

Mikroskopie  
des Zementklinkers  
Bilderatlas

Microscopy  
of Cement Clinker  
Picture Atlas

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## Contents

1.	The nature of clinker microscopy . . . . .	3	3.7.	Sources of errors . . . . .	14
1.1.	General remarks . . . . .	3	1.	Pores . . . . .	14
1.2.	Application of microscopy to the manufacture of cement . . . . .	3	2.	Internal reflections . . . . .	14
2.	Preparation of the samples . . . . .	4	3.	Newton rings (Interference stripes) . . . . .	14
2.1.	Methods of examination . . . . .	4	4.	Grinding scratches . . . . .	14
2.2.	Sampling . . . . .	4	5.	Ground clinker material . . . . .	14
2.3.	Preparation of samples for examination on the microscope . . . . .	4	6.	Grains of abrasive . . . . .	14
1.	Polished sections . . . . .	4	7.	Ground lead . . . . .	14
1.	General hints . . . . .	4	4.	Structure of clinker . . . . .	15
2.	Embedding media . . . . .	4	4.1.	Synopsis . . . . .	15
3.	Grinding and polishing . . . . .	5	4.2.	Macroscopic characteristics . . . . .	15
2.	Thin sections . . . . .	5	4.3.	Microscopic characteristics . . . . .	15
3.	Powder preparations . . . . .	5	1.	Porosity . . . . .	15
2.4.	Etching . . . . .	5	2.	Homogeneity . . . . .	15
1.	General hints . . . . .	5	1.	Variations in compositions . . . . .	16
2.	Etching methods . . . . .	6	2.	Spots in clinker . . . . .	16
3.	Clinker-phases . . . . .	7	3.	Nests . . . . .	16
3.1.	Synopsis . . . . .	7	4.	Streaks ("Schlieren") . . . . .	16
3.2.	Alite . . . . .	7	5.	Variations of the crystal-sizes . . . . .	17
3.3.	Belite . . . . .	9	6.	Differentiation of the molten mass . . . . .	17
3.4.	Ground mass (Interstitial phase) . . . . .	10	7.	Reaction borders on the surface of pores . . . . .	17
1.	Glass . . . . .	11	3.	Structure of the ground mass . . . . .	17
2.	Aluminate . . . . .	11	5.	Quantitative determinations . . . . .	18
3.	Alkalialuminate . . . . .	11	5.1.	Linear measurements . . . . .	18
4.	Ferrite . . . . .	12	5.2.	Square measurements . . . . .	18
5.	Further constituents . . . . .	12	5.3.	Determination of particle sizes . . . . .	18
3.5.	Additional phases . . . . .	12	5.4.	Quantitative determination of the percentage of the clinker phases . . . . .	18
1.	Free lime . . . . .	12	6.	Determination of the clinker and slag content of cements . . . . .	18
2.	Periclase . . . . .	12	6.1.	General hints . . . . .	18
3.6.	Special phases . . . . .	12	6.2.	Microscopical characteristics . . . . .	19
1.	Alkali-phases . . . . .	12	1.	Clinker . . . . .	19
2.	Phases formed under reducing firing conditions . . . . .	13	2.	Slag . . . . .	19
1.	Wuestit (FeO) . . . . .	13	7.	Mineralogical expressions . . . . .	19
2.	Metallic iron . . . . .	13			
3.	Calcium sulfide . . . . .	13			
4.	Iron sulfide . . . . .	13			
5.	Coke and graphite . . . . .	13			
3.	Phases with low content of CaO . . . . .	13			
4.	Phases with unknown composition . . . . .	14			

## Foreword

The light refraction and the double refraction of crystals – and thereby the theoretical principles of microscopical mineralogy and petrography – had already been discovered in the middle of the seventeenth century. However, only in the middle of the nineteenth century it became possible to prepare thin sections and to examine loosely scattered powder preparations in transmitted light on the microscope. Microscopical examinations of polished sections of ores and metals began only at the turn of the century. H.C. Sorby made first observations in about 1865, but they only became known by the examinations of A. Martens in 1875.

The evolution of clinker and cement microscopy was similar. H. Le Chatelier identified tricalcium silicate in a thin section on the polarization microscope in 1882. In 1897 A.E. Toernebohm called the four major clinker phases Alite, Belite, Celite and Felite.

In 1908 E. Stern introduced the examination of polished clinker sections in reflected light. By etching he made the different phases evident. The simultaneous examination of the same sample in transmitted

and reflected light was first carried out in 1938 by H. Insley and H.F. McMurdie. However, a comparably simple method of preparing thin polished sections has been introduced only in 1952 by F. Gille.

A group of mineralogists within the working committee "Zementchemie" (chemistry of cement), the former laboratory committee, began in 1960 to work out directions for the microscopical examination of clinkers. Thereby so many instructive pictures of polished sections have been collected, that the working committee decided to publish the most important of them in a picture atlas. This was an idea of the chairman of the Verein Deutscher Zementwerke e. V.

Dr.-Ing. E.h. Dipl.-Ing. Erich Plassmann

who died before it was realized. Revisors and editor remember him with grateful respect.

This picture atlas wants to give a survey of the actual position of clinker microscopy to colleagues and friends in the different branches of science and technology and serve them as basis and guide for their own work.

## 1. The nature of clinker microscopy

### 1.1. General remarks

Microscopical examinations have been indispensable in cement-research for a long time. They are used more and more for operational controls in cement works, – in addition to the usual chemical and mechanical-technical controls. Microscopical examinations can often give evidence of the causes of disturbances which occur in manufacturing of clinker and in working with cement.

This atlas gives a synopsis of the microscopy of Portland cement clinker. The microscopy of setting and hardened cement is not treated.

It is especially written for mineralogists, chemists and their collaborators. The subject of its first paragraphs is the special technique of clinker microscopy. In later chapters 151 illustrations are briefly described and interpreted.

Readers who are not familiar with the principles of crystal optics and microscopical procedures may find on page 69 explanations of important technical expressions and references to textbooks which are recommended for studies going into more details.

All the micro-photographs are in the same size of 70 x 99 mm. Two numbers in parentheses in the description of the illustrations give the exact position of the respective places: They are axial intercepts of a rectangular coordinate system, i.e. they give the distance of the respective point from the left hand bottom corner of the picture. The number at the left hand bottom corner gives the respective magnification. At the right hand bottom corner the etching reagent is specified.

### 1.2. Application of microscopy to the manufacture of cement

The microscopical examination of cement clinker gives evidence of kind, formation and distribution of the clinker phases. The percentage of the phases may be determined by measuring or by counting.

The percentage of the different phases is chiefly determined by the composition of the raw material. The structure of the clinker, i.e. formation and distribution of the phases, shows details of the procedure of manufacturing. For example high concentrations of free lime (Fig. 121), Periclase (Fig. 122) or Belite nests (Fig. 123) point to large lime, Dolomite or quartz grains resp., and accordingly mostly to an insufficient fine-grinding of the raw materials. Free lime nests in the vicinity of high concentrations of Belite (Fig. 117) and lots of small pores point to a too low degree of firing. Reducing firing conditions can be determined by means of the corrosion of Alite (Figs. 39–41) and the disintegration of Belite (Figs. 64, 65), or – in particularly clear cases – by means of the typical reduction phases (see paragraph 3.6.2.). Belite streaks, usually on the surface of grains, may point to an enrichment of acid coal ash (Fig. 131). The state of the interstitial mass (see paragraph 4.3.3.) and the formation of Belite gives information about the rate of cooling, – and accordingly to the effectiveness of the cooler.

As well as for examinations of clinker, the microscope may be used for examinations of cement. Additions of hydraulic materials – such as blast furnace slag (see paragraph 6) or trass – can quite often only be determined by means of the microscope. Even the clinker itself may still be examined in the cement: For these examinations an adequately coarse fraction is separated by sieving and embedded in resin.

The way of the microscopical examination has to be adapted to the respective problems. For operational control-purposes the examination of polished sections of average samples usually proves to be suitable. The preparation and etching of the samples and the interpretation of the microscopical pictures require a considerable experience, which can only be achieved by frequent work with the microscope.

## 2. Preparation of the samples

### 2.1. Methods of examination

Cement clinker is almost always examined on polished, etched sections in vertically incident light (reflected light). The clinker phases are essentially distinguished by different reflecting power, hardness and behaviour to etching. In some cases phases may be determined by means of the colour of their reflection or their reflection-pleochroism (bireflection).

Light refraction, double refraction, character of the double refraction, pleochroism, axial angle and colour have to be determined on thin sections or powder preparations in transmitted polarized light. However, these examinations are quite often disturbed by the small size of the clinker phase grains. As usually several phases cover each other, the samples must be ground very fine, — a work which requires considerable experience and manual skill. In thin sections the small double refraction of Alite can hardly be observed. The determination of the character of the double refraction and the axial angle of the crystals with small-double refraction in convergent light becomes very difficult or even impossible.

Polished thin sections can be examined as well in transmitted as in reflected light. Figs. 1–6 illustrate this technique.

**Fig. 1 (reflected light):** Laboratory clinker containing 5 % MgO. The photograph shows no Aluminate. Alite (70/50), Belite (40/40), pore (80/20).

**Fig. 2 (transmitted light):** Same place as in Fig. 1. The brown colour of the Ferrite phase to be noticed. Alite (65/35), Belite (50/30), pore (90/20).

**Fig. 3 (transmitted light):** Same place as Fig. 1. The sample has been turned around 90°. The considerable variation of the colour of the Ferrite phase from brown to brown-black to be noticed (Pleochroism). Alite (50/60), Belite (60/35), pore (80/60).

**Fig. 4 (reflected light):** Part of a laboratory clinker without MgO-content, showing few Aluminate. Alite (35/20), Belite (55/20).

**Fig. 5 (transmitted light):** Same place as Fig. 4. The brown colour of Ferrite to be noticed. Alite (35/20), Belite (50/20).

**Fig. 6 (polarized transmitted light):** Same area as Fig. 4. Alite (35/20), Belite (50/20).

### 2.2. Sampling

Usually the same methods of sampling as for chemical analysis are used. For treating special problems they can be modified in a suitable way.

In order to get complete information an average sample — according to DIN 53 711 — has to be taken. It must be especially prepared and divided: The clinker is divided into different fractions by sieving. Fractions smaller than 4 mm may be immediately prepared for the microscopical examination. The fractions larger than 4 mm are crushed to grains of 4–5 mm diameter. Care must be taken to produce as little grains smaller than 4 mm as possible.

Beside the examinations of average samples special problems may be observed, too:

1. Determination of the differences between certain clinker fractions or between different clinkers. The respective samples are separated from the production and examined on the microscope.
2. The examination of whole grains gives information about porosity and homogeneity, — for example about construction in shells or formation of streaks. Results of such tests must only be applied to the whole production, if all the sizes of grains are examined and interpreted according to their respective percentages.

### 2.3. Preparation of samples for examination on the microscope

#### 2.3.1. Polished sections

##### 2.3.1.1. General hints

For examinations on the microscope in reflected light the clinker has to be embedded in order to get a sample free from pores which can be ground and polished. There are several methods of embedding which have to be adapted to the nature and the size of the sample:

*Samples in form of dust* require a particularly careful preliminary treatment. They have to be agglomerated in an embedding medium of low viscosity, such as Bakelite powder dissolved in alcohol (Fa. Bakelit AG., Lemathe, Westfalen, Germany) or Palatal thinned with styrene. The powder is stirred up with the embedding medium and allowed to settle. After hardening the sample is broken in small pieces and embedded again. In this way a disintegration according to the sizes of the grains (which may occur due to sedimentation during embedding) is excluded. In the resulting sample all the sizes of grains appear according to their relative amounts.

*Powdery, granulated samples* (larger than 30  $\mu\text{m}$ ) may be directly mixed up with the embedding medium.

*Small pieces* of clinker may be directly put into a mould and covered with the resin. Large clinker grains are first ground plane by means of a coarse grinding wheel in order to obtain a larger surface of the sample and more pores filled with resin. Further treatment depends upon the nature of the embedding medium.

*Incompact samples* have to be reinforced by means of a suitable embedding medium before further treatment. The reinforcement is effected by the same solutions which are used for treating samples in form of powder. The samples are impregnated, — if necessary under vacuum — and then allowed to harden. According to the respective problem they may be broken in pieces or sawed in order to get oriented samples.

*Large samples* may be directly embedded in an appropriate mould. After impregnating and reinforcing they may undergo further treatment as complete pieces.

#### 2.3.1.2. Embedding media

*Sulfur:* The sample is cleaned by washing in alcohol and boiling in xylene. Then it is transferred — still hot and humid of xylene — into a crucible, covered with ground sulfur and heated up to 120–130 °C in a vessel which can be evacuated. As soon as the sulfur is molten the vessel is evacuated until no more air-bubbles are evolved. Then the vacuum is removed and the sample cooled down to room-temperature. After cooling it should be immediately ground and polished, as the sulfur tends to become brittle. (Ref. F. GILLE, N. Jhb. Min., Mon. Hefte 10 (1952), p. 277–287; Schriftenreihe Zementindustrie, Heft 10, (1952))

*Plexiglass* (M 330, milled, Fa. Roehm and Haas, Darmstadt, Germany): Plexiglass is hot pressed. It is particularly recommended for quick embedding of granulated or compact, not very porous materials. The sample is mixed with Plexiglass in the ratio 1 : 5 and filled into a press mould. Then pure Plexiglass is added in order to obtain a 2–3 cm thick plate. The press is heated up to 170–180 °C. The press power is increased until the sample is compact. After cooling the sample can undergo further treatment.

*Warm hardening resin:* (for example Araldit Giessharz B of Fa. DIBA AG., Wehr/Baden, Germany): Pieces of the sample are filled homogeneously into a mould (Preferably plastic rings which fit tightly on a bed-plate, supplied for example by Fa. Duerener, Maschinenfabrik, Dueren, Germany) and heated up to about 130 °C. A mixture of 10 g resin, molten at 130 °C, and 3 g hardener 901 is poured into the warm mould. The sample is evacuated until all the air is removed from the pores (With care! The resin can be evaporated, too!). The sample is now hardened during about 12 hours at 100–110 °C; then it is ready for further treatment.

