Optimization of the method for determination of the single periclase crystal size

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Abstract

Periclase crystal size of magnesia is an important characteristic parameter for magnesia raw materials, it will strongly influence the properties of these raw materials, especially the corrosion resistance. In this thesis, two methods for the crystal size measurements, the grid method ASTM E 112-96 (Reapproved 2004) and the lineal analysis are compared. Both methods show credible and accurate measurement results. The grid method is recommended as the general method for routine measurements in test work due to its efficiency. Lineal analysis can be used as an auxiliary method for more accurate requirements. To identify crystal boundaries clearly, etching of the polished sections with HNO3 or H2SO4 solution was applied. For the results of the grid method, the statistical analyses of crystal size measurements of fused magnesia differed for various brands. The crystal size of the blend material of magnesia clinker and fused magnesia always shows a higher standard deviation than that of the normal type of fused magnesia raw material. The secondary phases in the magnesia samples could be identified by chemical analyses and mineralogical characterization. For the samples investigated here mainly monticellite, merwinite, dicalcium silicate and tricalcium phosphate have been identified. The amount of the secondary phases is determined by the raw material purity.

Key word: Periclase crystal size; Grid method E 112-96 (Reapproved 2004); Lineal analysis; secondary phases; etching techniques

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1 Problem definition

For the basic refractories, magnesia is the most important raw material worldwide. Periclase crystal size of magnesia is an important characteristic parameter. The crystal size of periclase strongly influences the properties of the raw material, especially, the corrosion resistance. How to find accurate, effective and economical method of the periclase crystal size (PCS) measurements and to optimize this method is going to be investigated in this thesis.

In this thesis, the grid method for the periclase crystal size measurements has been used. For one magnesia type the grid method and lineal analysis are additionally compared here. Investigations of the statistical evaluation of deviation of the measurement results for the grid method are also included. Additionally optimizations of the visibility of single crystals at high purity magnesia clinker are carried out. At same time, the properties of fused magnesia raw materials are specifically characterized.

2 State of art

2.1 Fundamentals of crystal size measurements

In the period from 1852 until 1859 [1], dead burned magnesia was used for basic refractories in Upper Styria of Austria for the first time. Now magnesia products are applied all over the world. Magnesia clinker of refractory grade is already the most important raw material for basic refractories.

The mineral structure of periclase has been investigated by electron-microscopic micrograph since 1956 [2]. With the further developments for sintered and fused magnesia, the crystal size of the periclase became a very important parameter of evaluating raw material quality [3].

For the magnesia raw materials, the periclase crystal size is a basic quality classification and characterization feature of the raw material.

There are two major methods for periclase size measurement, the grid method and the lineal analysis. They both are used in the studies.

2.1.1 Grid method

The grid method is based on the ASTM standard E112-96 (reapproved 2004) [4] - Standard Test Methods for Determining Average Grain Size.

In ASTM standard E112-96, there are basic procedures for grain size estimation: comparison procedure, planimetric procedure and intercept procedure. The grid method is used for the comparison procedure.

The comparison procedure does not require counting of each crystal, but involves comparison of the grain structure to a series of grade images. There is a general deviation in this comparison. According to the ASTM standard, repeatability and reproducibility of comparison chart rating are generally ±1 crystal size number.

After the comparison between the average crystal size of one grain and a proper standard grid, the number of the gird can be noted. For a general measurement of a type of magnesia raw material, at least 60 grains in the polishing

samples should be measured. After the measurement, an average periclase crystal size of this material can be obtained.

2.1.2 Lineal analysis

As the ASTM standard E112-96 (2004) mentioned, the lineal analysis is a kind of intercept procedure [4]. This involves an actual count of the intercepted grains by a line or the number of grain boundary intersections within a test line, used to calculate the mean lineal intercept length.

According to H.Harmuth [5], the calculation of the mean crystal diameter is:

$$d_{mean} = 1.5 \times l_{mean} \quad (2\text{-}1)$$

d_{mean}: mean crystal diameter

l_{mean}: mean chord length

The mean chord length is the whole length of the line divided by the number of the chords.

With the above equation, the mean crystal diameter along the line is obtained. Then, with the measurements of several lines, the average crystal size of the whole sample can be calculated. To get liable results in minimum 500-2000 single crystals have to be measured [6].

2.2 Preparation techniques of samples for microscopical investigation

A polished sample is necessary for the microscopical investigation. The following is a usual process for the sample preparation by polishing [7]:

1) Crushing of the raw materials and screening into the different fractions.
2) Impregnation of the crushed raw materials with resin on a hot embedding press.
3) Pre-grinding of the samples.
4) Lapping the sample with cloth laps.
5) Etching of the polished sample for a better visibility of the single crystals during measurement (to clearly see small crystal boudaries).

For the accurate measurements on periclase crystal size, above step 4) and 5), it is very important to get higher polished quality and better visibility of the crystal boudaries. By the research of W.E.Lee and W.M.Rainforth [8]: cloth laps (felt, cotton or silk) have been successfully used for grinding and polishing. The surface of cloth is so sufficiently compliant that it can well keep in contact with the surface of the polishing. Due to the difference of hardness between periclase crystal and the secondary phase in the crystal boundary, a relief effect on the polished surface can be reached, which is favorable for the PCS measurements. The following photo is a typical polishing machine.

Fig. 1 polishing machine [resource RHI AG, Leoben]

Etching is also an important auxiliary method to improve the visibility of various crystals and their boundaries of the polished samples [9]. Etching techniques used for polycrystalline ceramics are chemical etching, thermal etching and plasma etching. For the periclase crystal size measurement in laboratory, chemical etching is a very efficient method and frequently used. Chemical etching of ceramics usually requires particularly corrosive fluids since ceramics are generally corrosion resistant [8]. The fluids normally used include strong acids, alkalis and molten salts. By the attack of the fluids, the boundary between the crystals will partly be dissolved. A relief effect will be present. This is beneficial for the visibility under the microscope. Strong acid is recommended for PCS measurement, because of the basicity of magnesia crystal itself and the secondary phase.

2.3 Characteristics of magnesia clinker and fused magnesia

Magnesia refractories are the most important type of basic refractories [10]. The general manufacturing processes and characteristics of sintered and fused magnesia raw materials are described as follows:

2.3.1 Manufacturing of magnesia clinker and fused magnesia

Magnesia clinker is classified as two mainly groups: natural magnesia clinker, and synthetic magnesia clinker. Natural magnesia clinker is fired in the shaft kiln or rotary kiln at 1800-1900˚C, Synthetic magnesia clinker is produced from seawater or salt brine, After the decomposition of the $Mg(OH)_2$ from the seawater or salt brine, MgO will be fired in shaft or rotary kiln at 1500-1900˚C [10].

The process could be one calcination step or two calcination steps that include pre calcination. According to the reference [11], sintered magnesia with pre calcination (850˚C, 1hour) could help the firing of the magnesia to increase the density and decrease porosity.

Fused magnesia is produced in the electric arc furnaces (EAF). The raw material is molten by the high voltage of three graphitized carbon electrodes of the electric arc furnace. The following is a schematic diagram of a Higgins type EAF [12].

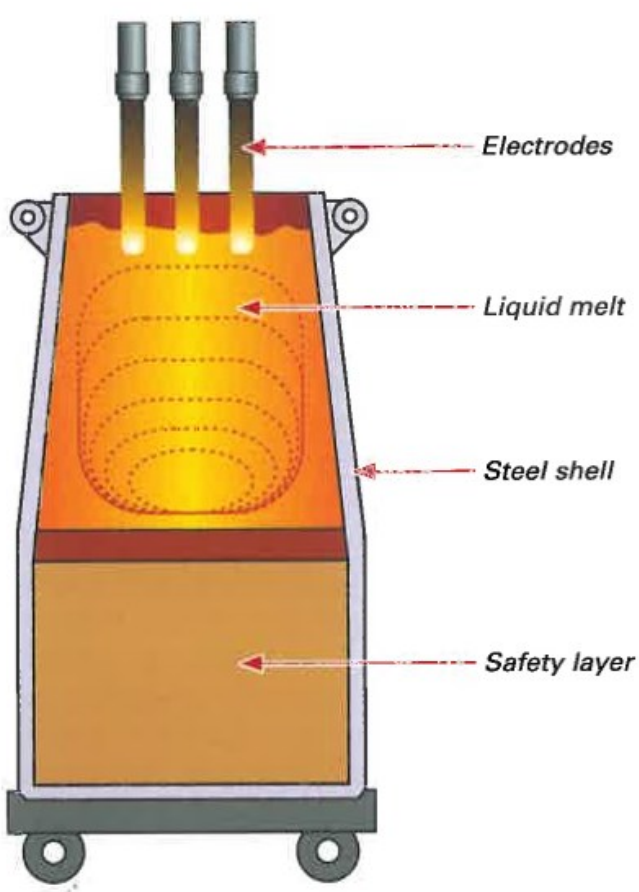


Fig. 2 Schematic diagram of a Higgins type EAF (RHI Bulletin 2011-2)

The Higgins type electric arc furnace includes a water-cooled steel shell. To start the process, a carbon layer is used. After the starting sequence (i.e, heating up of the vessel and formation of the first melt), the raw material will be fed into the furnace and fused stepwise.

According to the reference [12], the fusion line production steps are as follows:

1) Mixing, the feed material for the melting process will comprise magnesia raw material and recyclable material.

2) Melting: Starting phase and fusion of magnesia raw material.

3) Water-cooling: to enable safe handling of the block it needs to be water-cooled.

4) Stripping: Removal of the steel shell.

5) Air cooling: Since the block is still too hot for furnace processing, it will be left to anneal in air.

6) Breaking and crushing: Breaking the block with jackhammer, and crushing to grain size <90 mm.

7) Optical sorting: Separation of fused magnesia from the crust.

High quality of the fused magnesia is characterized by a low silica and iron oxide content, a medium lime content, high density and large periclase crystal sizes.

2.3.2 Physical characteristic of magnesia clinker and fused magnesia

Bulk density and porosity are evaluation targets for the quality of magnesia clinker and fused magnesia. In this thesis, they are an important parameter to evaluate the homogeneity and quality of the magnesia raw materials.

Because of the grained material a particular method of the measuring bulk density and porosity has been applied in the test.

The method is based on DIN 993-17 [13], methods for testing dense shaped refractory products -part 17: determination of bulk density of granular materials by the mercury method with vacuum, in short, mercury method.

The general process of the method is as follows:

i) Preparing the magnesia raw material sample with the grain size between 2.0 mm and 5.6 mm and weight of 100g. In the present investigation a grain fraction 3-4 mm and 5-8 mm has been used.

ii) Drying the sample grains at 110 ℃ and then measuring the weight m_P [g].

iii) Measuring the weight of empty vacuum pyknometer m_L [g].

iv) Measuring the weight of pyknometer filled by mercury m_G [g].

v) Measuring the weight of pyknometer filled by the sample grains and mercury m_T [g].

vi) Calculation of the sample volume V_R [cm^3] by the equation:

$$V_r = \frac{m_G + m_P - m_T}{\rho} \tag{2-2}$$

m_G: weight of pyknometer filled by mercury [g]

m_P: weight of sample [g]

m_T: weight of pyknometer filled by mercury and samples [g]

ρ: density of mercury at room temperature [g/cm^3]

vii) Determination of the bulk density ρ_R [g/cm^3]

$$\rho_R = \frac{m_P}{V_R} \quad (2\text{-}3)$$

m_P: weight of sample [g]

V_R: sample volume [cm^3]

The following table shows the examples for typical physical properties of sintered and fused magnesia [14]:

Properties	**Bulk Density [g/cm^3]**	**Porosity [vol. %]**		**Average PCS [µm]**
		Open	Total	
Sintered magnesia	3.35-3.46	1-5	3-7	60-200
Fused magnesia	3.50-3.54	<1	<2.5	400-2000

Table 1 Physical properties of sintered and fused magnesia

2.3.3 Chemical characterization of magnesia clinker and fused magnesia

The main chemical component of sintered and fused magnesia is MgO. Also CaO, Fe_2O_3, Al_2O_3 and SiO_2 could be included in the raw material. B_2O_3 has a negative impact to the refractoriness and other hot properties of magnesia products. B_2O_3 as impurity often appears in synthetic magnesia, from seawater as the raw starting material. A B_2O_3 content decreases the invariant point in the system C-M-S-B significally. Due to the negative effect, the content of B_2O_3 in basic products should not be larger than 0.1%. [15]

The following table gives an example for typical chemical compositions of sintered and fused magnesia [14]:

Chemical analysis [wt %]						
Compositions	MgO	Fe_2O_3	CaO	SiO_2	Al_2O_3	B_2O_3
Sintered Magnesia	88-97	0.4-8	0.4-8	0.3-5	<1	<0.06
Fused Magnesia	96-99	<0.8	<2.5	<0.8	<0.3	<0.02

Table 2 Chemical analysis of fused and sintered magnesia

2.3.4 Microscopic characteristic of magnesia clinker and fused magnesia

i.) Periclase crystal size

The periclase crystal sizes depend on the purity of the raw materials and the calcining temperature [16]. The microstructure of magnesia is also influenced by the ratio of CaO to SiO_2 and their amount. The different C/S ratio will lead to the different content of liquid phase that could influence calcination quality and growth of the periclase crystals [12]. It is reported that periclase crystal size of magnesia clinker is normally between 60-200 μm.

The periclase crystal size of fused magnesia is normally between 400 and 2000 μm, the different crystal size depends on the position of the whole raw material in EAF. Normally, the raw material grains in the centre area of EAF can form very large periclase crystals, with sizes of >1400 μm and can be selected by visual inspection [17].

ii.) Secondary phases in magnesia clinker and fused magnesia.

A grain boundary is the interface between two grains, or crystallites, in a polycrystalline material [18]. During the firing process, the crystal grains grow. For fused magnesia, the crystal size range is normally between 400-2000 μm. When the crystal size is large enough, the single crystal gains are found in grained material. In this case there are no grain boundaries in this situation.

To microscopically identify the chemical compositions of the secondary phases of fused magnesia, Energy-dispersive X-ray spectroscopy (EDX) is being used to analyze the material. Under the SEM, a very large magnification could help to take the images and also to accurately make the chemical analysis of each area of the grain boundaries [19]. The following image shows a grey scale SEM-BSE (Scanning electron microscope- back scattered electron image) photo of fused magnesia crust material and high amount of interstitial phases with the magnification of 200x.

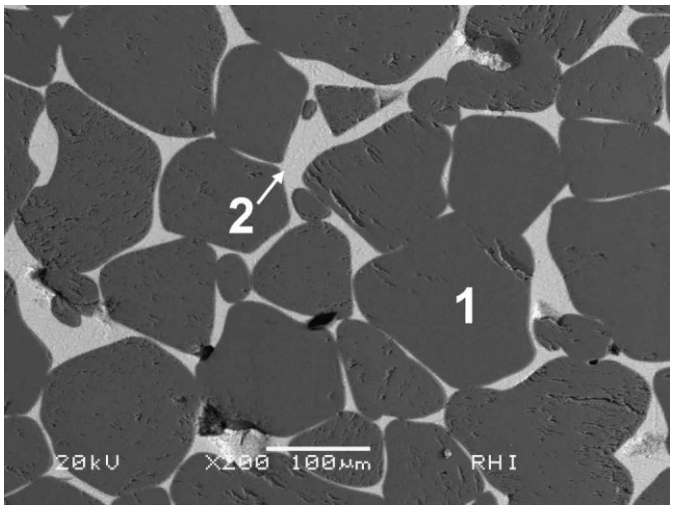


Fig. 3 SEM-BSE photo of Fused magnesia crust material

No.1: Marking 1 shows a periclase crystal in fused magnesia. The purity of the magnesia crystal is MgO>99%.

No.2: Marking 2 shows interstitial phase(s) between the periclase crystals. The chemical analysis of this area will be carried out by EDX. The impurity composition is going to be investigated here. The chemical compositions can directly be analysed by EDX analysis.

2.3.5 Ternary phase system CaO-MgO-SiO_2

The ternary system CaO-MgO-SiO_2 has important significance in technology for production and quality control of magnesia refractories and raw materials. The phase relations of the ternary system CaO-MgO-SiO_2, which are of importance for magnesia, are described in the following:

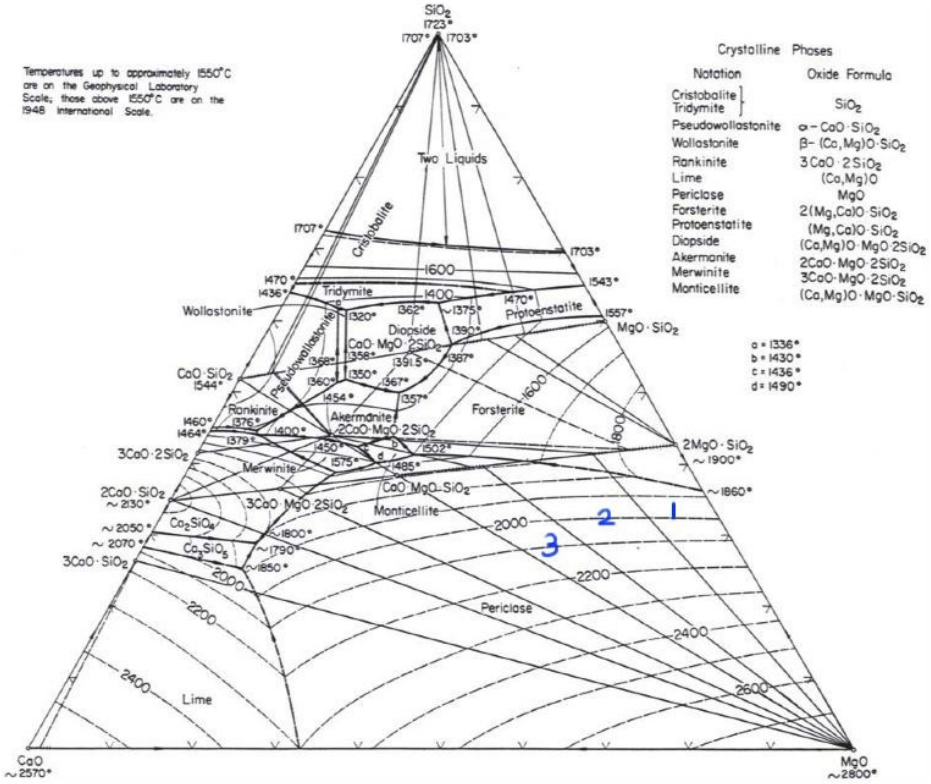


Fig. 4 CaO-MgO-SiO_2 System [21]

The Fig. 4 shows that forsterite, monticellite, merwinite and C_2S are stable in contact with magnesia.

The C/S ratio (mass ratio) in the system is a very important base of the determination of the crystalline phases. The following table 3 shows the relationship between the C/S ratio and their related phases [20]:

C/S ratio	0-0.93	0.93-1.40	1.40-1.87	>1.87
Phases	M_2S and CMS (*)	CMS and C_3MS_2	C_3MS_2 and C_2S	C_2S

Table 3 Relationship between C/S ratio and phases in system CMS

* Note: Between M_2S and CMS we can observe solid solutions (ss.). See Fig.4:

1. MgO+M_2S ss.

2. MgO+M_2S ss. +CMS ss.

3. MgO+CMS ss.

3 Investigations and results

3.1 Investigation of average periclase crystal size in magnesia clinkers

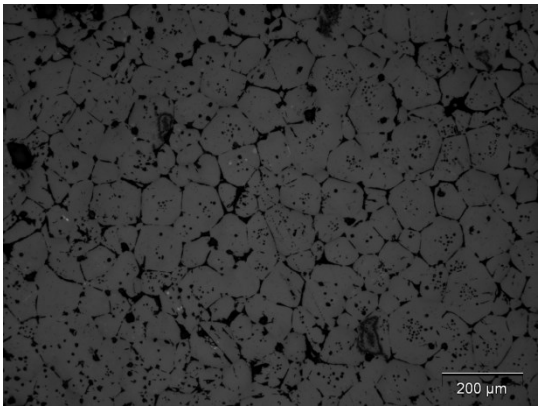
3.1.1 Grid method

The measurement procedure of the grid method is according to ASTM E 112-96 (reapproved 2004): Standard Test Method for Determining Average Grain Size [4]. It is a comparison procedure, which does not require counting on each gain but involves comparison of the grain structure with a series of grids.

