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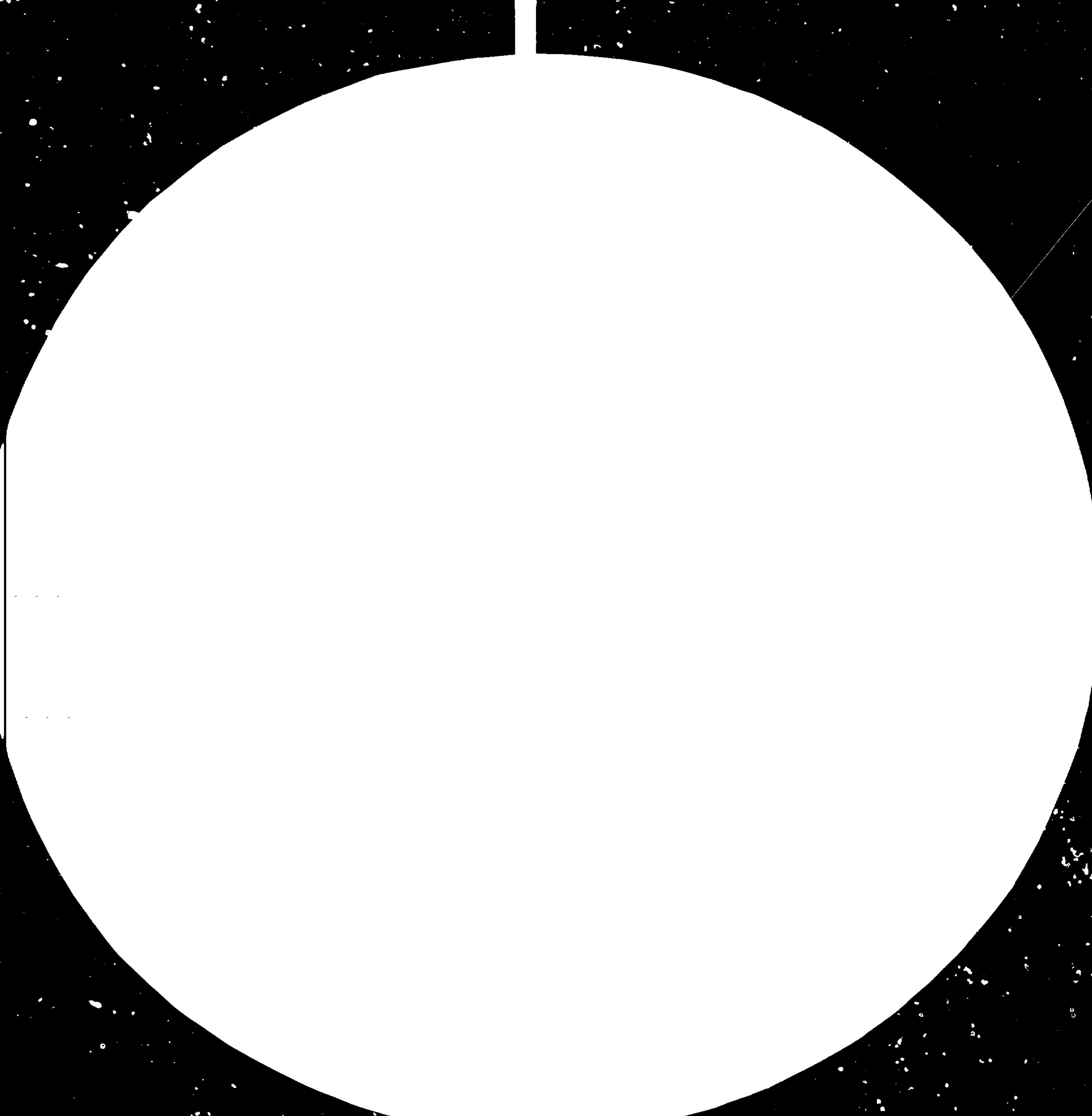

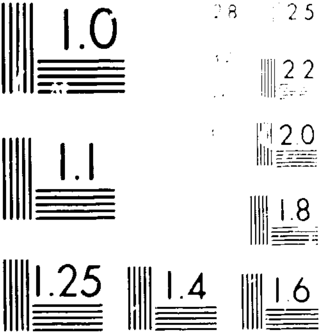
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APPLIED RESEARCH IN PROCESS CONTROL *

by

G. Roed **

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Introduction.

The title of the paper I shall have the pleasure of presenting for you is: Applied research in process control in cement productions. Under this heading I would like to report on a research program, I was asked to conduct, during a five month stay in one of the Middle East contries.

The program was intended primarily to be a training program for the scientific staff at a local central laboratory, and attempts were made, to relate characteristic diversities or anomalies observed, to relevant production stages. Due to the limited time available, the investigations were carried out on single sample-sets, each consisting of raw-mix, clinkers and cement. The work included physical tests and chemical analysis of cements, microscopic investigations on clinker-samples and fineness-analysis of raw-mixes. Because of the general difficulty of obtaining cement-samples, which originates from the clinkers under investigation (same period of burning), the results obtained on cements may contradict the results obtained on clinker-samples. It could therefore be argued that results from single samples, as used in these investigations, might reflect exceptional extreemes of fluctuations within the individual productions. However, for productions of high degree of stability such fluctuations are expected to be small, and contradictory data from cement- and clinker-samples are therefore believed to reflect the degree of instability in the clinker production.

The experimental work of the program was divided between two working groups, the microscopic group and the chemical-/physical-group as shown below:

Clinkers: a) determination of free lime. (Chem.)
          b) phase distribution of clinkers. (Micr.)

Cements: a) physical test of cement. (Chem.)
b) chemical analysis. (Chem.)

Raw-mixes: a) particle size distribution. (Micr.)
b) burnability test. (Micr.)

Sampling.

The raw-mix- and the cement-samples were considered homogeneous and were examined as received. For clinker-samples the situation is normally different. Each clinker-sample was therefore divided in homogeneous sub-samples according to clinker-size, colour and apparent porosity. The subsequent examinations were then carried out on the individual sub-samples and the final results calculated as weighted means of the sub-samples.

APPLICATION OF EQUILIBRIUM PHASE DIAGRAMS IN CEMENT RESEARCH.

It has been generally accepted for many years, that observations on model clinkers consisting of only CaO, Al_2O_3 and SiO_2 and burnt to complete equilibrium under laboratory conditions, could be satisfactorily interpretated by the help of the three component diagram $CaO - Al_2O_3 - SiO_2$ (C-A-S-diagram). This has also been the case for more realistic compositions containing Fe_2O_3 (10%) and minor amounts of other "impurities".

More recently it has been demonstrated that the application of equilibrium diagrams is also usefull in investigations of industrialy produced clinkers (ref. 3, 4 and 5). This was ealier questioned because industrial clinkers were not considered to be equilibrium samples and local inhomogenities normally exist. Investigations of the different steps of the clinker reaction have confirmed that the ratelimiting step is the reaction:

$$C_2S \quad + \quad CaO \longrightarrow \quad C_3S \quad (1)$$

This reaction takes place in the burning zone of the cement-kiln, after that much more rapid reactions, in lower temperature-zones in the kiln, have changed the raw-materials to a mixture of C_2S, liquid and great amounts of free CaO.

It has also been shown (ref. 3, 4 and 5) that reaction (1) is diffusion controlled and that locally equilibrium will exist. The concept of locally equilibrium means that equilibrium according to the phase-diagram exists at any boundary between different phases in the sample at the definite temperature. Fig. 1 shows the corner of the CAS-diagram of interest for cement-production. This diagram gives detailed informations about the equilibrium situation for different compositions at different temperatures.

Because reaction (1) is the far most important reaction in cement-production and since this reaction in practice can be assumed to take place at fairly constant temperature, a more convenient diagram may be constructed to give informations corresponding to one temperature only, (ref. 6). This is named an isothermal section, and is shown in fig. 2, for the temperature 1500^{o} C, which corresponds the burning temperature, approximately 1450^{o} C for realistic cement compositions.

In fig. 2 the composition space is divided into different fields designated D_1 - D_5. The fields D_1, D_3 and D_5 are two-phase fields where one solid (the component in the corner) is in equilibrium with one liquid phase. D_1 thus designates compositions in which CaO os in equilibrium with melt of composition L_3 - L_2, D_3 designates compositions consisting of C_3S in equilibrium with melt of composition L_2 - L_I and D_5, finally compositions where C_2S and melts on the isotherm are in equilibrium.