**Cold hardening resin** (for example Palatal P4 by BASF, Ludwigshafen, Germany): The preparation and manufacture is the same as for warm hardening resins, but the hardening temperatures are lower. They depend upon the portions of hardener and accelerator.

A good mixture for embedding clinkers is:

- 1/6 Palatal 5007 (Fa. Wirtz, Düsseldorf, Germany)
- 1/6 Legual N 50 S (Fa. Bayer, Leverkusen, Germany)
- 2/6 styrene, pure, stabilized with 0.0012 % hydroquinone (Fa. Chem. Werke Hüls, Köln, Germany)
- 2/6 Pleximon 808 (Fa. K. Roth, Karlsruhe, Germany)

15 drops hardener (Butanox, by Fa. Oxydo, GmbH., Emmerich, Germany) and 15 drops accelerator (Cobalt naphthenate diluted with styrene, by Fa. Wirtz, Düsseldorf, Germany) are added to about 100 ml of the mixture. The sample is embedded under vacuum at room temperature. Hardening is effected in an oil bath under a pressure of at least 10 atmospheres. It lasts about 12 hours at room temperature. (Ref. Publications of the suppliers of synthetics, where special mixtures, temperatures and variations can be found.)

### 2.3.1.3. Grinding and polishing

The microscopical examination of clinkers requires usually fairly high magnifications. Therefore the surface of the specimens has to be very clean, plane and without relief. The procedure of grinding and polishing and the time needed for the different steps depends upon the material as well as upon the available equipment. The sample has to be treated in several steps, — whether it is prepared by hand or by machine.

The sample is first ground with carborundum powder on an iron or glass plate, until the surface is plane and without scratches. For hygroscopic samples 1,4-Butane-diol (for instance supplied by BASF Ludwigshafen under the name Diol 14 B) is recommended as grinding lubricant.

Grinding is effected with different gradings in the following order:

250–300 $\mu\text{m}$	
125–150 $\mu\text{m}$	on iron plate
50– 60 $\mu\text{m}$	
20– 25 $\mu\text{m}$	
13– 16 $\mu\text{m}$	on glass plate
3– 7 $\mu\text{m}$	
0– 4 $\mu\text{m}$	

The sample is cleaned carefully after each grade of powder. Attaching grains of carborundum and swarf would cause scratches on grinding with finer grades. At the end of the procedure the surface must be free of any scratches.

Now the finely ground sample is polished either on a disk equipped with a hard cloth (Perlon) or on a linden wood disk. Chromic oxide, polishing alumina or magnesia, slimed either in alcohol or in 1,4-Butane-diol are recommended as polishing substances.

In this case grinding wheels and grinding powders should be used according to the propositions of the manufacturers. This procedure requires a particularly careful, intermediate cleaning of the samples, — as they all may be destroyed by scratches at the same time.

### 2.3.2. Thin sections

For examinations in transmitted light thin sections are needed. They are prepared in the following way: A sample — as thin as possible — is ground plane on one side and cemented on a microscope-slide. As cement canada balsam (hard as glass) or a similar material, — for example Araldite —, which can be molten on the slide is used. The melting point of canada balsam is about 80 °C. The slightly warmed sample is carefully impressed with the plane ground surface on the molten cement.

After cooling the other side of the sample is ground uniformly with different gradings, until a thickness of 0.02–0.03 mm is reached.

Finally the thin section is thoroughly cleaned and covered with a cover-glass, which is cemented with canada balsam (dissolved in xylene) or Araldite.

The preparation of thin sections requires some training, as they easily become rough and irregular and tend to crack, when the cover-glass is set up.

The preparation of samples which can be observed as well in transmitted as in reflected light is possible, too. According to the way of their preparation, two kinds can be distinguished:

- a) polished thin sections:  
The surface of the thin section is not covered, but polished.
- b) thin ground polished sections:  
The finished polished section (see paragraph 2.3.1) is cemented with the polished surface on a slide. Then it is thin ground from the back side. The finished “thin section” is cemented on another slide. The bed-plate is removed from the polished surface. The sample can be observed after short additional polishing.

This procedure requires a considerable manual skill and a lot of training.

(Ref. F. GILLE, N. Jhb. Min., Mon. Hefte 10 (1952), p. 277–287)

### 2.3.3. Powder preparations

Powder preparations are used for examinations in transmitted light. They are prepared in the following way:

First of all a fraction of grains larger than 30  $\mu\text{m}$  is separated from the total sample by sieving. This fraction is washed with alcohol, in order to get rid of dust particles attaching on the grains which make exact determinations difficult. Washing is not necessary if the separation has been effected by an airjet-sieve. For one preparation about 10 mg (= a small pinch) powder are needed. This is usually about a quarter of the sieved material. The sample is dispersed uniformly from low height on an embedding medium smeared over a slide. Finally it is covered with a cover glass. The amount of embedding medium should be just sufficient that no material flows out on covering. Otherwise grains of a certain size could be washed out preferentially and the remaining sample would no longer represent an average.

As embedding media dissolved canada balsam ( $n = c. 1.54$ ), cedarwood oil ( $n = c. 1.515$ ), oil of cinnamon ( $n = c. 1.602$ ) etc. are used. For samples which are to be stored for a longer time, the use of solid canada balsam is recommended. In this case the sample must be prepared on a hot plate, — but the procedure has two advantages: The preparation can be stored and the grains don't move during measuring. Solutions of synthetic materials can be used as embedding media, too. “Clearax” (manufactured by George T. Gurr, London SW 6, available through Fa. Merck, Darmstadt, Germany) is an example of a neutral embedding medium with high refractive index ( $n = 1.666$ ). These solutions must be heated (— like canada balsam) to effect hardening.

## 2.4. Etching

### 2.4.1. General hints

Examinations of phases and structures are made considerably easier by etching the polished sections.

According to their effects two types of etching can be distinguished: “Colour-etching”, by which the surface of the crystals is coloured, and “structure-etching”, by which the surface of the crystals is slightly dissolved. Most important is the fact that the crystals show a characteristic behavior against a certain etching reagent.

In a polished section, not etched, the following constituents only can be distinguished: Weakly reflecting alkalisulfate (see Figs. 87, 88), medium reflecting Alite, Belite and Aluminate (see Figs. 7, 11), moderately strongly reflecting CaO and MgO (see Figs. 7, 11, 83, 84, 85) and strongly reflecting CaS (see Figs. 94, 95), graphite (see Figs. 97, 98, 99), Ferrite (see Figs. 7, 11) and metallic iron (see Fig. 93).

The major phases of clinker, Alite, Belite and Aluminate can only be distinguished by means of one or several etching-methods. However, after strong etching the determination of certain minor phases and special constituents may be quite difficult.

Before etching the last traces of polishing oil have to be removed from the polished surface. This can be effected by short polishing (about 1 minute) with MgO or Al<sub>2</sub>O<sub>3</sub> suspended in absolute alcohol on a rotating disk which is covered with a soft cloth. Finally the polished surface is thoroughly cleaned with absolute alcohol.

Etching itself is effected, according to the respective reagent, by dipping the sample into the etching reagent, by spraying the reagent or by rubbing it on the sample by means of a piece of cellulose impregnated with the reagent. The time of etching depends upon the properties and the concentration of the etching reagent and upon the respective purpose. In case of structure etching it is recommended to start with short etching times. After checking on the microscope the sample is etched again, — if necessary. Every time after etching the sample is washed with absolute alcohol, which is removed finally by means of compressed air, a saw or by rubbing dry with cellulose (Kleenex).

#### 2.4.2. Etching methods

For general examinations water, nitric acid and water/dimethyl-ammonium-citrate are recommended as etching reagents. Descriptions of these methods are given in this section. Other etching methods which are used for special purposes are mentioned in following table.

*Etching with water:* The following phases are etched in decreasing order: Free lime Aluminate, Alite, Belite. Ferrite and Periclase are not etched.

Etching with water is preferably effected in several short steps of 5–10 seconds. Short etching (about 5 seconds) effects a strong blue-brown colour of Aluminate. Alite and Belite are hardly etched. By longer etching (10–20 seconds) Alite is coloured, too. The depth of the colour depends upon the position of the section in the crystal (Etching-anisotropy).

Belite is not coloured; only weak structure etching is effected.

*Etching with nitric acid:* Usually a 100 : 1 or 1000 : 1 solution of nitric acid in alcohol is used. The etching reagent must be prepared at least a fortnight before use. Free lime, Alite and Belite are etched

#### Etching methods

	I	II	III	IV	V	VI	VII	VIII	IX	X
Etching with:	dest. water	nitric acid	water + DAC	ammonium-polysulfide	hydrofluoric acid	potash lye	soda lye	oxalic acid	alcohol. borax solution	glacial acetate
Concentration		HNO <sub>3</sub> in alcohol 1:100/1:1000	see text	yellow, conc. (NH <sub>4</sub> ) <sub>2</sub> S <sub>1+x</sub> <sup>-</sup> solution (1:10)	(a) conc. HF (b) dil. HF (c) HF-Vap.	10 % KOH in water	8 cm <sup>3</sup> 10 % NaOH and 2 cm <sup>3</sup> 10 % Na <sub>2</sub> HPO <sub>3</sub>	10 % oxalic acid	1 % 0.4 %	glacial acetate in alcohol 1:100
Etching time	5–15 s or 10 s	2–15 s	5–10 s	15–30 s	(a) 2–3 s (b) 5–10 s 30–60 s (c) 10–20 s	15 s	60 s	5–15 s	10 min	2–5 s
Etching temperature	20 °C	20 °C	20 °C	20 °C	20 °C	30 °C	50–55 °C	20 °C	20 °C	20 °C
Author	Tavasci Trojer	Stern Tavasci Insley McMurdie Trojer	Gille	Trojer	Wetzel Tavasci Trojer Parker Heilmann	Insley	Tavasci	Tavasci	Tavasci	Stern* Gille
Alite	C	CS	S	C	(C)	–	C	–	C	S
Belite	S	CS	S	(C)	C	–	–	–	–	(S)
Aluminate	C	–	C	–	–	C	C	C	–	–
Ferrite	–	S	–	C	–	–	C	–	–	–
Free lime	C	C	C	C	–	–	C	–	C	S
Periclase	–	–	–	–	–	–	–	–	–	–

C = Colour-etching (C) = weak Colour-etching S = Structure etching (S) = weak Structure etching

\* E. Stern: Über mikrographische Zementuntersuchung. Stahl und Eisen, 28 (1908) Nr. 43, S. 1542 bis 1546.

\*\* T. Heilmann: Reactions of Coal Ash with Portland Cement Clinker During the Burning Process. Proceedings of the Fourth International Symposium Washington 1960, S. 87. U. S. Department of Commerce. National Bureau of Standards Monograph 43 – Volume 1.

in decreasing order. Aluminate, Ferrite and Periclase are etched weaker or not at all.

Etching with nitric acid is also preferably effected in short periods which can be repeated if necessary. Nitric acid acts both colouring and dissolving. If the polished section is rubbed dry with cellulose after etching, the colours are removed and structure etching can be observed. If the sample is carefully dried by simple touching, the colours are conserved.

In case of structure etching the interstitial mass is etched only weakly or not at all; Belite is weakly, Alite strongly etched.

#### *Etching with water and Dimethyl-ammonium-citrate (DAC):*

To a solution of 192.6 g citric acid in 1 l water 891 ml Dimethylammonium-solution (33 % in water) are added and filled up to 3 l.

Free lime and Aluminate are coloured by water; fetching with Dimethyl-ammonium-citrate shows the structure of Alite and Belite. Ferrite and Periclase are etched very weakly or not at all.

In a first step Aluminate is coloured by etching with water. The second step consists of etching with Dimethyl-ammonium-citrate for 5–10 seconds. Alite is strongly, Belite weakly etched.

Fig. 7: The interstitial mass contains beside fine, partially dendritic Periclase crystals (with positif relief), strongly reflecting Ferrite and Aluminate, which has about the same reflecting power as Alite. The Belite crystals contain finely interspersed enclosures of higher reflecting power. Alite (70/50), Belite (40/30), Aluminate (60/50), Ferrite (30/20), Periclase (40/5), fissure filled with resin (40/50).

Fig. 8: Aluminate in the interstitial mass is coloured by short etching with water.

Fig. 9: By longer etching with water Alite is coloured, too. The crystals are differently coloured according to the relative positions of the sections (Etching-anisotropy of Alite, compare Figs. 23, 24, 25).

Fig. 10: Alite is now stronger coloured. Belite is still not etched.

Fig. 11: The interstitial mass consists of fine Periclase crystals (with positif relief), strongly reflecting Ferrite and Aluminate, which cannot be distinguished from Alite. In the left hand bottom corner Belite crystals containing strongly reflecting enclosures. Alite (90/10), Belite (10/15), Aluminate (71/32), Periclase (77/25).

Fig. 12: Alite and Belite are etched, Aluminate and Ferrite are not attacked at all.

Fig. 13: Stronger etching of Alite and Belite.

Fig. 14: Aluminate in the interstitial mass has been coloured by etching with water. Belite and Alite show about the same reflecting power. Alite (70/40), Belite (20/40), Aluminate (30/25), Ferrite (30/15).

Fig. 15: Dimethyl-ammonium-citrate etches Alite strongly, Belite weakly. The Alite crystals contain Belite-enclosures. The Belite shows parallel striping.

Fig. 16: The structure of the surfaces of Alite and Belite are clearer to observe after longer etching.

### 3. Clinker-phases

#### 3.1. Synopsis

Alite, Belite, Aluminate and Ferrite are the major compounds of normal portland cement clinkers. Alite and Belite are formed essentially by solid state reaction. At the sinter temperature they exist in the solid state, while the ground mass is molten. The latter crystallizes on cooling mainly as Aluminate and Ferrite. The percentage of these four major phases may vary in wide ranges. In special clinkers one of these phases can even be completely absent. A white clinker, for example,

contains no ferrite, and a special clinker for cements with high sulphate resistance contains only a little or no aluminate.

