

## Energy saving cement production by grain size optimisation of the raw meal

### *Produção de cimento com economia de energia por otimização da granulometria da matéria prima*



**B. SIMONS**<sup>a</sup>  
BrunoSimons@brunosimons.de

#### Abstract

The production of cement clinker is an energy consuming process. At about 50% of the energy is associated with grinding and milling of the raw meal, that normally is in the range 100% <200  $\mu\text{m}$  with 90% <90  $\mu\text{m}$ . Question: is it possible to use coarser components of the raw meal without reducing the clinker quality. With synthetic raw meals of various grain sizes the clinker formation was studied at static (1100 - 1450°C) and dynamic conditions (heating microscope). A routine to adjust the grain size of the components for industrial raw meals is developed. The fine fraction <90  $\mu\text{m}$  should mainly contain the siliceous and argileous components, whereas the calcitic component can be milled separately to a grain size between 200-500  $\mu\text{m}$ , resulting in lower energy consumption for milling. Considering the technical and economical realizability the relation fine/coarse should be roughly 1:1. The energy for milling can be reduced significantly, that in addition leads to the preservation of natural energy resources.

**Keywords:** *Cement production, energy saving, electron microprobe, heating microscopy*

#### Resumo

A produção de clínquer é um processo que envolve alto consumo de energia. Cerca de 50% da energia é associada com trituração e moagem da matéria prima, que normalmente está no intervalo 100% < 200  $\mu\text{m}$  com 90% < 90  $\mu\text{m}$ . Pergunta: é possível usar componentes maiores da matéria prima sem reduzir a qualidade do clínquer? Com matérias primas sintéticas de granulometria variada a formação do clínquer foi estudada em condições estática (1100 – 1450°C) e dinâmica (microscópio de aquecimento). Uma rotina para ajustar a granulometria dos componentes para materias primas industriais foi desenvolvida. A fração fina < 90  $\mu\text{m}$  deve conter principalmente componentes silicáceos e argilosos, enquanto o componente calcítico pode ser moído separadamente para uma granulometria entre 200-500  $\mu\text{m}$ , resultando um menor consumo de energia para a moagem. Considerando a viabilidade técnica e econômica a relação finos/graúdos deve ser aproximadamente 1:1. A energia para moagem pode ser reduzida significativamente, o que adicionalmente conduz à preservação de recursos energéticos naturais.

**Palavras-chave:** *Produção de cimento, economia de energia, microsonda eletrônica, microscopia de aquecimento.*

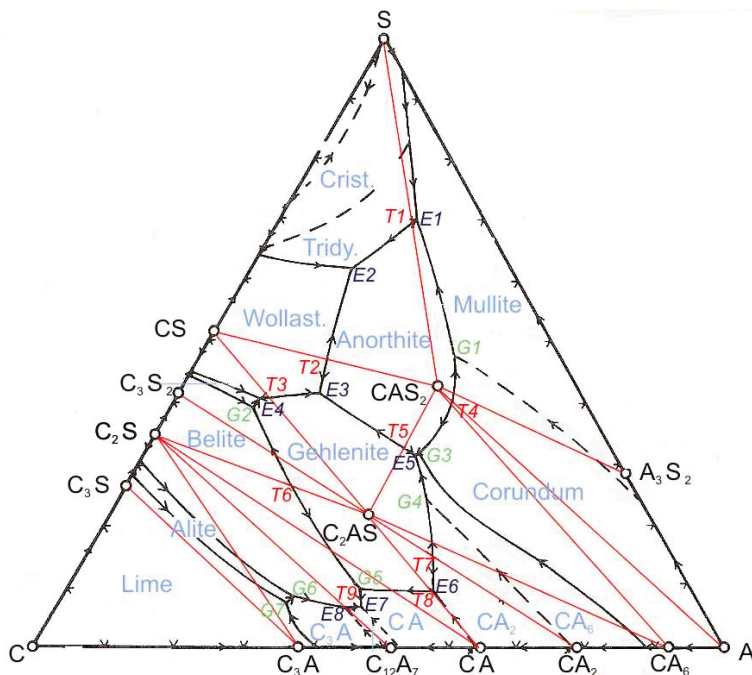
<sup>a</sup> *Institut für Geologie und Mineralogie, Abteilung für Angewandte Mineralogie, Universität zu Köln, BrunoSimons@brunosimons.de, Zùlpicher Strasse 49b, 50674 Köln, Deutschland*

### 1. Introduction

Compared to other industries cement production is an energy intensive process. Besides big energy reductions in the last years due to improvements in the preparation of raw materials, kiln development and heat recovery, a further reduction of energy by an extreme coarsening of the raw meal (up to 2000 µm grain size) is discussed. In the proposed process the energy consumption and operational costs shall be reduced by lowering the energy for milling, prolongation of the life time for the mills, lowering the sintering temperatures and shortening the reaction times in the rotary kiln,

resulting in at least 30% energy reductions. It was supposed in a patent (Lörke, 2001 [1]), that the raw meal should be milled separated in a fine fraction of grain size < 80 µm (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> rich) and a coarse fraction up to 2 mm (CaO rich) in a relation 1,5 : 1 up to 1 : 9. Thus at the sintering process the composition of the fine fraction is only sufficient to form CS and/or C<sub>3</sub>S<sub>2</sub> as well as C<sub>2</sub>AS, C<sub>3</sub>A, C<sub>12</sub>A<sub>7</sub> and C<sub>4</sub>FA. With respect to the system CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (CAS) (figure. 1) a first eutectic with CS (Wollastonite), C<sub>3</sub>S<sub>2</sub> (Rankinite) and C<sub>2</sub>AS (Gehlenite) at 1265°C will be established. A further eutectic would be C<sub>2</sub>AS (Gehlenite), C<sub>3</sub>A and C<sub>12</sub>A<sub>7</sub>. However, the later one is stably