D_2 and D_4 are three-phase fields corresponding two solid phases in equilibrium with a liquid phase of fixed composition. D_2 corresponds to C_3S and free CaO in equilibrium with melt L_2, and D_4 to compositions giving C_3S and C_2S in equilibrium with melt of composition L_1.

At a relative early stage in the burning zone, the individual regions of the clinker (approximately 100x100x100μm^3) will show a quantitative phase composition corresponding the isotherm diagram for the burning-temperature and the local composition concerned. However, general equilibrium still does not exist because of composition-differences between local regions. The reaction then taking place in the burning-zone is easily explained in the isotherm section in fig. 2.

In fig. 2, P is the total composition of the raw-mix. The equilibrium phase distribution of composition P is directly read from the diagram to be: (C_3S- a)%C_2S, (C_2S- b)%C_3S and (a- b)% liquid of composition L_1.

Because of the chemical inhomogeneity, the average composition P, may result from neighbour-regions of different compositions P_1 and P_2. The region of P_1 consists of C_3S, C_2S and liquid L_1, while P_2 consists of C_3S, free CaO and L_2. Because P_1 and P_2 are located in different fields of the isotherm section, D_4 and D_2 in fig. 2, they are not in mutual equilibrium and a transfer of materials between them will take place by a diffusion process. During this diffusion process an intermediate zone will develop in the contact zone between the two original regions P_1 and P_2.

N.H.Christensen (7) has shown, that this new diffusion zone will consist of compositions on the straight line between P_1 and P_2, and only those crossing the two-phase field D_3 in fig.2. According to the diagram, the diffusion layer then consists of C_3S and liquid only.

The two original regions will decrease in size, while the thickness of the intermediate zone will increase following a square roote of time dependency and equilibrium is not reached until one of them has disappeared. Consequently the rate of the over-all reaction $C_2S + CaO \rightarrow C_3S$ will also decrease proportional to the square roote of time, characteristic for diffusion processes.

For finely ground and homogeneous raw-mixes the diffusion distances can be kept very small ($< 200 \mu m$) and reaction times correspondingly short. This is not possible however, if coarse grains are present in the raw-mix, and the reaction time for complete reaction will therefore increase accordingly. Two types of coarse grains are of special interest in this connection, coarse $CaCO_3$- and coarse SiO_2-grains.

Coarse $CaCO_3$-grains.

If coarse $CaCO_3$-grains are present in the raw-mix, the reaction will proceed as illustrated in fig. 3a. The reaction layer of C_3S will increase during the reaction, but for $CaCO_3$-grains smaller than approximately 125 μm the CaO-grains are completely dissolved within the normal burning times and transformed to an area consisting of C_3S and liquid only.

Hereafter the clinker-structure will not change fundamentally during continued burning, but only show subsequent crystal growth of the equilibrium phases formed.

Coarse SiO_2-grains.

If coarse SiO_2-grains are present in the raw-mix, the final step of the clinker reaction can be illustrated by fig. 3b.

As mentioned above, the SiO_2-grains, when entering the burning zone, have already been transformed to C_2S-clusters containing some liquid. Because of the low CaO-content in such regions, the surrounding matrix must show a corresponding increased CaO-content, compared to the total composition P. The composition of the matrix may then fall inside the field D_2 of fig.2, where the phases in equilibrium are seen to be C_3S, free CaO and liquid L_2. The free CaO will in this case be finely distributed in the matrix. The further reaction between the C_2S-cluster and the free CaO-containing matrix will also here result in a diffusion layer around the coarse C_2S-particle, consisting of C_3S and liquid only.

However, for a given reaction layer-thickness, the reduction in size of the C_2S-cluster is insignificant compared to the grain-size reduction in the case of coarse CaO-particles. This is due to the random distribution of the reacting partner, the free CaO in the matrix, which in the case of coarse SiO_s-grains has to be transported from regions far away in the sample, in order to complete the reaction.

Therefore when SiO_2-grains, coarser than approximately 44 μm are present in the raw-mix, the above mentioned reaction will normally not be completed within the time available in the burning zone. Consequently a corresponding amount of free CaO (depending on the lime saturation factor) will be present in the clinker after leaving the kiln. Even a considerable increase in burning time will not affect this situation significantly, because of the rapid decrease in reaction rate by increased reaction layer-thickness.

From the discussion above it is understood, that the distribution of the clinker phases C_3S and C_2S will depend on the original distribution of CaO- and SiO_2-rich regions in the raw-mix, and that no change in the phase-distribution is to be expected after completion of the reaction (1).

An observation of an ununiform distribution of these phases in the microscopic examination, then reflects either insufficient homogenity or coarse-grains in the raw-mix.

By the rapid cooling, normally exerted in the clinkers upon leaving the burning zone, the liquid phase will crystallize forming mainly C_3A and also C_4AF in the realistic system.

EXPERIMENTAL.

Cement-samples from each sample-set were physically tested in accordance with the national specifications for cement testing. Only the autoclave test were omitted and additionally to the specification, the 28-day compressive strength were meassured. The results from the physical tests are shown in table I. Also on cement samples, complete chemical analysis has been carried out, following the standard proceedures normally used. The results are listed in table II.

Raw-mix samples were investigated for grain size distribution by meassuring the residues on sieves with No. 16, 18, 26, 72 and 170 corresponding mesh widths 1000, 850, 600, 210 and 90 microns respectively. The sieve residues are listed in table VII. On the basis of the accumulated residues, the grain size curves were constructed and graphs for the individual samples are shown in fig. 4.

<u>Clinker-samples</u> were examined for SO_3-content by chemical methods normally used. The results are included in table II. Clinker-samples from the individual factories were also examined qualitatively as well as quantitatively by reflection microscopy of polished sections. As mentioned earlier, the clinker-samples showed different degrees of inhomogenity with respect to modul size, colour and porosity. In order to improve the accuracy of the microscopic examinations, the clinker-samples were divided into groups, which then were examined individually.

Clinker fragments from each such group were impregnated in resin. After hardening of the resin the samples were ground to expose a cross-section of the clinker fragments, using 96% alcohol as a lubricant. To secure an absolute plane surface, the final steps of grinding were carried out in glass-plates, using SiC-powder and iso-butanediol. Finally the samples were polished automatically on petrodisc in a Struers DP-U polishing machine, using iso-butanediol and 1 μm and o.3 μm Al_2O_3-powder. Upon cleaning, the samples were surface-etched in HF-vapour for 5 - 15 sec. By using this etching technique the clinker phases are easily destinguished in the reflection microscop. Thus C_3S, C_2S, C_3A appear with brown, blue and grey colours respectively, while C_4AF and MgO remain completely unaffected by this treatment. The free CaO shows only a slightly change in colour and will also appear unetched white.

When not examined under the microscop the polished sections are carefully stored in dessicators equiped with silicagel. For further details in procedures for sample-preparations, see ref. 7 and 8.

<u>Qualitative microscopic examination</u>.

The clinker samples were investigated qualitatively under the microscop by estimating 10 characteristic clinker properties on three arbitrary levels. The selected properties were the following:

1. Crystalsize of alite. The alite crystals are regarded as medium size between 20 and 50 μm. Small alite crystals indicate incomplete clinker burning, while large sizes of alite indicate unneccessary intense burning, i.e. either too high temperature or too long time in the burning zone. Coarse alite surrounding belite clusters, typical for raw-mixes containing coarse silica is not considered here.

2. Crystalsize of belite. Belite crystals between 10 and 30 μm are regarded as medium size crystals. Smaller dimensions reflect an underburned situation, while oversize crystals of belite indicate coarse SiO_2-rich particles in the raw-mix.

3. "Belite".Under this point the frequency of belite with anomal etching behaviour is estimated on three levels, none, few and many. "Belite" denotes belite with a significantly lower reactivity than the β-belite usually found, when etched with HF-vapour. "Belite" is normally seen to form part of individual belite crystals, located in direct contact with sulphate liquid phase. It is known (ref. 9) that high concentrations of sulphates may stabilize α- or α'-modifications of belite. Also the temperature in the burning zone may affect the formation of certain modifications of belite, but more detailed investigations are needed to confirm the identity of "belite".