Besides these major phases, a normal clinker contains so-called minor constituents, chiefly free lime and Periclase. The amount of free lime can be used to measure the rate and the completeness of the reaction. It can be quantitatively determined by analytical chemical procedures, but only a microscopical examination will show the reason for an eventually incomplete reaction. Periclase usually exists only in clinkers with MgO contents above 1.5 % to 2.0 %, as most of the clinker phases are able to absorb more or less MgO. The maximum contents of Periclase are limited too; according to German standards, a linker may not contain more than 5 % MgO.

Under unusual conditions of firing other phases (not typical for normal clinkers), may be formed. Several compounds in clinkers with high Alkali contents, for example,  $K_2SO_4$  or compounds formed under reducing conditions of firing, for example, CaS, are examples for this type of constituent.

#### 3.2. Alite

'Alite' is a name for the different modifications of Tricalcium-silicate, which are stabilized in technical clinkers by formation of solid solutions. It is not yet possible to distinguish the different modification of  $C_3S$  by microscopical examination in reflected light. By means of X-ray diffraction one rhomboedric, two monoclinic and three triclinic modifications have been found.

Alite corresponds to  $C_3S$  of the calculation methods. It is the largest phase of normal portland cement clinkers (40–70 %).

Fig. 17: A relatively quickly cooled clinker with big, idiomorphic Alite crystals (e.g. 20/30) with mostly hexagonal cross-section. The Alite crystals are swimming' in a hardly differentiated ground mass. (Compare Figs. 18, 23, 31, 42, 46, 78.)

Fig. 18: Idiomorphic Alite crystals (e.g. 35/45) with mostly hexagonal cross-section in a fine crystalline ground mass (30/30) of a relatively quickly cooled clinker (white = Ferrite; dark grey = Aluminate) pores (5/25, 80/60).

Alite has the following optical properties:

Refraction index:  $n_x = 1.716$  to  $1.720$   
 $n_z = 1.722$  to  $1.724$

Double refraction:  $n_x - n_z = 0.005$

(Varying from about 0.002 to 0.005, measured on a crystal showing zones).

Axial angle (–)  $2V =$  very small

Colour transparent or weakly coloured.

In reflected light Alite appears grey. It cannot be distinguished from Belite and Aluminate without etching. Alite is etched by all usual etching reagents (Compare chapter 2.4 'Etching').

Alite forms idiomorphous, compact, tabular crystals with mostly hexagonal shapes (cross-section). The picture of the Alite crystals depends upon the present shape and habit, and, first of all, upon the accidental position of the section.

The above-mentioned shape of  $C_3S$  crystals are characteristic for Alite formed by solid state reaction at the sinter temperature (which is the normal way of formation of Alite in technical clinkers).

Occasionally larger amount of  $SiO_2$  are absorbed by the molten mass in technical clinkers too. This may occur either in case of an increased percentage of the molten mass (which has mostly a large iron content), or a high concentration of fluxing media or very high burning temperatures. On cooling the Alite crystallizes in a completely different habit: it forms thin tabular crystals, which appear in the section as long, narrow needles (Figs. 19–22).

Fig. 19: Long, narrow Alite needles (e.g. 40/25) in the part of the clinker containing a particularly large amount of ground mass. On the edges normal, compact Alite crystals (70/50). (Compare Figs. 20, 21, 22)

Fig. 20: Alite needles in completely molten laboratory clinkers.

Fig. 21: Long, narrow Alite needles (50/50) in a ground mass of big iron content. The dark grey, rounded crystals are Belite (35/40).

Fig. 22: Compact Alite crystals framed by fine Alite lamina (comparable to a skeleton) pores (30/0 and 80/10).

It is possible that both shapes occur together in the same clinker grain. The fine lamina used to grow on the compact crystals in a well defined, oriented way. Sometimes they grow over the old crystal edges, comparable to a skeleton (Fig. 22). The thin tabular crystals are usually more strongly etched than the compact ones.

Occasionally Alite tends to form simple twins. Twin formation can only be observed after etching. This is a consequence of an etching anisotropy. The surface of a section is differently etched according to its crystallographic orientation.

As already mentioned, Alite is a tricalcium silicate containing impurities (alien ions). The nature of these impurities, and thereby the chemical composition of the Alite, is dependent both on the available impurities as well as on the conditions of firing. Every change of these conditions varies the chemical composition of the Alite. Such variations during the growing of a crystal cause the formation of zones of different composition. These zones can be observed under the microscope after etching.

At the sinter temperature Alite is always formed in its highest symmetrical modification. On cooling several polymorphic conversions occur. At room temperature technical Alite exists, apart from a few exceptions, in its monoclinic or triclinic form. Typical conversion lamina can be observed occasionally under the microscope. After etching, the Alite shows stripes comparable to spindles or lancets. These stripes occur in triclinic Alite crystals exclusively. So they must be attributed to the conversion of the monoclinic into the triclinic modification.

Fig. 23: In the middle of the picture, an Alite-twin (60/30). The two individual parts of the twin are distinguished by different grey shades (consequence of the etching-anisotropy). The other Alite crystals show distinctly differentiated grey shades, too. Lighter grey, rounded grains are Belite (70/40). Dark grey, rough spots are pores (40/30). (Compare Figs. 24, 44).

Fig. 24: Large, twinned Alite crystals (30/30) amongst other, untwinned Alites. Dark grey, fingered ("gelappte") parts are Belite (80/40). Beside that light grey Aluminate (20/10) and whitish Ferrite (30/5).

Fig. 25: Alite showing zones (50/40) with different behaviour to etching. (Compare Figs. 26, 46, 79, 81, 86).

Fig. 26: Alite showing rhythmical zones. Pictures of this kind are fairly unusual. They can easily be confused with striped Belite (see Fig. 56).

Fig. 27 (reflected light), Fig. 28 (transmitted, polarized light): Photographs of the same part of a thin section in reflected and transmitted light. The stripes (resembling lancets) in the Alite are due to polymorphic transformations. The stripes in the reflected light correspond to different behaviours to extinction in the transmitted light. This observation leads to the conclusion that this Alite consists of several crystals of different orientation penetrating each other. (Compare Figs. 29, 50).

Fig. 29: Stripes resembling lancets in Alite crystals (55/35). Not to be confused with stripes in Belite! Same sample as in Figs. 27 and 28. (Compare Fig. 30).

Fig. 30: Typical transformation-laminas in an Alite crystal with strong etching-anisotropy. The crystal originally formed by solid state reaction, has further grown while the molten mass solidified. In this way a fringe with distinctly different behaviour to etching was formed.

The first product of the reaction between  $\text{SiO}_2$  and  $\text{CaO}$  during the firing process is always dicalcium silicate. Only at temperature above

$1200^\circ\text{C}$  Alite is formed by solid state reaction between the first-formed dicalcium silicate and  $\text{CaO}$ . During the formation of the Alite, crystal residues of Belite are often enclosed. Under the microscope these residues are shown as Belite knobs. This Belite can hardly react with free lime, if once it is completely enclosed by Alite; it is 'armoured'. Alites of production clinkers contain, almost without exception, Belite knobs in very different amounts and sizes. Like Belite, all the other clinker phases can be enclosed in Alite.

The melted phase of normal Portland cement clinker has at the temperature of sintering a low content of  $\text{CaO}$  in comparison with the solid phases in equilibrium with it; this is more definite the higher the content of alumina and the lower the content of iron of the clinker. (This rule must not be applied to Ferrari clinkers of high content of iron; at an alumina modulus smaller than 0.6 even the contrary is true!)

Aluminate, Ferrite and to a smaller extent also Belite crystallize on cooling. The  $\text{CaO}$  needed therefore, which is lacking in the melted phase, will be re-sorbed from either free lime ( $\text{CaO}$ ) or Alite. The corrosion of the Alite crystals enables us to detect this process under the microscope. The re-sorption of Alite needs time. Therefore corroded Alites are usually found only in slowly cooled clinkers.

Fig. 31: Alite-crystals (60/20) with numerous Belite-knobs. Beside that round Belites (80/10) in a ground mass of whitish Ferrite. Dark grey smooth parts are pores filled with resin (35/20). Bright, diffusely reflecting spots (15/10) are air-holes which have been filled with polishing paste during the polishing process. (Compare Figs. 10, 16, 32, 47, 73).

Fig. 32: Large, dark grey Alite crystal with enclosures of light-grey Belite and whitish Ferrite. It fills almost the whole field of vision.

Fig. 33: Light-grey Alite with black knobs of free lime and whitish Ferrite. The ground mass is Ferrite. Medium-grey parts are pores filled with resin (20/10).

Fig. 34: Medium-grey Alite crystal of untypical shape (comparable to an atoll) with small knobs of Belite and a big enclosure of ground mass.

Fig. 35: Alite crystals showing typical phenomena of corrosion. The original outlines of the crystals are still evident, but their edges are more or less corroded. (Compare Figs. 50, 60, 72).

Fig. 36: These Alite crystals are partially corroded to such an extent that the original edges can hardly be detected. Large, dark-grey parts of Alite (50/40), small round Belite crystals (85/30), whitish Ferrite. The fine points in the Ferrite parts (50/65) are Belite crystals, secondarily formed by disintegration.

Fringes of Belite around Alite crystals are formed by re-sorption of Alite by a molten phase with a low content of lime. Alite is removed pseudomorphously by Belite, i.e. The shape of the Alite crystals is still conserved. Fig. 35 shows it most clearly. Solidified Belite acts usually as a nucleus for the still molten  $\text{C}_2\text{S}$ . This behavior, which is typical for Belite favours the crystallization of Belite on the Belite layer already existing on the surface of the Alite crystals. The result is a fringe around the  $\text{C}_3\text{S}$  crystals. As the formation of this fringe needs time, it is only to be expected in relatively slowly cooled clinkers.

Alite is only stable above about  $1200^\circ\text{C}$ . As a consequence, Alite formed at the sinter temperature should be decomposed into Belite and free lime on cooling. However this decomposition is usually a very slow reaction. A production clinker is normally cooled just enough to freeze the Alite in a metastable state. However, there are exceptions: impurities in the Alite crystal can increase the speed of the decomposition. Reaction to such an extent that even normal cooling rates are not sufficient to freeze it in 'myrmekitische' (= intimate mixture, like worm casts) mixtures of Belite, free lime and sometimes residues of Alite, which are still pseudomorphous to Alite can be observed under the microscope.

This decomposition of the Alite can be caused either by higher contents of alkali or by  $\text{Fe}^{2+}$  ions built into the lattice of the Alite. In fact moderately reductive conditions during firing and thereby the



presence of Fe<sup>2+</sup> have been found in many cases to cause the decompositions of Alite in production clinkers.

Fe<sup>2+</sup> will be oxidised to Fe<sup>3+</sup> if an Alite containing a certain amount of Fe<sup>2+</sup> reaches an oxidizing atmosphere at a temperature above 1200 °C (limit of decomposition). As the Fe<sup>2+</sup> had substituted the Ca<sup>2+</sup>, the crystal is now lacking in a certain amount of Ca or other bivalent substituting ions resp. To reconstitute the equilibrium, some Belite is separated by the Alite crystal. This process cannot be observed on the microscope if it occurs at the sinter temperature. At lower temperatures (still over 1200 °C) a complete separation of Belite is no longer possible: Belite will be separated in slender lamina on crystallographic planes (rhombohedral planes) within the Alite crystal. Mostly three different groups of strictly parallel Belite lamina, crossing each other, can be observed. (The angles between the three groups of lamina depend upon the present position of the section. It is also possible, that one group does not occur at all.)

As a rule, these Belite lamina point to reducing conditions in the sinter zone. Only later, e.g. on the outlet of the furnace, the clinker has been completely oxidised again.

Fig. 37: Medium-grey Alite (50/20) with light-grey Belite fringes. The ground-mass consists of whitish Ferrite and dark-grey Aluminate (60/40). It contains – especially in the Aluminate phase – enclosures of secondary Belite. Grinding-scratches on Alite.

Fig. 38: Regular fringe of grey Belite crystals with internal reflections around black Alite. In the ground-mass light-grey Aluminate, whitish Ferrite and secondary Belite in very small enclosures.

Fig. 39: Formation of an intimate mixture of Belite and free lime from Alite. The products of this disintegration cannot be resolved by optical means. The disintegration starts at one point and diffuses like an "infection" over the whole crystal. In their centre the crystals still contain some non-decomposed Alite. Beside grey Aluminate and white Ferrite.

Fig. 40: A single Alite crystal is partially disintegrated to light-grey Belite and free lime. A third product formed by this dissociation is whitish Ferrite. A residue of Alite with black polishing-scratches lies on the top of the picture. The surroundings are formed mainly by grey reflecting resin.

Fig. 41: The surface of this sample has been exposed to the normal air-moisture for some hours. This procedure made the free lime coloured or black. The Alite crystals in the clinker are considerably disintegrated. The "myrmekitische" (= resembling worm-casts) structures of the free lime show the original outlines of the Alite crystals. These structures are relatively large in the first centres of the disintegration and become finer and finer in the outer areas, until the decomposition is frozen in.

Fig. 42: Large, idiomorphous Alite crystal with fine capillary fissures and cracks. Inside the crystals Belite knobs (for example 55/5). This must not be confused with the disintegration of Alite.

Fig. 43: Three groups of Belite laminas in an Alite crystal. The identity of the materials is evident, where the laminas combine with Belite knobs. (Compare Figs. 44, 45).

Fig. 44: Belite laminas in Alite crystals. The largest Alite crystal (55/30) is twinned. The different orientation of the lamina-groups in the two parts of the twin shows at the same time the different orientation of the two individuals of the twin. Beside that several Belite knobs (55/20).

Fig. 45: Small enclosures of Belite, – early stages in the formation of laminas – usually point to lack of air in the sinter zone. Beside that larger Belite knobs (50/23) within the same Alite crystal.

### 3.3. Belite

"Belite" is the name for Dicalcium silicate in technical clinkers. It contains small amounts of impurities in solid solutions. Certain physical properties, for example the colour may vary according to the kind and amount of these impurities. Four different modifications of dicalcium silicate ( $\alpha$ ,  $\alpha'$ ,  $\beta$ ,  $\gamma$ ) have been found up to now. As a rule C<sub>2</sub>S exists in clinker in a stabilized  $\alpha'$  or  $\beta$  form. The other modifica-

tions may occur under unusual conditions too. In reflected light they cannot be distinguished, except the  $\gamma$ -modification. The often fairly complex phase transformations corresponds to similarly complicated transformation structures. It is not yet possible to correlate the various forms of Belite to definite phases and phase transformation in an unequivocal way.

