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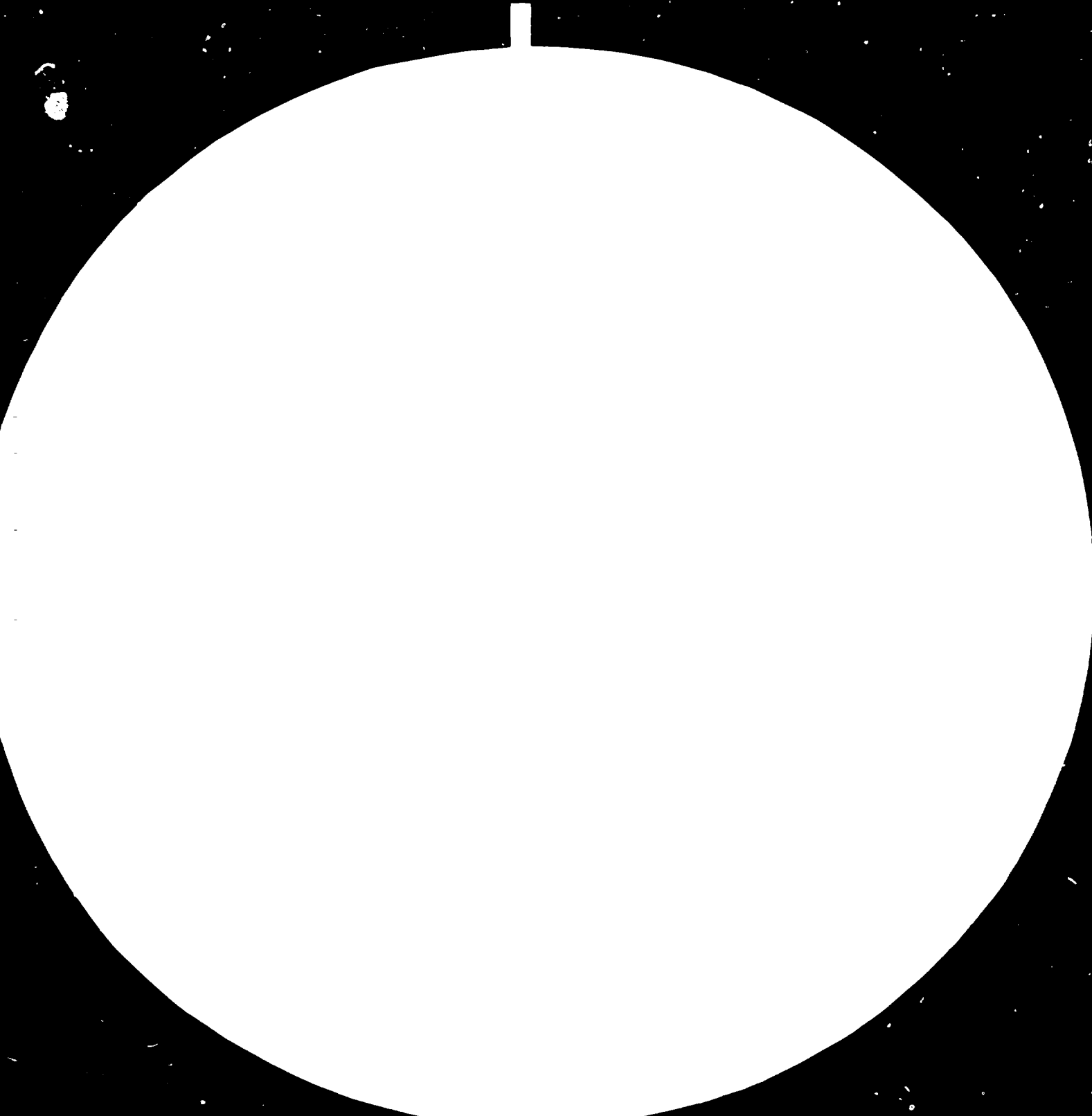
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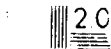
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GRINDING AND BURNABILITY OF OOLITIC LIMESTONE*

by

R.A. Marei**

and

K.M. Hanna***

003_56

Oolitic limestone plays a strange role in burning and grinding the raw mix due to its unique physical property i.e texure. Before studying these effects it is worthy first to study the termal behaviour and the grindability of this type of limestone.