The points 1 - 3 are related to the burning temperature and burning time. The following two points 4 and 5 deals with homogenity.

4. Streaks or bands of belite forming an interconnected pattern in the clinker, indicate insufficient homogenization of the raw-mix or in more rare cases, contamination of the clinkers with SiO_2-rich constituents in the kiln. This feature is also characteristic for raw-mixes with coarse $CaCO_3$-grains, especially when the lime saturation factor is relatively low, i.e. < 87.

5. Clusters of belite is a specific indication of the presence of coarse SiO_2-grains in the raw-mix. It has previously been discussed that this particular phase-distribution is an equilibrium phenomena for raw-mixes with lime saturation factors lower than 98.

Point 6 and 7 give informations about the cooling rate of the clinker.

6. The crystallinity of the interstitial phase will be highly influences of the cooling rate in all the temperature range down to the eutectic temperature about 1200° C. If slowly cooled, the liquid, which is completely melted at the clinker reaction temperature, will crystallize to well developed crystals of C_3A and C_4AF.

On the contrary, if clinkers are quickly cooled the liquid phase will show a fine grained structure.

The stoichiometric composition of the crystals formed from the clinker liquid is known to be more complex, but a more detailed differentiation than mentioned here will be outside the scope of this work.

7. Secondary precipitation of belite around alite crystals is occasionally observed in industrial clinkers and results from slow to moderate cooling rates at temperatures just below the maximum temperature in the kiln. It can be shown (ref. 6), that this particular belite structure must be expected, when passing the peritectic temperature (1455° C in the CAS-system) with a moderate rate of cooling. The reaction taking place in this point is the resorbtion reaction $C_3S + liq \rightarrow C_2S$.

In practical cement-production this undesirable reaction is avoided by installation of "cam-lines" in the kiln, which ensures the proper rapid cooling of the clinkers in the actual temperature-range.

The last points 8, 9 and 10 convey a qualitative estimate of the presence of the remainder minor constituents.

8. Clusters of free CaO are an unmistakable indication of coarse $CaCO_3$-particles in the raw-mix.

9. MgO-crystals, periclase are to be expected as an equilibrium phase in clinkers with high MgO-contents, ($>$ 3% MgO). The amount quantitatively estimated here, represents the coarse primary crystals (size $>15\,\mu m$) formed at the maximum temperature in the kiln. Additionally small amounts of finely crystallized periclase may be formed during the cooling of the clinker.

10. The sulphate phase, mainly K-, Na- and Ca-sulphates, is observed as separated inclusions in the interstitial phase. This characteristic distribution is due to immiscibility of the two liquid phases at the high temperature in the kiln. A larger amount of sulphate phase indicates high alkalicontent in the clinkers.

    Recently published data (ref. 10) also seem to indicate, that even small amounts of sulphate phase (water soluble sulphates) may have a negative influence on the long termed compressive strength of the cement.

The results of the qualitative examination are listed in table IV.

Quantitative microscopic examination.

The HF-vapour-etched polished sections of clinkers were after the qualitative examination investigated quantitatively for the content of clinker phases, by optical pointcounting.

The OPC-method is based on the fact that the area, occupied by any constituent in an cross section of a sample, corresponds to the volume percent of the particular constituent in the clinker.

Of statistical reasons this area is easily determined by placing a number of random grid points over the sample, and then count the relative number of points falling within the particular phase in question. Then, knowing the densities of the clinker phases, the weight percents are easily calculated from the volume percents measured.

In the present work a counting technique was used, by which the samples were automatically moved in steps, when the push buttons on a counting keyboard were pressed. A certain clinker mineral was counted by pressing the corresponding button when the mineral appeared under the cross-hairs of the microscops eye-piece. Normally the 50 x objective lense was used and the clinkerphases counted were C_3S, C_2S (C_3A + C_4AF), free CaO, MgO, sulphate phase and pores. The C_3A and C_4AF were counted in one group (liquid phase) and the relative amounts estimated from the average appearance of the liquid phase in each case. From the optical-point-counting data, the average volumetric content of each constituent in a clinker-sample is calculated as the weighted mean of the contents in the individual clinker-fractions. The results are listed in table V.

RESULTS.

Optical point counting.

From the volumetric data, the corresponding weight percentages are calculated in table V using the following equations:

$$\text{WT \% (component i)} = \text{Vol \% (i)} \times \frac{\rho_i}{\bar{\rho}}$$

$$\text{where } \bar{\rho} = \frac{\text{Vol \% (i)} \times \rho_i}{100}$$

The densities ρ_i, used for the different clinker-minerals were: C_3S, 3.13; C_2S, 3.28; C_3A, 3.0; C_4AF, 3.77; CaO, 3.32; MgO, 3.58 and sulphate, 3.22

For the contents of clinker minerals determined by optical point counting, confidence limits on a 95 % level have been claculated. In principle two different sources of error should be considered, the statistical counting-error and the error of sampling.

For the statistical error of counting, the standard deviation, s_{count}, can be deduced from the data in ref. 11, using the equation $\delta_{95\%} = 1.96 \times s_{count}$. $\delta_{95\%}$ is here the 95 % confidence limit, listed in ref. 11 as a function of the total number of counts and the relative content of the phase counted.

Using 3000 as the total number of counts, which has been exceeded in all cases in the present work, s_{counts} is calculated for the individual clinker-phases and listed in table VI (1).

Applying the "mean range method for grouped samples", ref. 12, p. 48, the sampling error can be estimated from the OPC-data from the individual clinker pieces in different polished sections. The groups are here polished sections containing the same number of clinker pieces (four). The individual pieces in a polished section represents the same particular fraction of the complete clinker sample from the factory.

From the OPC-data the mean range $\bar{W}$ is calculated for each of the clinker-phases and listed in table VI (2). From the mean range $\bar{W}$, the standard deviation of sampling is found using

$$s_{sampl.} = \frac{\bar{W}}{d_4}$$

where d_4 = 2.o6 (ref. 12).

The s-values of sampling for the different clinker-phases are listed in table VI (3).

The overall standard deviation is now calculated in table VI (4) from

$$s_{OPC} = \sqrt{s^2_{count} + s^2_{sampl}} \; .$$

Using now the overall standard deviations, the 95 % confidence limits are finally calculated in table VI (5) from

$$\delta_{95\%} = \pm \frac{t \times s_{OPC}}{\sqrt{N}}$$

where N is the total number of clinker pieces counted in a complete clinker sample and t takes the value 2 for the degree of freedom of s, i.e. N - (number of groups).

Chemical analysis.

In table V also the mineral contents are listed, which have been calculated from the chemical analysis data on cements, using following set of modified Bogue-formulas:

$$C_3S = 4.o \times CaO - (6.59 \times Al_2O_3 + 1.47 \times Fe_2O_3 + 7.39 \times SiO_2 + 2.8 \times SO_3 + 4.0 \times \text{Free } CaO)$$

$$C_2S = 3.11 \times SiO_2 - o.8 \times C_3S$$

$$C_3A = 2.78 \times Al_2O_3 - 1.86 \times Fe_2O_3 - 0.02 \times C_3S$$

$C_4AF = 3.3 \times Fe_2O_3 - 0.06 \times C_2S$

$CaSO_4 = 1.7 \times SO_3$

The modified formulas are taking into consideration the pronounced tendency of solid solution formation in clinker minerals, documented in litterature in recent years.

BURNABILITY.

Standard Burnability index.

In this part of the investigation the burnability of the raw-mixes from the different factories has been compared. The burnability model applied here is suggested by V. Johansen and Fundal, ref. 2 and 13, and is closely related to the clinker reaction mechanism discussed previosly in this report. According to the model a standard burnability index for at given raw-mix is defined as the amount of free CaO in the clinker after burning under standardized conditions, i.e. 1400°C, 30 min.

A relatively higher burnability index then stands for a raw-mix more difficult to burn into equilibrium condition.

Fundal (ref. 13), has established a relationship from which the standard burnability index can be calculated from chemical and physical parameters of the raw-mix. The equation is

$$CaO^{30}_{1400} = 0.33\ (LSF - LSF(M_s)) + 0.93 \times SiO_{2+44} + 0.56 \times k \times CaCO_{3+125} + 0.2 \times Aq \qquad (2)$$

Where LSF is the lime saturation factor, $(LSF(M_s) = -5.1 \times$ silica modulus + 107, and SiO_{2+44} and $CaCO_{3+125}$ are the fractions of SiO_2 - and $CaCO_3$ - grains coarser than 44 and 125 μm respectively. k is defined as

$$k = \frac{\text{titration (limestone)} - \text{titration (raw-mix)}}{100 - \text{titration (raw-mix)}}$$ and

Aq is the acid-insoluble residue - quartz.