**Figure 1 - The system CaO - Al<sub>2</sub>O<sub>3</sub> - SiO<sub>2</sub>, (modified after Rankin and Wright, 1915 (2)) in weight percent. Alkemadelines, red, connecting the subsolidus phases, and the resulting Alkemade triangles point to the according eutectics resp. peritectics listed above.**



Thermal divide		Distributary point		Eutectic	
T1: Tri/Ano	1368°C	G1: Cor/Mul/Ano	1512°C	E1: Tri/Ano/Mul	1345°C
T2: Wol/Ano	1307°C	G2: Ran/Geh/C <sub>2</sub> S	1315°C	E2: Tri/Ano/Wol	1170°C
T3: Wol/Geh	1318°C	G3: Ano/Cor/CA <sub>6</sub>	1405°C	E3: Geh/Ano/Wol	1265°C
T4: Ano/Cor	1547°C	G4: Geh/CA <sub>2</sub> /CA <sub>6</sub>	1475°C	E4: Wol/Ran/Geh	1310°C
T5: Ano/Geh	1385°C	G5: C <sub>2</sub> S/Geh/CA	1380°C	E5: Ano/Geh/CA <sub>6</sub>	1380°C
T6: Geh/C <sub>2</sub> S	1545°C	G6: C <sub>3</sub> S/C <sub>2</sub> S/C <sub>3</sub> A	1455°C	E6: Geh/CA/CA <sub>2</sub>	1500°C
T7: Geh/CA <sub>2</sub>	1552°C	G7: CaO/C <sub>3</sub> S/C <sub>3</sub> A	1470°C	E7: C <sub>2</sub> S/C <sub>12</sub> A <sub>7</sub> /CA	1335°C
T8: Geh/CA	1512°C			E8: C <sub>12</sub> A <sub>7</sub> /C <sub>3</sub> A/C <sub>2</sub> S	1335°C
T9: C <sub>2</sub> S/C <sub>12</sub> A <sub>7</sub>	1365°C				

**Abbreviations:** Crist. = Cristobalite; Tridy. = Tridymite; Wollast. = Wollastonite; C<sub>3</sub>S<sub>2</sub> = Rankinite

Table 1 – Composition and fine/coarse ratio

Synthetic mixture with CAS 65/10/25			
Component	Source	Weight %	µm
CaO	Calcite (Merck, 102066) Warsteiner Kalk	74,58	< 14 200 - 500
Al <sub>2</sub> O <sub>3</sub>	Kaolinite (Amberger Kaolinwerke, TEC FF840)	18,37	< 0,9
SiO <sub>2</sub>	Quartzpowder (Quarzwerte Frechen, Sikron SF600)	7,02	< 3
Sample	ratio fine/coarse		
fine	1 : 0	Calcite + Warsteiner Kalk	
coarse	1 : 1	only Warsteiner Kalk as	
“super coarse”	1 : 2,94	CaO component	

non existent, since the kinetic favoured formation of C<sub>2</sub>S (Belite) establishes the peritectics C<sub>3</sub>S<sub>2</sub>/C<sub>2</sub>AS/C<sub>2</sub>S (1315°C) and C<sub>2</sub>S/C<sub>2</sub>AS/CA (1380°C), as well as the eutectics C<sub>2</sub>S/C<sub>12</sub>A<sub>7</sub>/CA (1335°C) and C<sub>2</sub>S/C<sub>12</sub>A<sub>7</sub>/C<sub>3</sub>A (1335°C).

Right here it should be emphasised, that in a conventional rotary kiln process the first melt formation at about 1280°C (Taylor: „Cement Chemistry“, 1997 [3]) occurs, thus in the range of the eutectic CS/C<sub>3</sub>S<sub>2</sub>/C<sub>2</sub>AS.

This paper describes experimental results on synthetic and industrial raw meals, where the attempt was made to coarsen one or more components of the raw meal and achieve a lower eutectic.

The basics of the experimental results and the thermodynamically background of the observed equilibria and the technical realization is described.

## 2. Materials and experimental program

The respective portions were weight for a total of 100g and the samples were then homogenized for 2 hours. Aliquots of 5 g were then pressed to tablets 2 cm in diameter. Two of each mixture were heated up in a high temperature furnace with a rate of 15°C/min and held for 30 minutes at 1150, 1250, 1300, 1350 and 1450°C. The samples were quenched in a stream of compressed air. Sample preparation and experimental procedure for the Heating micro-scope is described in section 4.

### 2.1 Sample analysis

The samples were microscopically inspected in reflected light (etched samples), by x-ray diffraction (XRD) and by electron probe micro analysis (EPMA). Free lime was analysed wet-chemically.

## 3. Results

### 3.1 Calculation of Phase content from free lime content

From the analysed free lime content and the initial composition

of the sample the composition of the “remaining sample” can be calculated and the resulting Alkemade-triangle determined, thus the eutectic/peritectic at a sufficient temperature can be precast (figure 2).

