to avoid any humidity penetrating either from outside through the outer walls or resulting from the new concrete;

(b) The main factor creating lumps in the LCC cement silos is a chemical one and these lumps will be formed whether the inner walls are painted or not (the chemical factors affecting lump formation were discussed previously);

(c) The painting will cost a great deal and its application will not lead to a full solution.

At the end of discussions, it was agreed that, as the lumps are formed chemically or physically, it is preferable to try to solve the problem chemically or physically and to postpone painting the inner silo walls.

F. Laboratory tests on various additives

The operational tests carried out in the cement plant on using limestone as an additive did not give any clear result. This is partly because gypsum with a relatively-high percentage of impurity is used as an additive in LCC during clinker grinding. This influences the percentage of limestone which needs to be added during cement grinding. It was decided that laboratory tests should be carried out to assess the effect of adding limestone to the impure and pure gypsum respectively.

Tests were also carried out in the LCC laboratories to investigate the behaviour of other types of additives on the flowability of LCC cement.

In total, the following additives were tested:

1. Limestone
2. Limestone associated with high-quality gypsum
3. Polar chemical compounds (ethylene glycol)
4. Commercial additives known as HEA
5. Hydrophopic materials (stearates)

The laboratory results can be summarized briefly as follows:

Limestone

The laboratory results showed no wide range of difference from those produced in the operational tests on LCC large-scale production.

Limestone associated with pure gypsum

When limestone is associated with high-quality gypsum, good results are achieved, especially using 30% of the normal amount of gypsum added. Here, the compressive strength of the cement mortar increases while the cement also shows better flowability.

Ethylene glycol

Ethylene glycol was used in percentages of 0.02, 0.04, 0.06, 0.08 and 0.1 and the grinding was carried on for 20, 30, 40, 50 and 60 minutes. It was found that the fineness increased by increasing the time of grinding for all the percentages, but that the 0.06% addition of ethylene glycol was the critical percentage. When more was added, the blaine fineness decreased in all the grinding periods.

For the sample ground with 0.06% ethylene glycol, the compressive strength was increased by 14% after three days and by 10% after seven days.

Commercial additives (HEA)

The same procedure used with ethylene glycol was followed. The results were very encouraging, especially in respect of fineness, compressive strength and flowability. The critical percentage used was also 0.06%.

Hydrophopic materials (stearates)

Commercial hydrophopic material was tested in the laboratory but unfortunately these tests gave no reliable results. This may well have been due to the fact that the hydrophopic sample had been stored for more than 10 years.

The co-ordinator discussed the results of the laboratory tests with the LCC authorities and it was agreed to contact the Italian company, GRACE, to carry out some large-scale tests on LCC cement production, using some of the more promising additives. This company accepted to carry out these tests and will be sending two of its representatives to Benghazi to discuss the procedure of their work.
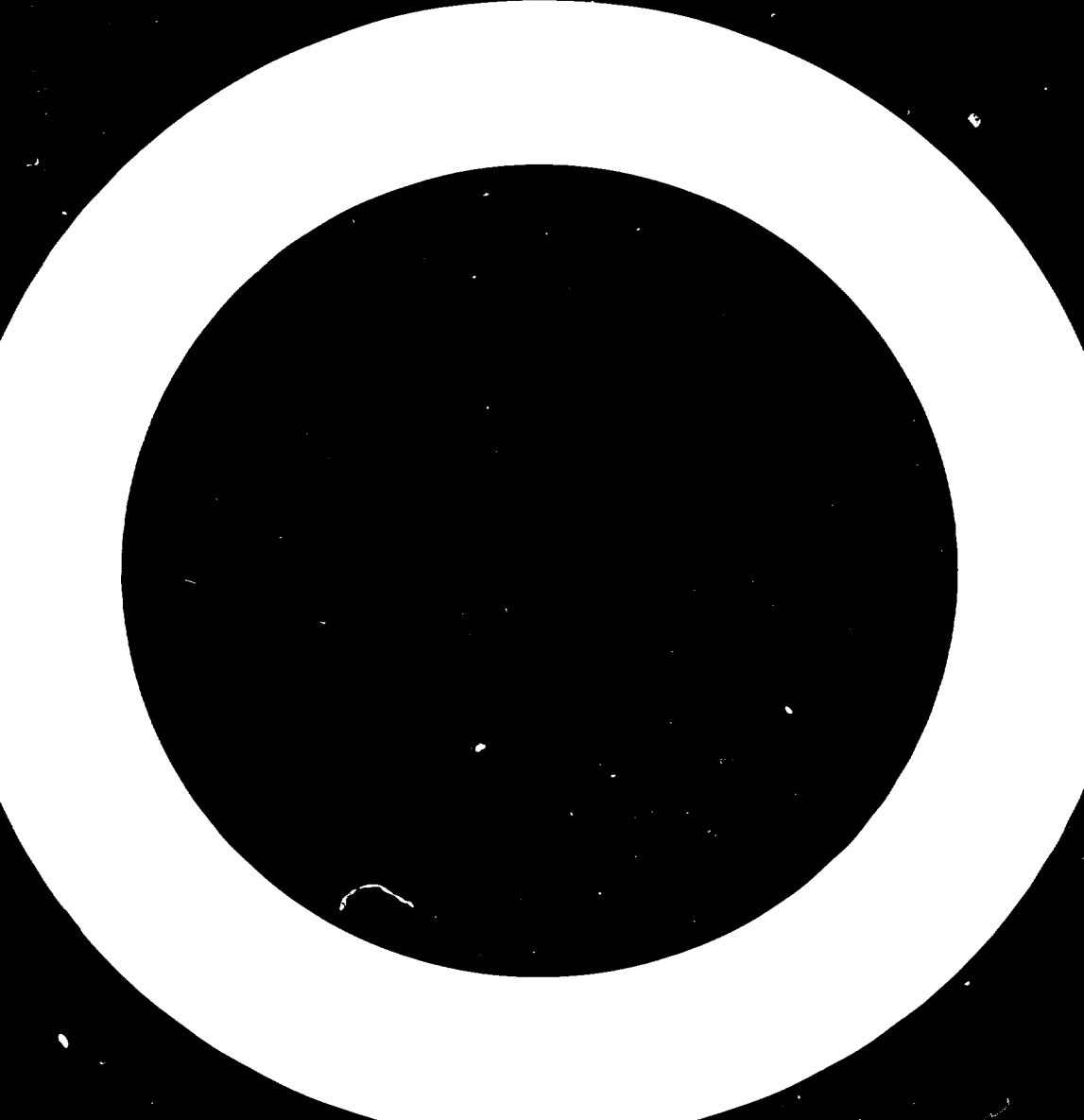
REPORTS ISSUED UNDER THE PROJECT TF/LIB/75/002 OR TF/LIB/82/002