Using equation (2) the standard burnability index were calculated for the nine raw-mixes investigated and the results are shown in table VIII. The chemical parameters in eq. 2 were calculated from the data in table II and the coarse $CaCO_3$ - fraction were read from the grain size curves in fig. 4, assuming that the fraction coarser than 125 μm consists of $CaCO_3$ particles only. The correction factors, k, used in the calculation, are included in table VIII.

The term related to "coarse silica" in eq. 2 had to be considered in five cases, where coarse silica were indicated from the qualitative investigation. In these cases, the amount of coarse silica was determined as the HCL-insoluble residue on sieve mesh no. 270 (cf. table VII).

The term Aq was neglected in all cases.

Effect of temperature and time.

Furthermore, Vagn Johansen (ref 2) has demonstrated that burnability indexes corresponding temperatures and burning-times, different from the standard conditions, can be calculated on the basis of the standard burnability index and the grain size distributions of the raw-mix.

The equation to be applied in this case is

$$\mathrm{CaO}_T^t = \frac{{}_T^t\Sigma(1 - X_i)\ Ri}{{}_{1400}^{30}\Sigma(1 - X_i)\ Ri} \times \ \mathrm{CaO}_{1400}^{30} \qquad (3)$$

where ${}_T^t\Sigma(1 - X_i)R_i$ represents the summation of the non-reacted fractions of CaO-grains, extended over all grain sizes in the raw-mix, for the temperature and time indicated. CaO_{1400}^{30} is the standard burnability index previously defined.

The non-reacted fractions $(1 - X_i)R_i$ are calculated individually for the average grain sizes d_i of a number of intervals, using following equation established in ref. 2:

$$1 - \frac{35.5 \times 10^{-5}}{K} \times \frac{t}{d^2} = (1 + 5X)^{2/3} - \frac{10X}{3} \qquad (4)$$

In eq. (4), K is a temperature dependent constant related to the diffusion - coefficient in the clinker liquid (= 1 for 1500°C, 2.3 for 1400°C); R_i is the weight-fraction of $CaCO_3$ with grain size d_i in the raw-mix.

On the basis of eq. (3) and (4) the effect of burning time at 1500°C has been calculated for the seven raw-mixes investigated.

The procedure in the calculation appears from appendix I and the results are shown in table VIII.

The burnability equation (3) considers the reaction of coarse $CaCO_3$ - particles only.

Therefore, if also coarse grains of silica are present in the raw-mix, a certain amount of free CaO should be added, corresponding the contribution from this constituent. According to the previous discussions in this report about the consequences of coarse silica in the raw-mix, this amount of free CaO will be influenced by the chemical parameters but are expected to be a naerly constant function of temperature and time. This contribution to the burnability index may therefore be estimated from equation (2) as $CaO(SiO_{2+44}) = 0.33(LSF - LSF(M_s)) + 0.93 \times SiO_{2+44}$. These corrections for the relevant cases are included in table VIII and a graphical reprensentation of the time-dependency of the 1500° - burnability index is shown in fig. 6.

Effect of fineness.

In one case of an extremely coarse raw-mix, sample no. 3, the effect of grinding has been demonstrated. By grinding by hand in a mortar, the 170 mesh sieve-residue, originally amounting 24% of the raw-mix, was changed to 10% (cf. fig. 4), without changing the total chemical composition.

Using the burnability model discussed in the proceeding section, the burnability indexes were calculated for the two different fineness-situations for three different temperatures and fixed burning-time, 30 min.

For the same conditions of temperature and time an experimental burnability test series was accomplished. Laboratory clinkers of the two raw-mixes were here calcinated for 30 min. at 1000°C and subsequently burned in a laboratory kiln under strictly controlled conditions at 1365°C, 1400°C and 1450°C for 30 min. Upon rapid cooling the amount of free [illegible] in the clinkers was determined by chemical analysis.

The calculated and experimentally determined free CaO-contents in the two cases are shown in table IX. A good aggreement is found between calculated and axperimental values. - It should be noticed, that variation of burning temperature only has a minor influence on the amount of free CaO, compared to the effect of improved fineness for this raw-mix.

COMBINATION OF RESULTS.

Discussion of the Sample No. 1.

The physical test results for Sample No 1 (cf. table I), shows a cement which satisfy all specification-properties tested.

The relative amounts of clinker minerals (cf. table V) may also be regarded as normal.

The considerable discrepancy between the OPC-data and the Bogue-data in table V reflects a significant difference in chemical composition between the clinkers and the cement-samples investigated, which again indicates an anomal fluctuation in the lime-saturation factor of the kiln feed.

This conclusion has been confirmed in a communication with the factory, and efforts were made to overcome these temporary difficulties.

Special attention has been payed to the unusual high MgO-content in these clinkers (determined to 4,4%).This amount exceeds the amount, that can be incorporated either in the clinker-minerals as solid solutions or dissolved in the liquid phase. Consequently a residual amount must remain in the clinker as a primary formed equilibrium phase of periclase. If slowly cooled an additional amount may precipitate from the saturated liquid phase.

By optical point counting the content of primary formed periclase has been determined to 1.12%, while no indication of periclase precipitated during cooling has been observed. The periclase crystals have a grain-size > 20 μm and C_3S-MgO "growing together" phenomena, characteristic for primary crystals, were frequently seen.

The maximum acceptable amount of coarse periclase crystals may be a function of production-conditions and has not been stated in the present work, but may be determined by additional microscopic examinations in connection with autoclave test on cement samples.

Discussion of Sample No 2.

From the physical test results (cf. table I) it appears that the cement conforms to the specifications in all properties tested.

From the qualitative microscopic examination it was revealed that substantial amounts of C_2S-clusters were present in the fine fraction of the clinker-sample, the dusty part, which fraction amounts for more than 50% of the whole sample. This observation is consistent with the finding of 6.5% silica-grain coarser than 50 µm in the raw-mix.

A substantial part of the belite-crystals is of the "Belite" type, but the practical importance of this observation is not clear at the present moment. The OPC-determination of clinker-minerals (cf. table V) was in excellent agreement with the Bogue-calculated values.

The relative high content of coarse silica in the raw-mix, is seen to have great influence on the burnability (cf. fig. 6), making this raw-mix very difficult to burn.

This difficulty is intensified because of a relatively high LSF (92). The matrix between the C_2S-clusters in the dusty clinkers consists of C_3S only, and the crystals here show exagerated grain-growth due to intensive burning.

In order to reduce the problems with the coarse silica-grains it was suggested to lower the lime-saturation to about 90.

A consequence of this moderate change should be a matrix between the C_2S-clusters more easy to burn and less sensitive to LSF-fluctuations, and the resulting minor reduction in the C_3S-content seems to be acceptable, if coarsening of C_3S can be avoided at the same time and a more "safe" production could be secured.

However, because of the limited range for the LSF, caused by coarse silica, and because of the absence of the mineral C_3A

in sulphate resistant cement, early strengths , far beyond the specifications can not be expected in this difficult case. This property seems only possible to improve in this case by increasing the specific surface (Blaine) of the cement.

Discussion of Sample No 3.

From the physical test results (cf. table I) it is seen that the cement does not fulfil the specifications with respect to compressive strengths and with respect to the fineness of the cement.

It is likely that the low specific surface found may have influenced the compressive strength data in this test.

However, from the microscopic examination, observations have been made, which is consistent with the physical test results. Big clusters of free CaO in amounts of 2,7% are characteristic for the clinkers. These clusters are impossible to dissolve by continued burning because of their coarse nature, and a corresponding decrease of approximately 10% in the C_3S-content is the consequence.

The reason for this major problem in this particular production is the extremely coarse-grained slurry used (cf. fig. 4).

The detailed burnability test program conducted especially on this raw-mix has been discussed in a preceding section. As a conclusion it was therefore only recommended here, that the particle size distribution in the slurry was improved to a residue on mesh 170 sieve of e.g. 11-13%. This change will improve the burnability sufficiently to secure a completed clinker reaction for an increased clinker-production. An increased fineness of the slurry also allows for a minor adjustment of the LSF to e.g. 89 - 90% without any risk of exceeding amounts of free CaO in the clinker.