### 3.2 Reaction paths of the analysed samples

#### 3.2.1 Sample “fine”

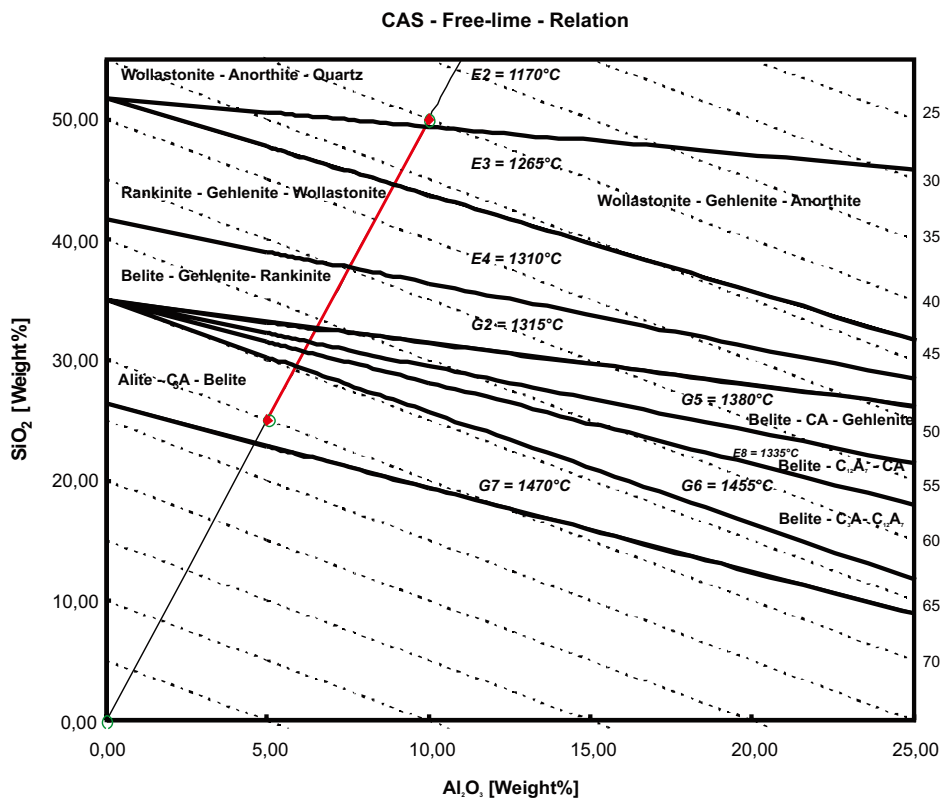
The sample “fine” develops in the temperature range 1150 - 1450°C in accordance to the phase relations in the CAS system. The free-lime calculation as shown in figure 2 leads at 1150°C to a composition CAS 58,09/11,97/29,94 and thus in the Alkemade-triangle Belite - CA - Gehlenite. With increasing temperature and consumption of CaO the Alkemade-triangles Belite - C<sub>12</sub>A<sub>7</sub> - CA; Belite - C<sub>3</sub>A - C<sub>12</sub>A<sub>7</sub> are passed and finally the clinker-assemblage Alite - Belite - C<sub>3</sub>A is established resulting in a homogeneous clinker.

#### 3.2.2 Sample “coarse”

The sample “coarse” composition at 1150°C is CAS 50,7/14,08/35,21 (after free-lime reduction) and thus in the triangle Rankinite – Gehlenite – Wollastonite. However, at 1150°C beside Gehlenite Belite is observed by XRD as a result due to its kinetically favoured formation at low temperatures (Lindner, 1955 [4]). At 1250°C Rankinite and Wollastonite in addition are observed, in especial by EPMA.

Finally at 1300°C a CAS 54,09/13,12/32,80 is calculated and due to its phase relation Belite - Gehlenite - Rankinite a melt is observed (nominally at 1310°C in the eutectic E4, see figure 1). With increasing temperature the melt composition develops to the tributary point G2 (1315°C), then follows the cotectical line Belite - Rankinite and then passes the liquidus of Belite to the cotectical line Belite – Gehlenite. The thermal divide T6 (1545°C) must be “tunnelled” by partial recrystallisation of the melt before it reaches the cotectical line Belite – Gehlenite again, passing the Belite liquidus at the 1450°C to the cotectical line Belite – C<sub>3</sub>A. Further incorporation of CaO finally leads to the formation of Alite.

**Figure 2 – CAS-Free-lime relation, modified system CAS. After subtraction of the analysed free-lime content from the initial composition (lower red dot) the remaining CaO reduced composition (upper red dot) results.**



The red line is the CaO-reaction line. CaO-isopleths are given by dotted lines.

Solid lines are Alkemade-lines. The resulting subsolidus paragenesis and melting temperatures are given.

(The calculation is available as an Excel-worksheet and can be requested from the author).

**Figure 3 – Sample “coarse” 1300°C. Semi quantitative EPMA. Note the strong maxima for Belite and melt. Gehlenite is weakly developed. At the CaO apex is free lime. Also note the trends following the Alkemade lines to C<sub>3</sub>A and C<sub>12</sub>A<sub>7</sub>.**