The equipment used by the grid method investigation generally is reflected light microscopy, which is supplied by the department of mineralogy, RHI AG Technology Center, Leoben. The microscope is equipped with 2x, 5x, 10x, 20x and 50x times objectives. For the investigation of the average periclase crystal size in magnesia clinkers 10x and 5x objectives are usually required.

For periclase crystal size measurement a polished section of the magnesia clinker sample is made and observed under the microscope. The rotatable grid is adjusted to match the investigated grain structure. So the proper irregular ASTM grid can in excellent agreement with the image of the periclase crystal boundaries serve as standard. The grid that matches best with the respective section of microstructure is selected and its number is noted.

The following two images (Fig.5 and 6) are typical comparisons of magnesia clinker samples under the microscope. The used magnification is 100x. It is shown that the crystal size of this grain very good matches with the grid number 4.



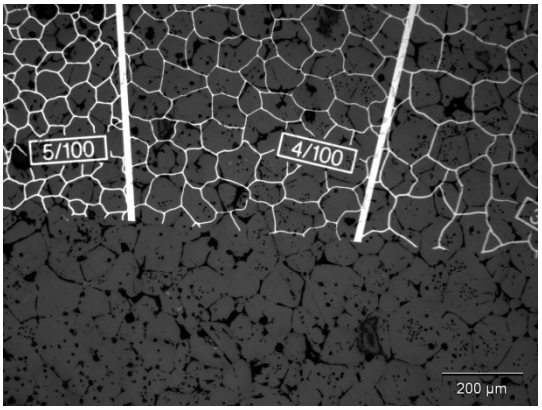


Fig. 5 Polished section of typical magnesia clinker crystals in one grain

Fig. 6 Appearance of magnesia clinker crystals compared with ASTM grids no.4 and no.5

For determination of an average crystal size in magnesia clinker, there are at least 60 magnesia grains needed to be measured for one brand material. The fraction of the material is normally 3-4 mm. In other words, this means at least two polished sections should be investigated to exclude the influence of inhomogeneities in raw material and to reach the number of 60 grains in minimum.

The samples of 3 different magnesia clinker brands are investigated in this thesis work. The results of these average crystal size measurements are shown in Table 4.

Brand	B1	B2	B3
Average crystal size [µm]	132	177	58

Table 4 Average crystal size of Brand 1, 2 and 3

The Fig.7 to 8 show the distribution of the average crystal size measured according to the amount of grains of magnesia clinker Brand 1, 2 and 3:

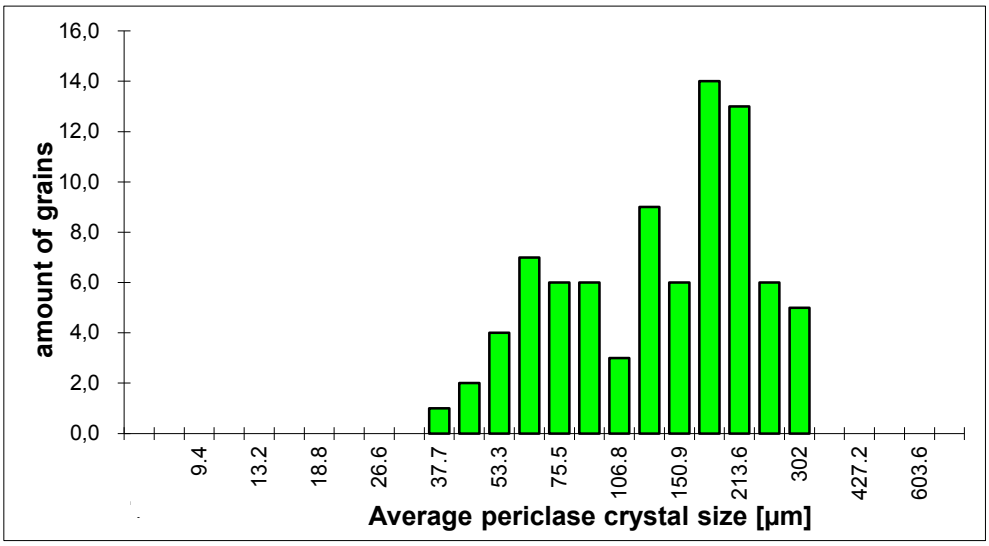


Fig. 7 Average periclase crystal size distribution of brand 1

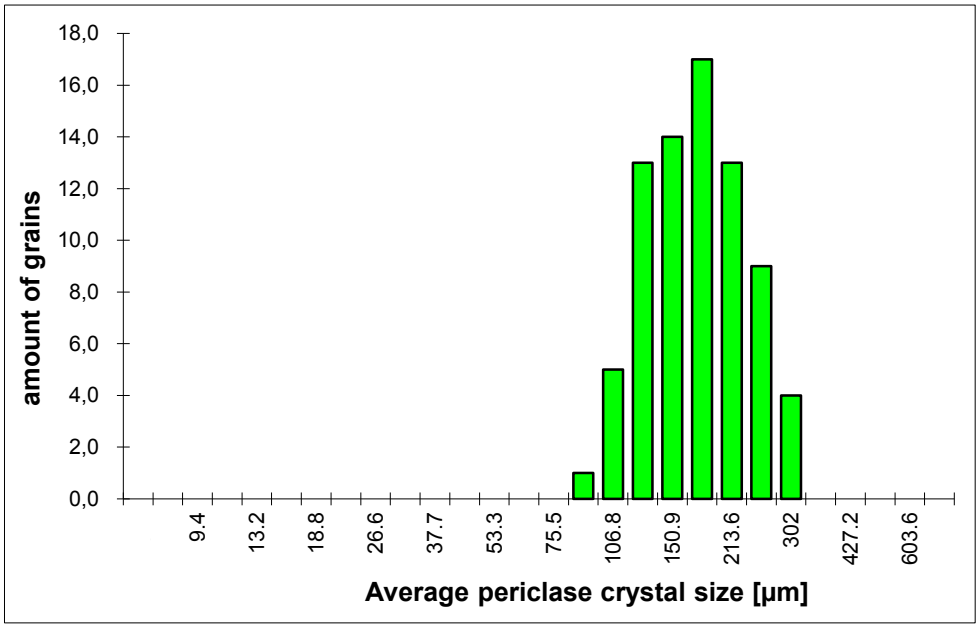


Fig. 8 Average periclase crystal size distribution of brand 2

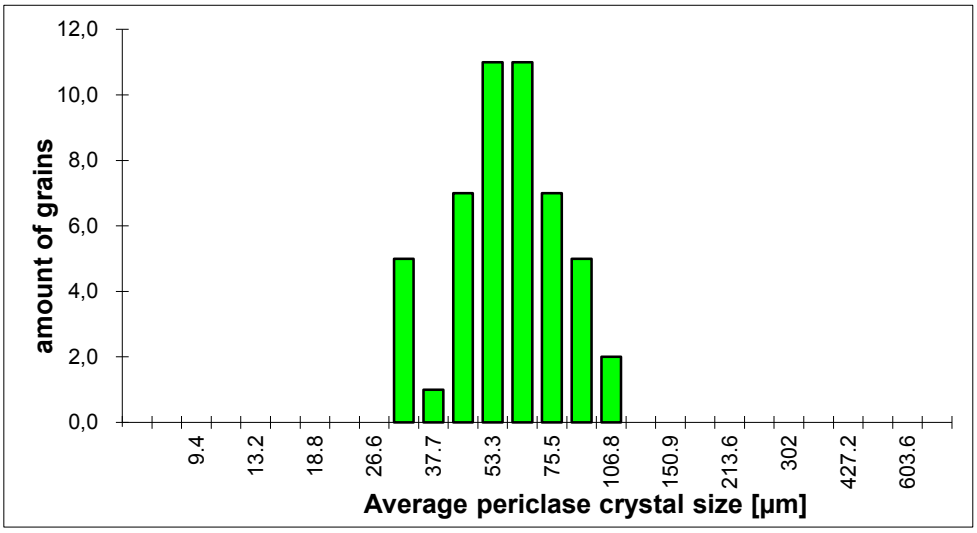


Fig. 9 Average periclase crystal size distribution of brand 3

The following images show different features of typical crystals of brand 1, 2 and 3 under the microscope with relevant ASTM grids:

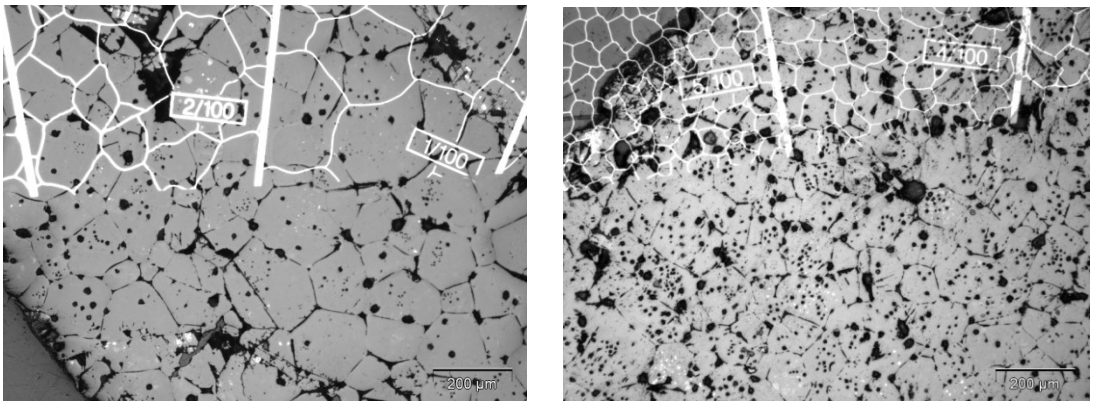


Fig. 10 Typical crystal features of Brand 1 with relevant ASTM grids

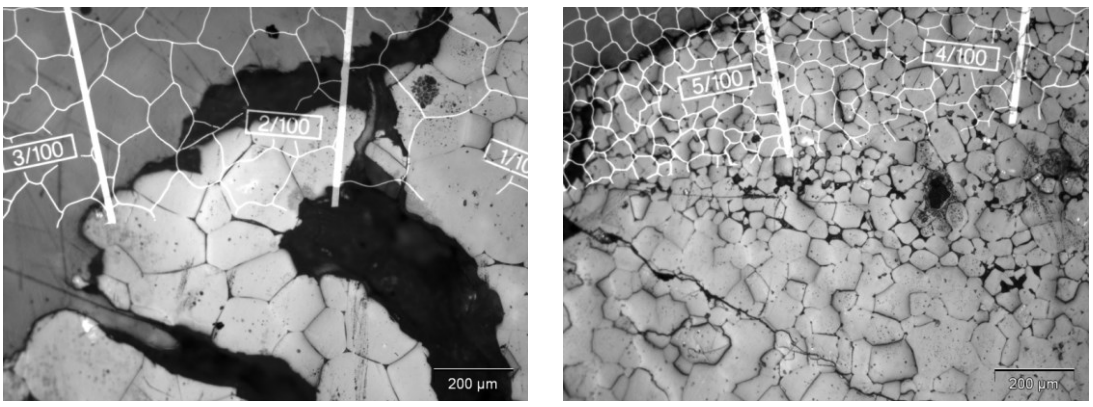


Fig. 11 Typical crystal features of Brand 2 with relevant ASTM grids

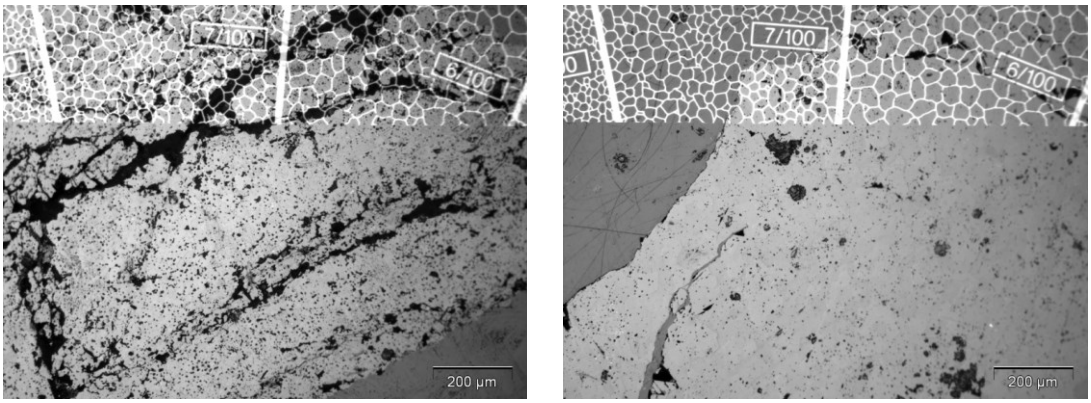


Fig. 12 Typical crystal features of Brand 3 with relevant ASTM grids

3.1.2 Lineal analysis for average periclase crystal size measurement

3.1.2.1 Introduction

Lineal analysis is another possible method for periclase crystal size determination. According to this method, the polished section of the magnesia raw material is investigated by reflected light microscopy. A parallel straight line is drawn in regular distance through the whole polished section. Along this line the chord length of each crystal is measured. Based on the chord length distribution the mean crystal size of the grain can be calculated [5]. The major part of this chapter is a crystal size measurement example of magnesia clinker, to compare the result with the measurement result achieved by grid method.

3.1.2.2 Procedure

A polished sample with a particular smooth surface is prepared for the microscopical observation. For preparation procedure of the polishing sample see chapter (2.2). The equipment of this investigation is a reflected light microscope which is supplied by the department of mineralogy, RHI AG Technology Center, Leoben. The used analysis software is Analysis Docu 5.0 by Olympus Soft Imaging Solutions GmbH. The raw material of the polished sample is magnesia clinker brand 1 according to chapter 3.1.1, the fraction of Brand 1 is 3-4 mm.

The investigation procedure is as follows:

(i.) Dividing the polished section of the sample into 4 parts under the microscope, and taking a general photo of each part by a 6x6 multi-photo function.

Sketching the straight parallel lines of the 1/4 section photo, the distance of each line is 0.5 mm (Fig.13), the magnification is 50x.

Fig. 13 1/4 Part photo of a polished section.

Rectangle: Detail see Fig.14

(ii.) Due to the limited magnification by the computer of such a 6x6 multi-image, it is necessary to take the single photo of each grain which is marked on the Fig.13.

The following Fig. 14 is an example image of a single grain photo area No.4 in Fig.13

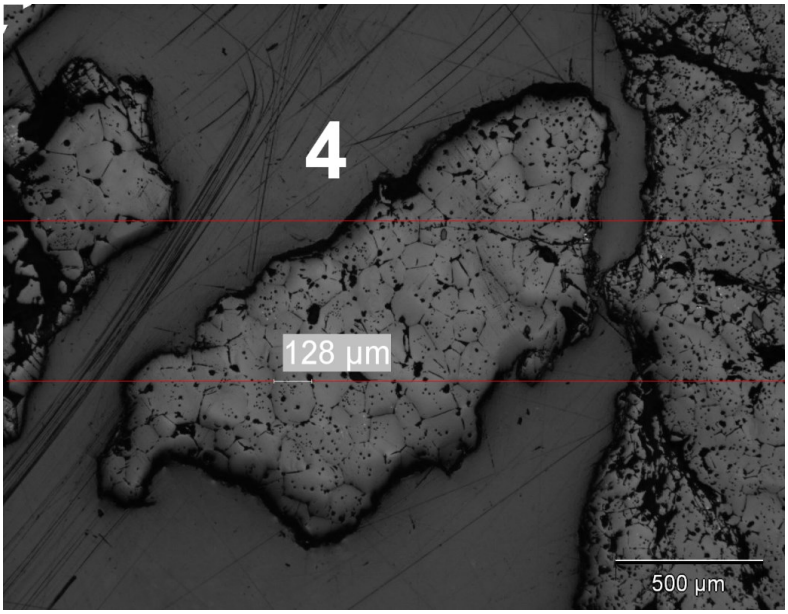


Fig. 14 Single grain photo, (detail from Fig.13)

(iii.) Magnifying the single images 200%-400% to get a clearer image of the crystal distribution of the grains. Then measuring the chord length of every crystal along the straight line. (Fig.15)

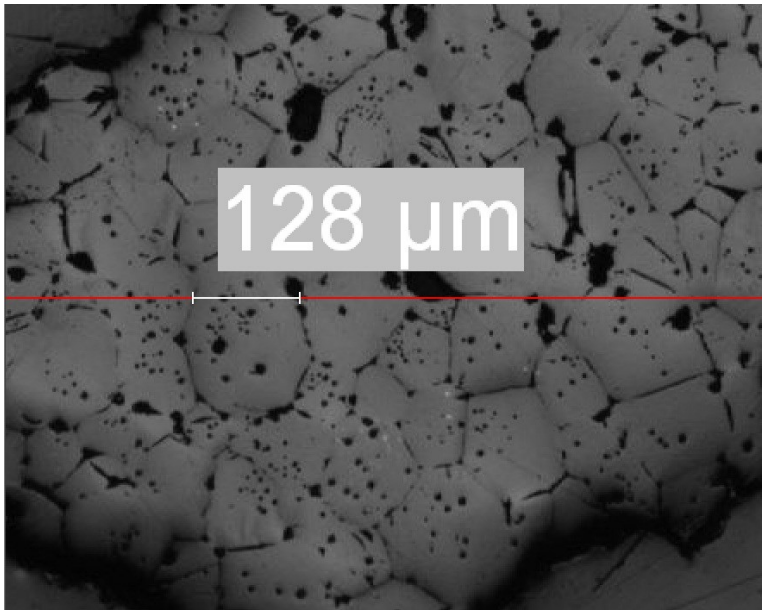


Fig. 15 Chord length measurement of a crystal

(iv.) According to a published paper by Steinwender/Harmuth: Measurement and Characterization of the Periclase Crystal Size in Products of the Magnesite Industry and in Sintered Magnesia [6], in minimum 500 to 2000 single crystals

have to be measured to get liable results for the average periclase crystal size. The more inhomogeneous the average periclase crystal size is, the more crystals have to be measured. The previous material is comparably homogeneous, nevertheless 2200 single crystals were measured.

(v.) Summary of the results of the chord length measurement of the crystals and calculation of the mean crystal diameter according to the mean chord length should be done. The calculation equation is:

$$d_{mean} = 1.5 \times l_{mean} \qquad (3\text{-}1\text{-}1)$$

Gathering the statistics results of 30 gains for the crystal size measurements and getting the mean crystal diameter of this material.

(vi.) Finally, making a histogram of the crystal size distribution, and comparing with the distribution histogram achieved by grid method.