The structures are therefore simply described in the following paragraphs without any further interpretation.

In transmitted light, Belite is normally colourless to black-brownish, but sometimes rather yellowish or greenish.

#### Optical properties of the dicalcium silicate modification

Modification	Crystal System	Light refraction	Double refraction $n_z - n_x$	Axial angle
- C <sub>2</sub> S*	trigonal	$n_x = 1.702$ $n_z = 1.712$	0.010	(+) 2V = 0°
- C <sub>2</sub> S (bredigit)	rhombohedral	$n_x = 1.713$ $n_y = 1.717$ $n_z = 1.732$	0.019	(+) 2V = 30°**
$\beta$ - C <sub>2</sub> S (larrit)	monoclinic	$n_x = 1.717$ $n_y = 1.722$ $n_z = 1.736$	0.019	(+) 2V = 64° to 69°**
- C <sub>2</sub> S (shannonit)	rhombohedral	$n_x = 1.642$ $n_y = 1.645$ $n_z = 1.654$	0.012	(-) 2V = 60°

\* Stabilized with Na<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub>

\*\* Measured values

The tendency of Belite to form mixed crystals may cause considerable deviations from these values.

At higher alkali content alkali Belite of the formula K<sub>2</sub>O 23 CaO 12 SiO<sub>2</sub> is formed. It cannot be distinguished from Belite in reflected light. Its light reflection is  $n_x = 1.694$ ;  $n_z = 1.702$ ; its double refraction  $n_z - n_x = 0.008$ ; 2V = 20°.

In reflected light Belite looks grey, like Alite and aluminate, from which it cannot be distinguished without etching. Belite is attacked by all usual etching reagents, but weaker than Alite. (Compare with paragraph 2.4 'Etching'.)

Belite crystals are almost always idiomorphous. They are usually globular and by this they are typically distinguished from Alite.

After structure etching different Belite types, according to the way of their formation, can be observed. In a few cases only, chiefly in clinkers cooled very quickly, as for example laboratory preparations, the crystals do not show any structure at all after etching (Fig. 47).

Fig. 46: Rounded Belite crystals (for example 20/10) beside Alite (for example 55/50) with typical hexagonal or rectangular cross-section and zonal construction. (Compare Fig. 31).

Fig. 47: Smooth, round Belite crystal (40/25) without stripes beside Alite, showing grinding-scratches. Fine ground-mass of a quickly chilled clinker. (Compare Fig. 31).

Crystals without stripes – which obviously were not subjected to any phase transformation during cooling – tend to split and to crack. Apparently this is a consequence of the stresses caused by quick cooling.

Above all, cross-stripe structure is typical for Belite crystals. It is formed by several groups of lamina crossing each other. In the section they appear like a lancet, spindle or needle shaped striping.

The tendency of Belite to collective crystallization can cause certain lamini to grow at the cost of others over the original limits of the rounded crystals. In this way fingered (gelappte) Belites are formed. This phenomenon can only be observed in relatively slowly cooled clinkers, as the recrystallization needs time.

Parallel stripes on Belite crystals, which are caused by formation of polysynthetic twins, are considerably rarer than the crossed stripes (Figs. 55–57).

Fig. 48: Non-twinned Belite (50/40) with concentric, radial fissures. Beside Belite with cross-laminas (80/10). (Compare Figs. 49, 52).

Fig. 49: Typical cross-stripping of Belite crystals. This form removes the original, not striped, smooth one, which has been conserved in the centre of the one crystal (65/40).

Fig. 50: Alkali-containing laboratory-clinker; Belite showing very broad laminas, beside strongly corroded Alite (80/60 and 15/45), partially with cooling-cracks and stripes resembling lancets. Dark-grey, laminar Aluminate (20/30). Pores (40/15 and 96/30).

Fig. 51: Belite showing finest cross-stripping; in each crystal several groups of laminas, crossing each other. (Compare Figs. 71, 123).

Fig. 52: Certain groups of laminas in a cross-stripped Belite grow at the cost of other ones. The final result is a complete transformation of the original crystal to single laminas with spindle-like cross-section.

Fig. 53: Transformation of the original Belite crystal into fingered ("gelappten") Belite. The ground-mass consists of light-grey Ferrite and medium-grey Aluminate. (Compare Figs. 16, 54, 62).

Fig. 54: Fingered ("gelappt") Belite. Almost complete resolution-process.

Fig. 55: Parallel-stripping of Belite. (Compare Figs. 16, 56, 63).

Fig. 56: Belite-crystals with non-typical outlines and marked parallel-stripping. Care must be taken to avoid confusion with Alite.

Fig. 57: Parallel-stripping of Belite. (Compare Fig. 65).

All the afore-mentioned forms of Belite can be removed by another type, which is obviously not able to absorb the same amount of impurities as the crystals from which it resulted. Thus a present excess of impurities will be separated as new phases which appear as enclosures of foreign substances. With the exception of free lime, all the clinker phases may occur as foreign enclosures. The largest part always consists of Alite. This means that Belite is able, at higher temperatures, to absorb, besides other components, above all an excess of CaO. Ferrite follows at the next position aluminate seems to be rare. Its presence has not yet been definitely proved. Often the enclosures are so small that they cannot be resolved by optical means. Such a structureless, new-formed crystal shows a diffuse reflection and reflecting enclosures. Structures which point to a further transformation of this Belite type are not known.

The fact that during the above-mentioned recrystallization Alite enclosures are separated in the newly formed Belite, leads to the conclusion that this process must have occurred in the stability range of Alite, i.e. above 1200 °C. A transformation of  $\beta$ -C<sub>2</sub>S into  $\beta$ -C<sub>2</sub>S, which should occur at 670 °C, cannot be detected by means of the Belite structures.

Fig. 58: Belite (50/40) with enclosures of foreign substances. At the edges hexagonal Alite crystals (for example 10/10). In the ground-mass whitish Ferrite (30/5) and dark-grey Aluminate (15/40). The coarser enclosures can be identified by means of their behaviour to etching as Alite; beside are finer Ferrite-enclosures.

Fig. 59: Belite with Alite- and Ferrite-enclosures is removing an older type, which has been partially conserved in the form of non-striped residues (55/15).

Fig. 60: Belite crystals showing cross-stripping are removed (starting from the edges) by another Belite type. Alite crystals at the edges of the picture. The ground-mass consists of whitish Ferrite and dark-grey Aluminate. (Compare Fig. 61).

Fig. 61: Belite showing cross-laminas (30/55) is removed by diffusely reflecting Belite (50/25). The enclosures are very small and cannot be resolved by optical means. Pores (50/10, 10/50, 85/60).

Fig. 62: Fingered Belite, completely removed by another type with simultaneous separation of foreign phases. With the exception of the Ferrite phase, these enclosures cannot be definitely identified. Beside, Alite with numerous grinding scratches, Ferrite and Aluminate.

Fig. 63: Belite with parallel-stripping is nearly completely removed by diffusely reflecting Belite containing enclosures. Only in the middle of the picture a residue has been conserved. Pores (60/20, 80/20).

Fig. 64: In the middle of the picture (50/35 and 53/15) two dark-grey  $\gamma$ -Belite crystals with several cracks and fissures which are filled (– also in the surroundings!) with dark-grey smooth resin (60/25 and 35/45). Starting from this crystal the whole clinker is cracked. Beside, decomposed Alite (for example 85/20). Only the primary Belite is disintegrated, not the "decomposition-Belite", which has been formed by decomposition of Alite. (Compare Fig. 65).

Fig. 65: A single, parallel-striped Belite crystal is partially transformed into  $\gamma$ -C<sub>2</sub>S. Simultaneously it disintegrates. The crystal is cracked parallel to the twin-stripping.

Figs. 58–63 show that several Belite types can exist at the same time in the same clinker. This is a fairly general rule, and concerns not only the incomplete removal of one Belite type by another one. Sometimes cross laminated and fingered ("gelappt") Belite can be observed close together in a single sphere of clinker.

In reflected light only  $\gamma$ -Belite can be definitely distinguished from the other modifications. As the transformation to  $\gamma$ -C<sub>2</sub>S brings along an increase of volume, a clinker containing  $\gamma$ -C<sub>2</sub>S will be cracked. The disintegration is a quite typical phenomenon, which arouses the suspicion that  $\gamma$ -Belite could be present. In a disintegrated clinker the Belite crystals themselves also show cracks and fissures, which cannot be overlooked.  $\gamma$ -Belite reflects distinctly weaker than the other silicate phases of clinker. The usually frozen transformation to  $\gamma$ -Belite is strongly accelerated by Fe<sup>2+</sup>-ions. It leads to the conclusion that the clinker has been burned under reducing conditions. (Further continuous tempering of clinker leads also to disintegration.)

If Belite is separated in larger amounts from the molten phase, fairly typical dendritic Belite crystals are formed. The dendritic structure is usually very fine, but larger crystals can be found too.

The composition of alkali Belite is, according to W. C. Taylor, K<sub>2</sub>O. 23CaO.12SiO<sub>2</sub>. In reflected light it cannot be distinguished from Belite as it shows the same behaviour towards etching and the same structures. However, the transformation lamini, which are quite typical for normal Belite can only seldom be observed. Alkali Belite is usually not striped and smooth. Opposite to normal Belite, Alkali Belite does not react with free lime to form Alite at normal sinter temperatures. The presence of free lime in the vicinity of Belite is the only criterion to identify Alkali Belite definitely under the microscope (Figs. 67, 88, 89).

Fig. 66: Dendritic Belite with unusually coarse structure. The Belite crystal in the middle of the picture shows a distinct parallel-stripping. This clinker has been made from raw material containing feldspar. Consequently it has a high content of alkali.

Fig. 67: On the right and on the left side of the picture Alite-parts with grinding-scratches. In the middle a streak ("Schliere") of higher alkali-content with medium-grey Belite and black free lime. The picture shows only a few ground mass: Whitish Ferrite and dark-grey Aluminate. The large, rough, dark-grey parts are pores (for example 65/30).

#### 3.4. Ground mass (Interstitial phase)

A normal clinker contains at 1450 °C about 30 % molten phase, besides the primary phases formed by solid state reaction at the sinter temperature. On cooling, the so-called secondary phases crystallize from the molten mass. Amongst other compounds namely aluminate and ferrite belong to these phases.

After aluminate and ferrite Belite is by far the commonest secondary phase, but, according to the respective conditions, all the other clinker phases may occur in the molten mass too. These separated phases are called 'formation of the second generation', in order to distinguish them from the primary phases already formed at the sinter temperature. 'Ground mass' is a comprehensive name for all the compounds crystallising from the molten mass.

The composition of the ground mass is determined chiefly by the "Alumina-modulus", the ratio being  $Al_2O_3$ . Clinkers with a high Alumina-modulus have a high content of Aluminate, clinkers with a low Alumina-modulus have a low content of Aluminate, but a high content of Ferrite. If the Alumina-modulus is smaller than 0.7, Aluminate can completely disappear.

The sequence of the separations is determined by the composition, too. At a high Alumina-modulus, Aluminate will crystallize first. In this way iron oxide is enriched in the residual molten mass. As soon as the composition of the molten mass reaches an Alumina modulus of about 1.5, Aluminate and Ferrite will crystallize together. This process can be observed on the microscope. The first separated Aluminate forms large, idiomorphous crystals, which are surrounded by younger, finely crystalline Aluminate and Ferrite in intimate mixture (see Figs. 71, 72). At a lower Alumina-modulus idiomorphous Ferrite will be separated in analogous way. When the ratio  $Al_2O_3 : Fe_2O_3$  has reached 1.5, Aluminate and Ferrite will crystallize together, too.

These situations are only valid in a strict sense, if the crystallization occurs under conditions of equilibrium, which are only rarely found in technical clinkers. Usually the molten mass is super-cooled by quick chilling the clinker. As a consequence Ferrite, which has a considerably higher tendency to crystallize, can be found as the first separated phase even in clinkers with fairly high Alumina-modulus (see for example Fig. 137).

### 3.4.1. Glass

The interstitial mass can solidify in an amorphous, glassy state, if the clinker is chilled very quickly. The composition of the glass corresponds to the composition of the molten mass, i.e. it can vary in wide ranges. In the same manner its properties, for example its reflectivity or its behavior to etching, change.

However, the molten phase of Portland Cement clinker has an extremely high tendency to crystallize, — the more, the higher its iron content. Under normal conditions of manufacturing it will hardly be possible to freeze the molten mass in the glass-state.

### 3.4.2. Aluminate

Aluminate in Portland Cement clinker corresponds essentially to Tricalcium-aluminate ( $C_3A$ ), but its properties are more or less modified by formation of solid solutions:

In clinkers with low or no alkali content Aluminate crystallizes in a cubic form. In transmitted light it appears colourless or — if it contains impurities — slightly coloured. Its refractive index is  $n = 1.710$ . In reflected light Aluminate appears grey. It can only be distinguished from Alite and Belite after appropriate etching. Aluminate is etched particularly strongly by water. This procedure gives quickly a deep blue to blue-brown colouring. KOH has a similar effect, but doesn't etch silicates and free lime (Compare paragraph 2.4. Etching).

Aluminate of a clinker with low alkali content is almost without exception xenomorphous, i.e. it shows no own, typical crystal faces. It fills the interstitial spaces between other crystals and shows in the section only irregular outlines. Idiomorphous Aluminate crystals occur only as rare exceptions.

Though Aluminate only seldom occurs in larger, coherent sections, the crystals are usually oriented in a uniform way over large ranges. Unfortunately this property is much harder to observe on the optically isotropic Aluminate than on Ferrite, whose uniform orientation can

be detected in a thin section by means of the extinction between crossed Nicols and by means of the pleochroism (see Fig. 6).

Fig. 68: Very quickly chilled white-clinker. Large Alite crystals (for example 40/25) in a ground mass of dark-grey Aluminate-dendrites (60/30) in not yet crystallized, medium-grey reflecting glass. The large, smooth, medium-grey areas at the edges of the picture are resin-filled pores. Some bright, small points in the ground mass are internal reflections. Ferrite is not present in this iron-free sample.