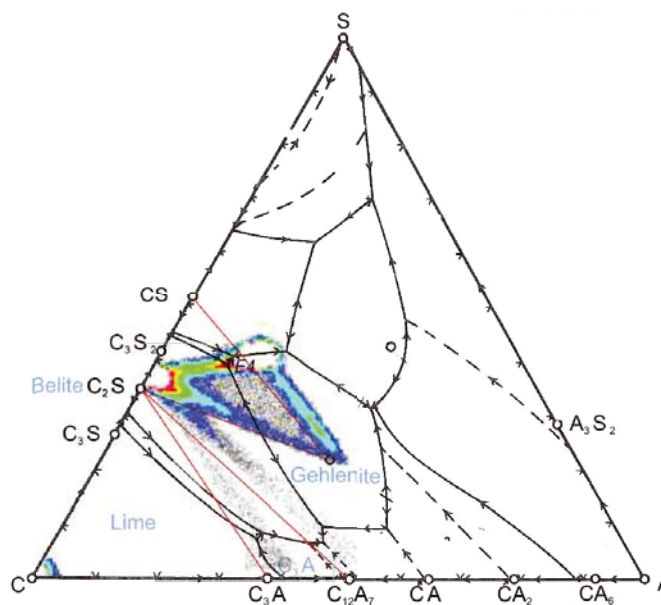
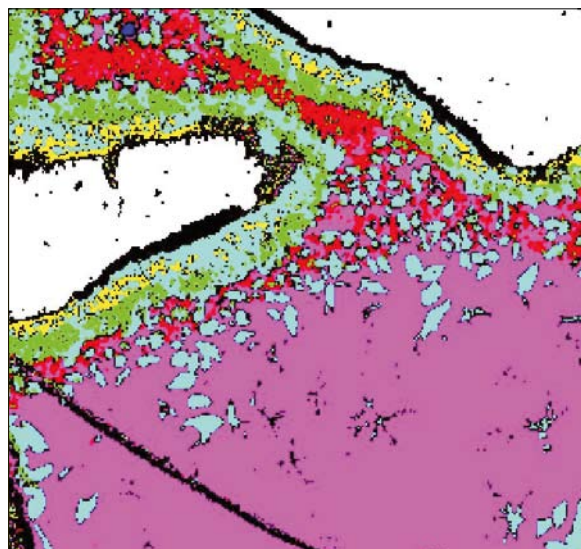
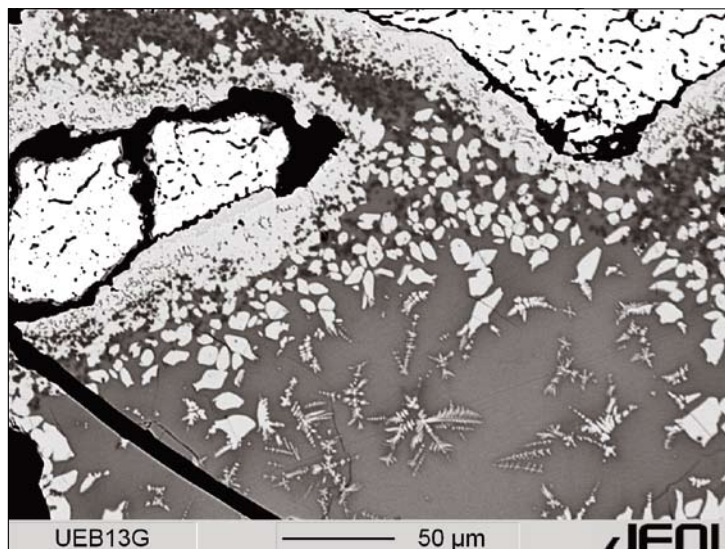


Figure 4 - a), b) (below) | Sample "coarse" 1300°C



a) Elementmapping: White: free lime; Magenta: melt; light blue: Belite; red: Gehlenite; yellow and green: nonstoichiometric Belites.



b) Backscattering image: note the typical Belite exsolutions (quench crystals) in the melt.

### 3.2.3 Sample "super coarse"

The sample "super coarse" composition at 1150°C is with CAS 17,86/23,47/58,67 in the triangle Wollastonite – Anorthite – SiO<sub>2</sub>. By EPMA only a limited reaction of the sample and no partial melting is observed.

At 1250°C by EPMA beside Wollastonite and Gehlenite a melt is detected. The composition of the melt is within the thermal divide T3. In addition Belite is observed, which by reaction of free CaO with Wollastonite due to kinetic reason develops. Due to this kinetically favourable reaction to Belite, Rankinite is not

Figure 5 - sample "super coarse" - 1250°C. Ternary plot of semi quantitative EPMA super-positioned on the CAS system. Note the maxima for Belite, Gehlenite and Wollastonite. On the thermal divide T3 the maximum for the melt composition is shown. The maximum in the CaO apex is free lime.

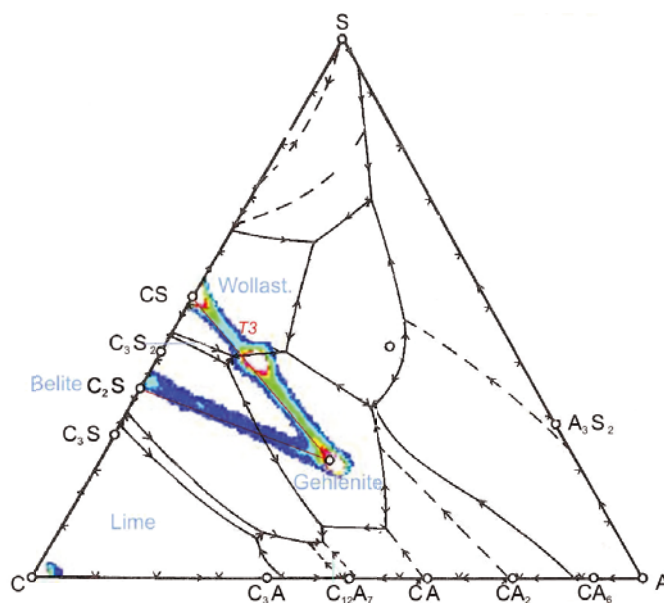


Figure 6 - sample "super coarse" - 1250°C. Elementmapping: light-blue: Belite; yellow: Wollastonite; magenta: Gehlenite; green: trend to Aluminat; pink: free lime; red: melt.