3.1.2.3 Results

The data of the chord length measurement of single periclase crystals, the number of measurement of each grain and the mean crystal diameter which is calculated according to above equation (3-1-1) are listed in the following table:

Magnesia grain	Mean chord length [μm]	Number of crystals being measured	Mean crystal diameter [μm]
1	64.3	74	96.5
2	80.8	60	121.2
3	49.4	69	74.1
4	78	82	117.0
5	52	118	78.0
6	51	118	76.5
7	89.7	70	134.6
8	84	37	126.0
9	71.5	79	107.3
10	84.5	81	126.8
11	130.3	47	195.5
12	100.1	68	150.2
13	87.6	52	131.4
14	80.5	58	120.8
15	90.4	56	135.6
16	118.1	58	177.2
17	100.3	14	150.5
18	96.9	41	145.4
19	63.7	112	95.6
20	134.8	77	202.2
21	118.2	105	177.3
22	76.1	68	114.2
23	114.9	61	172.4
24	50.7	109	76.1
25	81.1	49	121.7
26	53.4	120	80.1
27	72.5	80	108.8
28	117.7	53	176.6
29	38.3	78	57.5
30	69.5	106	104.3
	Mean value=83.3	∑ 2200	Mean value=125.0

Table 5 Statistic results of crystal size measurement by lineal analysis

According to Table 5, the histogram of crystal size distribution for Brand 1 could be specified:

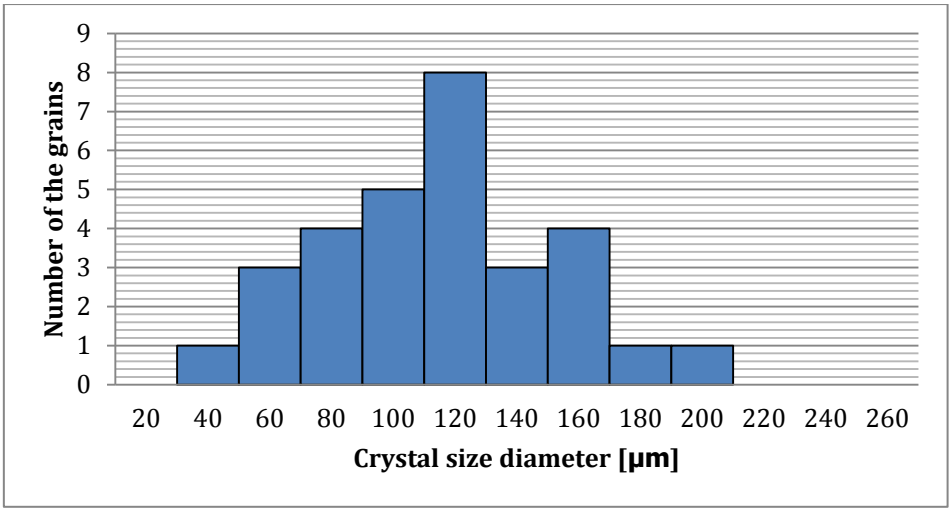


Fig. 16: crystal size distribution histogram

The mean chord length l_{mean} is 83.3 µm; the mean crystal size d_{mean} calculated by equation (3-1-1) is 125.0 µm.

The highest frequency of the grains appears in the range of 120 µm-140 µm, which is perfectly matching the result of the mean crystal size measurement by grid method of this material Brand 1.

3.1.3 Etching techniques

In chemically very pure magnesia raw materials with MgO contents >98% the single periclase crystals can hardly be distinguished. The crystal boundaries are not clearly visible anymore and therefore essential crystal size measurement can hardly be carried out.

Etching is a method to improve the visibility of the single periclase crystals of magnesia in polished sections [9]. Common techniques used for polycrystalline ceramics are chemical, thermal and plasma etching. For the periclase crystal size measurement, chemical etching is a very efficient method. Chemical etching of ceramics usually requires particularly corrosive fluids with one major requirement [8]. The fluid should attack the boundary lines between crystals faster than the crystals themselves.

Fluids normally used include strong acids, alkalis and molten salts. By the attack of the fluids, the boundary line between the crystals will partly be dissolved. A so-called relief effect will be achieved, which is highly beneficial for the visibility of the crystals under the microscope. Due to the basicity of periclase crystals and secondary phases in the magnesia with high C/S ratio, strong acid is recommended for etching.

The etching procedure of a magnesia clinker polishing samples in a laboratory generally is:

(i.) Drop the etching solution on the surface of the polished section (3~5 drops).

(ii.) Dwell time on demand (between a few seconds and several minutes).

(iii.) Take pure to water clean up the surface, and then clean up the surface by pure ethanol.

(iv.) Observe the etched polished section under the microscope.

(v.) Step ii.) and iii.) could be repeated in case that no sufficient etching occurred.

Because of the corrosivity of the strong acid, the etching procedure must be carried out by following the safety instructions for the used acid (according technical data sheet and safely data sheet)

In the following figures there are comparative results of the etching by two different etching fluids. In contact with chemically very pure clinker brand Brand 3 (chemical composition: see Table 6).

Fluid 1: 1% HNO_3 in ethanol

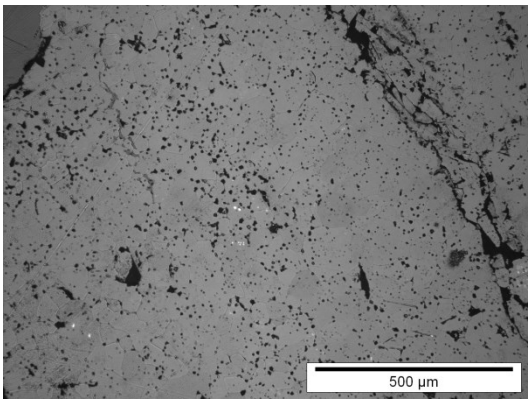


Fig. 17 Polished section before etching with 1% HNO_3 in ethanol

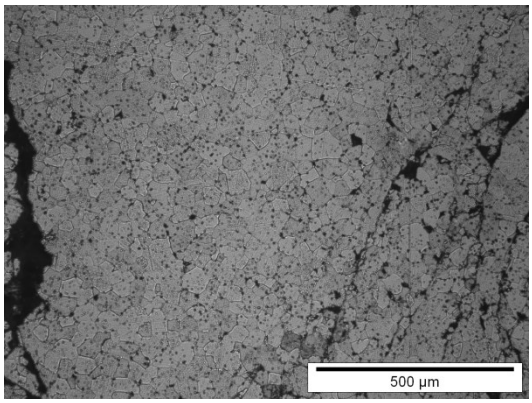


Fig. 18 Polished section after etching with 1% HNO_3 in ethanol, 30 seconds.

Fluid 2: 1% H_2SO_4 in 95% ethyl alcohol

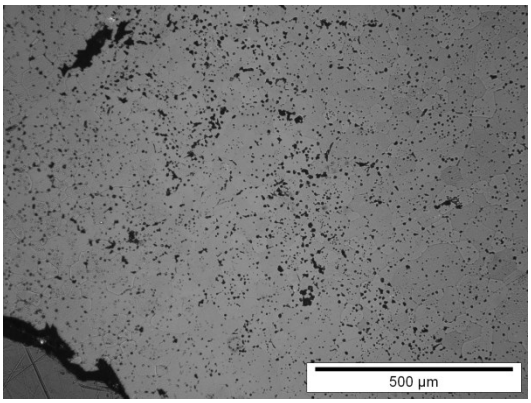


Fig. 19 Polished section before etching with 1% H_2SO_4 in ethanol

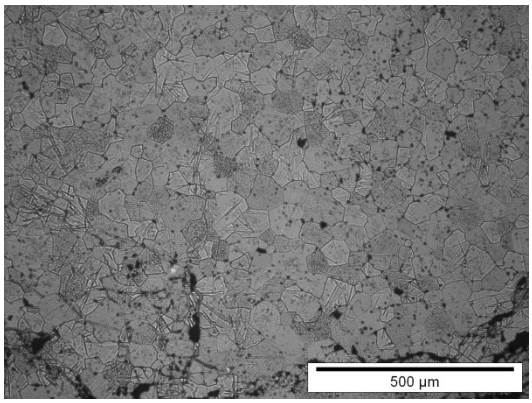


Fig. 20 Polished section after etching with 1% H_2SO_4 in ethanol, 30 seconds.

Typical chemical analysis of Brand 3:

	MgO	SiO_2	CaO	Al_2O_3	Fe_2O_3
Content [wt %]	98.5	0.13	0.72	0.06	0.49

Table 6 Chemical analysis of magnesia clinker Brand 3

3.2 Investigation of fused magnesia

3.2.1 Classification of fused magnesia by visual inspection

When the periclase crystal size is measured, especially for the fused magnesia crystal size, it can be seen that single crystals and fracture residuals of very large single crystals (diameter>1435 μm) frequently appear. The average size of these periclase crystals is difficult to be measured by grid method because of the upper limitation of the grid size and the unknown size of original crystals in the raw material before crushing. The following figures show typical grains of single crystal fused magnesia, and normal crystal size fused magnesia:

Fig. 21 Single crystal fused magnesia

Fig. 22 “Normal” crystal size fused magensia

The influence of the single crystals on the results of the periclase crystal size measurements is studied; the experimental procedure is as follows:

(i.) Crushing of the raw material of fused magnesia and sieving it into two fractions: 3-4 mm and 5-8 mm. Both fractions have to be investigated for comparison.

(ii.) Measuring the regular weight of the fused magnesia.

(iii.) Sorting the regular fused magnesia (see Fig.23) by hand and separation into two groups: single group and residual group. Single group magnesia grains are characterized by one grain, which represents one single crystal (see Fig.24), residual group are the grains which are not one single crystal (see Fig.25).

(iv.) Weighting of the single group and residual group.

(v.) Making the polished sample of the residual group and single group.

(vi.) Measuring the average crystal size of the single crystal grain amount of each group.

(vii.) Calculation with an equation described in the following to get the theoretical amount of single crystals (C_{theo}).

(viii.) Making the polishing sample of the regular grains.

(ix.) Measure the crystal size and the single crystal grain amount (C).

(x.) Comparing the results of vii) and ix), and find the possible relationship between C_{theo} and C.

The following photos show typical examples of the regular, single and residual group of fused magnesia with the fraction of 5-8 mm.

Fig. 23 Fused magnesia in regular group

Fig. 24 Fused magnesia in single crystal group

Fig. 25 Fused magnesia in residual group

The group of single crystals shown in Fig.24 is obviously clearly to be identified. The single crystal group and the residual group are sorted from the bulk material of the two grain fractions by visual inspection.

In order to calculate the theoretical amount of single crystal (C_{theo}), an equation according to the weight measurement and the single crystal amount measurement by microscopy can be obtained. The following procedure is the figure of the equation:

(i.) The experimental objective is fused magnesia samples which are separated into two fractions: 3-4 mm and 5-8 mm. Both fractions have to be investigated.

(ii.) First measurement of the weight of the sample (showing with m), then the single crystal grains distinguished by eyes are sorted out for determination.

(iii.) Second measurement of the single crystal grains weight (showing with m_1) and the residual grains weight (showing with m_2). The relation among them is

$$m = m_1 + m_2 \qquad (3\text{-}2\text{-}1)$$

Where: m: weight of Regular group [g]

m_1: weight of Single group [g]

m_2: weight of Residual Group [g]

According to the weight measurement, the weight amount can be calculated:

$$X_1 = \frac{m_1}{m_1+m_2}\ 100\% \quad (3\text{-}2\text{-}2)$$

$$X_2 = \frac{m_2}{m_1+m_2}\ 100\% \quad (3\text{-}2\text{-}3)$$

Where: X_1: Single crystal grains weight amount of single group [%]

X_2: Single crystal grains weight amount of residual group [%]

With $X_1+X_2=100\%$

(iv.) Periclase crystal size is here measured with grid method for the regular group and the residual group. (The single group here is 100% single crystal.) Then the crystal amount >1435 µm of each group is obtained by microscopic measurement.

Where: A: Single crystal amount of single group (100%) [%]

B: Residual group >1435 µm (percentage of grains) [%]

C: Regular group>1435 µm (percentage of grains) [%]

(v.) Theoretical calculation of the single crystal amount

Total weight of crystal amount >1435 µm:

$$m_{>1435\mu m} = m \times \frac{C}{100} \quad (3\text{-}2\text{-}4)$$

The theoretically total single crystal weight could be calculated:

$$m_{>1435\mu m} = m_1 \times \frac{A}{100} + m_2 \times \frac{B}{100} = m_1 + m_2 \times \frac{B}{100}\ (A=100\%) \quad (3\text{-}2\text{-}5)$$

From formula (3-2-4) and (3-2-5) the following equation is obtained:

$$m \times \frac{C}{100} = m_1 + m_2 \times \frac{B}{100} \quad (3\text{-}2\text{-}6)$$

then

$$C_{theo} = 100 \times \frac{m_1}{m} + B \times \frac{m_2}{m} \quad (3\text{-}2\text{-}7)$$

Combining of equation (3-2-7) with (3-2-1), (3-2-2) and (3-2-3) results in:

$$C_{theo} = X_1 + X_2 \times \frac{B}{100} \quad (3\text{-}2\text{-}8)$$

The result received from equation (3-2-8) is the theoretical amount of single crystals. The following parameter are obtained by measurement and used for calculation of C_{theo}.

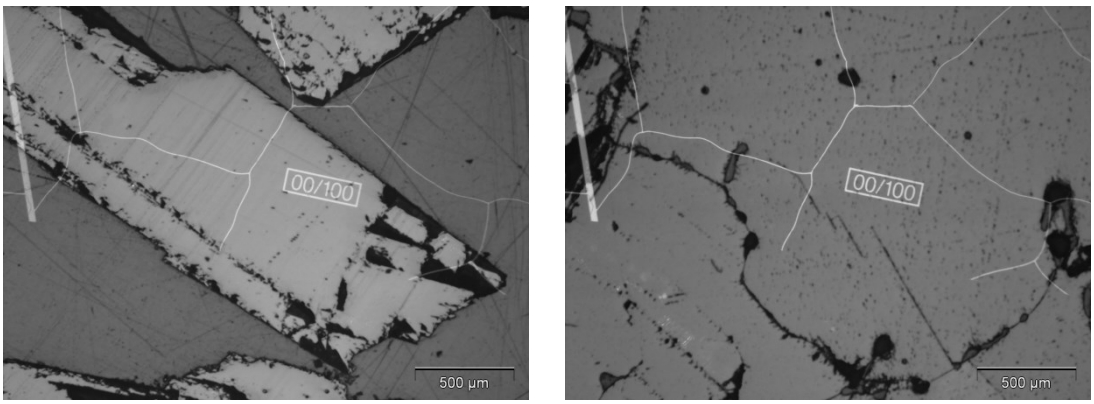
X_1: Single crystal grains weight amount of single group [%]

X_2: Single crystal grains weight amount of residual group [%]

B: Residual group >1435 μm (percentage of grain) [%]

The following photos show typical examples of the regular, single and residual group of fused magnesia with the fraction of 5-8 mm.

Among the periclase grains, the crystal size larger than 1435 μm appear in two kinds of grains: single crystal grain and “very large crystal grain”. The single crystal grain which talked above is the grain which only contains one crystal, and the crystal size is >1435 μm. The so-called “very large crystal grain” is a grain containing several crystals, and these crystals sizes are >1435 μm. The following two images are typical examples of the single crystal grain and “very large crystal grain” under the microscope:



(A) Single crystal grain (B) “Very large crystal grain”

Fig. 26 Comparison of Single crystal grain (A) and “Very large crystal grain”(B)

Truly, fused magnesia in the residual group contains some amount of the “very large crystal grains” (diameter>1435 µm) that is difficult to distinguish. But this situation is already considered and included with B in the above equations for calculation on theoretical amount of single crystals.

The definition of the parameters in the following tables and figures:

X_1: Single crystal grains weight amount of single group [%]

X_2: Single crystal grains weight amount of residual group [%]

B: Residual group >1435 µm (percentage of grains) [%]

C: Regular group >1435 µm (percentage of grains) [%]

C_{theo}: Theoretical amount of single crystals [%]

No.	Material	X_1	X_2	B	C	C_{theo}
1	Type 1	39.66	60.34	50	60	70
2	Type 2	17.12	82.88	38	42	49
3	Type 3	14.33	85.67	49	38	56
4	Type 4	11.96	88.04	49	33	55
5	Type 5	0.00	100.00	5	4	5

Table 7 1-5 type fused magnesia fraction 5-8 mm

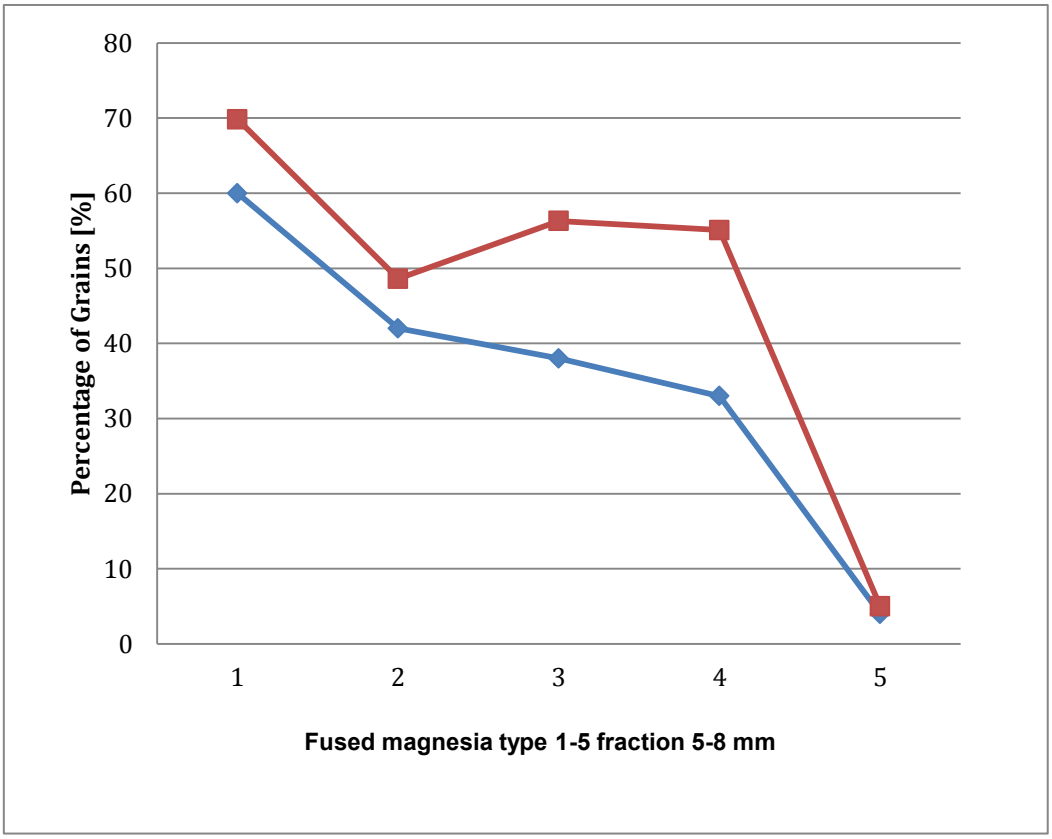


Fig. 27 Comparison of the results between C (blue) and C_{theo} (red) from table 7

3.2.2 Classification of average periclase crystal size by grid method including statistical variations of results

For average periclase crystal size determination by grid method, the results are often not identical, and swing in a range. The reason for this is that the grid method is measured by personal comparison with a standard grid. The subjective determination by this method could influence the results and lead to deviations. This chapter is an investigation of the deviation of the results achieved by different persons technical staff who measured. The purpose is to define a deviation range to clarify the data, which of them are acceptable due to the measurement method deviation and which of them are not acceptable by mistake measurement. With this investigation we can evaluate and rank the results of average periclase crystal size measurement by grid method achieved by multiple measurement of one and the same material.