UNIDO/IOD.37 24 May 1976	Report on the first part (February to April 1976) of a year's mission by a building-materials adviser to the cement industry in Benghazi Aly Afify
UNIDO/IOD.174 11 July 1977	Report on the second part (November 1976 to August 1977) of a year's mission by a building-materials adviser to the cement industry in Benghazi Aly Afify
UNIDO/IOD.264 1 August 1978	Planning a system of mechanical maintenance Alfred Madsen
UNIDO/IOD.345 16 March 1979	Preventive maintenance planning in the mechanical maintenance service Mehmet A. Basman
UNIDO/IOD.354 15 August 1979	Assistance in instrument maintenance Boguslaw J. Walczenko
UNIDO/IOD.361 12 December 1979	Report of the project co-ordinator for the period up to October 1979 A.M. Afify
UNIDO/IOD.383 16 September 1980	Assistance to the electrical engineering staff in organizing and carrying out electrical maintenance Boguslaw J. Walczenko
UNIDO/IO.437 16 January 1981	Report on a one-month mission (from 11 November 1980) to review and evaluate the progress of the project A.M. Afify
UNIDO/IO.475 13 March 1981	Instrument maintenance systems at the Benghazi complex: final summary Boguslaw J. Walczenko
UNIDO/IO.472 6 July 1981	Report of a one-month mission (from 19 May 1981) to review and evaluate the progress of the project A.M. Afify
UNIDO/IO/R.7 30 July 1981	Raw materials deposits at Wadi Ash Shati and Al Jufrah Abd El R. Marei
UNIDO/IO/R.14 17 December 1981	Preliminary study for long-term technical advice A.M. Afify
UNIDO/IO/R.33 28 October 1981	Progress of the project from 10 May 1980 to 31 July 1981 A.R. Marei

UNIDO/IO/R.17 2 November 1981	Feasibility of producing sulphate-resisting cement A.R. Marei
UNIDO/IO/R.29 26 March 1982	Replacing cylpebs by grinding balls in Benghazi I and Hawari cement mills A.R. Marei
UNIDO/IO/R.34 26 March 1982	Progress of the project from 1 August 1981 to 31 December 1981 A.R. Marei
UNIDO/IO/R.42 26 March 1982	Formation of cement lumps and aggregation in cement silos A.R. Marei
UNIDO/IO/R.53 26 March 1982	New gypsum deposits A.R. Marei
UNIDO/IO/R.84 24 January 1983	Progress of project from 1 January 1982 to 30 June 1982 A. R. Marei
UNIDO/IO/R.85 24 January 1983	Feasibility study on plant for ready-mixed concrete and prefabricated concrete products A.R. Marei
UNIDO/IO/R.99* 27 October 1983	Evaluation of the raw material situation of the Al Khums I Cement Plant A.R. Marei

---

* Forthcoming.