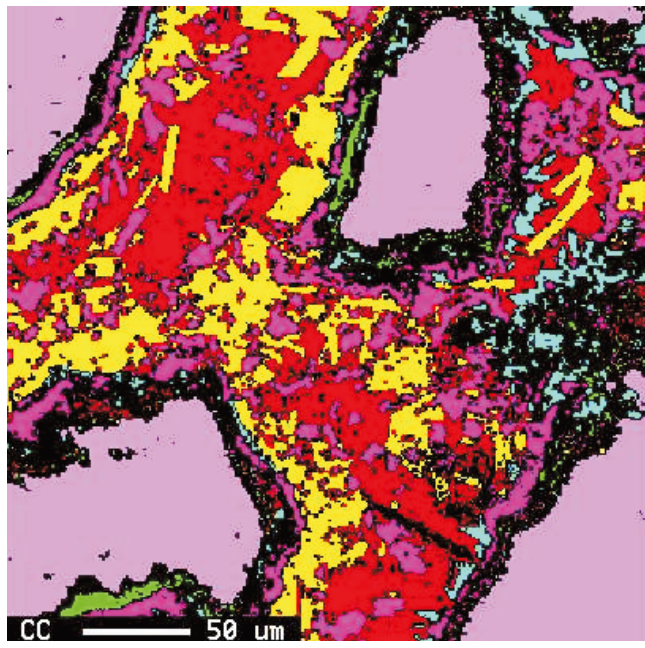


Figure 8 - Sample "fine" - 1150°C, EPMA Elementmapping. A coarse Metakaolinite (green) is surrounded by a rim of Anorthite (yellow).

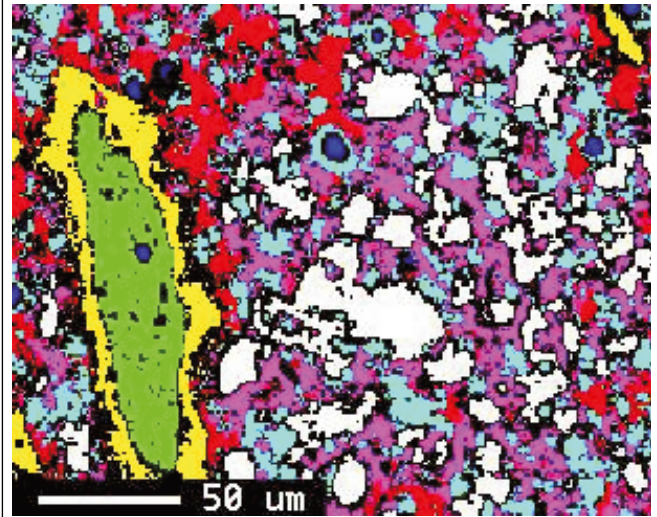


Figure 9 - Sample "fine" - 1250°C. Now a metakaolinite (green) is surrounded by Gehlenite (red).

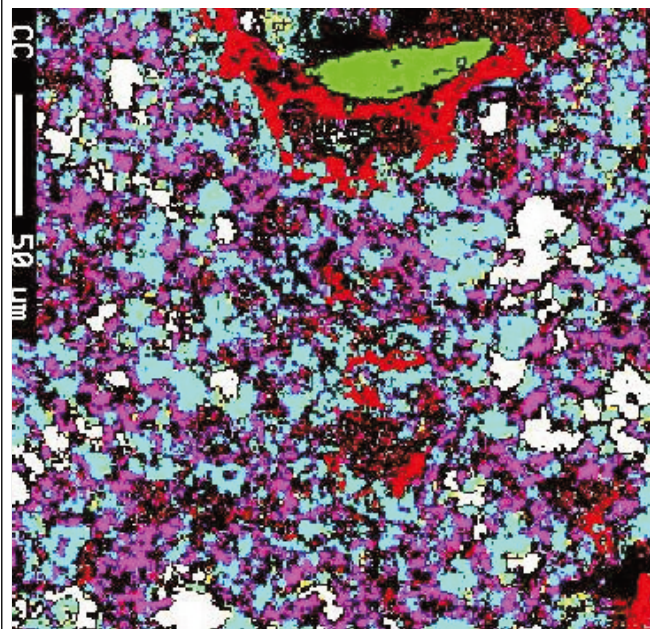
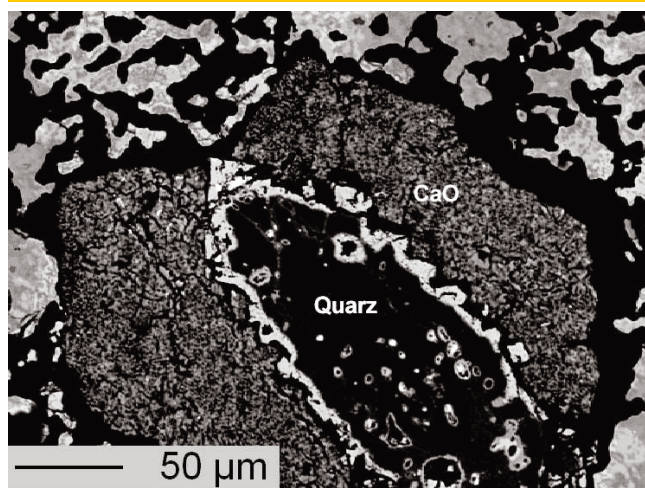


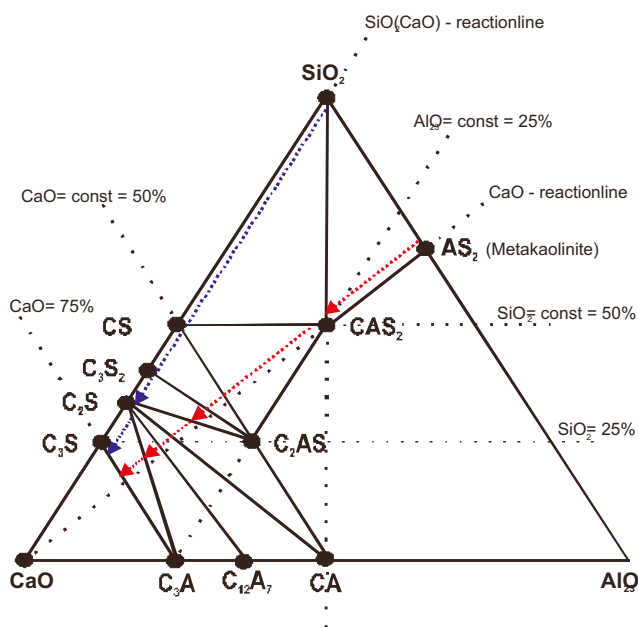
Figure 7 - sample "fine" - 1250°C, EPMA Backscattering image. In a decarbonised Calcite a Quartz-crystal with well developed pyramidal ends is embedded. The reaction-rim (about 1,5 - 2 μm) is analysed to be Belite. In addition Gehlenite, Wollastonite and Rankinite is observed.



observed. The composition of the melt seems to remain at the thermal divide.