This investigation includes 11 different brands of fused magnesia. Five brands are typical fused magnesia with different raw material origin and different quality. These 5 brands are named as Type 1, Type 2, Type 3, Type 4 and Type 5. The other 6 brands are so called “blend” brands, which means one brand of this material includes at least two different types of magnesia, the crystal size distribution of each blend brand could include a wide range. These 6 brands are named as Blend A, Blend B, Blend C, Blend D, Blend E and Blend F. These 11 brands are crushed and separated into 2 fractions: 3-4 mm and 5-8 mm. All of them are investigated here.

In order to find the deviation range by personal error, there are five times measurements of each brand. The measurements were carried out by 4 persons. These five measurements are named as H1, H2, H3, H4 and H5. Among the test, H1 and H2 are finished by one person with two measurements. All these measurements are done at the department of mineralogy, RHI AG Technology Center, Leoben.

With this 22*5(*) data, we can have a general analysis for the deviation by grid method. In the following there is the method of the deviation calculation:

Note: (5 brands+6 brands)* 2 grain sizes * 5 persons.

Deviation calculation:

The standard deviation calculation equation for all the four parameters of the results of the periclase crystal size measurements is:

Nr.	H1	H2	H3	H4	H5	Mean
n	X_1	X_1	X_1	X_1	X_1	$\bar{x}$

Table 8 Example parameter for deviation calculation

$$\sigma = \sqrt{\frac{1}{N-1} \times \sum_{i=1}^{N} (x_1 - \bar{x})^2} \qquad (3\text{-}2\text{-}9)$$

σ: standard deviation

Due to the different unit of the 4 parameters, the coefficient of variation COV is applied here:

$$COV = \frac{\sigma}{\bar{x}} \times 100\% \qquad (3\text{-}2\text{-}10)$$

COV: Coefficient of variation [%]

Considering of the unit of the measurement result parameter, for the results of grain portions, the standard deviation is applied, for the results of average grain size, the coefficient of variation COV [%] is applied here.

The following tables list the measurement results and the figures show the statistical analyses of the measurement results. Among the tables the “Maximum difference” is the maximum absolute difference among H1-H5 [%]*[µm]$^{-1}$.

Grain portion which average crystal size is >1435 µm [%]										
No.	Material	Fraction	H1	H2	H3	H4	H5	Mean	Standard Deviation [%]	Maximum difference [%]
1	Type 1	3-4 mm	76	73	79	84	82	79	3.97	11
2	Type 1	5-8 mm	59	61	60	65	57	60	2.65	8
3	Type 2	3-4 mm	86	91	82	80	77	83	4.87	14
4	Type 2	5-8 mm	41	41	44	41	47	43	2.40	6
5	Type 3	3-4 mm	31	37	31	34	49	36	6.68	18
6	Type 3	5-8 mm	38	33	43	31	28	35	5.31	15
7	Type 4	3-4 mm	65	66	60	56	58	61	3.90	10
8	Type 4	5-8 mm	33	30	37	36	45	36	5.04	15
9	Type 5	3-4 mm	5	4	6	3	4	4	1.02	2
10	Type 5	5-8 mm	5	5	3	10	7	6	2.37	7

Table 9 Type 1-5; Grain portion which average crystal size is >1435 µm in [%]

Grain portion which average crystal size is >1435 µm [%]										
No.	Material	Fraction	H1	H2	H3	H4	H5	Mean	Standard deviation [%]	Maximum difference [%]
11	Blend A	3-4 mm	26	27	26	23	44	29	7.52	18
12	Blend A	5-8 mm	42	35	35	48	45	41	5.25	13
13	Blend B	3-4 mm	65	63	64	62	66	64	1.41	4
14	Blend B	5-8 mm	25	27	26	35	29	28	3.56	10
15	Blend C	3-4 mm	43	46	32	40	51	42	6.34	14
16	Blend C	5-8 mm	31	33	33	44	43	37	5.53	13
17	Blend D	3-4 mm	14	13	14	14	15	14	0.63	2
18	Blend D	5-8 mm	19	18	18	22	22	20	1.83	4
19	Blend E	3-4 mm	30	27	31	41	44	35	6.65	17
20	Blend E	5-8 mm	35	43	31	53	41	41	7.53	21
21	Blend F	3-4 mm	70	68	69	69	76	70	2.87	7
22	Blend F	5-8 mm	55	58	53	55	61	56	2.80	8

Table 10 Blend A-F; Grain portion which average crystal size is >1435 µm in [%]

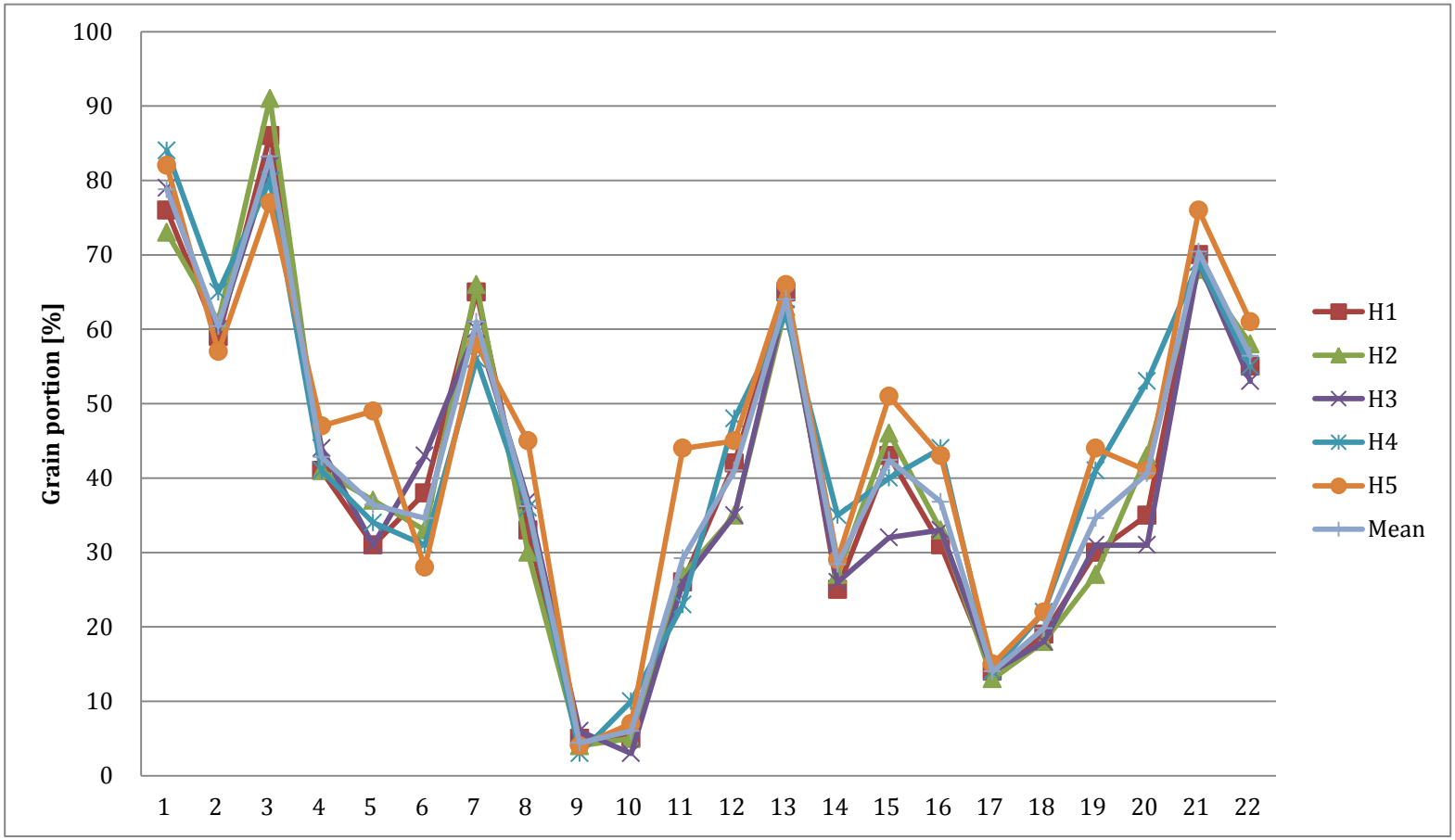


Fig. 28 Grain portion which average crystal size is >1435 µm in %

Note: No.1-No.22 are the mean value of different types of fused magnesia from table 9 and 10.

Grain portion which average crystal size is >718 µm in [%]										
No.	Material	Fraction	H1	H2	H3	H4	H5	Mean	Deviation [%]	Maximum difference [%]
1	Type 1	3-4 mm	95	94	95	93	96	95	1.02	3
2	Type 1	5-8 mm	87	86	90	93	85	88	2.93	8
3	Type 2	3-4 mm	94	96	90	94	90	93	2.40	6
4	Type 2	5-8 mm	85	82	87	88	83	85	2.28	6
5	Type 3	3-4 mm	80	80	80	76	84	80	2.53	8
6	Type 3	5-8 mm	82	74	80	78	85	80	3.71	11
7	Type 4	3-4 mm	91	95	89	89	88	90	2.50	7
8	Type 4	5-8 mm	91	86	90	76	90	87	5.57	13
9	Type 5	3-4 mm	35	25	34	22	22	28	5.75	12
10	Type 5	5-8 mm	21	26	23	29	22	24	2.93	7

Table 11 Type 1-5; Grain portion which average crystal size is >718 µm in %

Grain portion which average crystal size is >718 µm in %										
No.	Material	Fraction	H1	H2	H3	H4	H5	Mean	Deviation [%]	Maximum difference [%]
11	Blend A	3-4 mm	43	42	43	46	58	46	5.95	16
12	Blend A	5-8 mm	54	50	49	58	53	53	3.19	9
13	Blend B	3-4 mm	75	77	72	85	84	79	5.08	13
14	Blend B	5-8 mm	43	53	52	63	65	55	8.01	22
15	Blend C	3-4 mm	70	76	73	71	80	74	3.63	10
16	Blend C	5-8 mm	64	64	64	78	78	70	6.86	16
17	Blend D	3-4 mm	18	17	16	14	17	16	1.36	4
18	Blend D	5-8 mm	26	22	27	30	33	28	3.72	11
19	Blend E	3-4 mm	42	42	44	53	54	47	5.37	12
20	Blend E	5-8 mm	52	57	47	65	61	56	6.37	18
21	Blend F	3-4 mm	81	84	83	86	89	85	2.73	8
22	Blend F	5-8 mm	79	84	80	80	88	82	3.37	9

Table 12 Blend A-F; Grain portion which average crystal size is >718 µm in %

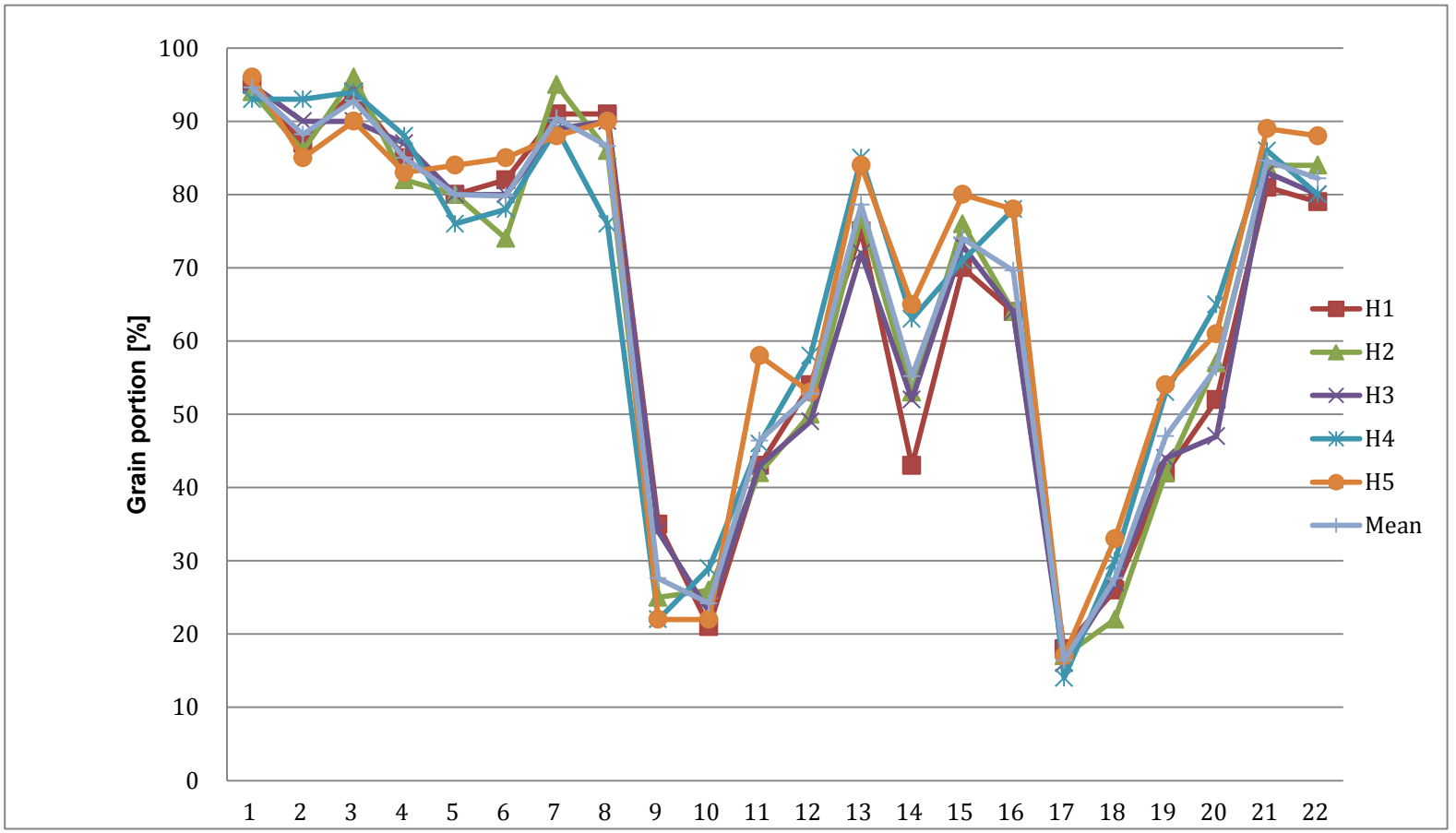


Fig. 29 Grain portion which average crystal size is >718 µm in %, from table 11 and 12

Note: No.1-No.22 are the mean value of the different types of fused magnesia from table 11 and 12.

Average periclase crystal size of portion < 1435 µm in [µm]										
No.	Material	Fraction	H1	H2	H3	H4	H5	Mean	COV [%]	Maximum difference [µm]
1	Type 1	3-4 mm	992	1111	959	864	1007	987	8.07	247
2	Type 1	5-8 mm	1004	1001	1013	1090	922	1006	5.30	168
3	Type 2	3-4 mm	683	711	645	990	1045	815	20.59	400
4	Type 2	5-8 mm	955	932	995	990	894	953	3.94	96
5	Type 3	3-4 mm	913	895	927	907	825	893	4.00	102
6	Type 3	5-8 mm	925	920	907	956	948	931	1.95	49
7	Type 4	3-4 mm	962	974	970	980	929	963	1.87	51
8	Type 4	5-8 mm	1111	1096	1124	960	1100	1078	5.56	164
9	Type 5	3-4 mm	616	604	605	592	589	601	1.62	27
10	Type 5	5-8 mm	586	593	572	561	587	580	2.01	32

Table 13Type 1-5; Average periclase crystal size of portion < 1435 µm in [µm]

Average periclase crystal size of portion < 1435 µm in [µm]										
No.	Material	Fraction	H1	H2	H3	H4	H5	Mean	COV [%]	Maximum difference [µm]
11	Blend A	3-4 mm	326	305	326	383	344	337	7.78	78
12	Blend A	5-8 mm	292	309	292	299	263	291	5.27	46
13	Blend B	3-4 mm	683	654	635	770	752	699	7.63	135
14	Blend B	5-8 mm	671	688	691	712	759	704	4.31	88
15	Blend C	3-4 mm	743	727	726	786	846	766	5.97	120
16	Blend C	5-8 mm	733	715	715	747	847	751	6.56	132
17	Blend D	3-4 mm	168	153	168	184	153	165	6.99	31
18	Blend D	5-8 mm	220	213	224	221	215	219	1.84	11
19	Blend E	3-4 mm	263	252	267	311	312	281	9.03	60
20	Blend E	5-8 mm	309	297	303	331	358	320	7.00	61
21	Blend F	3-4 mm	737	759	747	834	838	783	5.60	101
22	Blend F	5-8 mm	894	913	952	976	1002	947	4.18	108

Table 14 Blend A-F;Average periclase crystal size of portion < 1435 µm in [µm]

Fig. 30 Average periclase crystal size of portion < 1435 µm in [µm], from table 13 and 14

Note: No.1-No.22 are the mean value of different types of fused magnesia from table 13 and 14.