Fig. 69: Typical section of a clinker with low alkali-content. Idiomorphous, dark-grey Alite crystals (80/60) in a ground-mass of xenomorphous, medium-grey Aluminate (70/35) and whitish-grey Ferrite (20/30). In the ground-mass finest disintegration-particles of secondary Belite. (Compare Figs. 24, 29, 35, 39, 53, 70).

Fig. 70: Dark-grey Alite crystals (70/40) in a ground-mass of whitish Ferrite and smooth, medium-grey Aluminate (45/30). The black spots are fine Belite disintegration-particles in the ground-mass.

Fig. 71: Medium-grey Aluminate (35/50) with distinct crystal-faces (primary separations from the molten mass). Beside, finely crystalline mixtures of whitish Ferrite, dark Aluminate and small enclosures of secondary Periclase (30/40) with clear relief. In the area of high Ferrite-content (20/63) several small Belites showing stripes, separated from the molten mass. In the right-hand part of the picture large, cross-striped Belite crystals.

Fig. 72: Idiomorphous, dark-grey Aluminate crystals beside whitish Ferrite and corroded Alite crystals. The zonal construction of the Aluminate crystals is due to the varying composition of the different layers (see p. 8). Enclosures of Ferrite in the Aluminate phase. Aluminate with zonal construction is very rare.

Fig. 73: In this picture the percentage of ground-mass is particularly high. Dark-grey Aluminate crystals (55/40) are grown to big individuals. They enclose typical, light-grey Alite-crystals (70/18). The same applies to the whitish Ferrite-crystals (40/20). Black-grey, rough spots are free lime (50/30). Aluminate and Ferrite crystals are able to grow around the silicates even if the percentage of ground mass is smaller.

### 3.4.3. Alkalialuminate

In the presence of alkali an Alkalialuminate is formed in the clinker instead of the pure Tricalciumaluminat. Alkalialuminate tends to form idiomorphous crystals, — contrary to pure  $C_3A$ . It forms laminas or thin, tabular crystals, which in the section usually appear as long needles. These needles have led to the incorrect name "prismatic" Aluminate.

Alkalialuminate has the following optical properties:

Light refraction:  $n_x = 1.702$ ,  $n_z = 1.710$   
 Double refraction:  $n_z - n_x = 0.008$   
 Axial angle:  $(-)\ 2V$   
 Colour: colourless

The crystals do not belong to the cubic system; they are lower symmetric.

The behavior of Alkalialuminate in reflected light and its behavior to etching are analogous to the behavior of Aluminate in alkali-free clinkers.

Fig. 74: Long needles of medium grey Alkalialuminate (70/25) beside whitish Ferrite (60/25) in the ground-mass of the clinker. Beside, dark-grey Alite crystals (20/15) and rounded Belites (40/15). The rough parts are resinfilled pores (80/0 and 0/60).

Fig. 75: Idiomorphous laminas of dark-grey Alkali-aluminate beside rounded free lime (65/5), Alite (20/20) (a little darker coloured than free lime) and whitish Ferrite. — The picture illustrates also the corrosive action of KOH: Aluminate is dark coloured, Ferrite is slightly dissolved, the other phases don't react at all. (Compare Figs. 139, 140).

Fig. 76: Aluminate laminas with different colours in a slowly cooled clinker. Beside, Ferrite and corroded Alite crystals with Belite knobs. The light-grey parts of the ground mass are Belite (30/25), which partially borders the Alite.

### 3.4.4. Ferrite

$\text{Fe}_2\text{O}_3$  in cement clinker is bound – apart from unimportant formation of solid solutions with other phases – in Ferrite. Ferrite is a part of the uninterrupted series of solid solutions between the end points  $\text{C}_2\text{F}$  and  $\text{C}_6\text{A}_2\text{F}$ . Bogue uses the point  $\text{C}_4\text{AF}$  as base for his phase calculation. This is in fact the approximate composition of Ferrite in normal clinker with an alumina-modulus of about 2. In clinkers with particularly high content of iron (alumina-modulus smaller than 0.6) a Ferrite with a corresponding high iron-content is formed.

The Ferrite phase in normal clinker appears in transmitted light dark-brown to yellow. It shows a variable pleochroism. Magnesium-impurities have an effect upon colour and pleochroism: With increasing magnesium content the colour changes from green-brown to green-yellow. The colour of the cement changes from brown to green-grey, too.

The pure solid solution  $\text{C}_4\text{AF}$  has the following optical properties:

Light refraction:	$n_x = 1.98; n_y = 2.05, n_z = 2.08$
Double refraction:	$n_z - n_x = 0.10$
Axial angle:	(-) $2V = \text{medium}$
Pleochroism:	$n_z = \text{strongest absorption}$

In reflected light Ferrite appears beside Alite, Aluminate and Belite whitish, slightly blueish. Thus it can be identified without any etching. The reflecting power increases with higher iron oxide contents and decreases in case of reducing firing conditions. The usual etching reagents hardly attack Ferrite. The Ferrite occurs – together with Aluminate – as interstitial material between the silicates; against Aluminate it can be either idiomorphous either simply interstitial, “wedge-filling” material. Ferrite can be seen in the ground mass on almost every photograph.

A gigantic growing of the Ferrite crystals – similar to Alite crystals (Fig. 73) – can often be detected in the thin section by means of the uniform extinction over large areas (see Fig. 6).

Fig. 77: Whitish Ferrite (for example 50/20) in idiomorphous prisms. The cross-section of these prisms is usually rhombic, only exceptionally extended. Beside that, the ground mass contains interstitial Aluminate and black spots of secondary Belite. Alite of primary generation, partially with skeleton-like or laminar shape.

Fig. 78: Idiomorphous prisms of whitish Ferrite (for example 85/10) beside light-grey Aluminate in the ground mass. Beside, Belite with cross-laminas (65/5) and idiomorphous Alite crystals (20/50) with zonal construction. The varied behaviour to etching of Alite, – even within one crystal – to be noticed. (Compare Fig. 42).

Fig. 79: Dendritic Belite (75/30) as secondary separation from the molten mass. Beside, Alite-crystals with zonal construction. In the ground-mass, beside larger, not etched Aluminate crystals (60/30) an intimate mixture of fine crystals of Aluminate and Ferrite. (Compare Fig. 66).

Fig. 80: In the middle of the picture finest secondary separations of Belite (from the molten mass), embedded in Ferrite. Beside that, Alite (70/10) and primary Belite. The definite identification of such small enclosures is often very difficult. The best way to solve this problem is to prove the identity of smaller and smaller enclosures, starting from larger, known ones (see Fig. 43). Often new polishing and new, stepwise etching will be inevitable. Pores (20/45). (Compare Figs. 36, 69, 70).

### 3.4.5. Further constituents

The molten mass contains parts of all constituents occurring in clinker, above all  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ , but also  $\text{SiO}_2$ ,  $\text{MgO}$  and others. Thus silicate, Periclase and eventually free lime crystallize in smaller amounts beside Aluminate and Ferrite on cooling.

Beside that, additional phases can be formed – after complete solidification of the clinker, but still during cooling – by disintegration in solid state: A crystal may separate again a constituent absorbed before at higher temperatures. This disintegration can be detected by the often very strict orientation in the large crystal (Examples: Belite laminas in Alite, Figs. 43, 44, 45 and disintegration knobs of Belite and Periclase in Aluminate, Fig. 147).

### 3.5. Additional phases

#### 3.5.1. Free lime

$\text{CaO}$  not chemically bound is called free lime. In transmitted light it appears colourless or slightly brownish coloured. It is optically isotropic. Its light refraction is about  $n = 1.83$ . In a freshly polished sample free lime reflects a little brighter than the silicates and slightly yellow-tinted, but considerably less strong than Ferrite (see Fig. 75). The normal air-moisture attacks free lime quickly. It is covered with an iridescent film of  $\text{Ca(OH)}_2$  which finally becomes grey and rough. Free lime is etched by all the usual etching reagents.

Fig. 81: In the middle of the picture free lime as secondary separation from a molten mass with high iron-content. Beside, Alite (25/50) and Belite (60/20).

Fig. 82: Typical, rounded free lime crystals, covered with a grey film of  $\text{Ca(OH)}_2$  (“air-etching”). With the exception of the Ferrite phase, the other phases cannot be determined without etching. (Compare Figs. 88, 110, 117, 118, 120, 121).

#### 3.5.2. Periclase

Periclase is  $\text{MgO}$  which can be slightly modified by impurities. In a normal clinker up to 1.5–2 %  $\text{MgO}$  can be built into silicates and aluminates. Thus Periclase is only to be expected in clinkers with  $\text{MgO}$  contents higher than about 2 %, either generally in the whole clinker, or locally in case of inhomogeneities (see Fig. 122).

In a thin section Periclase appears colourless or slightly yellowish or greenish coloured. The colours are difficult to observe, because the crystals are usually very small. Pure periclase is isotropic with a refractive index of  $n = 1.736$ . If it has absorbed some Fe or Mn, the refractive increases.

In reflected light Periclase appears grey, usually slightly brighter than the silicates. It can be definitely identified by means of the marked relief which is a consequence of its extreme hardness. Periclase is not attacked by the usual etching reagents.

Fig. 83: Periclase crystals with sharp, black edges, caused by the positif relief. The big black areas are air-holes (50/30, 90/50). Ferrite is whitish. Alite, Belite and Aluminate cannot be determined without etching. (Compare Fig. 122).

Fig. 84: Periclase dendrites in the ground-mass of a clinker. The dendritic shape is typical for secondary separations. Bright areas are pores filled with sulfur (for example 60/45). (Compare Figs. 7, 91).

Fig. 85: Dendritic Periclase crystals. Black areas are open pores.

Fig. 86: Under varying conditions of firing the resorption of already formed Periclase is possible, too. Corroded Periclase crystals (60/35) in an Alite crystal showing a well marked zonal construction, which gives further evidence of extremely varying conditions during the formation-period. Pores, for example 90/45.

### 3.6. Special phases

Special phases occur only in case of unusual firing conditions. The following groups can be distinguished:

1. Alkali-phases
2. Phases formed under reducing firing conditions
3. Phases with low content of  $\text{CaO}$
4. Phases with unknown composition.

#### 3.6.1. Alkali-phases

Alkali-containing compounds have already been mentioned in the paragraphs about Alkalibelite and Alkalialuminate. These compounds are in fact silicates and aluminates with a low content of alkali. As a real alkali compound potassium sulfate may occur in clinker in case of relatively high potassium- and sulfate-concentrations.

Potassium sulfate reflects weaker than the silicates, – and so weaker than every other clinker phase. It is dissolved by every etching reagent.

Even in short times of etching it is completely washed out. Therefore the polished sample must be carefully examined for potassium sulfate before etching.

Alkali sulfate has a low melting point. It crystallizes always together with the last phases, mostly as interstitial material, more seldom dendritic.

Fig. 87: Alkali sulfate (for example 35/15) in relatively large, slightly dark-grey reflecting crystals. Grey-white reflecting areas are Ferrite. Beside that, small, rounded Periclase grains with positif relief. Silicates and Aluminate cannot be distinguished without etching. The larger white spots (for example 15/65) are pores filled with sulfur. (Compare Figs. 88, 89, 90, 91).

Fig. 88 (etched by air), Fig. 89 (same area, but etched by DAC): Laboratory clinker with Alite, Alkalibelite, free lime and alkalisulfate. The large, diomorphous Alite crystals contain free lime- and Belite-enclosures, which appear after etching black or grey respectively, with marked relief. The small Alkalibelites – probably  $KC_{23}S_{12}$  – show about the same reflecting power as Alite. The round free lime crystals appear dark-grey. The alkali sulfate is black-grey and shows jagged-outlines. After etching alkalisulfate and free lime are completely washed out. In spite of firing temperatures of 1450 °C, free lime exists in the direct vicinity of Belite. On the top of Fig. 88 several pores filled with resin; open pores at (5/65, 45/13, 60/55).

Fig. 90: Dark-grey reflecting, dendritic alkali sulfate (40/30) in the ground-mass. Beside, large Alite crystals.

Fig. 91: Black potassium sulfate (40/29) in wedges of a finely crystalline ground-mass of light-grey Ferrite and medium-grey Aluminate. Enclosures of dendritic Periclase (73/41).

### 3.6.2. Phases formed under reducing firing conditions

Lack of air during firing causes reducing firing conditions. The trivalent iron is usually the only constituent which can be reduced. It can be reduced either to bivalent or metallic iron. Small amounts of sulfates, which occur in every natural raw material, may form sulfides under reducing conditions. Beside that, not burned combustible can be embedded in clinker.

If bivalent iron is formed under moderately reducing conditions, it is usually absorbed by other clinker phases by formation of solid solutions. Thereby their properties are modified. For example the decomposition of Alite into Belite and free lime is accelerated (see p. 26), the tendency of Belite to disintegrate is increased (see p. 35) and the reflecting power of Ferrite is diminished (see p. 40).

#### 3.6.2.1 Wuestit (FeO)

FeO is only very rarely observed as an independent phase: It can only occur in clinkers with high iron content which have been very quickly chilled. On slow cooling the following reaction occurs:

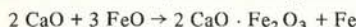


Fig. 92: Brightly reflecting Wuestit dendrites (30/35) beside medium-grey Ferrite, black free lime and white metallic iron. Beside, idiomorphous Alite crystals with polishing scratches. Wuestit appears brighter than Ferrite and shows a marked orange-tinge; Ferrite beside Wuestit appears dark-blue-grey. The transformation to the equilibrium Ferrite/iron metal is already considerably advanced.

#### 3.6.2.2. Metallic iron

Iron compounds may be reduced to iron metal under strongly reducing conditions. As such clinkers contain no iron oxide they are white or light grey coloured. On the microscope metallic iron can be identified by means of its form of small drops and its extremely high reflecting power which excludes a confusion with other phases.

Fig. 93: White drops of metallic iron in a clinker burned under highly reducing conditions. As the clinker is not etched, Alite, Belite and Aluminate cannot be distinguished. (Compare Figs. 92, 97).