Discussion of Sample No 4.

From the physical test results (cf. table I) it is seen, that the cement conforms to the specifications in all properties tested with the exception of the 3-days compressive strength.

The relatively low C_3S-content of 48% from the Bogue calculation (cf. table V), in connection with the very low C_3A-content, seems to give an adequate explanation for this failing property. The minor disagreement between the mineral contents from OPC and Bogue-calculations in table V, is explained by fluctuations in the LSF.

By the qualitative microscopic examination the presence of coarse silica in the raw-mix was indicated by 100 - 300 µm C_2S-clusters in the medium and the very small clinkers (75% of the total clinker-sample). From the burnability data (cf. table VIII and fig. 6) this content of silica-grains is seen to be the limiting factor in the clinker reaction. This conclusion is supported by the finding of C_3S and liquid only in the clinker matrix between the C_2S-cluster, showing that eventual residues of free lime here are very difficult to react.

Exaggerated grain growth of the alite crystals observed in the medium sized clinkers (typical sizes 60 - 80 µm) seems to support the prediction, that intensive burning has been necessary to keep the free lime content very low.

Therefore in order to improve the 3-days compressive strength, an increase of the LSF to approximately 90 was recommended, but in order to compensate for the corresponding increase in the burnability index, a simultaneous lowering of the silica modulus to about 3.0 was suggested.

Discussion of Sample No 5.

From table I it is seen that the cement from Sample No 5 easily fulfils all requirements within the specifications.

The particle-size distribution in the raw-mix is suitable and the burnability (cf. table VIII and fig. 6) is seen to be excellent.

The microscopic examinations reveal an ideal clinker-structure in the small size clinkers. In the big and medium clinkers, clusters of C_2S (200 - 400 µm) were frequently observed, indicating a certain amount of coarse silica particles (100 - 200 µm) in the raw-mix (the amount was not estimated). This observation is far from reflecting any difficulties, but because the clinker-matrix between these C_2S-clusters was seen to consist of C_3S + liq. only, it can be stated that the content of coarse silica in the raw-mix is the limiting factor in the clinker burning reaction in this case. Therefore the lime saturation factor 92, used at the present, is believed to be close to the maximum (and optimal) value for this raw-mix, if the free CaO should be kept at the same low value.

The excellent agreement between the OPC-data and Bogue calculated clinker mineral contents (cf. table V), seems to indicate a production of high stability.

Discussion of Sample No 6.

From the physical test results (cf. table I) it appears that the cement fulfils all requirements within the specification.

The good agreement between OPC-results and Bogue-calculated mineral-contents seems to indicate a stable production.

In the microscopic investigation the presence of coarse silica in the raw-mix was indicated by 100 - 500 µm C_2S-clusters in the clinkers. The amount of this constituent was 3.2% (cf. table VII).

However, because of a correct choice of a relatively low lime saturation factor, the negative effect on the burnability from these coarse particles is reduced. This is also supported by the observation of a matrix between the C_2S-clusters containing C_2S as well as C_3S and liquid.

There should therefore be no reason for any changes in the conditions in this production.

Discussion of Sample No 7.

The cement is found to fulfil all requirements within the specification easily (cf. table II).

The calculated burnability index is seen to predict a very easy burnable raw-mix (cf. table VIII and fig. 6). This is mainly because of the good grinding condition for the raw-mix.

The microscopic examinations confirm this situation in revealing a clinker structure without any anomalities. A homogene phase distribution is observed in all clinker fractions and the high content of C_3S found by OPC explains the excellent early strength for this cement. The discrepancy between the OPC-data and the Bogue calculated mineral-contents is not clear at the present time. It might reflect fluctuations in the LSF, but no other observation supports this possibility.

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TABLE I. RESULTS; PHYSICAL TESTS ON CEMENTS.

	compressive strength (lb/in^2)			le chat.	Blaine
Cement sample No	3 days	7 days	28 days	exp.	(cm^2/g)
1	3470	4807	5900	-	3051
2	2600	3550	5163	1	2554
3	1019	2586	4550	2.5	1909
4	1850	3300	5900	1	2933
5	3513	5120	6150	0	3000
6	2588	3940	6500	1	2573
7	3015	4509	6850	0	3044
Specifications	2134	3271	-		2250

TABLE II. RESULTS; CHEMICAL ANALYSIS OF CEMENTS.

Cement-sample No	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	loss
1	20.45	5.80	2.70	62.45	4.39	1.14
2	21.17	3.52	5.57	62.81	3.78	0.75
3	22.22	4.70	2.70	62.40	3.5	1.20
4	23.70	3.02	3.02	64.05	0.88	1.10
5	21.46	3.66	5.24	64.27	1.86	0.90
6	22.47	4.69	2.67	62.33	3.44	0.98
7	21.22	5.96	3.00	62.26	3.05	1.07

x) SO_3-content in clinkers.

in.res.	Na_2O	K_2O	SO_3	SO_3 x)	free CaO	LSF	M_s
-	-	-	2.51	o.77	1.43	o.93	2.4
o.17	o.48	o.62	1.83	o.88	1.27	o.92	2.3
o.16	o.68	o.64	2.45	1.18	1.5o	o.87	3.o
o.37	o.32	o.26	3.73	o.31	o.64	o.86	3.9
-	o.86	-	1.8o	1.1o	o.86	o.92	2.4
-	o.73	-	2.39	1.1o	o.58	o.86	3.1
-	-	-	2.51	o.46	o.41	o.88	2.4

TABLE IV. RESULTS; QUALITATIVE MICROSCOPIC EXAMINATION.

Clinker-sample No	(1) Crystal size, alite	(2) Crystal size, belite	(3) Frequency of "belite"	(4) Streaks of belite	(5) Clusters of belite	(6) Crystal size interstitial phase
1	XX	XX	00	00	0	X
2	XX	XX	000	(0)00	(0)00	X
3	XX	XX	000	00	00	X
4	XXX	XXX	00	(0)00	(0)00	X
5	XX	XX	000	00	(0)00	X
6	XX	XX	000	000	000	XX
7	XX	XX	0	00	00	XX

X = small
XX = medium
XXX = large

(7) Sec. precipitation of belite	(8) Free CaO-clusters	(9) MgO, periclase	(1o) Sulphate-phase
000	00	000	00
0	00	000	00
00	000	00	00
0	00	0	0
0	00	0	000
0	00	0	00
(0)0	00	0	00

0 = none
00 = few
000 = many

TABLE V. PHASE DISTRIBUTIONS IN CEMENTS AND CLINKERS.

Clinker-sample No		C_3S	C_2S	C_3A
1	Bogue	50.8	22.9	10.1
	OPC	62.6±2.6	16.7±2.6	12.1±1.0
2	Bogue	55.3	21.9	0
	OPC	51.2±4.0	28.1±4.0	2.1±0.2
3	Bogue	44.3	39.9	8.3
	OPC	39.2±3.0	41.34±3.0	8.8±1.2
4	Bogue	48.3	41.3	2.1
	OPC	54.0±3.0	36.0±3.0	6.7±1.5
5	Bogue	59.3	19.0	0.0
	OPC	61.0±3.0	17.0±3.0	2.7±0.2
6	Bogue	42.5	32.9	7.2
	OPC	44.4±4.7	33.2±4.7	9.8±2.0
7	Bogue	41.3	33.0	10.2
	OPC	61.0±3.0	21.0±3.0	10.9±1.2

C_4AF	free CaO	MgO periclase	Sulphate phase
7.5 6.2±1.o	1.43 1.1±o.4	1.1±o.13	2.1±o.2
17.1 16.6±2.o	1.2 o.6±o.6	1.6±o.2	-
7.8 7.5±1.3	1.5 2.7±o.4	-	-
8.4 9.3±1.5	o.64 o.o±o.5	-	-
16.2 19.o±1.4	o.86 o.16±o.4	-	-
6.8 12.4±2.2	o.6 o.3±o.7	-	-
7.9 8.4±1.4	o.41 o.13±o.4		

TABLE VI. STATISTICAL ANALYSIS OF ERROR FROM OPC-METHOD.