1. Thermal Behaviour of Oolitic Limestone

The differential thermal curve of the oolitic limestone sample as shown in Table I , Fig 1 , shows.

Table 1 : <u>Thermal Analysis Data of Oolitic Limestone</u>

DTA Peak Temp.				Total Weight loss
Endothermic C^o	Exothermic C^o	Temp. Range C^o	Weight Loss%	
130		25 – 525	2.0	42.3
641		525 805	3.9	
690				
739				
980		805 1000	36.4	

a- Storng effects with endothermic peak temperature at $130C^o$

b- Very week effects with endothermis peak temperature at 641, 690, and 739 C^o

c- Very strong effects with endothermic peak temperature at $980C^o$ The endothermic effects with peak temperature of $130C^o$ is the consequence of humidity leaving the sample. The very weak effects with peak temperatures at 641, 690 and 739 C^o may be due to the loss of the structural hydroxylation present in small quantities of clay minerals (Brown,1961).
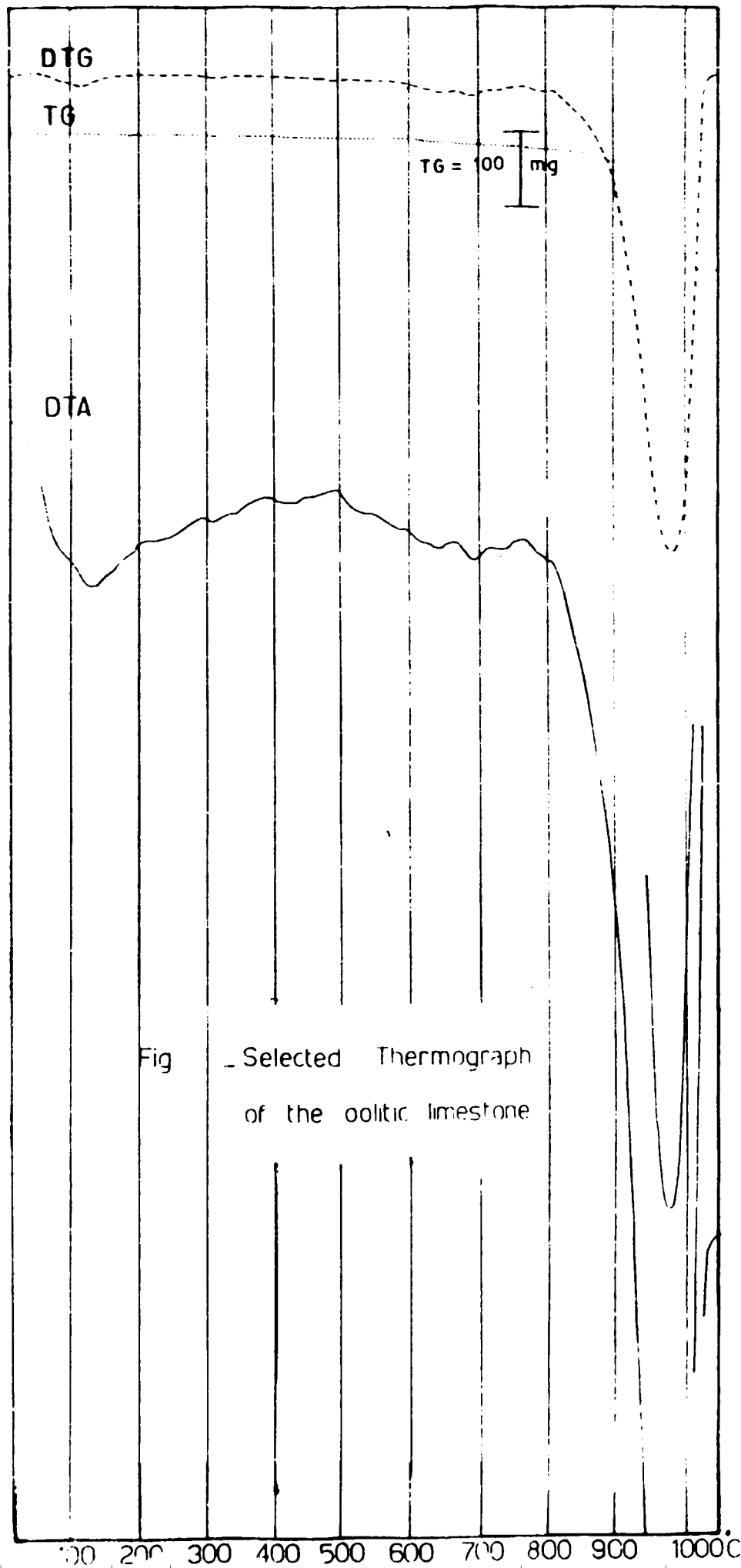
DTG