#### 3.6.2.3. Calcium sulfide

Even under moderately reducing conditions Calcium sulfide may appear. Its reflecting power is quite similar to Ferrite's. These two phases are therefore easily confused. Calcium sulfide crystals are usually rounded and dendritic. They are easily etched by DAC. Ferrite appears either in idiomorphous prisms with plane crystal surfaces or xenomorphous.

Fig. 94: Whitish calcium sulfide dendrites in a clinker burned under reducing conditions. Pores are black; the other clinker phases cannot be distinguished without etching. The dendrites are – independent of the interstitial silicates – uniformly oriented over large areas. (Compare Fig. 25).

Fig. 95: Whitish calcium sulfide dendrites with brighter reflecting borders.

#### 3.6.2.4. Iron sulfide

In clinkers fired under reducing conditions another phase can be observed quite often: On the strength of its paragenesis (– the history of its formation, its surroundings etc.) it must consist of a complex iron sulfide. (FeS and  $\text{FeS}_2$  must be excluded because of their optical properties.) F. Trojer, loc. cit., says the composition of this phase is  $\text{KFeS}_2$ .

This potassium iron sulfide is very soft. On polishing care must be taken, not to produce a too strong relief. Iron sulfide can be definitely identified by means of its extremely high reflection pleochroism. It reflects stronger than the surrounding Ferrite in the colours grey-yellow, greenish-grey, copper-red.

Fig. 96: Iron sulfide. Photograph of a sample in oil-immersion. Polarized light. Under these conditions Silicates and Aluminate are black; only the iron sulfide crystals can be seen. They show an extremely high reflection-pleochroism, which appears in polarized light as different grey tinges of differently oriented crystals.

#### 3.6.2.5. Coke and graphite

In case of acute lack of air the solid fuel is not completely burned. Thus residues of coke and graphite are enclosed in clinker. Their direct surroundings are always strongly reduced.

The internal structure of the coke particles depends upon the coal which is used and can therefore vary in wide ranges. A fairly high reflective power, a bright, yellowish colour and a marked reflection pleochroism (yellowish-white – dark-grey) are always typical.

Fig. 97: (polarized reflected light): Coke residue in a blast furnace clinker. The medium-high reflecting power and the undulous reflection-pleochroism, which is a consequence of the different orientation of the particles in the coke residue, are fairly typical. Near the edge (20/55) lies another piece of coke with "smooth" surface and entirely different structure.

The burning coke pieces have been slowly consumed; they shrunk. In this way a fissure around the coke residue has been formed, which is filled with resin. The finely interspersed stars of metallic iron in the surroundings of the coke pieces point to reducing conditions; accordingly Ferrite is lacking in this sample.

Fig. 98, Fig. 99 (polarized, reflected light): Coke enclosures in clinker. The original cellular structure has been partially conserved. The two pictures are rectangular to each other and show the reflection-pleochroism of coke. (Compare Figs. 97, 101, 102).

### 3.6.3. Phases with low content of CaO

Sometimes extreme inhomogeneities are found in clinker: Locally the content of CaO may be too low to make the formation of a normal clinker paragenesis possible. In this case Gehlenite-glass, a dark-grey, uniform interstitial mass between large Belite crystals is fairly typical (see Fig. 100).

Fig. 100: Band of acid coal ashes between two pieces of clinker. Within the band Melilith and dendritic Belite have been separated. Between the ash-band and the clinker a Belite fringe has been formed (contact-zone).

### 3.6.4. Phases with unknown composition

Even in well investigated cement clinker phenomena which cannot be explained and phases which cannot be determined may occur. In practice such single observations are hardly important. However, these marginal phenomena may become important, too, — and therefore they should be examined. In this paragraph only few examples are mentioned.

Several hygroscopic compounds which are preferably formed under reducing conditions belong — amongst others — to these “unknown” phases. As these constituents are immediately covered with a film of water when exposed to the normal air-moisture, special methods are needed to observe them.

Fig. 101, Fig. 102 (polarized reflected light): Section of a blast furnace clinker burned under reducing conditions. Fig. 102 has been rotated clockwise around 90°.

The strongly reflecting part in form of a “J” (40/42 in Fig. 101, 51/40 in Fig. 102) is probably titanium carbide or titanium nitride carbide  $Ti(C,N)$ . It is fairly common in metallurgical products, but, — as it requests unusually high titanium contents — not to be expected in normal cement clinker. Beside, graphite in typical spheruliths, particularly clear in the direct vicinity of the  $TiC$  crystal. The reflection-pleochroism and the migration of the dark and bright areas of the spherulith according to the respective plane of vibration of the incident light beam to be noticed. In the surroundings Alite and ground-mass.

Fig. 103: Formation of a drop (50/30) on the surface of the sample, caused by an unknown hygroscopic constituent.

Fig. 104: Hygroscopic constituents cause the formation of drops in form of black beads on the surface of the sample, especially on the edges of Alite crystals, i.e. in the ground mass. The latter consists mainly of Aluminate, which is darker than Alite. Beside, white, metallic iron and grey-white calcium sulfide.

## 3.7. Sources of errors

Beside the above mentioned clinker phases, phenomena which are quite difficult to explain for beginners can be observed quite often on the microscope. A large part of them is caused either by anomalous optical effects or by wrong methods of preparation. Some of these phenomena are treated in the following paragraphs.

### 3.7.1. Pores

Every normal cement clinker contains a lot of pores. When embedding, as many pores as possible should be filled with the embedding medium. According to the respective reflecting power of the impregnating medium the pores appear brighter or darker, but mostly with smooth, structureless surface (see Figs. 1, 33, 41, 64, 68, 135). However, it is usually not possible to impregnate all the pores entirely with resin. Open pores appear black on the microscope. The edges of these air-holes are characteristically rounded off; so they cannot be brought into focus (see Figs. 47, 61, 116, 133, 145).

Other pores can be filled partially with impregnating mass. It is also possible that the resin contains air-bubbles, which appear as rounded, black spots (see Figs. 117, 120).

Sometimes open pores are filled up with polishing paste during polishing. In this case they reflect diffusely in the colour of the polishing agent: Magnesia and Alumina white, chromic oxide green (see Fig. 31).

### 3.7.2. Internal reflections

All the normal clinker phases are transparent in thin sections. Only a small part of the incident light is reflected. A much larger part is absorbed or transmitted resp. through the transparent phases. It may

occur that an incident beam is reflected from a crystal face or a cleavage surface in such a way, that it reaches again the path of rays of the microscope. In this case the crystal lights up brightly. This so called “internal reflection” shows the colour which would appear in smallest fragments of the crystal. Apart from this possibility to determine the colour, internal reflections have no further importance.

Sometimes it may be difficult to decide whether a brightly reflecting area is an internal reflection or another phase. This question is easiest to answer by “playing” with the fine adjustment. Internal reflections don’t get out of focus, but they “undulate” restlessly.

Fig. 105: Large internal reflection in an Alite crystal (40/40). (Compare Figs. 46, 49, 59, 71, 123, 140).

### 3.7.3. Newton rings (Interference stripes)

If a crystal is cut in very small angle to its surface, the appearance of so called Newton rings at its border with the next crystal is possible. They are a consequence of an interference between the beam reflected at the surface of the section and the beam reflected at the crystal face below. Newton rings may sometimes be confused with zonal construction of the crystal (see Figs. 7, 15, 52, 140).

### 3.7.4. Grinding scratches

Almost every normally prepared polished section shows grinding scratches. Especially after etching these scratches are clearly to observe.

Sometimes it may be difficult to distinguish scratches from structural characteristics, as for example cross-stripping of Belite. Scratches are always straight lines over wide ranges of the field of vision, and accordingly over several crystals, while cross-laminas in Belite are strictly determined by the orientation of a single crystal. They cannot continue in a neighbour crystal with different crystallographic orientation. Numerous pictures show examples of grinding scratches (for instance Figs. 15, 16, 19, 29, 35, 37, 40, 60).

### 3.7.5. Ground clinker material

If a piece of clinker is not thoroughly cleaned after preliminary grinding, swarf may remain in its pores, where it is embedded by the impregnating agent. In this case fine splinters of clinker material, which partially fill the pores, can be observed on the microscope.

### 3.7.6. Grains of abrasive

Sometimes grains of abrasive (for example carborundum or corundum) may be stuck into the embedding medium during the grinding process.

After polishing they may easily be identified by means of their extremely strong relief. They could only be confused with Periclase, but Periclase crystals would not be loosely embedded in the resin (see Fig. 106).

Fig. 106: Two grains of corundum (45/25 and 50/65), embedded in resin. The broad, black edges, — a consequence of the positif relief — to be noticed. Beside corundum, splinters of ground materials (50/30) are embedded, too. They consist mainly of Alite.

Fig. 107: Ground lead (40/30) in the pores of the clinker.

### 3.7.7. Ground lead

If samples are ground mechanically by means of lead-polishing-wheels, ground lead is quite often found within the pores. It can be identified by means of its fairly high reflecting power and — above all — by means of its always coarse, irregular, often iridescent surface.

## 4. Structure of clinker

### 4.1. Synopsis

The structure of clinker is the manner of its construction of the different constituents, their composition, size and distribution. The structure is determined by the respective history of the formation of the clinker. So a critical examination of the structure may give as well informations about the chemical composition and the preparation of the raw material as about the firing and cooling process.

### 4.2. Macroscopic characteristics

Previous to the examination in transmitted or reflected light the *external appearance* of the clinker should be observed. The following phenomena may be found:

1. single clinker grains
2. clinker grains sintered together to a structure resembling to a bunch of grapes
3. larger, tight, compact clinker pieces ("blocks")
4. partially molten, usually brightly shining pieces, so called "Schmolz" (= molten mass)
5. irregular aggregates; — above all fragments of the above mentioned types; usually small splinters, formed by suddenly chilling of clinker grains.

The *form* of the clinker grains depends largely on the type of the kiln:

Single clinker grains are typical for rotary kilns. Clinkers from Lepol kilns show usually a much uniform distribution of the grain sizes than clinkers from other types of dry- or wet-rotary kilns. On the other hand compact clinker blocks and molten pieces ("Schmolz") occur quite rarely in normal rotary kiln plants, but much more frequently — together with bunches of clinker grains — in blast furnace plants.

Beside the form the *surface* of the clinker should be observed, too. It can be:

1. smooth
2. rough, more or less easy to abrase
3. dull
4. glistening, due to undisturbed growing of small crystals on the surface, or
5. rounded and knobby.

The *colour* of the clinker may be a very sensitive indicator for the conditions of firing. It is estimated on a cross-section which should be moistened. As water attacks the clinker strongly, it should be moistened by glycerine or — even better — by 1,4-Butane-diol.

The raw material goes during firing through different shades: Earth-brown (khaki) — bright yellow-brown — deep brown — dark brown. A normal clinker becomes finally blackish with a green-brown tinge. So, weak firing may be detected by means of the colour.

Every cement containing iron oxide is more or less intensively coloured. All the major phases are brown coloured due to — mostly very limited — formation of solid solutions with  $Fe_2O_3$ .

Ferrite is the constituent which gives the clinker its colour. While pure Ferrite is deep brown coloured (with a slight reddish tinge), even small impurities of magnesium change its colour to brown-green. As all the raw materials for the production of clinker contain a certain amount of magnesium, the brown-green Ferrite is quite typical for normal technical clinker: It gives the cement its characteristic, slate-grey colour. The brown-green colour of Ferrite is removed by traces of  $Fe^{2+}$ : It becomes red-brown again, just like in magnesium-free clinker (compare colour photographs 2, 3, 5).

The clinker is coloured dark grey with a reddish tinge if the iron is partially substituted by manganese. Ferrite containing manganese is red-brown coloured even in presence of magnesium.

A clinker can be uniformly coloured, but sometimes it is irregularly spotted. Regular, concentric colour-zones can be observed quite often, too. These colour-variations point to differences of the chemical composition or of the firing conditions.

Every normal Portland Cement clinker contains holes and pores. Their shapes and their arrangements should be observed, too. A lot of important information about the relative sizes of the pores and their distribution across the cross-cut may be obtained from big clinker pieces. The pores are usually irregularly arranged in streaks and bands or in concentric rings (shells).

### 4.3. Microscopic characteristics

#### 4.3.1. Porosity

In a wider sense the pores of clinker can be interpreted as an additional, gaseous phase. At the sinter-temperature materials are exchanged between the solid and liquid phases, while the pores are inert. Under normal conditions of firing a diffusion of — for example — Ca or Si through the pore is not possible (however, see Fig. 135). Parts of Belite and free lime which are separated by a pore can be observed quite often. Belite and free lime would certainly have combined, if they would have been in contact with each other (see Figs. 108, 109).

Size and distribution of the pores are easiest to observe at low magnifications (see Figs. 110–114).

Fig. 108: Part of a very porous clinker. Materials can only be exchanged imperfectly over narrow "bridges". (Compare Fig. 109).

Fig. 109: Clinker with an unusually large content of pores and consequently imperfect reaction. Numerous black free lime nests (35/35), beside light-grey Belite (65/35) and etched Alite. The pores are filled with medium-grey resin.

Fig. 110: Fairly porous clinker. The pores are filled with medium-grey reflecting resin. Beside, more or less dark-coloured free lime nests (73/15) with strong relief.

Fig. 111: Rotary kiln clinker with a low content of pores.

Fig. 112: Rotary kiln clinker with a high content of pores.

Fig. 113: Rotary kiln clinker made from not granulated raw material. Formation of a larger grain by winding up smaller grains. Accumulation of finer clinker grains on the surface of a larger one.

Fig. 114: Pores and concentric shrinkage cracks. The contrasts are improved by colouring the resin with white  $TiO_2$ . Inclined light.

Shape and distribution of the pores depend essentially upon the chemical composition of the clinker, the distribution of the particle sizes in the raw material and the system of furnace. Therefore conclusions from the distribution of the pores to the firing conditions are only to be drawn, if the clinkers in question have been burned in a kiln of the same type and — exactly — of the same work.

The determination of the specific gravity (weight per liter) has proved in practice to be a fast and useful method for the comparison of the degree of firing. The specific gravity measures the whole pore space of a certain clinker fraction. These specific gravity values depend upon the system of the kiln, too. Clinkers burned in kilns of different systems cannot be compared in this way. The decisive value is not the total volume of the pores, but the form and distribution of the air-holes which separate two reactive clinker parts.