Theoretically the melt should consume CaO with increasing temperature and develop to the eutectic E4 at 1310°C. In fact, at 1300°C a CAS 53,80/13,20/33,00 indicates the distribution point

**Figure 10 - Reaction path in the CAS system (mole %). Solid lines are Alkemade-lines. Black wide dotted lines as indicated. The narrow dotted blue line indicates the reaction of SiO<sub>2</sub> with CaO; the red dotted line indicates the reaction of Metakaolinite with CaO.**



G2 with coexisting Belite - Gehlenite - Rankinite. Further increase in temperature up to 1450°C, consumption of free CaO, leads to the cotectic line Belite - Gehlenite and develops as described above for the sample "coarse".

At 1450°C the Clinker-assemblage is observed.

By reflected light microscopy as by EPMA as well typically rounded Belites in the range of 20 - 50µm and prismatic Alites up to 60 µm are observed. The axial ratio is 2:1 for the Alites. A free lime content of 1,45 is within an acceptable range for industrial clinkers. The texture is homogenous with low porosity.

It thus seems possible with the above experimental approach to achieve a "lower melting" eutectic (E3: 1265°C) despite intense coarsening of the calcitic component of the raw meal; however, resulting in a technical acceptable clinker.

But it has to be mentioned, that the fine fraction of the above raw meals was < 10µm in the average, thus by one decade lower as for industrial raw meals.

### 3.3 Reaction paths in the System CaO – Al<sub>2</sub>O<sub>3</sub> – SiO<sub>2</sub>

The analysed synthetic samples, especially those in the subsolidus region demonstrate that two different primary reactions occur. At one hand the reaction of Quartz with CaO (figure 7), which leads to the kinetically favoured formation of Belite (see 3.4); at the other hand the reaction of Metakaolinite with CaO (figure 8 and 9), leading over the formation of an anorthitic component to the Alkemade relations shown in figure 10.

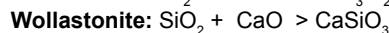
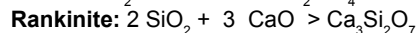
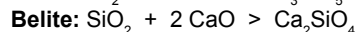
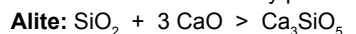
Assuming a heterogeneous sample, where after decarbonatisation of the calcitic component and dehydration resp. dehydrolisation of the argileous components to in exemplo Metakaolinite, the free SiO<sub>2</sub> reacts

with CaO to Belite (kinetically favoured) and Metakaolinite reacts with CaO to an anorthitic phase and consequently to Gehlenite and Belite, a first melt will establish in one of the Alkemade-triangles Belite - Gehlenite - (Wollastonite/Rankinite). A paragenesis Wollastonite - Anorthite - SiO<sub>2</sub> at nominally E2 = 1170°C will never be achieved. However, when reactions of SiO<sub>2</sub> with CaO at higher temperatures lead to the formation of Wollastonite and/or Rankinite occur, local heterogeneities may lead to a partial melting with the anorthitic component to E3.

### 3.4 The Belite „problem“

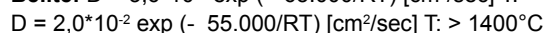
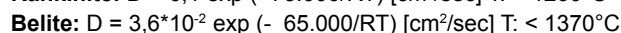
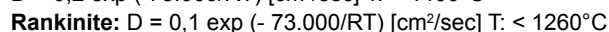
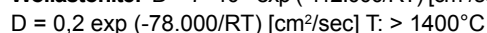
At the binary join CaO - SiO<sub>2</sub> the phases Lime, CaO; Alite, Ca<sub>3</sub>SiO<sub>5</sub>; Belite, Ca<sub>2</sub>SiO<sub>4</sub>; Rankinite, Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub>; Wollastonite, CaSiO<sub>3</sub>; and Quartz, SiO<sub>2</sub> occur.

The reactions of the binary phases from the oxides are given with:



Considering the available Cp data, the free energies of reaction demonstrate that Belite has the lowest values over the whole temperature range.

The self diffusion constants for Calcium were given by Lindner (1955 [4]):



and are sketched in figure 11.