Average periclase crystal size of all grains in [µm]										
No.	Material	Fraction	H1	H2	H3	H4	H5	Mean	COV [%]	Maximum difference [µm]
1	Type 1	3-4 mm	1303	1299	1303	1311	1353	1314	1.52	54
2	Type 1	5-8 mm	1232	1240	1246	1300	1176	1239	3.19	124
3	Type 2	3-4 mm	1262	1330	1204	1327	1245	1274	3.82	126
4	Type 2	5-8 mm	1122	1101	1165	1148	1107	1129	2.16	64
5	Type 3	3-4 mm	1046	1056	1057	1054	1063	1055	0.52	17
6	Type 3	5-8 mm	1085	1054	1096	1075	1058	1074	1.48	42
7	Type 4	3-4 mm	1239	1201	1219	1205	1190	1211	1.39	49
8	Type 4	5-8 mm	1204	1186	1226	1102	1238	1191	4.03	136
9	Type 5	3-4 mm	644	621	638	609	612	625	2.23	35
10	Type 5	5-8 mm	612	618	585	616	624	611	2.22	39

Table 15 Type 1-5; Average periclase crystal size of all grains in [µm]

Average periclase crystal size of all grains in [µm]										
No.	Material	Fraction	H1	H2	H3	H4	H5	Mean	COV [%]	Maximum difference [µm]
11	Blend A	3-4 mm	454	437	450	498	586	485	11.24	149
12	Blend A	5-8 mm	512	491	472	599	506	516	8.48	127
13	Blend B	3-4 mm	1084	1039	1040	1107	1129	1080	3.32	90
14	Blend B	5-8 mm	811	836	830	900	908	857	4.59	97
15	Blend C	3-4 mm	913	971	892	988	1089	971	7.11	197
16	Blend C	5-8 mm	887	885	886	975	1049	936	7.05	164
17	Blend D	3-4 mm	241	238	241	267	303	258	9.63	65
18	Blend D	5-8 mm	318	306	313	340	321	320	3.57	34
19	Blend E	3-4 mm	472	477	417	530	563	492	10.26	146
20	Blend E	5-8 mm	485	529	459	637	566	535	11.72	178
21	Blend F	3-4 mm	1156	1151	1161	1196	1249	1183	3.11	98
22	Blend F	5-8 mm	1150	1182	1173	1189	1291	1197	4.08	141

Table 16 Blend A-F; Average periclase crystal size of all grains in [µm]

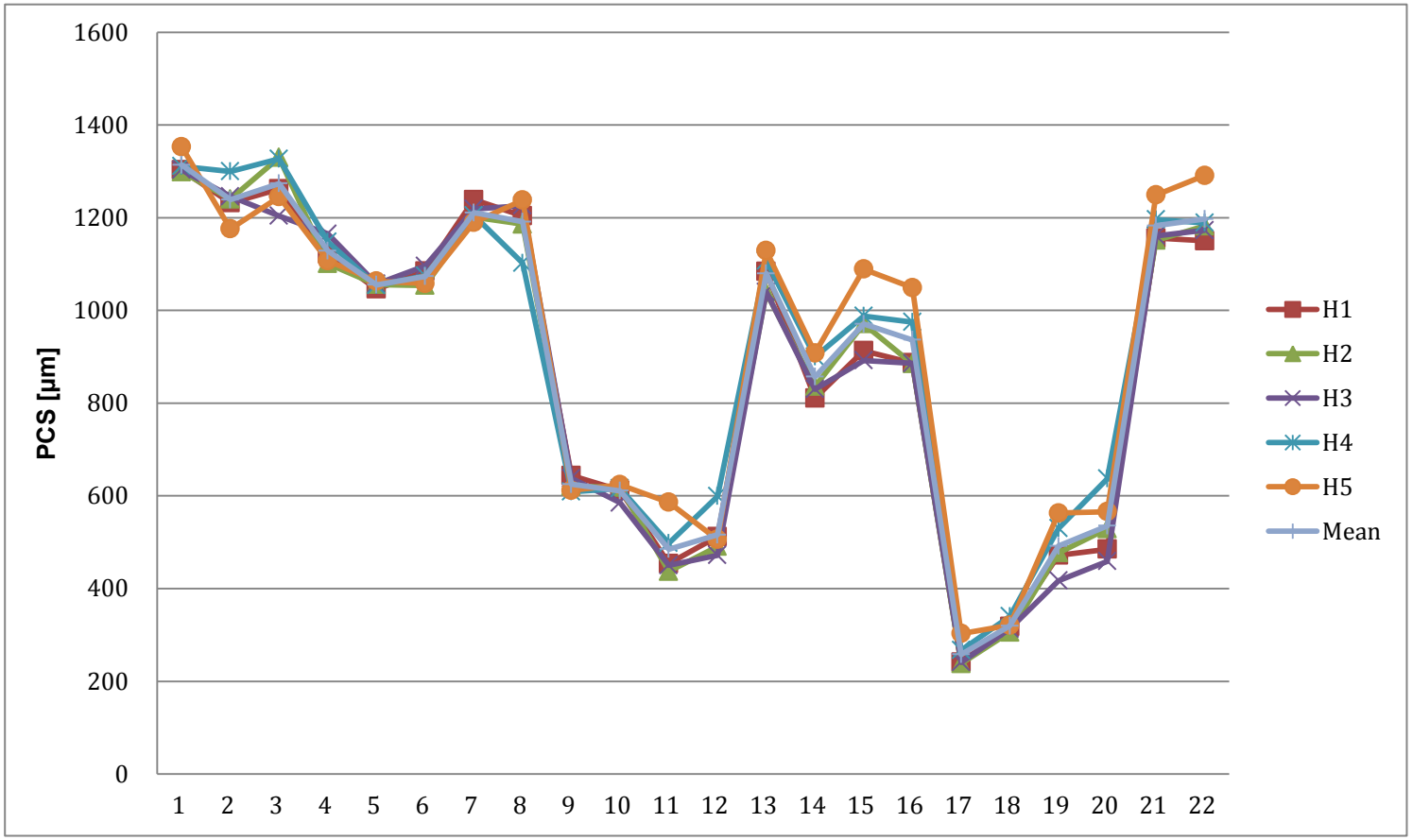


Fig. 31 Average periclase crystal size of all grains in [µm], from table 15 and 16

Note: No.1-No.22 are the mean value of different types of fused magnesia from table 15 and 16.

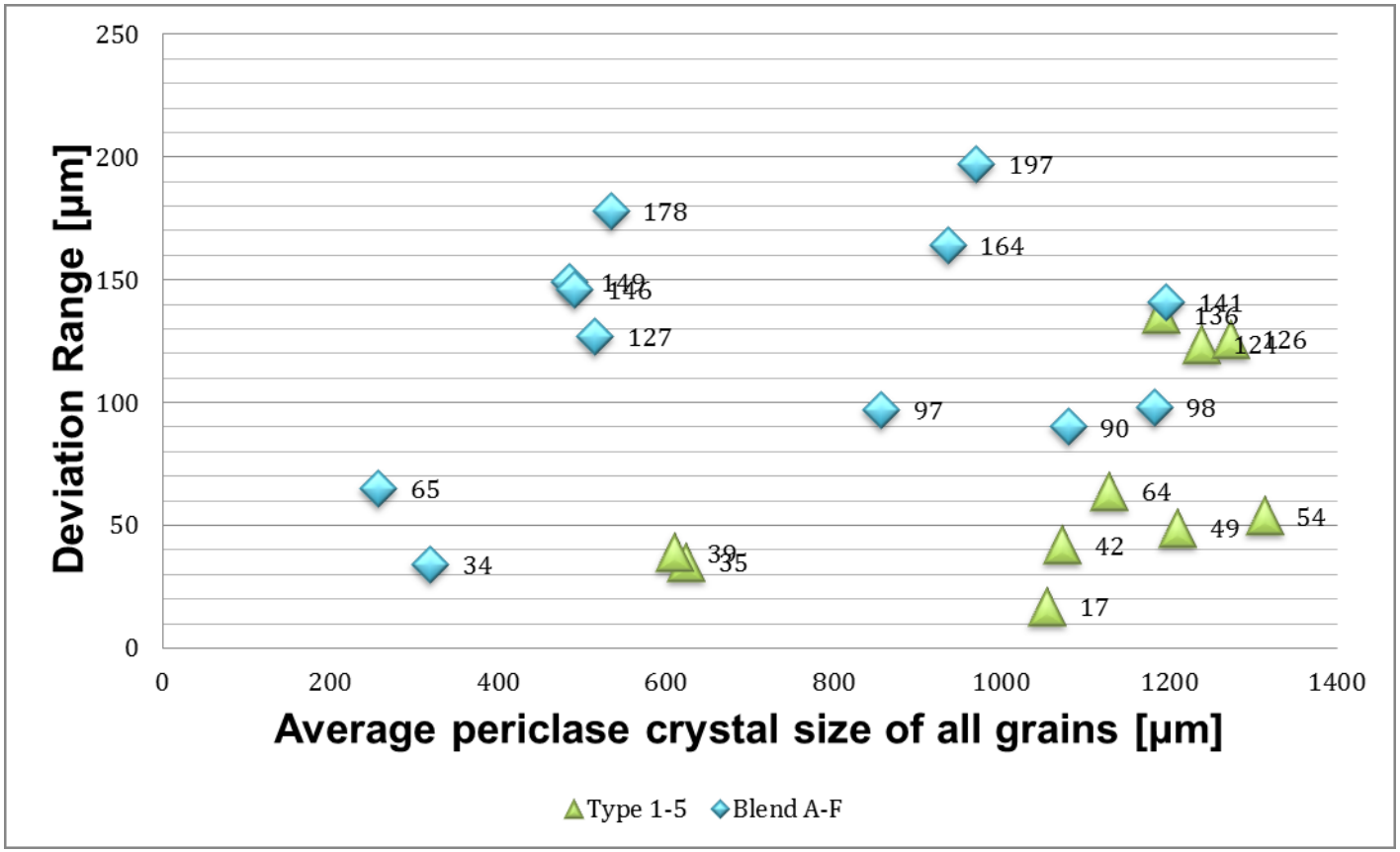


Fig. 32 Deviation range area of average periclase crystal size of all grains according to raw materials

Note: The actual measurement value is the mean value of H1-H5 from table 15 and 16 in [µm].

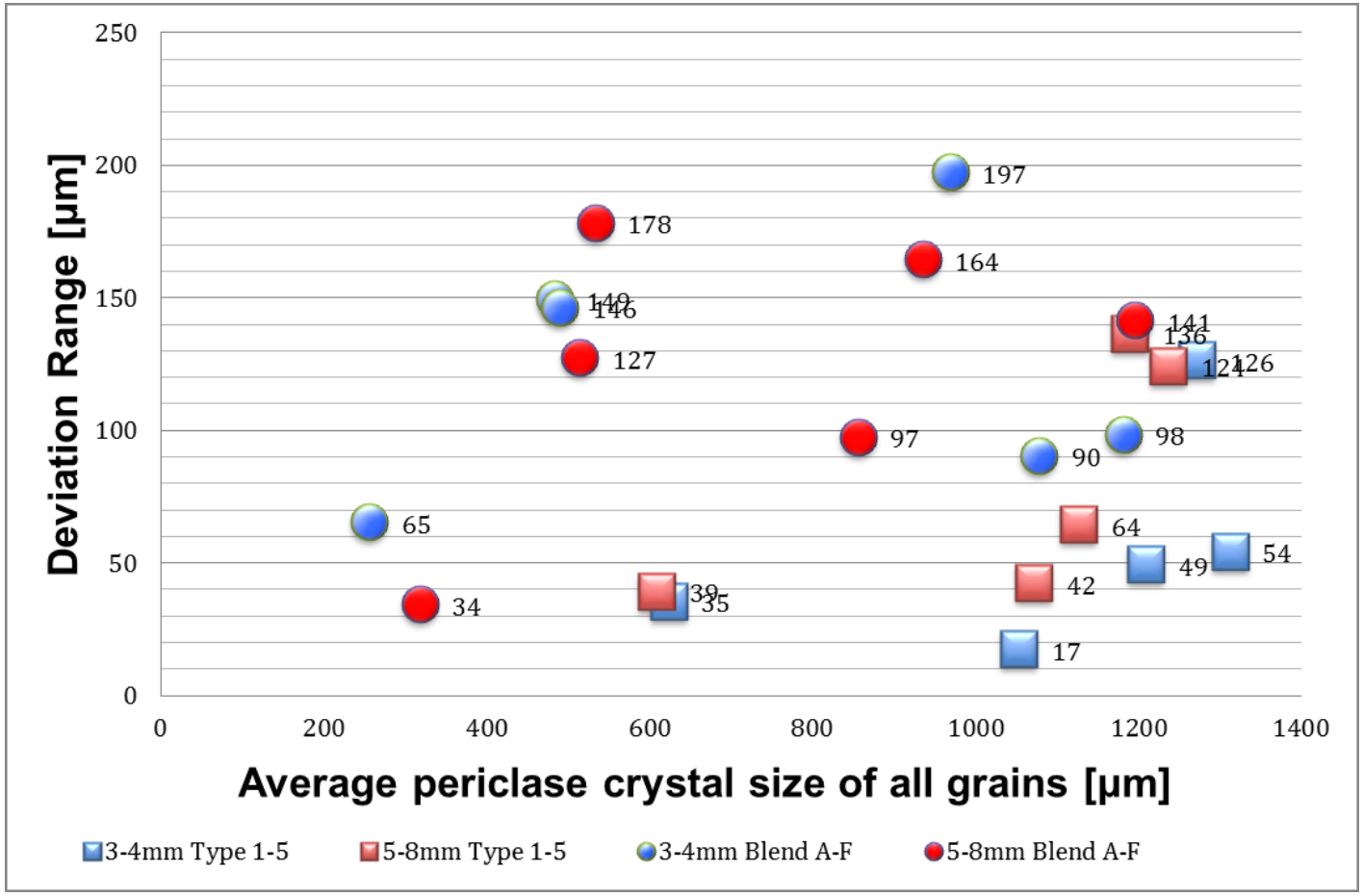


Fig. 33 Deviation range area of average periclase crystal size of all grains according to different fractions

Note: The actual measurement value is the mean value of H1-H5 from table 15 and 16 in [µm].

For analysis of the deviation the result, the following maximum absolute difference of the average periclase crystal size of all grains has been calculated and shown in the above tables. By all appearances the Type 1-5 of the normal type of magnesia raw materials shows a lower maximum difference range than the Blend material.

According to the ASTM standard E112-96 (2004) [4], the repeatability and the reproducibility are applied for the average crystal size measurement evaluation.

The repeatability is defined as the maximum permissible difference due to test error between two test results obtained by one operator on the repeatability interval (r) and the relative repeatability interval (r%).

The maximum difference due to test error between two test results obtained by two operators in different laboratories on the same material using the same test equipment is given by the reproducibility (R) and the relative reproducibility (r%).

For the accuracy evaluation of the measurement results, the parameter of average periclase crystal size of all grains [µm] has been analysed by Technology Center of RHI-AG, Leoben with the standard statistical analysis method DIN 38402 A45; the software of the analysis is PRO Lab.

The following figures are the results of the statistic analysis:

Sample	Standard deviation [µm]	COV [%]	Rep.(*) [µm]	Rel. Rep [%]
Type 1 3-4 mm	14.94	1.14	41.84	3.19
Type 1 5-8 mm	119.83	9.67	335.53	27.07
Type 2 3-4 mm	90.98	7.18	254.76	20.09
Type 2 5-8 mm	37.73	3.33	105.63	9.32
Type 3 3-4 mm	6.66	0.63	18.64	1.76
Type 3 5-8 mm	28.85	2.68	80.78	7.52
Type 4 3-4 mm	31.07	2.57	86.99	7.2
Type 4 5-8 mm	62.14	5.22	173.98	14.62
Type 5 3-4 mm	16.64	2.67	46.6	7.48
Type 5 5-8 mm	14.79	2.42	41.42	6.78
Blend A 3-4 mm	100.6	20.33	281.68	56.92
Blend A 5-8 mm	53.26	10.25	149.13	28.7
Blend B 3-4 mm	50.3	4.64	140.84	12.99
Blend B 5-8 mm	34.03	3.93	95.28	11.01
Blend C 3-4 mm	170.87	17.48	478.44	48.93
Blend C 5-8 mm	164.22	17.3	459.8	48.45
Blend D 3-4 mm	46.36	17.65	129.82	49.43
Blend D 5-8 mm	16.27	5.06	45.57	14.17
Blend E 3-4 mm	119.83	24.15	335.53	67.63
Blend E 5-8 mm	156.08	28.78	437.02	80.59
Blend F 3-4 mm	77.67	6.53	217.48	18.28
Blend F 5-8 mm	35.51	2.97	99.42	8.33

Table 17 statistical analysis results parameters

Note: Rep. is short for reproducibility
Rel.Rep is short for Relative reproducibility

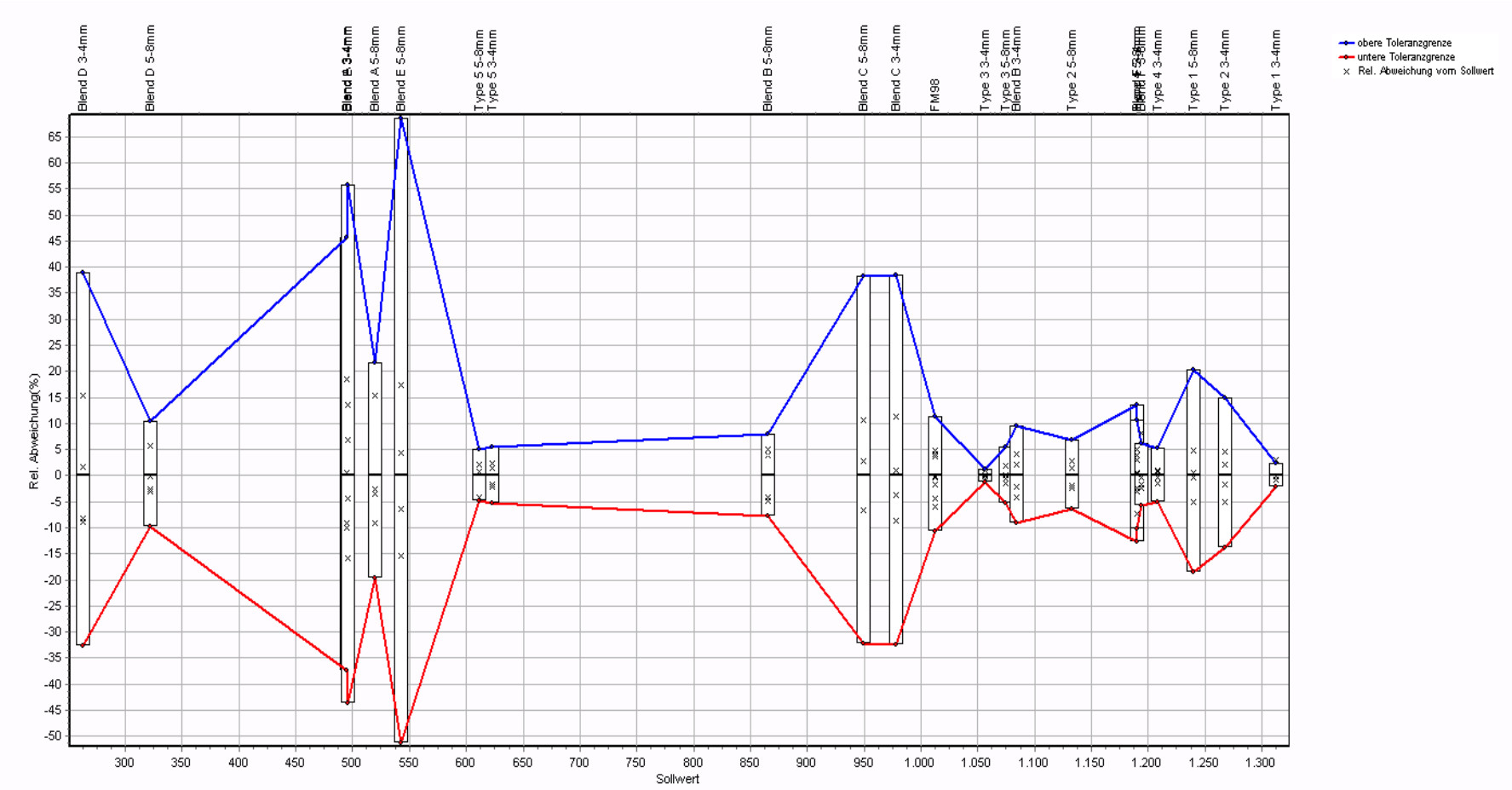


Fig. 34 COV result according to statistical analysis

Note: This figure shows the coefficient of variation result by every measurement. Red line: above the mean value. Blue line: under the mean value.