#### 4.3.2. Homogeneity

In a homogeneous clinker the distribution of the pores and the solid parts would be more or less statistical. Within the solid parts the distribution and the form of the clinker phases would be uniform, too. This ideal state can only be reached under laboratory conditions (see Fig. 127).

Technical clinkers are only seldom homogeneous in form and distribution of the phases.

The following paragraphs describe inhomogeneities in clinker and their possible causes:

#### 4.3.2.1. Variations in compositions

The chemical composition of a clinker may fluctuate around a certain theoretical value, — locally as well as temporarily. These inhomogeneities may be caused either by variations in the composition of the raw material or by phenomena such as oversize-grains, disintegration etc. They cause the formation of spots and streaks in the clinker.

A homogeneous distribution of free lime, — for instance — suggests a high CaO-content of the clinker. However, only checking of several samples over a longer period will show whether the CaO-content has been generally too high or just due to a temporary variation of the composition of the raw material. Chemical analysis can only seldom give an answer to this question.

#### 4.3.2.2. Spots in clinker

“Spots” in clinker are caused by very limited, local inhomogeneities: Certain constituents of the raw material have not completely reacted during firing or have not been resorbed homogeneously by the clinker. The nests can be interpreted as spots, too (see paragraph 4.3.2.3.). A spotty distribution of the clinker phases — above all Belite and free lime — may have many different causes:

Spotty structures may be caused by too low degrees of firing (either too low firing temperature or too short time of firing). A characteristic of both these causes is a small “depth of reaction”: Belite and free lime have only reacted in narrow spaces. An additional characteristic of too low firing temperatures is a high porosity.

Insufficient homogeneity of the raw material may also cause a spotty structure of the clinker. If this cause is suspected, the overall-composition of the clinker has to be examined: Spots of free lime could be caused by an excess of lime, and Belite spots could be a consequence of a too low lime-content. However, under normal conditions of firing an adequate “depth of reaction” is to be expected.

Fig. 115: Regular distribution of the clinker phases. Etched, medium-grey Alite and light-grey Belite. In the ground mass whitish Ferrite. The black spots are pores.

Fig. 116: Free lime, homogeneously interspersed in the clinker.

Fig. 117: Spotty distribution of free lime (for example 65/45) in a very porous clinker, caused by too low firing temperature. Beside, silicates and interstitial mass. The distribution of the light grey Aluminate and the whitish Ferrite in the ground mass is spotty, too. The pores are filled with resin, which is partially scratched. Dark spots in the resin are air-bubbles.

Fig. 118: Spotty distribution of the clinker phases. Narrow Alite border between parts of Belite (70/40) and free lime (25/40), caused by too short time of firing.

Fig. 119: Black and dark-grey spots of free lime. Beside, parts with high content of Alite in an interstitial mass of high Ferrite-content. Large, dark spots are pores (20/15 and 90/10).

Fig. 120: Spotty distribution of the clinker phases. Beginning formation of nests. Light-grey Belite (for example 50/15) and dark-grey Alite (45/30). In the surroundings of a free lime nest (20/40) Alite is etched weaker, because the etching reagent ( $\text{HNO}_2$ ) has been neutralized by CaO.

#### 4.3.2.3. Nests

“Nests” are sharply limited, irregular enrichments of a mineral in clinker. They are formed from larger grains (oversize grains) in the raw material which cannot be completely resorbed during firing. Under normal conditions of firing grains larger than 0.1 mm cannot be expected to be completely resorbed. The outlines of these nests are usually still those of the original grains. The composition of a nest depends upon the nature of the original grain.

Belite nests demonstrate places of low lime-content in the raw ma-

terial, such as — above all — splinters of quartz and drops of ash (from the flame of the furnace).

Fig. 121: Free lime nest (60/25), giving evidence of an original lime-splinter in the raw material.

Fig. 122: Nest of dark-grey free lime (50/40) and medium-grey Periclase (with positif relief), caused by an oversize grain of Dolomit.

Fig. 123: Belite nest with Belite showing crossed laminas. It contains no interstitial mass and gives evidence of an original quartz grain in the raw material.

Fig. 124: Belite nest, caused by a grain of blast furnace slag, which has been conserved in the middle of the nest (50/40).

In normal clinker quartz reacts always with CaO to form Belite. Silicates with lower content of lime or even residues of quartz or cristobalite are usually not existing.  $\text{SiO}_2$  is highly mobile at the sinter-temperature and migrates to places with higher lime contents. In this way fairly typical pores, surrounded by a thick border of Belite, are formed (see Fig. 125). As details about this migration are not known, it is not possible to derive the original shape of the  $\text{SiO}_2$ -source (the quartz grain) from the outlines of a Belite nest.

A Belite nest containing a lot of interstitial mass demonstrates usually an enclosure of ash, while a Belite nest with a low content of interstitial mass can be brought back to a quartz oversize-grain. A clear distinction between these two types of Belite nests is rather difficult, as beside quartz and ash other constituents (for example feldspar and blast furnace slag) may cause the formation of Belite nests, too.

Free lime nests (Fig. 121) are formed, if a large grain of lime is not completely resorbed during the reaction period. Sometimes these nests show still the outlines of the original grains.

Nests formed due to dolomite grains contain beside free lime periclase crystals.

It is often very difficult to distinguish variations in the composition from a distribution in form of spots or nests.

The different shapes and the formation of nests can be observed in Figs. 125–128, where clinkers are compared with the respective raw materials.

Fig. 125: Laboratory-clinker, fired 20 minutes at 1450 °C, prepared from normal raw material. Different sizes of the Alite crystals and an accumulation of Belite around a fairly large pore are characteristic.

Fig. 126 (polarized reflected light): Normally prepared raw material, containing larger pieces of lime and round residues of lime-organisms. The structure of the fragments is clearly shown due to the high reflection-pleochroism of Calcite (35/55).

Fig. 127: Clinker prepared from the same raw material as the clinker in Fig. 125. The raw material has been reground in a colloid mill and fired 20 minutes at 1450 °C. Alites of approximately uniform size; among them homogeneously interspersed Belite. The distribution of all the constituents has become more homogeneous.

Fig. 128 (polarized reflected light): The same raw material as in Fig. 126, reground wet during 5 $\frac{1}{2}$  hours in the colloid mill.

For reasons of economy the raw materials for technical clinkers cannot be ground as finely as an ideal homogeneity would request. In order to obtain a clinker with a high content of lime, but a low content of free lime, the raw material has to be particularly homogeneous.

#### 4.3.2.4. Streaks (“Schlieren”)

“Streaks” are accumulations of a phase formed due to variations of the chemical composition within a clinker grain. They can be caused by insufficient homogeneity of the raw material. It is to be noticed that a well homogenized raw material may disintegrate again, — for instance — due to formation of dust during pneumatic conveying or



on running out of silos. Disintegration in the kiln is possible, too. The different reasons for the formation of streaks cannot always be distinguished on the microscope.

Typical Belite streaks are quite often formed on the surface of clinker-grains which have been burned from granulated raw material with coal rich in ash. The ash falls on the surface of already preformed grains, where it forms a zone with low content of lime. On firing Belite is formed in this zone. Similar Belite streaks can be formed if furnace dust with low content of lime is deposited on the clinker grains.

The surface of such a clinker grain is usually formed by a covering layer of "normal" composition. It consists of ground, abraded material which has been wound up — on the Belite layer — within the kiln.

**Fig. 129:** Large streaks of free lime (30/20), caused by disintegration of the raw material.

**Fig. 130:** Typical Belite streak (15/20) on the periphery of a clinker grain burned in a Lepol-kiln.

#### 4.3.2.5. Variations of the crystal-sizes

The size of the crystals in a clinker may vary in wide ranges. The crystal-growth depends upon the temperature, the time and the chemical composition of the surroundings. Variations of these parameters may therefore cause different sizes of the clinker phases. Different sizes of Alite crystals in one clinker, for instance, point to absorbed nests or former inhomogeneities.

Larger crystals are usually formed at higher temperatures and during longer firing periods. In surroundings of low content of lime, i.e. in the neighbourhood of Belite, Alite tends to form larger crystals. On Fig. 132 the causes of the different sizes of the Alite crystals cannot be detected.

**Fig. 131:** Ash deposited on the surface of two Lepol-kiln-clinker grains has induced the formation of a Belite border (53/50). In the sinter-zone the two grains have been joined together. They have wound up together a cover-layer of ground material.

**Fig. 132:** Irregular formation of Alite crystals. (Compare Fig. 125).

#### 4.3.2.6. Differentiation of the molten mass

Differentiation is only possible in the molten ground mass. The molten phase can, for example, migrate from certain parts of the clinker to the peripheral zones where it will be enriched. It is also possible that certain constituents of the molten mass are separated from others.

#### 4.3.2.7. Reaction borders on the surface of pores

Sometimes higher concentrations of Belite or free lime can be observed on the surface of pores. The reasons for such a higher or lower contents of  $\text{SiO}_2$  (eventually also  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ ) may be various. They cannot yet be explained satisfactorily.

The formation of a Belite border around former quartz grains and the simultaneous formation of a pore have already been mentioned above.

Beside that, other, completely different kinds of reactions may occur. The formation of free lime borders is chiefly found in clinkers fired under reducing conditions. Reactions like for example the volatilization of Si as  $\text{SiO}$ , i.e. reactions in the gas phase, are supposed to be important in this case. Volatilization of Si is not possible in case of firing under oxidizing conditions.

**Fig. 133:** High concentration of interstitial mass in the marginal zone of a clinker grain (40/40).

**Fig. 134:** Black streak of free lime on the surface of a pore (35/30). (Si can diffuse into the clinker substance, if it is mobilized!) The free lime streak is followed by a narrow, etched Alite border (35/40). The normal clinker substance follows after a zone of not etched Belite. In the interstitial mass whitish Ferrite and dark-grey Aluminate.

**Fig. 135:** High concentration of light-grey Belite on the surface of a pore. Beside that, normal clinker substance with medium grey Alite and not differentiated interstitial mass.

#### 4.3.3. Structure of the ground mass

At the sinter temperature the ground mass is a fairly homogeneous, liquid phase. During cooling several phases crystallize from the molten mass, namely Aluminate and Ferrite, subordinately also Belite and sometimes even Alite or free lime and periclase.

These phases form large, individual crystals, provided they dispose of sufficient time. As the clinker is usually chilled in the cooler, the crystal growth is disturbed; instead of large crystals an intimate mixture of small crystals is formed.

The following illustrations (Figs. 136–147) give an impression of the large variety of structures which can be found. The first pictures show quickly chilled, the later ones slowly cooled clinkers. The structure is chiefly determined by the composition of the molten mass, especially by the alumina-modulus. However, other constituents, — for instance alkali — have a certain influence, too. For a critical examination of the cooling rate other phenomena — as for example corrosion of Alite, Belite fringes around Alite, secondary separations from the ground mass etc. — should be considered, too.

Separations of secondary Belite, free lime or Periclase and disintegration of crystalline phases point infallibly to a low rate of cooling (see Figs. 144–147).

**Fig. 136:** Quickly chilled clinker with an alumina-modulus of 2.0, prepared in a wet-rotary kiln. Beside Alite round Belite grains. The interstitial mass is hardly differentiated.

**Fig. 137:** Relatively quickly cooled clinker. The interstitial mass is clearly differentiated, but the crystals are still small. In some places Belite-borders around Alite-crystals.

**Fig. 138:** Relatively quickly cooled clinker. The ground mass consists of a typical intimate mixture of fine crystals.

**Fig. 139:** Normally cooled clinker. Aluminate and Ferrite are already clearly differentiated.

**Fig. 140:** Slowly cooled clinker. Aluminate and Ferrite are clearly differentiated. Belite-borders around Alite. Secondary Belite in the interstitial mass. (Compare Fig. 15).

**Fig. 141:** Slowly cooled clinker containing alkali. Laminas of idiomorphous, dark-grey Alkali-aluminate. Alite with polishing-scratches. Whitish Ferrite. Beside, rounded grains of free lime.

**Fig. 142:** This structure of the ground-mass cannot yet be explained satisfactorily.

**Fig. 143:** Different structures of the ground-mass. Between Alite and Belite Aluminate and Ferrite containing small enclosures of secondarily separated Belite (for example 85/15). This clinker shows all the characteristics of a low cooling rate. However, an enclosure in Alite (50/35) contains an intimate mixture of finely crystalline ground-mass, which cannot be quicker cooled than the interstitial mass surrounding the Alite crystal. Obviously the ratio Ferrite : Aluminate : Belite in the enclosure is essentially different from the ratio in the surrounding ground-mass. The picture demonstrates that the cooling rate cannot be derived from the structure of isolated parts of the ground-mass.

**Fig. 144:** Secondary Belite in very fine enclosures, especially in Aluminate (40/20), but also in Ferrite (65/42). Belite fringes around Alite.

**Fig. 145:** Small, dark, secondary Alite crystals in a ground mass of mostly Ferrite.

**Fig. 146:** Secondary separations of free lime (60/26) in the ground mass of a clinker with high iron content.

**Fig. 147:** Disintegration-particles of Belite (87/25) and Periclase (50/60) in Aluminate (80/35). The crystal edges of all the light-grey Periclase-enclosures are parallel to each other and to these of the medium-grey Belite particles which have been separated simultaneously. They correspond to the crystallographic orientation of the "host"-Aluminate crystal. This disintegration from Aluminate in solid state is not to be confused with secondary separations from a molten mass.

## 5. Quantitative determinations

### 5.1. Linear measurements

An ocular-micrometer fitted with a linear scale is used for linear measurements on the microscope. This instrument has to be calibrated with the scale of the ocular. Then the covered divisions are counted. Multiplication with the calibration factor gives the length in mm.

The determinations are carried out on microscopical preparations (see p. 12 et seq.). The particles to be measured are caused to coincide with the scale of the ocular. Then the covered divisions are counted. Multiplication with the calibration factor gives the length in mm.