TG

TG = 100 mg

DTA

Fig _ Selected Thermograph

of the oolitic limestone

100 200 300 400 500 600 700 800 900 1000 C

The very strong endothermic peak at 980C^o is due to the dissociation of calcite into CaO+ CO$_2$ (Webb and Heystek, 1957).

X-ray diffraction data as shown in Appendix I indicate that traces of Aragonite and quartz are present in this sample. Faust (1950) reported that the decomposition temperature of aragonite is between 870 to 959 C^o and that the calcite between 914 to 972 C^o. He added that subsidiary breaks were observed on the high temperature side of the peak in samples formed of mixtures of calcite and oragonite. This was attributed to different decomposition temperatures for the primary calcite and the trigonal calcite produced from the erthorhombic aragonite transformation at 400 - 450 C^o. The peak characteristic for this transformation did not appear in the DTA curve of the analysed sample, this may be due the presence of a very small quantity of aragonite. The characteristic peak is not detected when aragonite content is much below 35%. This may vary considerably with the sensitivity of the D.T.A. unit used.

The total loss in weight during heating from 25 to 1000C^o of the oolitic limestone is 42.3%. It is represented in three temperature regions on the DTG curve as shown in Table I, Fig. I. Weight loss of about 2.0% was estimated from the TG curve in the temperature region between 25 and 525C^o This loss in weight may be attributed to the moisture content leaving the sample during the first stage of heating It is represented by a very weak peak at about 110C^o on the DTG curve of the sample.

The loss in weight in the second temperature region (525-805 C^o) is about 3.9%. Two diffused very weak peaks were observed on the DTG curve (Fig.I) in this temperature region. This may be attributed to the loss of the structural hydroxylation present in very small quantities of clay minerals (Brown, 1961) and/ or due to the contamination of small amount of magnesite or dolomite. However, the presence of the clay is not proved by the X-ray diffraction. This means that: if there is any clay mineral, it could be represented by less than 5% as confirmed by chemical analysis of the sample.

The greatest loss in weight was detected in the 805-1000C^o temperature region. DTG curve indicated that this loss in weight took place in one stage. This is proved by the presence of one very strong peak at about 980 C^o on the DTG curve.

It is mainly due to the liberation of CO_2 as a result of the dissociation of calcite or aragonite caused by the reaction

$$CaCO_3 \rightleftharpoons CaO + CO_2$$
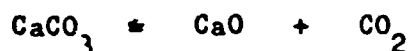
2. Evaluation of the Grindability of Oolitic Limestone

The raw materials introduced into the rotary kiln must be sufficiently fine so that the clinkering reaction can be completed without requiring excessive temperature or longer reaction Lime. Under commercial burning conditions, the coarse particles of limestone or silica may fail to react completely and hence cause excessive free lime to exist in the resulting clinker leading to unsoundness and excessive volume change of the mortar or concrete (Lea,1970). 90 micron is the maximum size for limestone at a clinkering temperature of $1350C^o$ (Pollitt, 1964).

Two processes, known as the wet and dry processes according to whether the raw materials are ground and mixed in a wet or dry condition, are used. Because of the soft nature of the marl and clay they can ground easily and converted directly into a slurry. On the other hand, the harder limestone requires rigid fineness control.

Grinding test were accordingly carried out to investigate the grindability behaviour of two kinds of limestone of approximately the same chemical composition but of different hardness. The diference of hardness range is not so much as we have chosen two types of the oolitic limestone classified as: white oolitic limestone (containing calcareous material cementing the ooids with each other) and brownish oolitic limestone (this type contains the ooids without or with small percentage of calcareous cementing material) i.e the only difference between the two types is the calcareous cementing material.