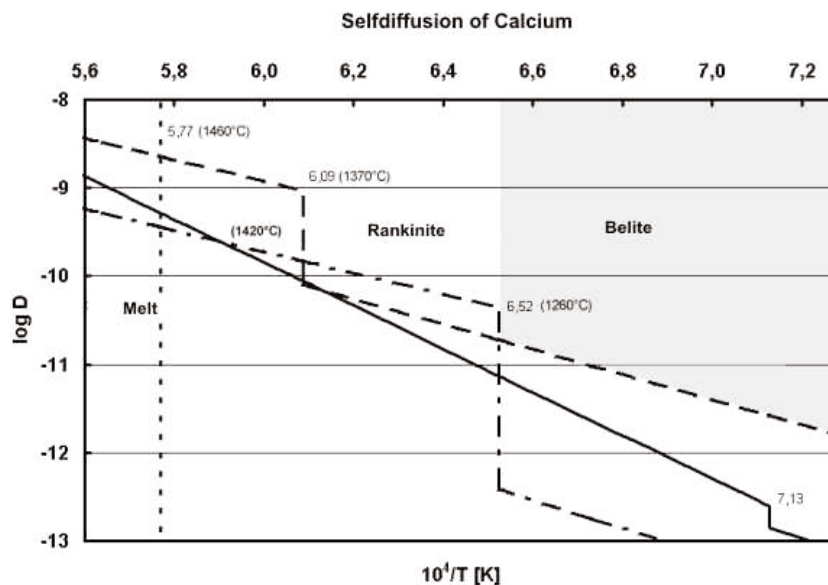
**Table 2 – Standard state values**

		H°298,1 (kJ/mole)	S°298,1 (J/mole*K)	reference
Quartz	SiO <sub>2</sub>	-910,70	41,46	Saxena et al. (4)
Lime	CaO	-634,26	38,10	Saxena et al. (4)
Wollastonite	CaSiO <sub>3</sub>	-1.632,00	82,03	Saxena et al. (4)
Rankinite	Ca <sub>3</sub> Si <sub>2</sub> O <sub>7</sub>	-3.842,60	210,90	Kubachewski et al (5)
Belite	Ca <sub>2</sub> SiO <sub>4</sub>	-2.305,98	127,61	Robie et al (6)
Alite	Ca <sub>3</sub> SiO <sub>7</sub>	-2.928,80	168,60	Kubachewski et al (5)

**Table 3 – Free Enthalpy of formation**

	$\Delta G^{\circ}_{298,1}$ (kJ/mole)	$\Delta G^{\circ}_{1000,1}$ (kJ/mole)	$\Delta G^{\circ}_{1750,1}$ (kJ/mole)
Wollastonite	-87,78	-89,51	-91,36
Rankinite	-122,50	-132,10	-142,36
Belite	-129,73	-136,71	-144,17
Alite	-119,15	-128,16	-137,79

**Figure 11 – Diffusion-constants for Belite (line - dot), Rankinite (dotted line) und Wollastonite (solid line). In addition a dotted line is shown representing the eutectic temperature with 1460°C for Rankinite and Wollastonite.**





**Figure 12. The heating microscope. On an optical bench the following major components are mounted (from left to right): Light source, vertical tubular furnace (max. 1650°C), video camera. At the lower left the programming and control unit is shown. The picture analysing system is not shown.**



According to Lindner (1955 [4]) the early occurrence of Belite is thus explained.

In the present study a sample of fine grain size, being with its overall chemistry within the ternary Alkemade triangle Rankinite - Gehlenite - Wollastonite, at 1150°C only Belite and Gehlenite could be detected; at an according coarse grained sample beside Belite, Rankinite and Wollastonite were observed. In fine as well coarse samples, having the overall composition in the ternary Alkemade

triangle Wollastonite - Anorthite -  $\text{SiO}_2$ , the respective subsolidus phase assemblage was achieved.

It thus has to be pointed out, given a composition above the Alkemade-line Wollastonite - Anorthite ( $\text{SiO}_2$ -rich), Wollastonite is formed. Consequently at CaO - contents below the Alkemade-line Wollastonite-Anorthite the formation of Wollastonite follows over the primary formation of Belite and then Rankinite. This is demonstrated in figure 7, where a  $\text{SiO}_2$  grain imbedded in the groundmass is surrounded by a Belite rim.

## 4. Heating Microscope

### 4.1 Sample preparation and experimental procedure

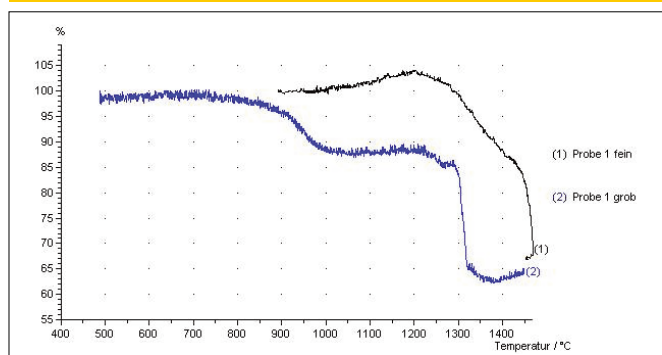
Synthetic samples fine and coarse as described in section 2 as well as various industrial raw meals were pressed to cubes with 3 mm length and placed on an  $\text{Al}_2\text{O}_3$  sample holder. The sample holder was sled into a tubular furnace preheated to 500°C. The temperature was registered with an EL18 thermocouple placed right under the sample. The temperature was then linearly raised with 10°C/min up to 1450 ~ 1500°C. The sample was illuminated inline of an optical bench, and its shadow was registered by a video device. Thus with a picture analysing system the surface resp. volume decrease was monitored. Thermal events as sintering, softening and others can be monitored.

### 4.2 Results

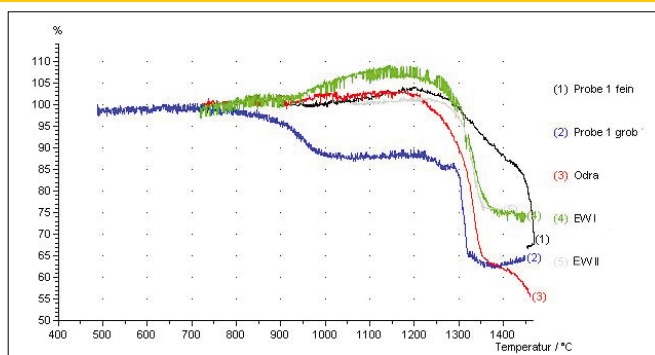
Sample „fine“ (1) only shows a decrease in volume at about 1200°C and then a drastic decrease at 1463°C - melting. However the coarse sample decreases in volume at about 800 - 900°C (decarbonatization, sintering), then shows a slight decrease at about 1230 - 1260°C (eutectic E3: 1265°C) and a softening temperature of 1310°C (partial melting in the eutectic E4). This is in total agreement with the static experiments.