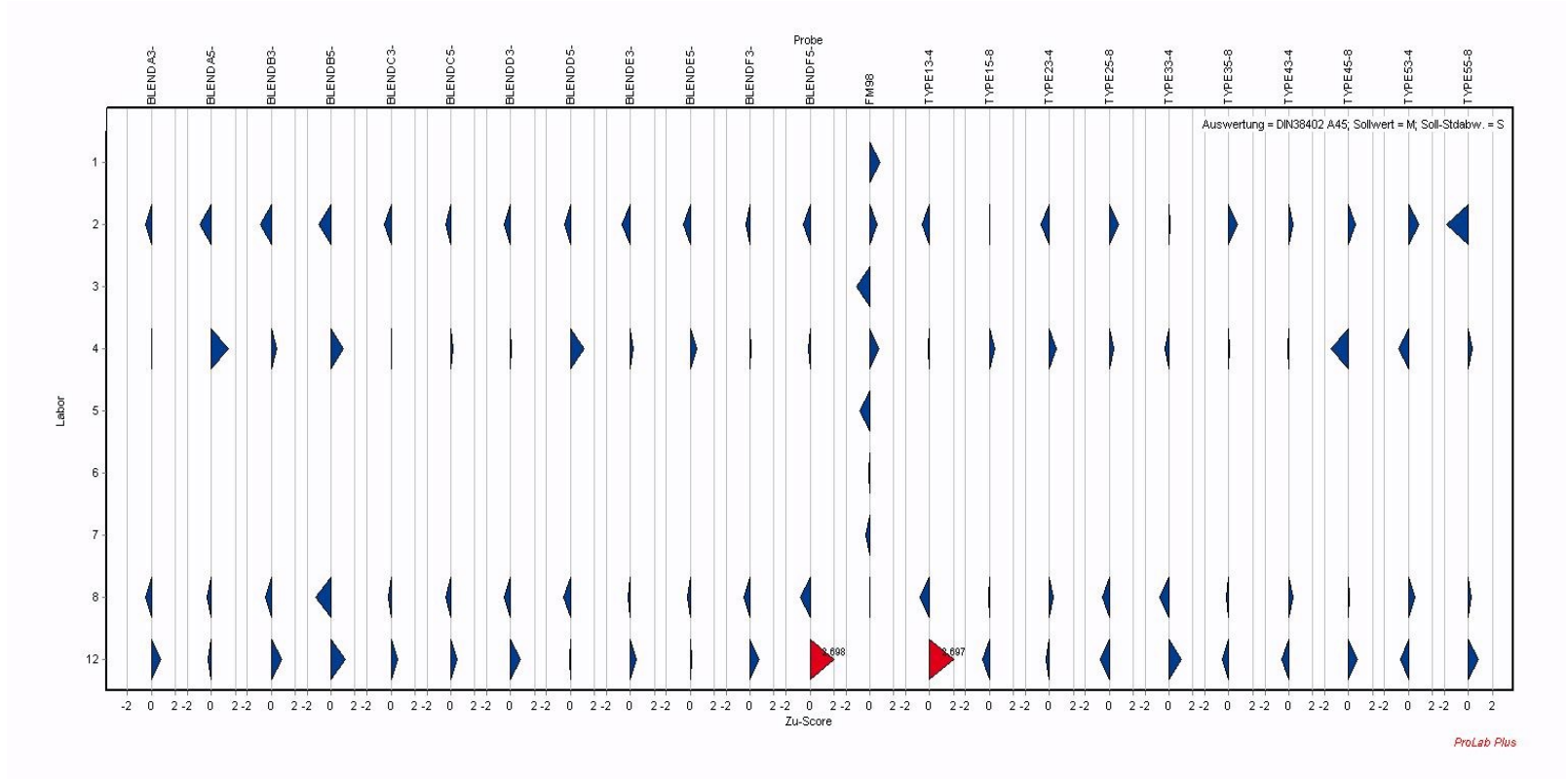


Fig. 35 Personal measurement evaluation according to statistical analysis

Note: The formation of the triangle described the deviation of every measurement result. The bigger the triangle is, the higher deviation there is.

“FM 98” represents a material measured by 8 persons twice

3.2.3 Physical properties

The aim of the bulk density and the open porosity measurement is to compare these properties of different groups of a material and receive at least a figure for homogeneity. A sampling survey of one brand of the 11 brands fused magnesia from chapter 3.2.1 is investigated here. This investigation includes the measurement of the regular, single and residual group of this brand.

The measurement is taken by the department of physics, RHI AG Technology Center, Leoben. The measurement method is mercury porosity method, according to DIN 933-17. The investigation sample of the sampling survey is brand F. Brand F represents concerning average periclase crystal size and microscopically observed porosity a comparably inhomogeneous material. The results are list in the following table:

	Regular Group	Residual Group	Single Group
True density [g/cm^3]	3.576	3.580	3.582
Bulk density [g/cm^3]	3.541	3.543	3.552
Open porosity [Vol%]	1.0	1.0	0.8
Weight [g]	190.1	151.6	38.5

Table 18 True density, bulk density and open porosity results of Brand F

Below the physical parameter are combined with the results of chapter 3.2.1, classification of the fused magnesia by visual inspection. The degree of homogeneity of the raw material can be calculated by the result of weight measurement and bulk density.

The following is the calculation of control procedure:

Total volume calculates by regular group:

$$V1 = \frac{190.1}{3.541} = 53.68\ \mathrm{cm}^3$$

Total volume calculates by single and residual group:

$$V2 = \frac{38.5}{3.553} + \frac{151.6}{3.543} = 53.62\ \mathrm{cm}^3$$

$$V1 \approx V2$$

Considering of the deviation of the physical properties measurement in this generally “inhomogeneous” material, the result is acceptable. The influence on the results of chapter 3.2.1 and 3.2.2 is negligible. Therefore no further bulk density and open porosity measurements have been carried out.

3.2.4 Chemical and mineralogical characterization

3.2.4.1 Chemical analysis

The chemical analyses are done by the chemical department of RHI AG Technology Center, Leoben, to have an overview about the chemical characteristic of the magnesia samples. The investigated samples are fused magnesia Type 1-5 and Blend A-F, with the fraction of 3-4 mm. Table 19 lists the chemical composition of Type 1-5:

[wt %]	Type 1	Type 2	Type 3	Type 4	Type 5
MgO	98,83	98,85	97,68	97,09	97,22
Al_2O_3	0,08	0,12	0,09	0,06	0,20
SiO_2	0,30	0,14	0,48	0,57	0,68
P_2O_5	0,03	0,00	0,08	0,00	0,07
CaO	0,52	0,75	0,92	2,00	1,25
MnO	0,01	0,00	0,02	0,11	0,03
Fe_2O_3	0,23	0,13	0,73	0,17	0,55
C/S ratio(*)	1.73	5.36	1.92	3.51	1.83

Table 19 Chemical analyses of fused magnesia type 1-5

B_2O_3 was not analyzed at the fused magnesia types because the raw material did not origin from seawater or brine deposits.

(*) Note: C/S ratio means the ratio of CaO content to SiO_2 content in wt%.

The following table 20 lists the results of the chemical analysis of Blend A-F:

[wt %]	Blend A	Blend B	Blend C	Blend D	Blend E	Blend F
MgO	97,04	98.04	97,16	97,00	96,96	97,56
AL_2O_3	0,12	0,12	0,11	0,10	0,08	0,12
SiO_2	0,49	0,38	0,54	0,36	0,64	0,51
P_2O_5	0,01	0,05	0,05	0,02	0,01	0,10
CaO	2,05	0,88	1,67	2,13	2,02	1,02
Cr_2O_3	0,02	0,00	0,00	0,07	0,02	0,00
MnO	0,10	0,02	0,07	0,09	0,10	0,02
Fe_2O_3	0,17	0,50	0,39	0,23	0,17	0,67
C/S ratio	4.18	2.32	3.10	5.9	3.16	2.00

Table 20 Chemical analyses of fused magnesia blend A-F

Comparing with the table 19 and table 20, generally the typical fused magnesia types 1-5 have a higher content of MgO than Blend A-F, and a lower content of CaO.

3.2.4.2 Mineralogical investigation

The mineralogical investigations of these 11 brands of fused magnesia include SEM (scanning electron microscope) investigation, chemical etching observation and EDX (energy dispersive analysis) analysis. The following figures show the results of the SEM investigation and the secondary phase after chemical etching by 1% HNO_3 in ethanol for several seconds. The following tables list the results of the EDX analysis. All of the following chemical composition analysis are in weight percentage [wt%].

Type 1

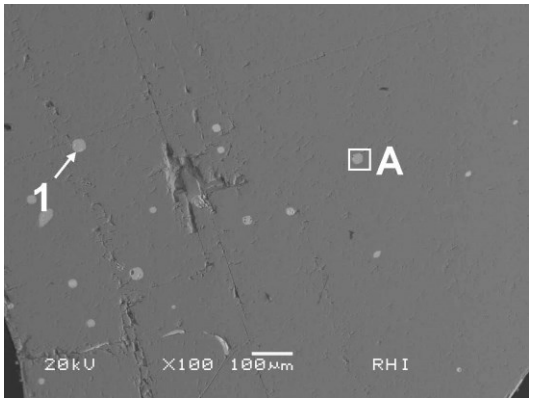


Fig. 36 Grain 1. SEM image of fused magnesia type 1

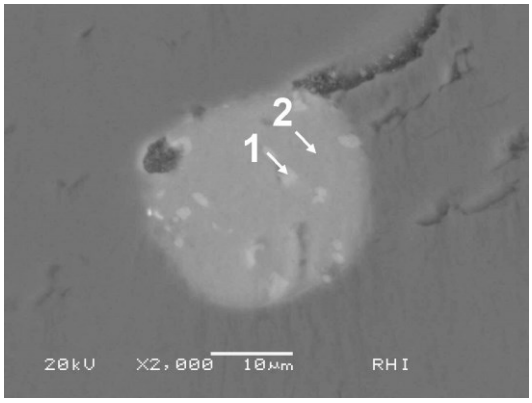


Fig. 37 Grain 1. Area from Fig.36……..

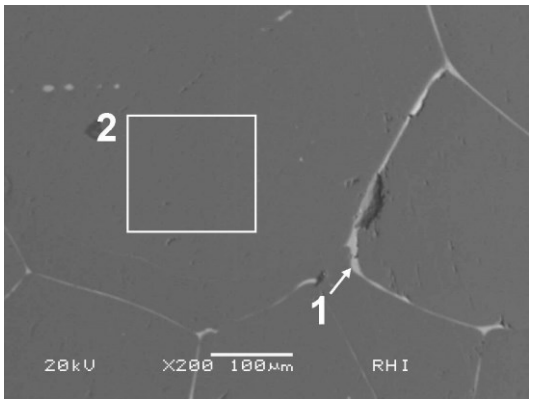


Fig. 38 Grain 2. SEM image of fused magnesia type 1

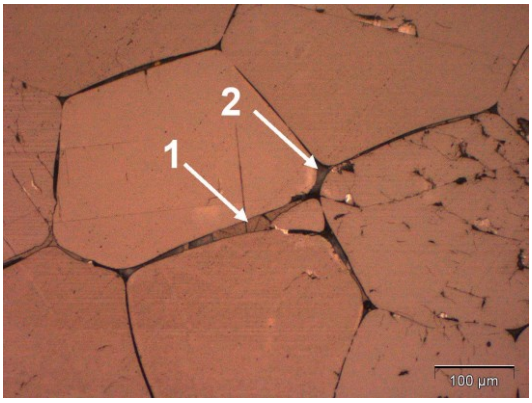


Fig.39 Grain 3. Chemical etching 1) Monticellite 2) Merwinite

Fig.	Area or spot	MgO	Al_2O_3	SiO_2	P_2O_5	CaO	Fe_2O_3(*)	Phase
		%	%	%	%	%	%	
36	1	26.6		38.8		35.6		Monticellite
37	1	11.6		18.2	24.0	45.3		C_3P+Monticellite
37	2	27.1		38.7		34.2		Monticellite
38	1	14.0		35.0	1.1	49.8		Merwinite
38	2	98.7		0.4		0.1	0.8	Periclase

Table 21 EDX analyses of fused magnesia type 1

(*): Total iron content, calculated as Fe_2O_3

Type 2

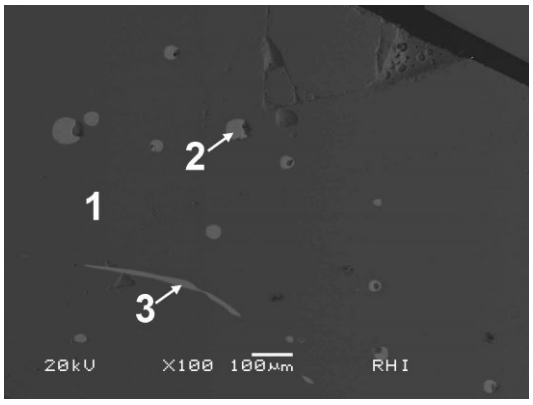


Fig. 40 Grain 1. SEM image of fused magnesia type 2

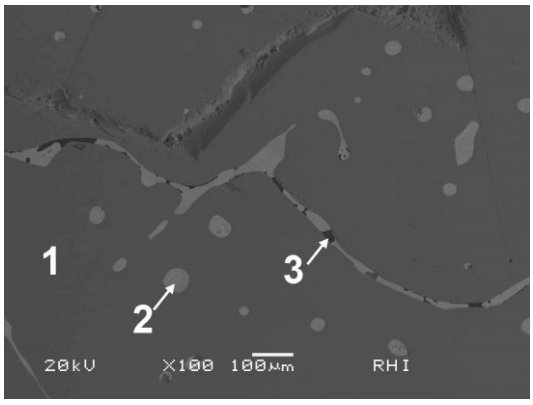


Fig. 41 Grain 2. SEM image of fused magnesia type 2 (Pore point 3)

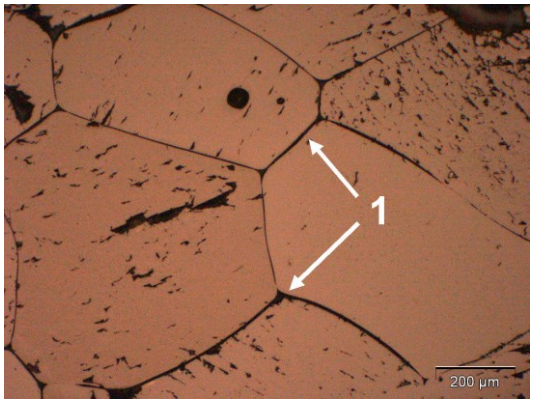


Fig. 42 Grain 3. Chemical etching 1) C_2S

Fig.	Area or spot	MgO	SiO_2	CaO	Phase
		%	%	%	
40	1	98.4		1.6	Periclase
40	2	5.9	35.7	58.4	C_2S+Merwinite
40	3	4.0	35.0	60.9	C_2S+Merwinite
41	1	99.0		1.0	Periclase
41	2		35.2	64.8	C_2S

Table 22 EDX analyses of fused magnesia type 2

Type 3

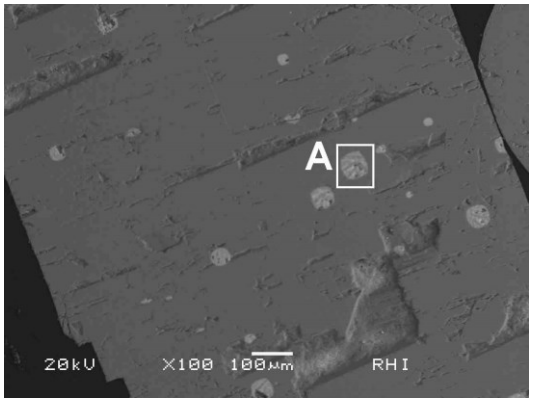


Fig. 43 Grain 1. SEM image of fused magnesia type 3

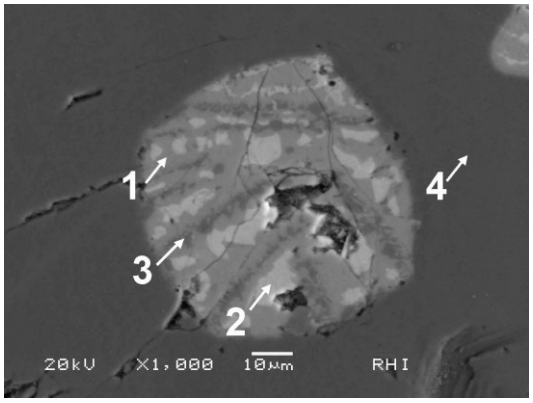


Fig. 44 Grain 1. Area A from Fig.4

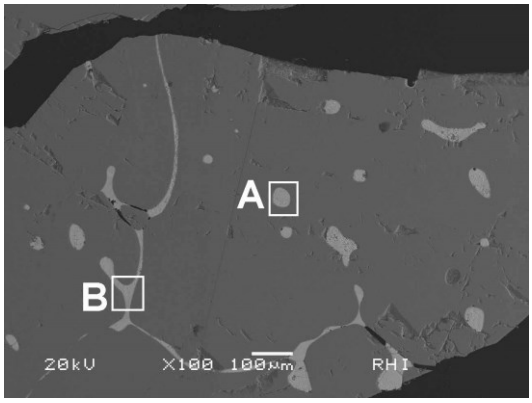


Fig. 45 Grain 2. SEM image of fused magnesia type 3

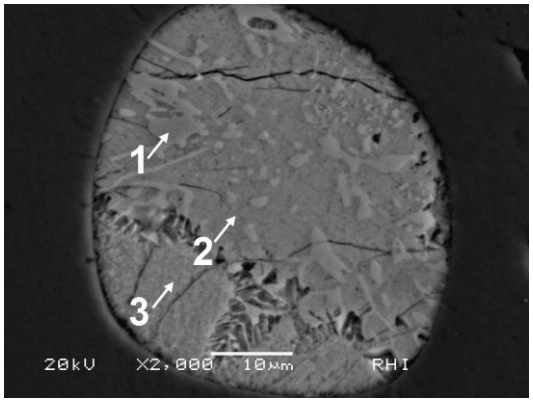


Fig. 46 Grain 2. Area A from Fig. 45

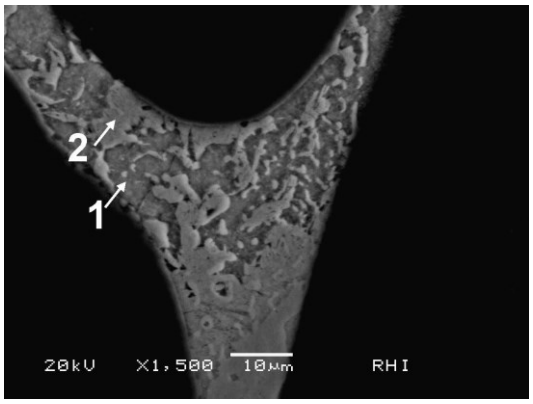


Fig. 47 Grain 2. Area B from Fig.45`

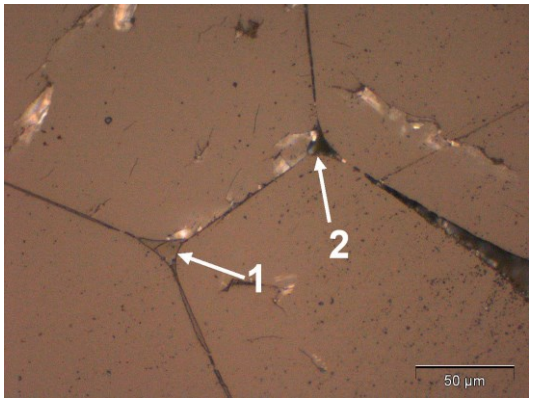


Fig. 48. Grain 3 Chemical etching 1) Monticellite 2) C_2

Fig.	Area or spot	MgO	SiO_2	P_2O_5	CaO	Phase
		%	%	%	%	
44	1	25.6	38.3	1.3	35.0	Monticellite
44	2	0.6	5.1	38.7	55.7	C_3P
44	3	42.4	39.8	1.5	16.3	M_2S(light area)+Monticellite(dark area)
44	4	100				Periclase
46	1	1.8	31.0	4.8	62.4	C_2S+ C_3P
46	2	5.4	32.1	3.9	58.5	Mixing composition,C_2S+C_3P mainly(*)
46	3	0.8	28.4	8.5	62.3	Mixing composition,C_2S+C_3P mainly(*)
47	1	5.2	29.2	7.8	57.8	Mixing composition,C_2S+C_3P mainly(*)
47	2	0.6	30.2	4.5	64.7	Mixing composition,C_2S+C_3P mainly(*)