The individual samples were crushed to pass a 4 mm sieve using a 3 inch jaw crusher. The crushed material was dried overnight at about 60 C^o. Dry grinding was conducted in a steel ball mill having an internal diameter of 24 inch and length of 22 inch. The mill speed was 50 rev/min. The ball charge was composed of 1/3 each by weight of 3/4, 7/8 and 1 inch diameter steel balls, totalling 100 kg.

The mill was operated with 10 kg materials batches. The products of the ginding tests were analysed for the percent finer than 56 microns and for the specific surface. The sepecific surface of the powder was determined by the air permeability method.

Separate batches of the brownish and white oolitic limestones were ground for 5,10,,15,20,30,45 and 60 minutes. The test results charted in Fig 2 indicat that the white limeston is easier to grind than the brownish limestone. The white limestone developed,.at all grinding times, a greater surface area and a more finer material than the brownish oolitic limestone.

These results can be attributed to the fact that the cementing material – mainly formed of fine needle like crystals of calcite or aragonite binding the individual oolites – is present in greater amounts than that present in the brownish oclitic limestone. When the needle – like crystals are subjected to the impact and attrition action of the comminution process, they become disentegrated and accordingly, new surfaces of the individual colites become available for future impact and attrition actions of the grinding media. Moreover, the individual oolite of the brownish limestone tend towords avality in shape than in the while oolitic limestone (plate I, Fig, A.). Since fine grinding is mainly brought about by attrition of the grinding media, it is expected that spherical oolities are ground to higher fineness by the spherical (ball) grinding media than the oval oolites. In oval oolites, attrition takes place at limited points. Oval oolites would be efficiently ground if cylindercial grinding media (cylpebs) or rod mill are used. It was found that both the rounded and oval oolites can escape the attrition action of the grinding media specially the balls and they can be considered as a part of this grinding media. The fact is that these rounded or oval oolites escape grinding action and appear in the slurry produced by the open circuit mills or appear in the separators or the back delivery products coming back to the raw mill to be ground again. Accordingly the oversize grains retained on both sieves go and 170 is compartively. of high percentage than when grinding normal hard limestone.

3. **Thermal Behaviour of Oolitic Limestone on Raw Mix:Four** different cament raw mixes containing white and brownish limestone were

selected from the computer result data. The proportions of the components of each raw mix were calculated by computer simulation. These raw mixes were subjected to thermal analysis. In general the chemical and physical changes which take place on heating the cement raw mixes (composed of oolitic limestone, marl and clay) from room temperature up to $1400C^o$ can be summerized as follows (Table II).

1- Loss on humidity, endothermic with peak temperature at about 130 C^o

2- Dehydroxylation of clays, endothermic with peak temperature at 525° - 535 C^o

3- Decomposition of carbonate, endothermic with peak temperature at 743° - 756 C^n and 940 C^o for the dolomite and calcite respectively.

4- Reaction between lime and clay to form belite in a solid phase is represented by an exothermic effect with peak temperature range between 1230 and 1250 C^o

5- Liquid formation followed by completion of cement compounds in three phases represented by endothermic effects between 1290 and 1340 C^o (clin kering temperatures)

6- On cooling an exothermic effect is indicated at 1230 + 2 C^o due to the crystallisation of the molten phase.

EVALUATION OF THE BURNABILITY OF THE RAW MIXURES

The facility of combination of the components of a portland cement raw mixures is designated as the "burnability". Burnability of the raw mix materials can be readily ascertained by estimating the percentage of free lime or uncombined calcium oxide which remains in the products (Bogue, 1955) following heat treatment. In the present work evaluation of the burnability of raw mixes was followed by determining both the uncombined lime and insoluble residue after subjecting the raw mixures to specific burning time and temperature. The insoluble residue represents the aluminosilicates of the clay mineral and/or silica which did not participate in chemical combination.

Evaluation of the burnability of the raw materials
is based on the following considerations:

-       Use of a raw mix characterized by a high lime
        saturation factor, 97.

-       Use of relatively coarse raw mix where the fraction
        coarser than 89 microns (retained on a 170 mesh sieve)
        was estimated to be about 17%.

-       Burning the mix at onl$_\cdot$ $1350^{o}C$ for 15 minutes.

The principle upon which the above conditions were
designed is that a mixture with a high lime saturation
factor- especially if coarse materials are used- requires
a higher heat consumption for clinker burning (Duda 1976).
accordingly, the reactivity of the raw materials under
these severe test conditions will give a true and clear
picture on the burnability rather than burning under
ideal conditions such as using low lime saturation factor,
higher fineness, higher temperature and longer burning
time.