	C_3S	C_2S	C_3A	C_4AF	CaO	MgO
$\overline{W} = \frac{\Sigma W}{N}$	8.ol	8.19	3.31	3.79	1.o4	o.41
$s_{sampling} = \frac{\overline{W}}{d_4} = \frac{\overline{W}}{2.o6}$	4	4	1.6	1.8	o.5	o.2
$s_{counting} = \frac{\delta}{2}$	o.9	o.8	o.7	o.7	o.3	o.1
$s_{OPC} = \sqrt{s^2_{count.} + s^2_{sampling}}$	4.1	4.1	1.7 x)	1.9	o.6	o.2

x) o.6 for sulphate resisten clinkers.

TABLE VII. SIEVE RESIDUES OF RAW MIXES, wt% OF DRY MATTER.

Sample No	Mesh No 16	18	26	72	172	270x)
1	0.50	0.07	0.27	4.04	6.16	1.38
2	0.28	0.14	0.38	5.7	13.1	6.5
3	1.4	0.16	1.1	9.7	11.9	1.98
4	0.09	0.16	0.25	6.5	12.8	2.0
5	0.02	0.01	0.02	3.77	9.31	-
6	0.05	0.09	0.09	2.04	7.70	3.2
7	0.03	0.03	0.1	1.86	9.39	-

x) Accumulated residue after HCL-treatment.

TABLE VIII. BURNABILITY INDEXES, CALCULATED.

Sample No	k-value	CaO^{30}_{1400} $-SiO_{2+44}$	CaO^{30}_{1500}	CaO^{60}_{1500}	CaO^{120}_{1500}	CaO^{240}_{1500}	ΔCaO (SiO_{2+44})
1	0.48	3.6	2.04	1.43	0.95	0.68	0.7
2	0.80	4.5	2.40	1.40	1.02	0.47	4
3	0.59	5.9	4.50	3.70	2.20	1.14	0.3
4	0.28	0	0	0	0	0	1.5
5	0.6	2.6	1.35	0.81	0.75	0.28	-
6	0.51	0.5	0.19	0.10	0.05	0.02	1.3
7	0.52	0	0	0	0	0	-

TABLE IX. FREE CaO-CONTENT IN BURNABILITY-TEST-CLINKERS.
(SAMPLE No 3)

	T = 1365°C t = 3o min		T = 14oo°C t = 3o min		T = 145o°C t = 3o min	
	Calc.	exp	Calc.	exp	Calc.	exp
Slurry as received 1)	6.1	5.7	6.2	5.6	4.9	4.9
Reground slurry 2)	1.7	1.6	1.6	1.3	1.1	1.2

1) 24% residue on 17o mesh sieve.

2) 1o% residue on 17o mesh sieve.

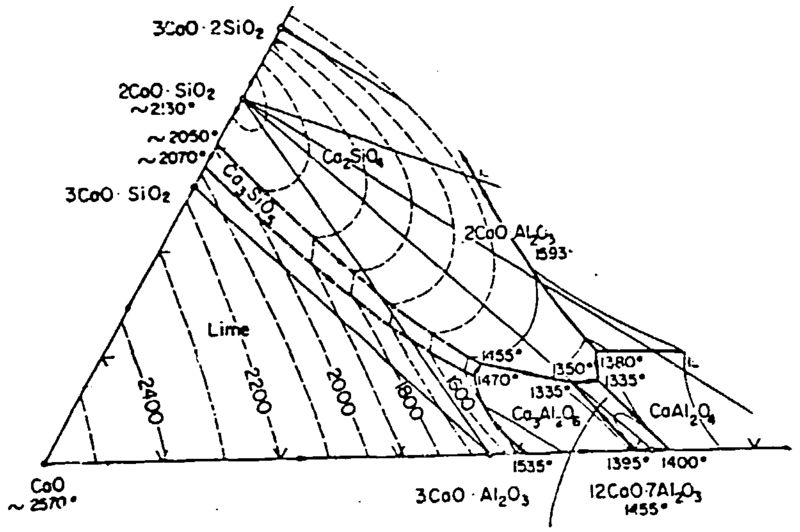


Fig. 1. Part of $CaO-Al_2O_3-SiO_2$ phase diagram.

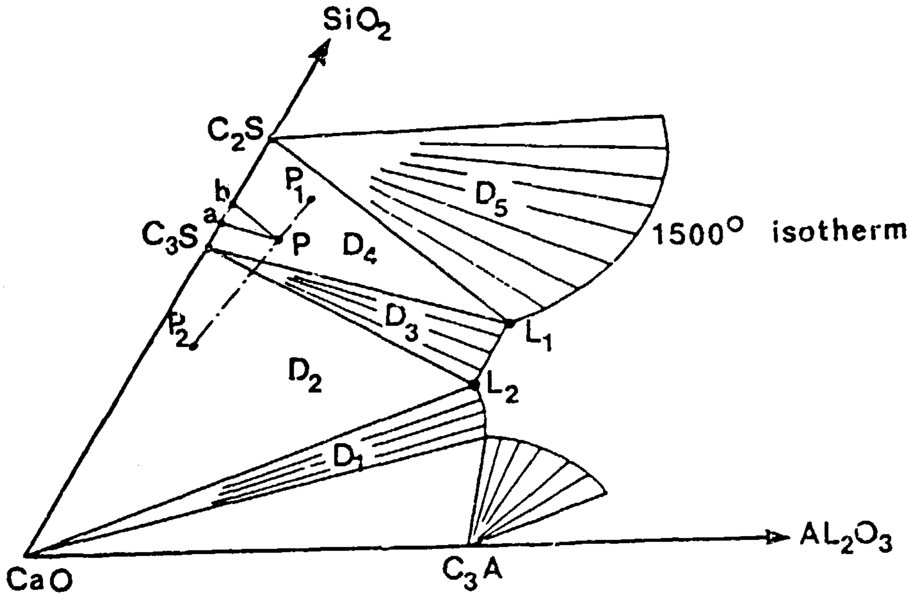


Fig. 2. 1500°- isotherm section of $CaO-AL_2O_3-SiO_2$- diagram

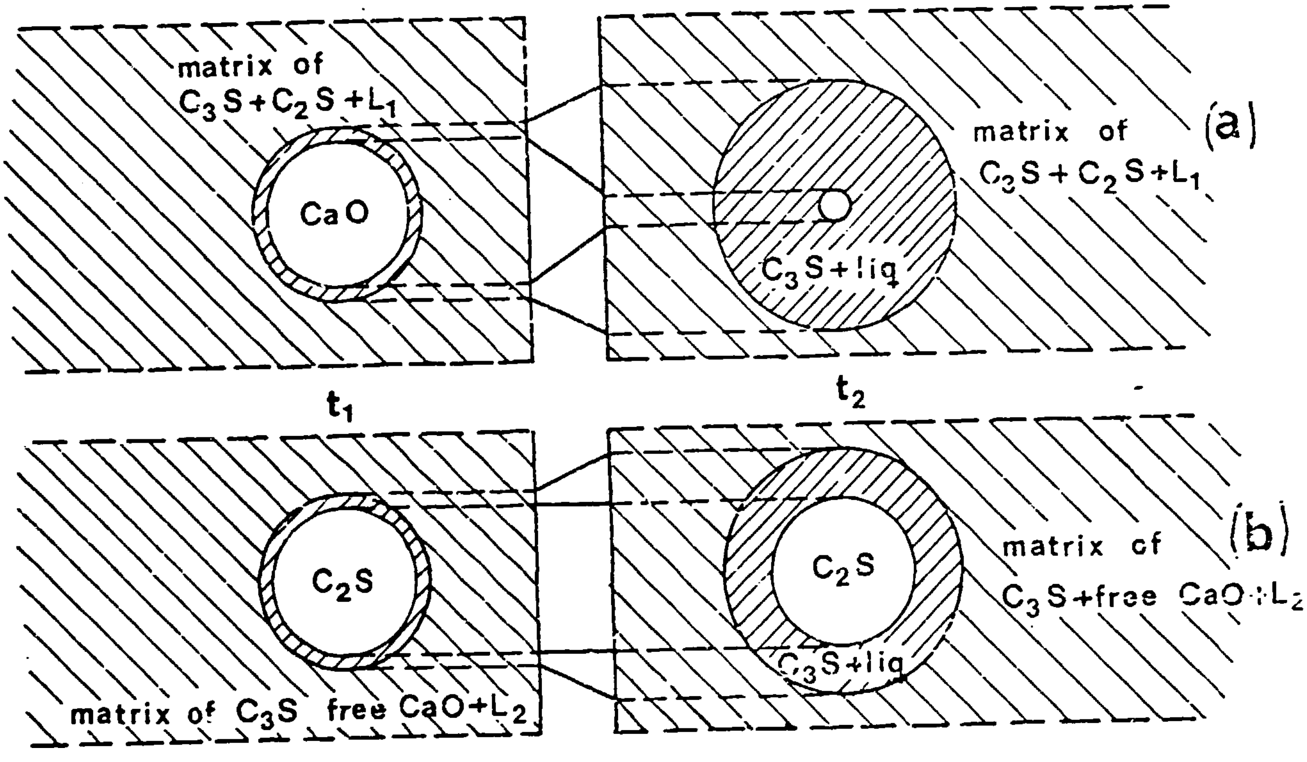


Fig. 3. Schematic representation of clinker-reaction for raw-mix containing: (a) coarse $CaCO_3$-particles (b) coarse SiO_2-particles.