Table 23 EDX analyses of fused magnesia type 3

* This mixing composition is possible due to the investigated area for the EDX chemical identification

Type 3 Single group

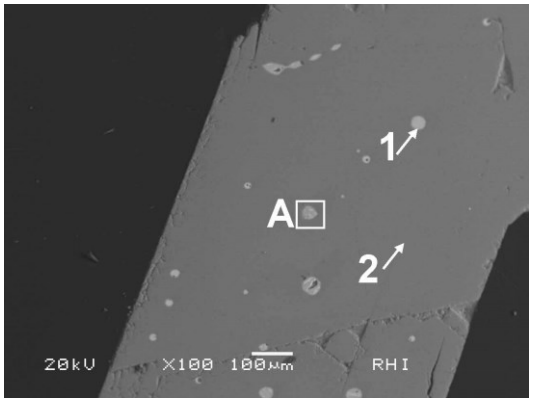


Fig. 49 Grain 1. SEM image of fused magnesia type 3 , single crystal group

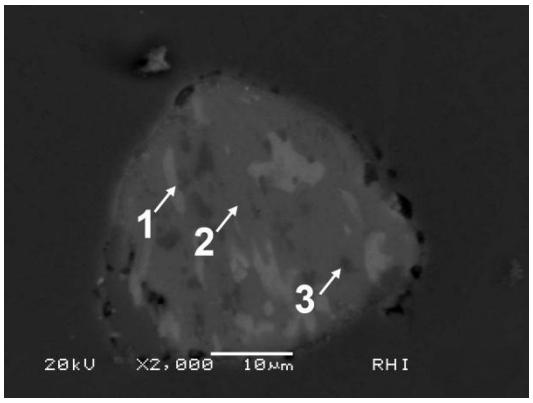


Fig. 50 Grain 2. Area A from Fig.49

Fig.	Area or spot	MgO	SiO_2	P_2O_5	CaO	Fe_2O_3(*)	Phase
		%	%	%	%	%	
49	1	99.1			0.3	0.6	Periclase
49	2	12.3	37.7	6.6	43.4		Merwinite+C_3P
50	1	13.9	20.2	21.6	44.3		Merwinite+Monticellite +C_3P
50	2	27.6	38.4		34.1		Monticellite
50	3	11.5	38.8		49.7		Merwinite

Table 24 EDX analyses of fused magnesia type 3 single crystal group

(*): Total iron content, calculated as Fe_2O_3

Type 4

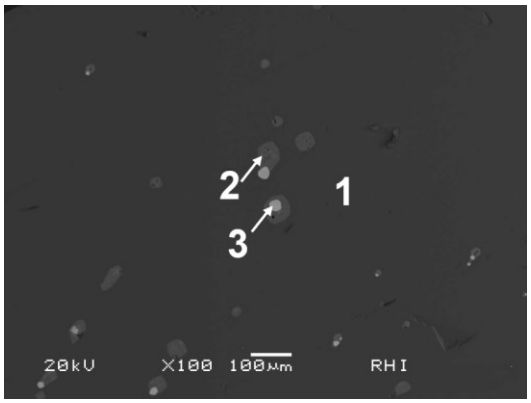


Fig. 51 Grain 1. SEM image of fused magnesia type 4

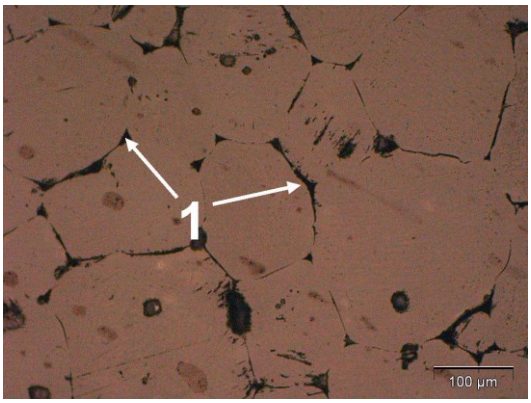


Fig.52 Grain 2. Chemical etching 1) C_2S

Fig.	Area or spot	MgO	SiO_2	CaO	Phase
		%	%	%	
51	1	99.2		0.3	Periclase
51	2	11.7	36.7	51.7	Merwinite
51	3	5.62	35.6	58.7	Merwinite+C_2S

Table 25 EDX analyses of fused magnesia type 4

Type 5

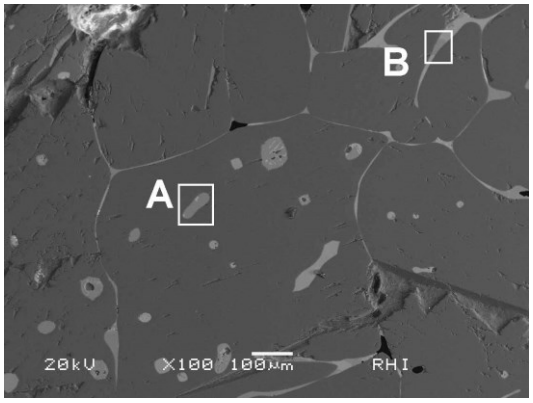


Fig. 53 Grain 1. SEM image of fused magnesia type 5

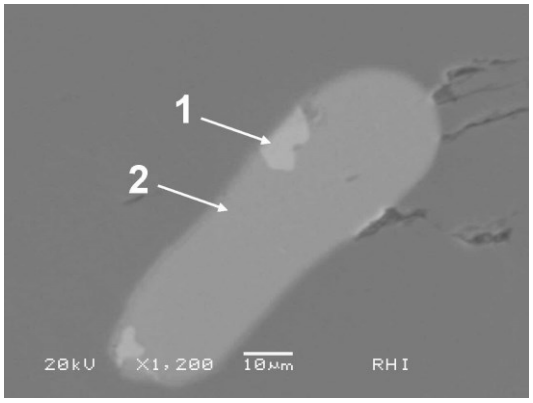


Fig. 54 Grain 1. Area A from Fig.53

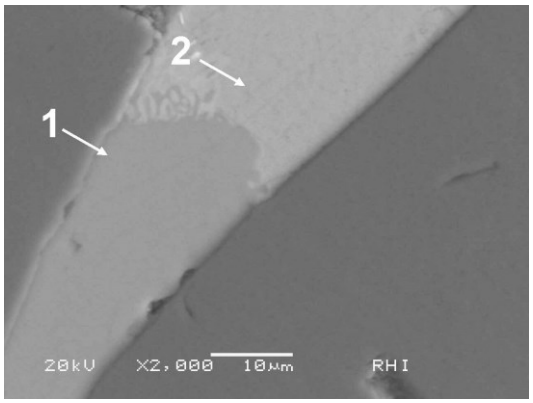


Fig. 55 Grain 1. Area B from Fig.53

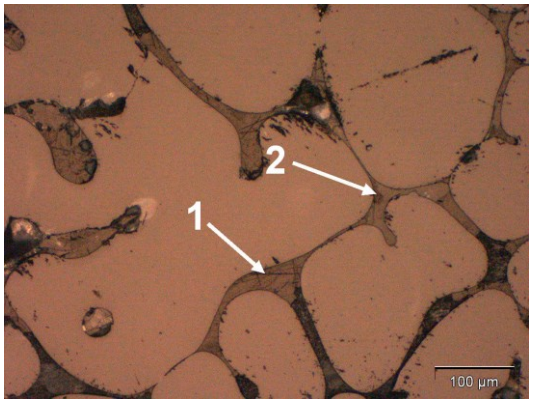


Fig. 56 Grain 2. Chemical etching 1) Merwinite 2) Monticellite

Fig.	Area or spot	MgO	SiO_2	P_2O_5	CaO	Phase
		%	%	%	%	
54	1	0.5		40.3	56.5	C_2P
54	2	27.9	38.6		33.5	Monticellite
55	1	25.7	38.6		35.7	Monticellite
55	2	12.0	35.4	1.3	51.2	Merwinite

Table 26 EDX analyses of fused magnesia type

Blend A

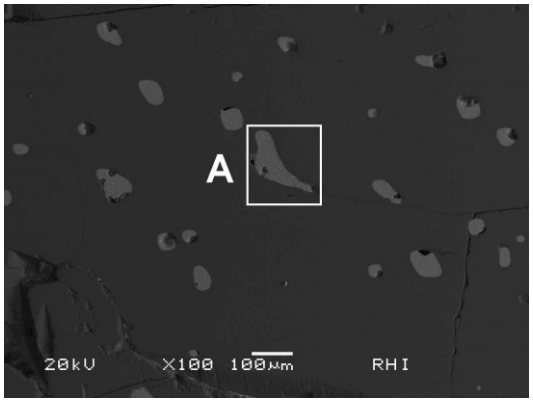


Fig.57 Grain 1. SEM image of fused magnesia sample Blend A

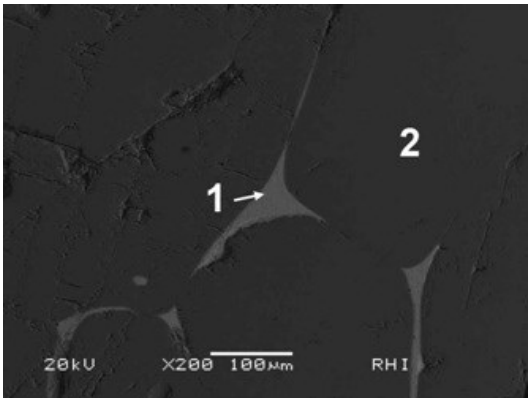


Fig. 58 Grain 2. SEM image of fused magnesia sample Blend A

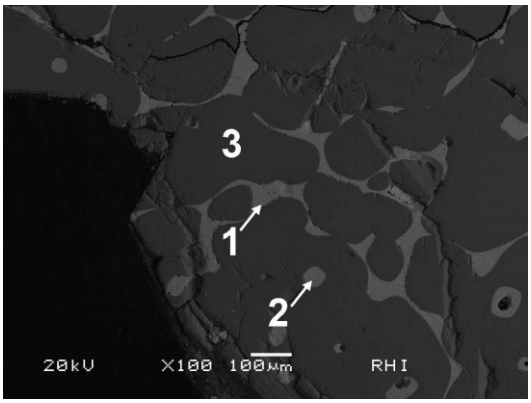


Fig.59 Grain 3. SEM image of fused magnesia Blend A

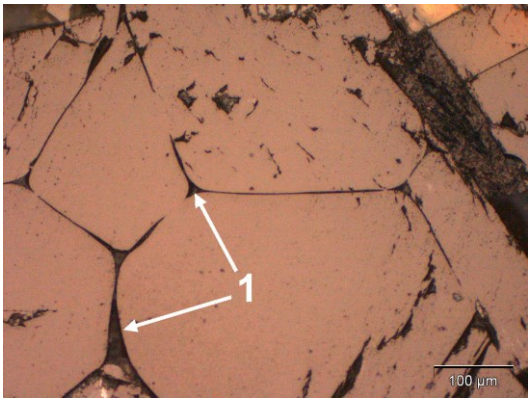


Fig. 60 Grain 4. Chemical etching 1) C_2S

Fig.	Area or spot	MgO	SiO_2	CaO	Phase
		%	%	%	
57	A	3.0	34.7	62.3	C_2S
58	1		34.9	65.1	C_2S
58	2	99.1		0.9	Periclase
59	1	4.4	35.8	59.9	C_2S+Merwinite
59	2	0.5	34.6	64.9	C_2S
59	3	98.5	0.5	1.0	Periclase

Table 27 EDX analyses of fused magnesia Blend A

Blend B

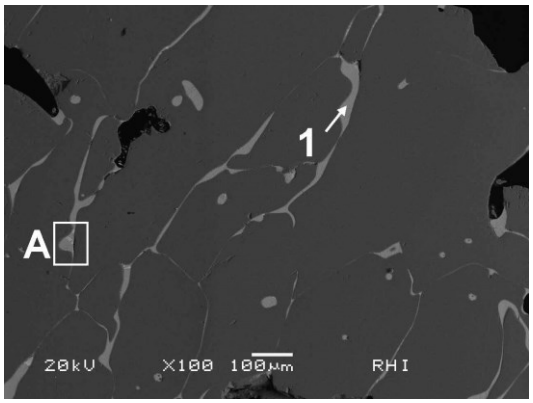


Fig. 61 Grain 1. SEM image of fused magnesia sample Blend B

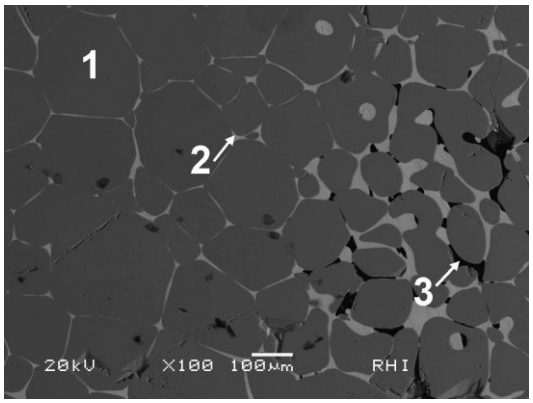


Fig. 62 Grain 2. SEM image of fused magnesia sample Blend B

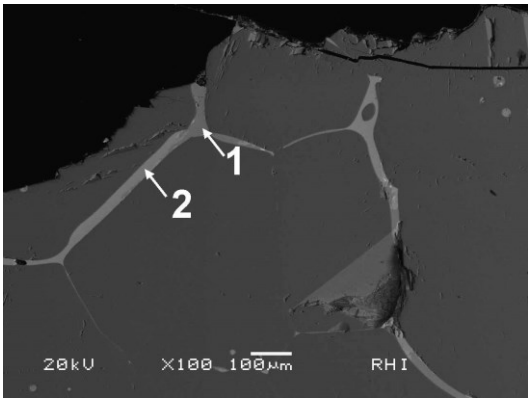


Fig. 63 Grain 3. SEM image of fused magnesia Blend B

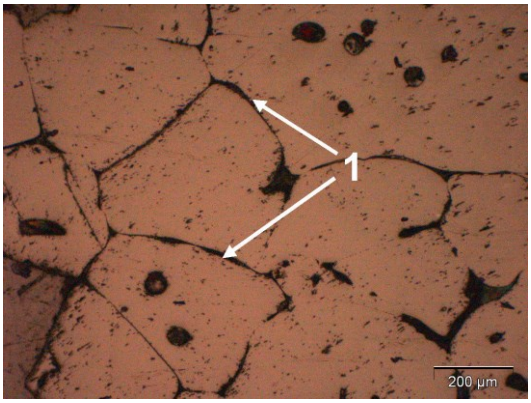


Fig.64 Grain 4. Chemical etching 1)C_2S

Fig.	Area or spot	MgO	SiO_2	P_2O_5	CaO	Fe_2O_3(*)	Phase
		%	%	%	%	%	
61	1		33.0	6.0	59.9		C_2S+C_3P
61	A	17.7	28.3	3.9	50.1		Area analysis
62	1	98.2				1.8	Periclase
62	2	12.6	36.2		51.3		Merwinite
63	1	26.6	38.9		34.5		Monticellite
63	2	11.9	35.2	2.6	50.2		Merwinite+C_3P

Table 28 EDX analyses of fused magnesia Blend B

(*): Total iron content, calculated as Fe_2O_3

Blend C

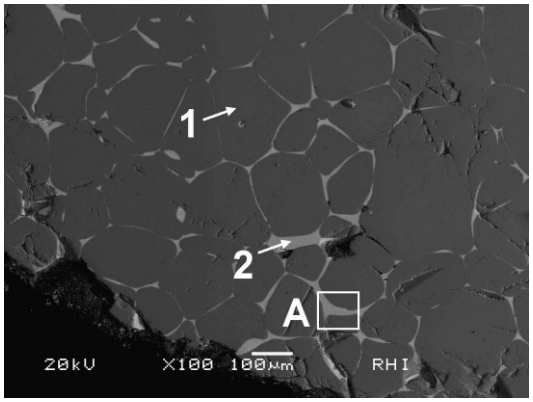


Fig.65 Grain 1. SEM image of fused magnesia sample Blend C

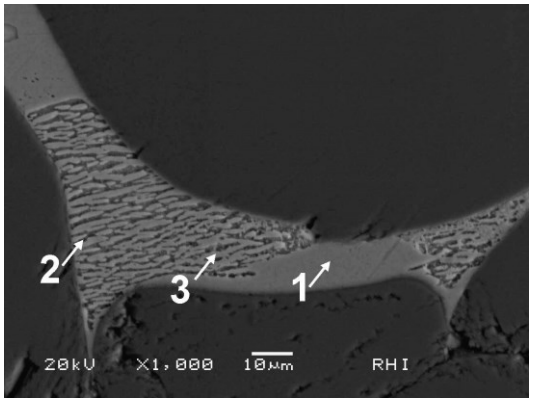


Fig. 66 Grain 1. Area A from Fig.65

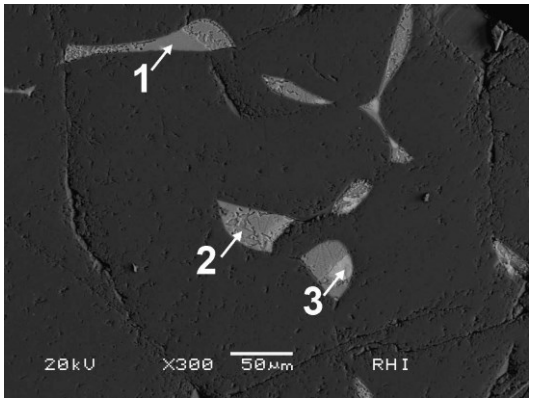


Fig. 67 Grain 2. SEM image of fused magnesia sample Blend C

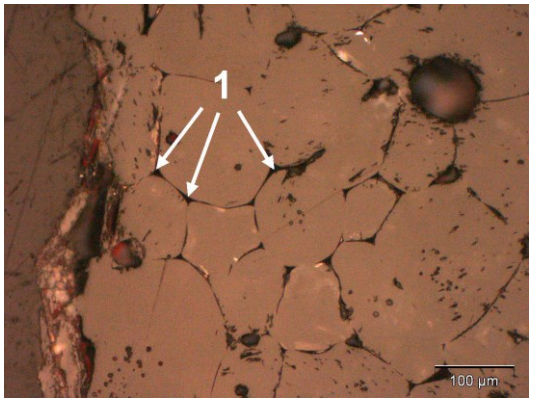


Fig. 68 Grain 3. Chemical etching 1) C_2S

Fig.	Area or spot	MgO	SiO_2	P_2O_5	CaO	Fe_2O_3(*)	Phase
		%	%	%	%	%	
65	1	98.1				1.9	Periclase
65	2	12.0	35.5	1.8	50.7		Merwinite+C_3P
66	1	12.1	36.5		51.6		Merwinite
66	2	3.3	28.7	5.9	59.5		Mixing composition,C_2S+C_3P mainly
66	3	10.8	34.2	2.7	52.3		Merwinite+C_3P
67	1	4.9	36.1		59.2		C_2S+Merwinite
67	2		33.6	1.3	65.1		C_2S+C_3P
67	3		32.4		67.6		C_2S