Four mixes were used in the first step of the
evaluation of the burnability of the raw materials. The
proportions of the raw materials components of these mixes
are given in Table 2. The four mixes had in common the same
lime saturation factor, the same silica modulus and the
same fineness (83% finer than 89 microns). The
characteristics and oxide composition of the four mixes
are summarized in Table 3 .

Table: 2. Composition of the Raw Mixes

Raw Material	First Series				Second Series			
	Mix I	Mix II	Mix III	Mix IV	Mix I	Mix II	MIX III	Mix IV
White Oolitic Limestone	72.24	74.93			70.36	73.25		
Brownish Oolitic Limestone			72.94	76.12			71.07	74.93
Desert Marl	20.01	15.67	18.08	12.92	21.36	16.71	19.45	14.01
Clay I	7.75		8.98		8.28		9.48	
Clay II		9.40		10.96		10.05		11.56

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Preparation of the Test Specimens:

*The proportions of the raw materials components of
each mix were thoroughly mixed and enough water was added
to obtain a homogenized plastic mass.   The plastic material was*

Table. 3   CHARACTERISTECS   OF   THE   FIRST   SERIES

OF   RAW   MIXES

Characteristic	Mix I	Mix II	Mix III	Mix IV
L.S.F.	97	97	97	97
S. M.	2.6	2.6	2.6	2.6
AM	1.88	1.98	1.59	1.68
CaO, %	41.87	41.75	41.38	41.22
SiO_2, %	13.56	13.51	13.44	13.37
Al_2O_3, %	3.41	3.45	3.17	3.22
Fe_2O_3, %	1.81	1.74	1.99	1.92
Ignition Loss, %	35.85	36.12	36.12	36.44
C_3S %	65.30	65.03	65.97	65.68
C_2S %	11.35	11.59	10.54	10.78
C_3A %	9.30	9.72	7.89	8.32
C_4AF %	8.59	8.30	9.50	9.20

Formed by hand into balls of 1 to 1.5 cm diameter. The balls were dried at 120 °C for about 4 hours then heated for one hour at 600 °C. About 100 grams of the preheated balls were placed in platinum dishes in an electrically heated laboratory muffle furnace of the Heraues type. burning was carried out for 15 minutes at 1300° and 1350°C soaking temperature). The dishes were introduced into the muffle furnace at 1000 °C.

The products of the burning were rapidly cooled, ground to pass a 100 mesh sieve and then analyzed for the insoluble residue and free lime.

The test results are summerized in Table 4.

Table 4. Insoluble Residue and Free Lime Contents of the First Series of Raw Mixes Burned at 1300 and 135°C

Burning	Mix I		Mix II		Mix III		Mix IV	
Temp., °C	I.R.	Free	I.R.	Free lime	I.R.	Free lime	I.R.	Free lime
1300	2.0	8.0	3.6	8.4	4.0	10.3	6.0	9.7
1350	2.0	6.4	3.1	6.5	3.0	7.4	2.2	8.6

I.R.: Insoluble residue

examination of the insoluble residue and the free lime data reported in Table 4 shows:

a -   Both the insoluble residue and the uncombined calcium oxide decrease at the higher burning temperature indicating the progress of chemical combination.

b -   Considering that the insoluble residue represents the uncombined or free aluminosilicates of the clays and/ or free quartz, then from the data shown in Table 5 it can be found that:

Table 5. CALCULATION OF THE EXTENT OF COMBINATION
OF SILICA + ALUMINA AND LIME IN RAW
MIXES BURNED AT 1350 ^{o}C

	:Mix I		Mix II:	Mix III	:Mix IV	:
	SiO_2 + Al_2O_3					
Original content, dry, %	:16.97	16.96	:	16.61	:16.59	:
" " ignited, %	:26.45	26.55	:	26.00	:26.10	:
Insoluble Residue at 1350 ^{o}C, %	: 2.0	3.1	:	3.0	: 2.2	:
Insol. residue x 100 / (Original SiO_2+ Al_2O_3); ignited	: 7.50	11.67	:	11.54	: 8.4	:
	CaO					
Original content, dry, %	:41.87	41.75	:	41.88	:41.22	:
" " ignited, %	:65.27	65.36	:	64.77	:64.65	:
Free CaO at 1350 ^{o}C, %	: 6.4	6.5	:	7.4	: 8.6	:
Free CaO: Original CaO (ignited); %	: 9.8	9.94	:	11.42	:13.26	:

a) About 90% of the sum of al_2O_3 + SiO_2 had combined at 1350°C

b) The ratio of the insoluble residue to the original
SiO_2 + Al_2O_3 (ignited weight) amounts to 7.5 to 11.6% at
the burning temperature of 1350 ^{o}C. In the same manner,
it can be seen that from 87 to 90% of the original calcium
oxide had combined with the acidic oxides.

oxide had combined with the acidic oxides.

c- Comparison of the free lime centerts of raw mix No. 1
and No. III and No. II and No. IV indicates that
compositions containing the white oolitie limestone
are easily burned (as can be seen from the free lime
contents) than those compositions containing the
brownish oolitic limestone, i.e., white limestone
has a higher reactivity towards combination with the
acidic oxides.

In general the results of the free lime contents
obtained in the present investigation indicate that
the four mixes are of "normal burnability" and are of
high reactivity according to the standards suggested
by Polysius. Polysius considers that raw mixes with
lime saturation factor of 95 to 98 are evaluated as
"normally burnable" according to the following free
lime centents (Polysius, 1974):

Free lime of 12 - 16 % on burning for 15 min. at $1350^{o}C$
Free lime of 8 - 12 % on burning for 15 min. at $1400^{o}C$
Free lime of 4 - 8 % on burning for 15 min. at $1450^{o}C$
Free lime of 2 - 4 % on burning for 15 min. at $1500^{o}C$

Actually the free lime contents suggested by Polysius (1974)
to be obtained at 1450 ^{o}C, were obtained at 100 ^{o}C lower
i.e., 1350 ^{o}C in the present work indicating good burnability
of the raw mixes.

The free lime and insoluble residue tests have shown
normal burnability of the raw mixtures having a lime
saturation factor of 97. Moreover, the tests have shown
very clearly a difference in the reactivity behaviour of
the white and the brownish limestones. A second series
of raw mixes was prepared and fired at 1400 ^{o}C.

*The lime saturation factor of this series was only 91, the
normal time factor commonly used in cement plants for the
production of Ordinary Portland cement. The silica modulus
was maintained 2.6, the same as in the first series of
raw mixes. In order to study the role of fineness, two
groups of samples were prepared from each raw mix. The
First group of samples was made from raw materials finer
than 89 microns, whereas the fineness of the second
(coarse) group was only 82% finer than 89 microns. The
proportions of the raw materials components of the second
group of mixes are given in Table, 6, the chemical
composition of the raw mixes and the computed phase com-
position of the clinker are reported in Table 6.*