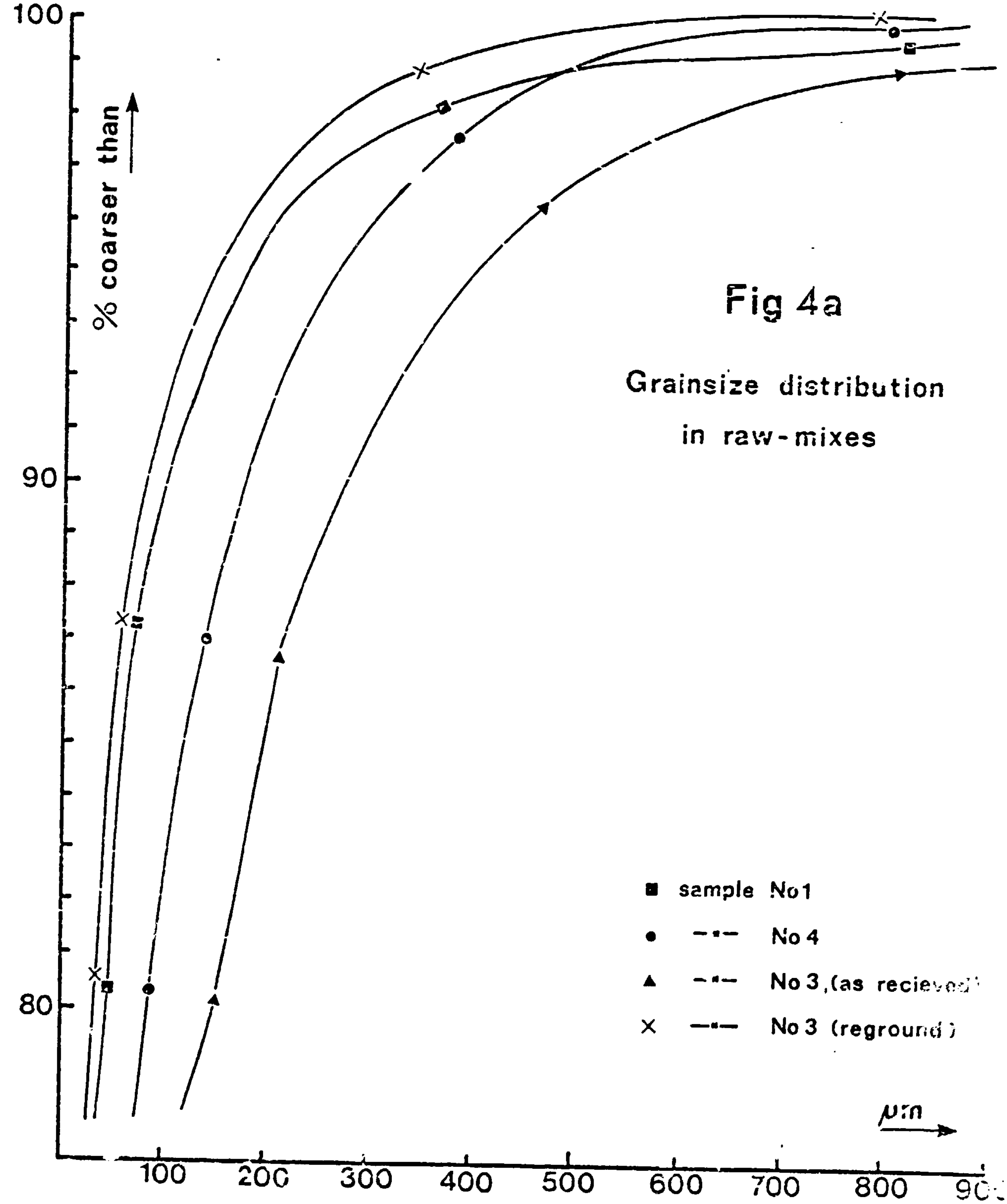


Fig 4a

Grainsize distribution in raw-mixes

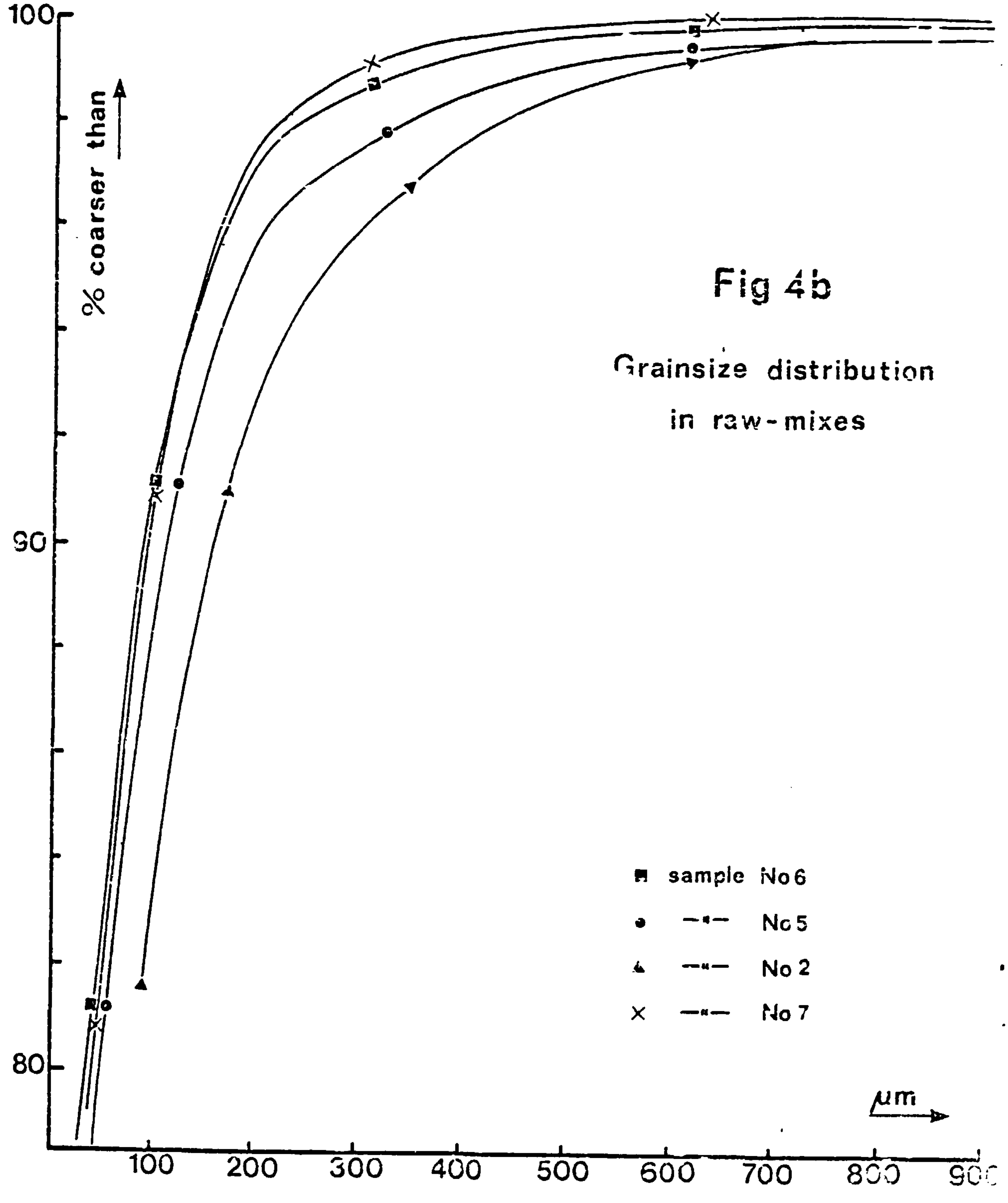


Fig 4b

Grainsize distribution in raw-mixes

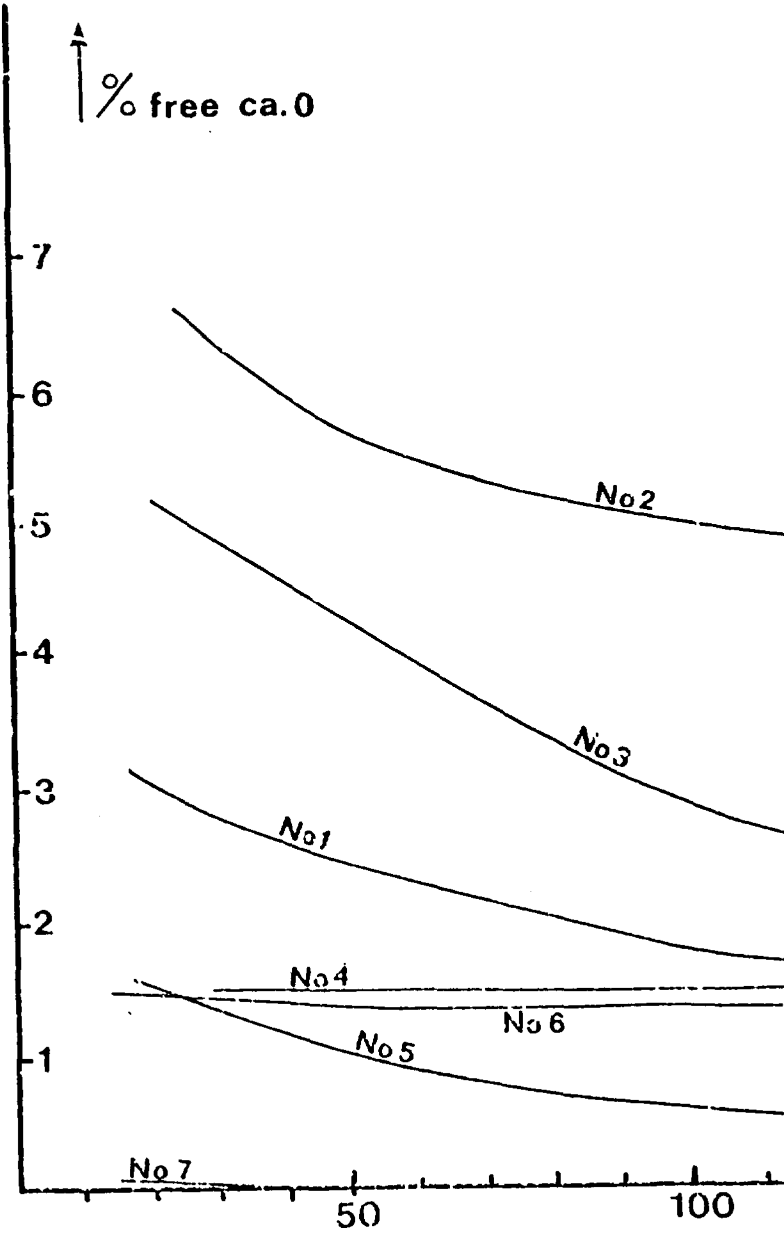
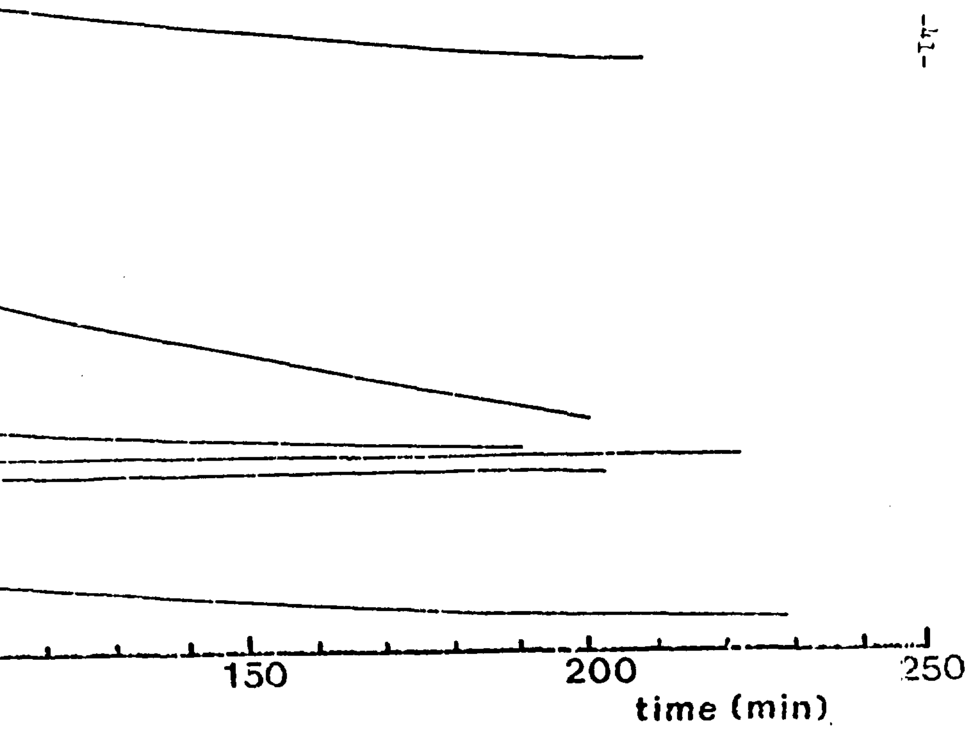

% free ca.0
7
6
5
4
3
2
1
No 2
No 3
No 1
No 4
No 6
No 5
No 7
50
100

Fig 6

Burnability - index (1500 °C) as a function of burning- time.



APPENDIX Ia. EXAMPLE OF BURNABILITY CALCULATION, SAMPLE No 2.

Grain size interval	R (wt% in interval)	$(1-x)^{30}_{1400} \times R$	$(1-x)^{30}_{1500} \times R$	$(1-x)^{60}_{1500} \times R$	$(1-x)^{120}_{1500} \times R$	$(1-x)^{240}_{1500} \times R$
40 - 60	0	0	0	0	0	0
60 - 80	3	0.3	0	0	0	0
80 - 120	10.1	4.55	0	0	0	0
120 - 160	3.7	2.15	1.37	0	0	0