Table 29 EDX analyses of fused magnesia Blend C

(*): Total iron content, calculated as Fe_2O_3

Blend D

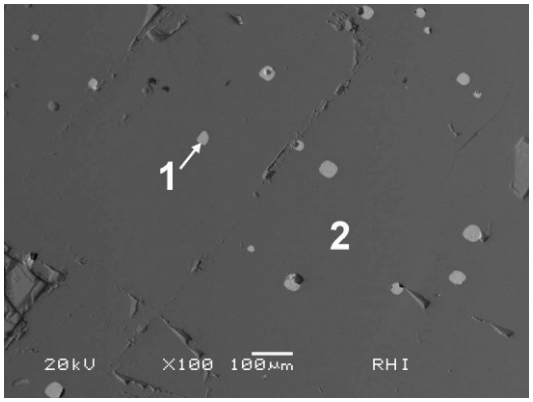


Fig.69 Grain 1. SEM image of fused magnesia sample Blend D

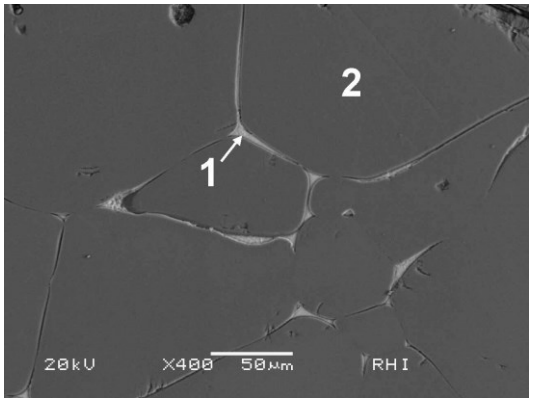


Fig.70 Grain 2. SEM image of fused magnesia sample Blend D

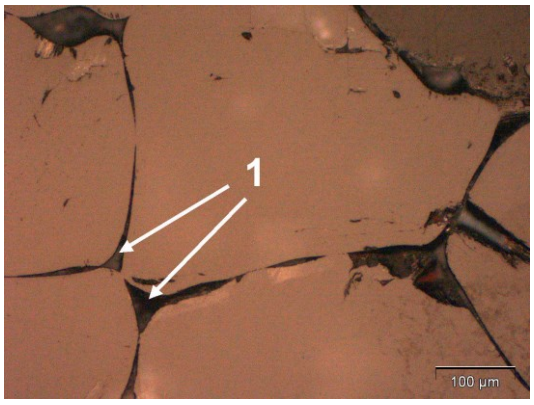


Fig.71 Grain 3. Chemical etching 1)C_2S

Fig.	Area or spot	MgO	SiO_2	CaO	Phase
		%	%	%	
69	1	7.1	36.2	56.7	C_2S+Merwinite
69	2	99.4		0.6	Periclase
70	1		31.3	68.9	C_2S
70	2	99.6		0.4	Periclase

Table 30 EDX analyses of fused magnesia Blend D

Blend E

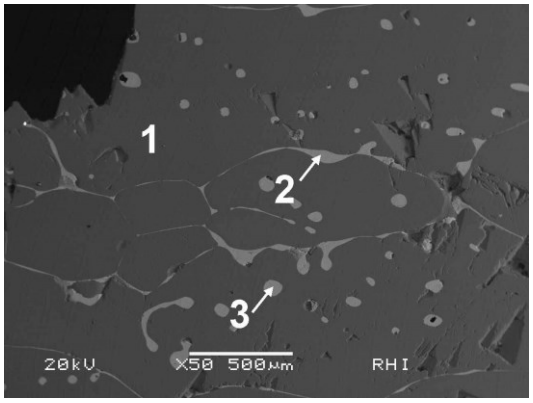


Fig. 72 Grain 1. SEM image of fused magnesia sample Blend E

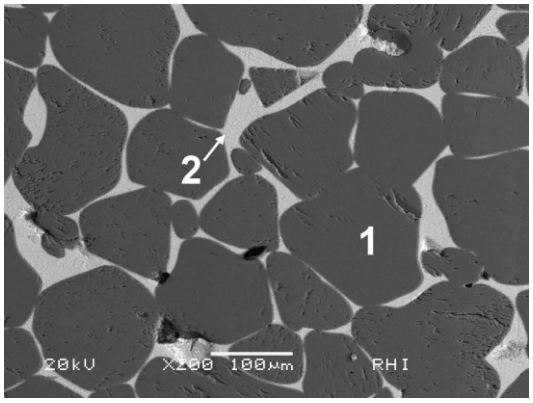


Fig. 73 Grain 2. SEM image of fused magnesia sample Blend E

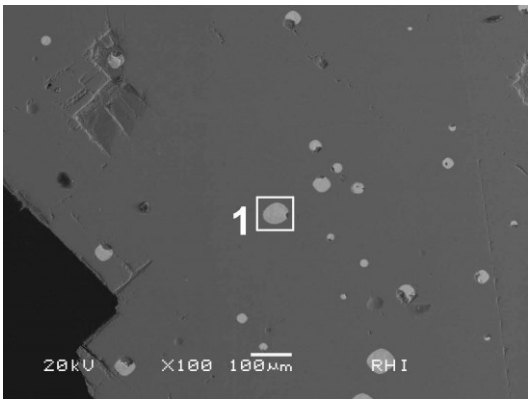


Fig. 74 Grain 3. SEM image of fused magnesia Blend E

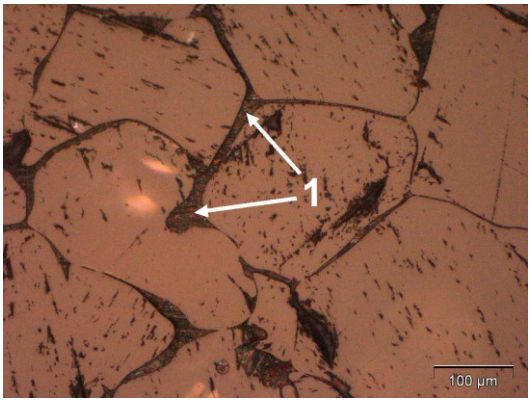


Fig.75 Grain 4. Chemical etching 1) C_2S

Fig.	Area or spot	MgO	SiO_2	CaO	Phase
		%	%	%	
72	1	98.7		1.3	Periclase
72	2	5.8	35.9	58.4	C_2S+Merwinite
72	3		35.0	65.0	C_2S
73	1	99.2		0.8	Periclase
73	2		34.5	65.5	C_2S
74	1	6.5	35.6	57.9	C_2S+Merwinite

Table 31 EDX analyses of fused magnesia Blend E

Blend F

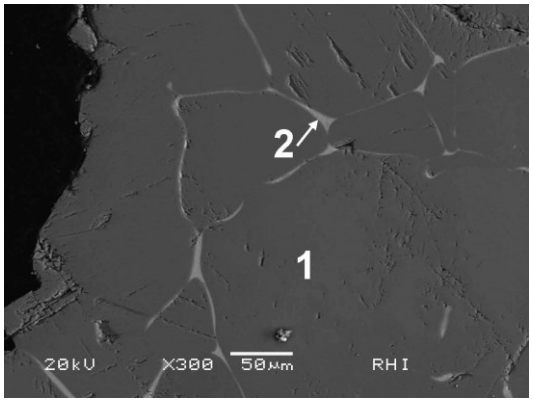


Fig. 76 Grain 1. SEM image of fused magnesia Blend F

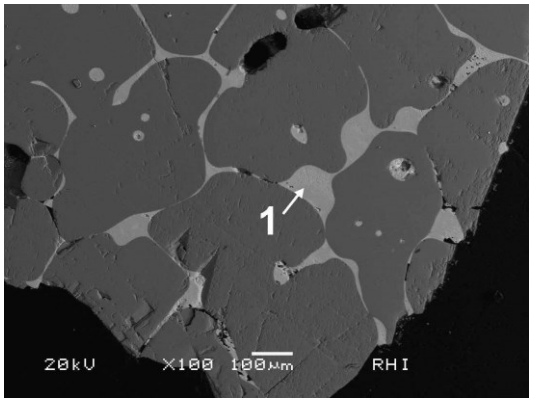


Fig. 77 Grain 2. SEM image of fused magnesia sample Blend F

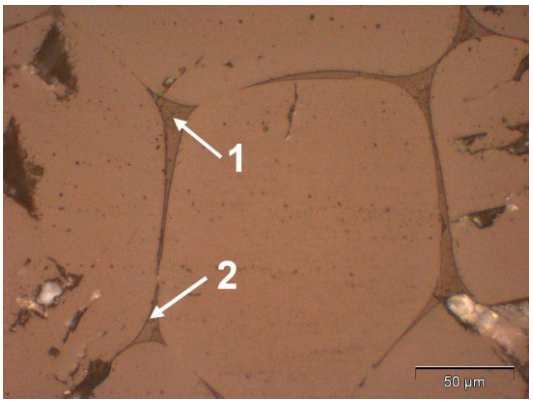


Fig.78 Grain 3. Chemical etching 1) Merwinite 2) Merwinite

Fig.	Area or spot	MgO	SiO_2	P_2O_5	CaO	Fe_2O_3(*)	Phase
		%	%	%	%	%	
76	1	98.7			0.4	0.9	Periclase
76	2	11.0	31.9	6.0	51.1		Merwinite+C_3P
77	1	11.6	34.7	2.0	51.7		Merwinite+C_3P

Table 32 EDX analyses of fused magnesia Blend F

(*): Total iron content, calculated as Fe_2O_3

Example for Residual group (Blend F)

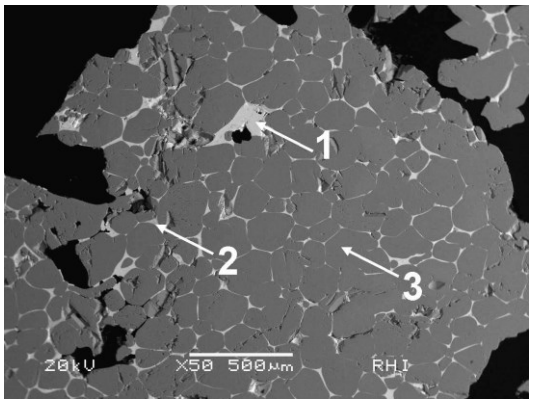


Fig.79 Grain 1. SEM image of fused magnesia Blend F Residual group

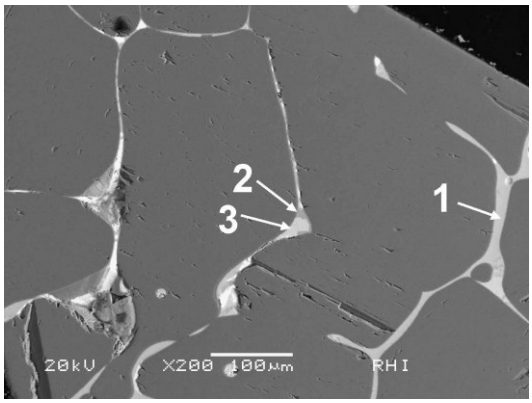


Fig.80 Grain 2. SEM image of fused magnesia Blend F Residual group

Fig.	Area or spot	MgO	SiO_2	P_2O_5	CaO	Fe_2O_3(*)	Phase
		%	%	%	%	%	
79	1	11.3	35.0	2.0	51.7		Merwinite+C_3P
79	2	24.0	37.2	1.8	37.0		Monticellite+ C_3P
79	3	99.2				0.8	Periclase
80	1	14.3	36.2		49.5		Merwinite
80	2	28.7	38.2		33.0		Monticellite
80	3		1,8	42.2	56.0		C_3P

Table 33 EDX analyses of fused magnesia Blend F Residual group

(*): Total iron content, calculated as Fe_2O_3

4 Discussion of results

4.1 Investigation of magnesia clinker

In chapter 3.1.1 and 3.1.2. The two methods for average periclase crystal size measurements are described. In the following are some discussions and comparisons about the two methods.

4.1.1 Average crystal size measurement results

In chapter 3.1.1, the grid method has been used for the average crystal size measurements of 3 different magnesia clinker brands. The results are shown in table 1, which correspond to the characterizations of the 3 magnesia clinker brands: Brand B1 has an average crystal size with 132 µm, and the crystal size distribution is quite wide. Brand B2 has a bigger average crystal size with 177 µm, but its crystal size distribution is narrower than that of brand B1. Brand B3 is a typical smaller size periclase with 58 µm average size; such chemically highly pure magnesia with smaller crystal size is often difficult to accurately be measured.

In chapter 3.1.2, the lineal analysis is taken for a same group of polishing samples of magnesia clinker brand B1. The details of the measurement process are described in chapter 3.1.2. The result for the average crystal size of the magnesia is 125 µm by using lineal analysis.

4.1.2 Comparisons of the results

Two methods are applied for average crystal size measurement for the same polishing samples of brand B1. The results show that crystal size obtained by grid method is 132 µm that by lineal analysis is 125 µm. There is only a very small deviation of the results. Compared with the distribution diagram obtained by the both methods (chapter 3.1.1 and 3.1.2), they also show a similar distribution histogram. The investigation proves that the both methods for the periclase crystal size are credible and accurate.

4.1.3 Advantages and disadvantages of the two methods

According to above studys and the reference from J.Mosser and K. Riepl [21], the advantages and disadvantages of the two methods are summarized as follows.

i.) Grid method

Advantage:

-Objective choice of objects
-Consumes little time (approx. 0.5h per 100 comparison measurements).
-Comparative estimation
-Subjective (invariable) margin of estimative error.
-Easily reproducible results.

Disadvantage:

-Reasonable but significant physical exertion.
-Reliable data, even for poorly discernible crystal boundaries.

ii.) Lineal analysis

Advantage:

-Accurate measurements possible as long as the crystal boundary is

-Discernible at the measuring point.

Disadvantage:

-One-dimensional measuring
-Danger of subjective selection of objects
-Time-consuming
-Physically strenuous
-Results only reproducible for a large number of measured values

4.2 Investigation of fused magnesia

4.2.1 Comparison of the theoretical single crystal amount and the single crystal amount

According to chapter 3.2.1, the results of the comparison between theoretical amount of single crystal C_{theo} and measured single crystal amount C of fused magnesia fraction 5-8 mm with is shown in the Table 7.

From the Fig. 27 of this chapter, the curve of C_{theo} and the curve of C always show the similar tendency and distribution. Most of the comparisons between C_{theo} and C show a small difference. C_{theo} is always higher than C.

4.2.2 Statistical analysis of average crystal size measurement by grid method

According to chapter 3.2.2, the investigation results of the standard deviation and the coefficient of variation are listed in table 9-16. Combining with Figure 28-31, the there is a general judgment of each measurement result.

Discussion:

(i.) According to Fig 32 the material of blend A-F fused magnesia obviously shows higher deviation range than the 1-5 type fused magnesia. That means the blend material that contains “wide range” crystal size is difficult to measure and the deviation can be larger than from normal type fused magnesia. By evaluation of the deviation range, the scale of the mean value of PCS must be taken into consideration. E.g. A difference range of 100 µm for the average PCS = 500 µm is very high, but for a material with PCS = 1200 µm, this could be acceptable.

(ii.) With respect to the material type 1-5, table 17 shows a small coefficient of variation and also a small number for relative reproducibility of the average periclase crystal size measurement of all grains, compared to the blend types.

(iii.) In table 13 there is a high deviation by H4 and H5. This high deviation appears in sample No.3, material type 3 in fraction 3-4 mm. The analysis of this high deviation is as follows:

Sample No.3:

	Average PCS of portion <1435 µm [µm]	Average PCS of all grains [µm]
Mean value	815	1274
COV	20.59	3.82

Table 34 Measurement results of sample No.3

Obviously, among the average periclase measurement of sample No.3, only the portion<1435 µm shows a high deviation, but the results of all grains is acceptable. In the following there are the results of average periclase crystal size of portion <1435 µm by all 5 measurements:

	H1	H2	H3	H4	H5
P3 [µm]	683	711	645	990	1045

Table 35 Results by five measurements of technical staff H1-H5

Clearly H4 and H5 show a big difference of the measurement compared with H1, H2 and H3. The reason for the difference can be explained by the following analysis:

(iv.) H1, H2 and H3 considered 2-3 grains with an average crystal size in the range of 200-300 µm. But among the measurement of H4 and H5, these grains are missing. The total number of grains is at least 60 in minimum, normally 2-3 grains missing will not influence the results very much. But in this investigation the grain portion with average PCS > 1435 µm is 83%, that means there are only 100%-83%=17% portion of all grains are <1435 µm. The very high deviation appears in the measurement of average crystal size of portion<1435 µm, which is exactly this 17% portion. The total grains of this measurement are only about 10 grains. The influence of the 2-3 grains to the

total number of 10 grains is large and leads to such a big difference in the result.

The deviation result of average PCS of all grains is little, because the denominator of this parameter is at least 60 grains. The influence by the missing grains is smaller.

(v.) Compared with all results of average PCS of grains <1435 μm and average PCS of all grains, average PCS of grains <1435 μm always shows a larger deviation than average PCS of all grains. This is also caused by the higher number of grains used for calculation. According to the definition of these two parameters, the grains that are measured for average PCS <1435 μm is a portion of average PCS of all grains. The lower the portion is, the larger the difference between these two parameters can be.

(vi.) From the above discussion, there are several important points which should be noted during fused magnesia crystal size measurement:

1. The deviation of the measurement results is influenced by the homogeneity of the raw material. The more homogeneous the raw material is, the smaller the measurement deviation is to be expected.
2. All of the four measurement result parameters are important for the results evaluation of fused magnesia. The results cannot only be judged by their average periclase crystal size of all grains.
3. During the periclase crystal size measurement by grid method, all grains on the polished samples should be measured. Do not forget any grains, especially those with very small crystal size.

5 Conclusions

In this thesis, the fundamentals of periclase average crystal size measurement are studied. Main works include optimization of the preparation techniques of samples for microstructural observation, influence on crystal size measurements by the single crystal amount in fused magnesia, statistical analyses on the results achieved by grid method and comparison of two methods of the crystal size measurements: grid method and lineal analysis. The characterizations of fused magnesia of different brands, which include physical, chemical and mineralogical properties, are also investigated. The obtained conclusions are summarized as follows:

i. During preparation of the polished samples for microstructure investigations, a soft cloth lap is recommended for the polishing. For the observation on smaller crystal size periclase, especially in chemically very pure material an etching technique with HNO_3 or H_2SO_4 solution on the polished section could help to identify clear crystal boundaries.

ii. The classification of fused magnesia by visual inspection shows that also grains with average crystal sizes <1435 µm are sorted out. The regularly measured portion >1435 µm is always smaller than the “calculated” C_{theo} one.

iii. The statistical analyses of crystal size measurements of fused magnesia with different brands show a deviation range of the results of grid method. For the statistical evaluation of the measurement results, the coefficient of variation, repeatability and reproducibility can be applied. The blend material always shows a higher deviation than the normal type of fused magnesia raw material.

iv. According to the results of chemical analyses and mineralogical characterization, the C/S ratio calculated from the chemical analyses is corresponding with the results from chemical etching microstructure observation and EDX analyses. The secondary phases in the magnesia

sample are mainly composed of monticellite, merwinite, C_2S and C_3P. The amount of the secondary phases is determined by the raw material purity.

v. Lineal analysis can be used as an auxiliary method for more accurate results requirements. But it is problematic for fused magnesia because of the high number of polished samples needed to achieve the required number of periclase crystals to be measured. For LC-sintered magnesia both measurement procedures lead to similar results. For further statistic confirmation significantly more measurement results with lined analysis would be required.

vi. Grid method and the lineal analysis show credible and accurate measurements results. The grid method is more efficient due to its comparison process. It is recommended as the general method for the large amount measurements in test work especially for fused magnesia. The results of pure type material measured by several well trained personal with grid method show low deviations.

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