By means of an integration-table or an integration-ocular the length of several constituents may be measured. Textbooks of crystal optics and the respective instructions for use give further information about these special instruments.

### 5.2. Square measurements

Square measurements are carried out similarly to linear measurements. Instead of oculars with length scales, oculars with squares or circles are used. These calibrated areas are caused to cover the object; then the covered areas are counted.

For more accurate determinations the surface-area of the objects is measured on micro-photographs by means of a planimeter.

### 5.3. Determination of particle sizes

Particle sizes can be determined by measuring lengths or areas. Accurate measurements are only possible on "scatter-preparations".

Polished sections usually show only parts of the real particle sizes, as the grains are only cut. The surface of the sections is usually not average, but smaller. So the measured particle size is smaller than the real one. An approximately correct result is only to be expected, if irregular, directionless granular samples are examined.

(The determination of the real particle size on random sections is described by H. Muenzner, Zur Ermittlung der Kornverteilung von An- und Duennschliffen, Mitteilungsblatt fuer math. Statistik, 5 (1953), p. 167-176.)

### 5.4. Quantitative determination of the percentage of the clinker phases

For quantitative determinations the surface shares of the different phases, which correspond to the volume shares, are determined. This procedure requires clearly discernible particle borders. For cement and clinker this is only possible in polished sections. Care must be taken to measure an area which is representative for the whole volume. This condition is usually only fulfilled in case of unoriented granular structures. Sufficiently large samples must be prepared from clinkers containing nests or zonal distribution of the mineral-phases.

The determination on the polished section can be carried out in different ways:

#### 1. by means of a planimeter:

The surface area of the different phases is measured on a micro-photograph of the sample. As this procedure is very complicated — it requires a large number of photographs and a lot of time —, it has no practical importance.

#### 2. by linear measurements:

Straight "guide-lines" are drawn in equal distances on the picture. Then the intercepts covered by the different phases are measured. The sum of all the intercepts ( $A$ ) of a phase, divided by the totally measured length, equals the percentage of the respective intercepts, which is proportional to the volume:

$$\text{Vol\% M}_1 = \frac{\sum A_{M1} \cdot 100}{\sum (A_{M1} + A_{M2} + \dots + A_{Mx})}$$

$x = 1, 2, \dots, n$  means the respective kind of mineral.

#### 3. by-counting points:

A regular grid of points is drawn on the picture. The different mineral phases are covered by a random, statistically determined number of points. These impacts are counted for each phase. The percentage of the respective volumes is calculated as in case of linear measurements.

Every ocular containing a grid can be used for this method of determination. Thereby the grid is projected on the picture already enlarged by the objectif. It is possible to count at very high magnifications; so even fine enclosures — as for instance Belite in Alite, free lime, Periclase etc. — can be determined, also the interstitial mass can be resolved clearly.

#### Interpretation of the measurements:

All quantitative determinations on the microscope give volume percentages. Multiplications with the respective densities gives weight percentages. Every volume is multiplied with the corresponding density and divided by the sum of the weights of all the volumes.

Density of the clinker phases in  $\text{g/cm}^3$ :

Alite	3.20
$\alpha$ -Belite	3.07*
$\alpha'$ -Belite	3.31**
$\beta$ -Belite	3.28
$\gamma$ -Belite	2.97
Aluminate	3.04
Ferrite: $C_4AF$	3.76
$C_2F$	4.01
$C_6A_2F$	3.71
Free lime	3.35
Periclase	3.58

\* at 1500 °C, \*\* at 700 °C

These densities are valid for the pure phases. They may differ from the densities of the actually existing phases. So small irregularities of the measurements can be entered into this calculation.

## 6. Determination of the clinker and slag content of cements

### 6.1. General hints

In this paragraph the name "slag cement" is used for standard (norm) cements consisting of cement clinker, granulated basic blast furnace slag and a sulfate containing constituent. Their compositions are defined in the German cement norms DIN 1164 and DIN 4210:

- Eisenportlandzement (Iron-Portland cement)
- Hochofenzement (Blast furnace cement)
- Sulfathuettenzement (Sulfuric acid plant cement)

The determination of the clinker and slag content serves to operational controls, controls of norms or quick checking on sites of construction, when they are used to mix concretes with special properties.

This paragraph gives only general hints for such determinations and microscopical characteristics of Portland cement clinker and slag.

The clinker and slag content can be determined as well in transmitted as in reflected light. Examinations in transmitted light are carried out on a polarization microscope. This instrument allows the observation of the double refraction — a very important property for the determination of minerals — beside external characteristics, as for example form of the grains, transparency, formation of single crystals and light refraction.

For non-glassy blast furnace slag counting in reflected light has proved to be most effective.

The composition of slag cements is determined on grain preparations. The samples must be especially prepared, as a satisfactory examination

of normal cement is not possible. The existence of particles of different size (under  $1\ \mu\text{m}$  – over  $100\ \mu\text{m}$ ) makes an observation very difficult. Besides every cement contains a large amount of finest particles (smaller than  $10\ \mu\text{m}$ ) which often tend to agglomerate and which cannot be definitely determined on the microscope. The quantitative determination of the constituents by simple counting of particles is impossible in samples containing particles of different size. The other methods of quantitative determinations of phases (planimeter, linear measurements, counting of points; see paragraph 5) give also inaccurate results when applied to such samples, as the finest particles are not considered.

The examination of grain fractions with very limited range of particle sizes has proved to be most suitable. These fractions must fulfill – above all – two conditions:

- a) the particles must be resolved by the microscope
- b) the composition of the fraction must correspond to the composition of the original cement.

Fractions of grains of  $30\text{--}40\ \mu\text{m}$  usually fulfill these conditions. The fraction of  $60\text{--}90\ \mu\text{m}$  used to be examined in former times. Modern cements are ground finer; so the composition of this fraction usually does no more correspond to the composition of the original cement.

(\* K. Grade, Die Bestimmung des Hüttensandgehaltes in Hüttenzementen, Schriftenreihe der Zementindustrie, Heft 29, p. 113–140 gives a detailed review of the determination methods mentioned till now in the literature.)

## 6.2. Microscopical characteristics

### 6.2.1. Clinker

The clinker grains of the fractions which are used for microscopical examinations show usually rounded outlines. Almost always they consist of several individual crystals. Due to their Ferrite content grains appear more or less brown coloured; sometimes green shades are observed. The refraction indices of the major clinker phases Alite and Belite are between 1.69 and 1.72, i.e. much higher than the refraction indices of the usual embedding media. Due to this big difference of the refraction indices the clinker grains show a very strong relief. So even slightly coloured grains and small fragments of not coloured single crystals appear relatively dark in transmitted light.

In polarized light between crossed Nicols Alite and Belite crystals light up four times in more or less bright light-grey to white-yellow shades when the stage is turned.

In polished sections clinker and slag grains can be distinguished after etching with one of the etching reagents mentioned in paragraph 2.4. For example 0.001 % alcoholic  $\text{HNO}_3$  etches the major constituents of clinker, Alite and Belite, more or less strongly. In the slag grains only dicalcium silicate and Merwinite, which occur only in small amounts, are etched. The large percentage of glass, which is characteristic for slag, and the predominant slag mineral Melilite are not etched at all (see Figs. 148–151).

### 6.2.2. Slag

By far the largest part of the slag grains is – due to the quick chilling of the liquid slag when granulating – amorphous (glassy). The grains show splintery outlines and shell-shaped surfaces of fractures. They are usually colourless and transparent in transmitted light. The slag glass has a refractive index between 1.62 and 1.67. These grains remain – due to the optical isotropy of the glass – dark when the sample is turned. Sometimes the amorphous ground mass contains enclosures of Millite, dicalcium silicate, Merwinite and other slag minerals. This is slightly more common in strongly basic slags. While dicalcium silicate is almost always rounded, the other slag minerals show quite often a skeleton-like shape. When turning the stage these crystalline constituents light up more or less brightly in white, grey or yellowish shades.

In polished sections the slag glasses are only etched by HF-solutions. By treating with HF-vapour they are coloured.

Entirely crystalline slag grains are only rarely found in slag cements. They consist of the above mentioned slag minerals. The light refraction of most of the slag minerals is about the same as the light refraction of the slag glass, i.e. between  $n = 1.61$  and  $1.67$ . So it is much smaller than the light refraction of the major clinker minerals. Therefore slag grains – amorphous or crystalline – show a much weaker relief in the embedding medium than clinker grains. Beside the shape, the weak relief is a second characteristic of slag grains. The formation of crystal skeletons, which has been already mentioned on the crystal enclosures in the slag glass, can often be observed in crystalline slag grains. It is a further characteristic of slag grains, as the constituents of clinker are usually well crystallized.

Sometimes the grains are as fine that it is impossible to determine their light refraction or their double refraction in transmitted light. Polished sections cannot be prepared neither. In such cases the examination of the sample in ultraviolet light proves to be suitable. Opposite to clinker grains, slag grains fluoresce in different colours when irradiated with ultraviolet light of short wave length, as it is emitted, for example, by a quartz burner. Glassy slag grains show pink, red or brown, crystalline slag grains blue or violet fluorescence colours. Clinker grains don't light up at all. Thus this fluorescence makes it possible to distinguish definitely the different constituents even in samples containing very finely crystalline fractions. Opposite to the normal technique these examinations must be carried out without embedding the scattered sample, as all the usual embedding media fluoresce themselves intensively in white to yellowish shades, which are brighter than the fluorescence colours of the slag grains embedded in it.

Fig. 148 (transmitted light): Polished thin section of a slag cement, fraction  $40\text{--}60\ \mu\text{m}$ . Slag (65/15, 70/40, 50/40, 35/40, 30/55, 20/0). All the other grains are clinker grains.

Fig. 149 (reflected light): Polished thin section of a slag cement, fraction  $40\text{--}60\ \mu\text{m}$ . Same area as Fig. 148, not etched.

Fig. 150 (reflected light): Polished thin section of a slag cement, fraction  $40\text{--}60\ \mu\text{m}$ . Same area as Fig. 148, etched with alcoholic  $\text{HNO}_3$ .

Fig. 151 (reflected light): Polished thin section of a slag cement, fraction  $40\text{--}60\ \mu\text{m}$ . Same area as Fig. 148, etched with alcoholic  $\text{HNO}_3$  and HF vapour.

## 7. Mineralogical expressions

### Anisotropy

Different behaviour of a body (for example a crystal) in different directions in space. The double refraction of non-cubic crystals is – for example – a consequence of different light refraction in different crystallographic directions.

### Dendrites

Crystal-“skeletons”, resembling branches, fern or trees. They are usually a consequence of fast growing. Typical examples are snow crystals or – in Portland cement clinker – calcium sulfide (see Figs. 94, 95) and secondary Periclase (see Figs. 84, 85).

### Habit

Overall-shape of a crystal, determined by the proportions of the different forms. For example Alite formed by solid state reaction is compact, whereas from a molten mass thin-tabular Alite crystals are separated.

### *Idiomorphous*

Crystals which have developed their own, typical shape during their formation are called idiomorphous. Examples: Alite (see Figs. 17, 23) or – very rarely – Aluminate (see Figs. 71, 72, 73).

### *Isotropy*

Similar behaviour of a body in all directions. Glass is usually isotropic. Cubic crystals are also optically isotropic. However, they can be distinctly anisotropic in other properties, as for example cleavability, growth, behaviour to etching etc.

### *Modification*

Different structures of one compound. See also "polymorphy".

### *Myrmekit*

Intimate, dendritic mixture of two or more crystals of different composition, resembling worm-casts. Fig. 41 shows a typical example of a myrmekit.

### *Paragenesis*

Association of minerals depending on a certain history of formation. For example the paragenesis Alite, Belite, Aluminate and Ferrite is typical for normal Portland cement clinker.

### *Pleochroism*

Anisotropy of the light absorption.

A double refracting, coloured crystal shows in polarized light (polarizer only) different colour intensities and different shade of colours according to its orientation against the plane of vibration of the incident light beam. For instance tourmaline absorbs only weakly parallel to its longitudinal axis (crystallographic *c*-axis), but strongly in the perpendicular direction (it can be completely nontransparent, opaque). Analogously a Ferrite crystal in a thin section can be light-amber-yellow to dark-red-brown in polarized light, depending upon its orientation to the incident beam (see Figs. 2, 3).

### *Poikiloblastic*

Younger, strongly growing formations often enclose older constituents. In this way a poikiloblastic structure is formed. Examples: Enclosures of Belite in younger, strongly growing Alite (see Fig. 32).

### *Polarized light*

Normal light vibrates in all the planes around the direction of propagation as axis. In linear polarized light all the vibrations are in one single plane (plane of vibration).

### *Polymorphy*

Some compounds form different kinds of crystals under different conditions (temperature, pressure, impurities). Dicalcium silicate, for example, can occur in four different modifications,  $\alpha$ ,  $\alpha'$ ,  $\beta$  and  $\gamma$ .

### *Pseudomorphosis*

One chemical compound is removed by another one, but the external shape of the original compound is conserved.

### *Reflection-pleochroism*

Variation of reflecting power and/or colour of reflection of an anisotropic crystal when it is turned in polarized reflected light. See also "pleochroism" (see Figs. 98, 99, 101, 102).

### *Spherulite*

Globular, radiating aggregate (see Figs. 101, 102).

### *Structure*

1. crystal structure: sterical arrangement of atoms or atom-groups in the crystal lattice.
2. rock structure: form, size etc. of the constituent parts and their arrangement in the conglomerate. (For example fine granular, coarse granular, dendritic structure.)

### *Texture*

Arrangement of constituent parts; structure, for example directionless or streaked, banded texture etc.

### *Twins*

Symmetric, regular intergrowth of two crystals of the same type (also double twins, multiple twins). In case of polysynthetic twinning several individual crystals are grown together in such a way, that every third, fifth, seventh etc. crystal is oriented like the first, and every fourth, sixth, eighth etc. crystal is oriented like the second one.

### *Undulous extinction*

Irregular extinction of the interference colours of a crystal in transmitted light between crossed Nicols. It is due either to varying chemical composition within the crystal or to disturbances (for example compressive stress).

### *Xenomorphous*

Opposite to idiomorphous. Xenomorphous crystals cannot develop their own, characteristic shape due to hindrance during growing.