160 - 200	2.3	1.63	1.27	0.67	0	0
200 - 240	0.9	0.72	0.58	0.29	0.14	0
240 - 300	2.1	1.76	1.51	1.22	0.74	0
300 - 400	1.6	1.42	1.25	1.12	0.88	0.42
400 - 600	1.6	1.46	1.36	1.28	1.23	0.85
600 - 800	0.3	0.28	0.27	0.25	0.24	0.21
Σ		14.27	7.62	4.83	3.23	1.48

APPENDIX Ib.

	t = 30 T = 1400	t = 30 T = 1500	t = 60 T = 1500	t = 120 T = 1500	t = 240 T = 1500
Σ_T^t	14.27	7.62	4.83	3.23	1.48
CaO_T^t	4.5	2.4	1.4	1.02	0.47

$CaCO_{3+125}$ = 12% (from graph)

LSF = 93

$LSF(M_S) = 95.12$

$$k = \frac{94.9 - 74.4}{100 - 74.4} = 0.8$$

$$CaO_{1400}^{30} = 0.33\,(LSF - LSF\,(M_s)) + 0.56 \times k \times CaCO_{3+125}$$

$$= 0.33\,(93 - 95) + 0.56 \times 0.8 \times 12$$

$$= 4.5$$

$$CaO_T^t = \frac{\Sigma_T^t}{\Sigma_{1400}^{30}} \times CaO_{1400}^{30}$$