*Table 6. CHARACTERISTICS OF THE SECOND SERIES
OF RAW MIXES*

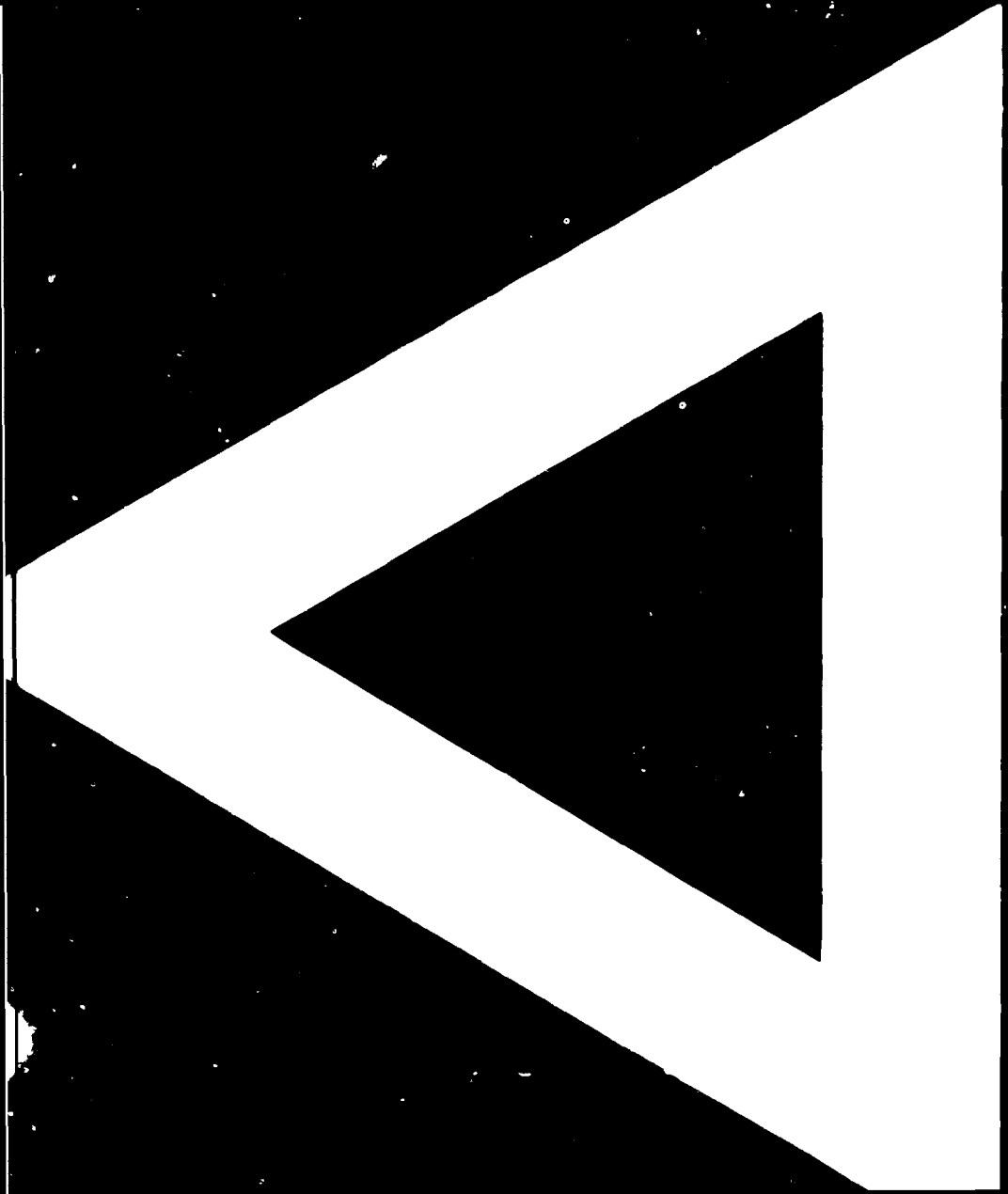| Component	Mix I	Mix II	Mix III	Mix IV
L.S.F.	91	91	91	91
S M	2.6	2.6	2.6	2.6
A M	1.89	1.99	1.61	1.70
CaO %	41.26	41.13	40.74	40.62
SiO_2 %	14.24	14.19	14.11	14.04
Al_2O_3 %	3.58	3.63	3.35	3.40
Fe_2O_3 %	1.90	1.83	2.08	2.00
Ign. Loss %	35.44	35.72	35.70	36.04
C_3S %	50.98	50.67	51.73	51.41
C_2S %	24.80	25.07	23.91	24.18
C_3A %	9.72	10.17	8.35	8.80
C_4AF %	8.95	8.64	9.83	9.52

The free lime and insoluble residue contents of the second series of mixes burned at 1400 ^{O}C are summarized in Table 7.

Table 7.   FREE   LIME   AND   INSOLUBLE   RESIDUE   CONTENTS
OF   THE   SECOND   SERIES   OF   RAW   MIXES   BURNED
AT   1400°C (LSF: 91)

Mix	Mix I		Mix II		Mix III		Mix. IV	
	In.Res	CaO	Ins.Res	CaO	In.Res	CaO	In.Res	CaO
Coarse	1.60	2.9	2.7	2.3	2.2	5.0	2.2	4.8
Fine	0.24	0.30	0.90	0.35	0.20	0.30	0.42	0.35

The   st results given in Table. 6 reveal clearly the importance of fineness, especially for the borwnish oolitic limestone, in burning cement raw mix.   The raw materials should be fine enough to bring the reactions to completion.   The results also show the marked difference in the reactivity behaviour of the borwnish oolitic and white oolitic limestone at the relatively low lime saturation factor.

The white oolitic limestone showed a higher reactivity than the borwnish oolitic limestone.