All industrial raw meals show similar behaviour to the synthetic sample „coarse“ (figure 13a) with softening temperatures in the range 1320 - 1330°C, clearly indicating partial melting.

**Figure 13 - a), b) - Heating curves for synthetic and industrial raw meals. Heating rate: 10°C/min in air. The volume decrease is shown on the ordinate.**



**a) Curve (1, black) sample “fine”, (2, blue) “coarse”**



**b) Curves (1, 2) as in figure 12a  
Curves (3, 4, 5) industrial raw meals**

## 5. Conclusions

Concerning the question, is it possible by coarsening the raw meal for cement production (going along with reduced energy consumption of the milling process) to achieve a controlled phase formation and eventually partial melting of a silica rich melt resulting in a "lower melting" eutectic, synthetic raw meals composed from Calcite p.a. resp. Warsteiner Kalk (pure limestone, Germany), quartz powder and pure Kaolinite were calcined. While in a first experimental run the components were in an average grain size of <14  $\mu\text{m}$ , in a second run the Calcite (Warsteiner Kalk) was chosen in the range 200 - 500  $\mu\text{m}$ . As expected the "fine" raw meal followed the phase-theoretical path and finally led to a clinker with the according phase assemblage Alite, Belite and Aluminate. Using a coarse calcitic component, however, led to a displacement of the remaining composition (CaO partially unavailable to the reaction) to higher  $\text{SiO}_2$  resp.  $\text{Al}_2\text{O}_3$  contents. In fact it was possible to shift the remaining composition as such, that for a coarse mixture with a relation fine/coarse of 1:1 (with fine <14 $\mu\text{m}$ , and coarse 200-500  $\mu\text{m}$ , Warsteiner Kalk) a low melting peritectic with 1315°C was approached. Macroscopically the sample was already recognised to be partially molten. Increasing the temperature to 1450°C results in the desired clinker assemblage with a homogenous texture. For a so called "super coarse" mixture, where the total calcitic component was added as Warsteiner Kalk with a grain size 200 - 500  $\mu\text{m}$ , the eutectic Wollastonite - Gehlenite - Anorthite with 1265°C was established. Thus it seems, that by coarsening the calcitic component of the raw meal a lower eutectic might be achieved.

Heating microscopy of the very same synthetic raw meals confirmed these observations. For a fine synthetic sample sintering was observed at 1223°C and weakening of the sample (partial melting) was observed at about 1463°C, whereas the onset of softening for a coarse grained synthetic sample was at 1310°C.

The onset of weakening for a coarse grained sample was at 1287°C.

Various industrial raw meals were subjected to heating microscopy (static experiments have been performed as well, not described in the present paper), demonstrating similar features to the coarse resp. super coarse synthetic sample of this study: the softening temperatures are in the range 1310 - 1330°C). Modifying one of the industrial raw meals with respect to the grain size of the calcitic component finally led to a softening onset at 1279°C.

It can thus be stated, that a coarsening of the calcitic component of a raw meal for cement production is advisable and may lead to a significant cost reduction.

Anyhow, this is strongly dependant on the available resources. For each location an optimisation routine has to be performed. Some of the given calculations within this project are suitable to give a quick access to the parameters.

For a given raw meal a quick test run can be performed showing the onset of weakening. A static clinker calcination and routine reflected light observation reveals the texture of the clinker. Stepwise the optimum of coarsening is detected.

It is proposed to separately grind resp. mill two significantly different grain fractions. A "fine" fraction <90 $\mu\text{m}$  should in principal contain the siliceous and argillaceous components, whereas the calcitic component may be according to the observations of this study in the range 200 - 500 $\mu\text{m}$ . Considering the technical and economical

realizability a ratio 4:1 lime-marl/limestone is proposed. However, increasing the pure limestone content eventually leads to a "lower melting" eutectic. The lime-marl and of course the limestone itself will be fractured during the rotary kiln process due to the decarbonisation of the calcitic component and thus increase the "fine" fraction. Coarsening the calcite bearing fraction of the raw meals thus results in significantly lower energy consumption for milling.

## 6. Acknowledgements

The preparative work of N. Nebolsin and the EPMA of I. Steinberger is highly acknowledged

## 7. References

- [01] Lörke, P.; Lörke, A.: Verfahren zum Herstellen von Zementklinkern sowie dessen Vorrichtung. Europäische Patentschrift EP 0 801 636 B1, 2001
- [02] Rankin, G. A.; Wright, F. E.: The Ternary System CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. Am. J. Sci., Ser. 4, 39, 1915; p.1-79.
- [03] Taylor, H. F. W.: Cement Chemistry. Thomas Telford Publishing, London. 2nd edition, 1997
- [04] Lindner, R.: Silikatbildung durch Reaktion im festen Zustand. Z. Phys. Chem., Neue Folge, Vol. 6, 1955; p. 129-142.
- [05] Saxena, S. K.; Chatterjee, N.; Fei, Y; Shen, G.: Thermodynamic Data on Oxides and Silicates. Springer Verlag, Heidelberg, 1993
- [06] Kubachewski, O.; Alcock, C. B.: Metallurgical Thermochemistry, 5<sup>th</sup> Ed., Pergamon Press, Oxford, 1979
- [07] Robie, R. A., Hemingway, B. S.: Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10<sup>5</sup> Pascals) pressure and at higher temperature. United States Geological Survey Bulletin, 2131, 1995