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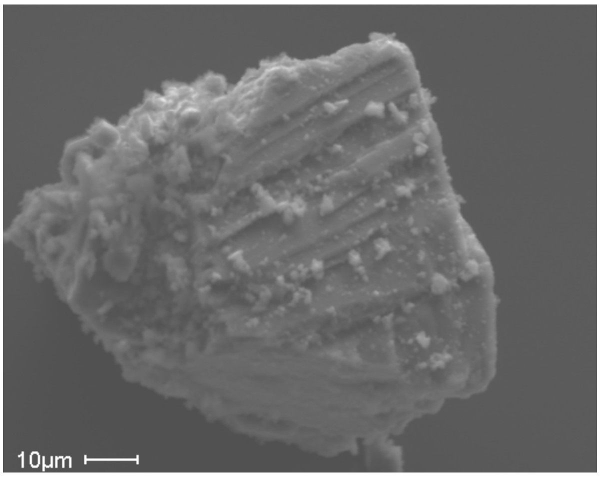
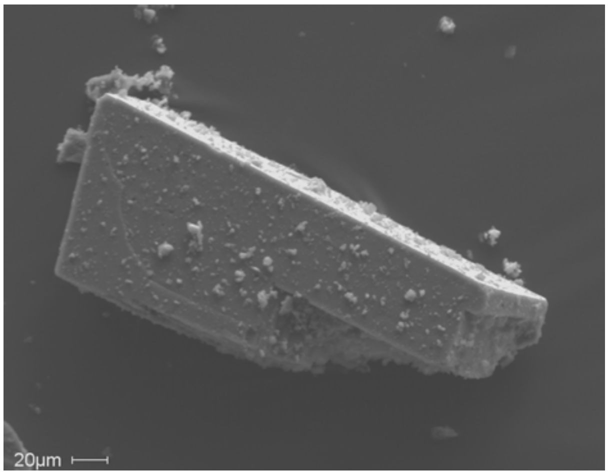
Område 2 **Rapport nr 2:2**

MinBaS projekt nr 2,2 Framtida betong
Delprojekt nr 2,22 Finpartikulära restprodukter som filler i cementbaserade material

The influence of limestone fillers´origin, surface texture and particle size distribution on cement paste properties





Helena Moosberg-Bustnes, Cement och Betong Institutet

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Abstract

It is known that particle size distribution, particle shape and surface texture are the main important physical parameters describing the effects of the filler material on the cement paste properties. In order to facilitate the use of mineral and metallurgical by-products as filler in concrete it is important to know which of the mentioned properties is the most important one for the filler materials function. To obtain base knowledge, 8 limestone fillers with different origin (genesis and metamorphose grade) and particle size distribution have been added to cement paste. Particle characterisation has been performed on the limestone particles with scanning electron microscopy, and the various limestone fillers effect on cement pastes' water demand, rheology, heat of hydration and strength have been investigated. It is clear that the particle size distribution plays a major roll, although the origin/surface texture affects water demand and rheology. The limestone fillers, particle size distribution and origins have a minor effect on the cement pastes' compressive strength.

INNEHÅLLSFÖRTECKNING **Sid.**

The influence of limestone fillers' origin, surface texture and particle size distribution on cement paste properties.

1 Background

The use of by-products as filler in concrete opens a whole new range of possibilities, at the same time as it raises a lot of questions. However, their behaviour in, and influence on cement paste has to be thoroughly evaluated before they can be put in to regular use.

It is known that particle size distribution, particle shape and surface texture are important physical parameters for how the filler affect cement paste. But it is not known which one of the parameters that is the most important one, or if they are equally important. To be able to choose the right type of by-products as filler material it is imperative it is known if the shape, texture or size distribution is the most important parameter. This study is made in order to obtain more knowledge in this area. Limestone fillers have been chosen as experimental materials since they are commonly used and they excist in different size ranges and have different origins.

2 Literature

2.1 The influence of the particle size distribution on rheology

Generally, the problems with segregation and sedimentation set the restriction on the maximum particle size of the filler materials that can be used in cement paste. High amounts of fines may increase the viscosity.

Poppe and De Schutter (2001) compared the effect on concrete rheology and strength of two limestone fillers that have the same characteristics with the exception for different particle size distributions. They found that small changes in the grading curves, caused by a different combination with cement, have little effect on the flowability of the mixture. Replacing a larger part of the cement by the limestone powder still results in a concrete with the same flowability. The strength seems to be influenced only by the cement content.

Clearly, the specific surface area of concrete aggregate is largely determined by the amount of finer particles in the mass. Even though particles < 125 μm normally only are present in minor amounts, their influence on the total specific surface area of the aggregate is significant. Bache (1973) asserts that, particularly in connection with superplastisized particle systems, it is meaningless to claim that the water requirement becomes greater with increasing specific surface area. On the contrary, dispersed silica particles for instance, reduce the volume of void space available for water by filling in the voids between cement grains. Thereby, more water becomes available for lubrication between coarser particles.

Opoczky (1992) claims that the main achieved effects when using limestone fillers are of a physical nature. It causes a better packing of the particles and a better dispersion of the cement grains.

Some carbonate fillers cause drastic and rapid losses of workability in superplasticized concrete while others do not (Nehdi, 2000). There is no feasible theory that explains this behaviour, the origin may lay in the material chemistry, surface chemistry or in its physical properties.

2.2 The influence of the particle shape on rheology

The particle shape of the filler influences the rheology of the cement pastes. Barnes et al. (1996) state that particle asymmetry has a strong effect on the intrinsic viscosity and maximum packing fraction, and hence on the concentration/viscosity relationship. A deviation from spherical particles means an increase in viscosity for the same phase volume. Figure 1 illustrates this point.

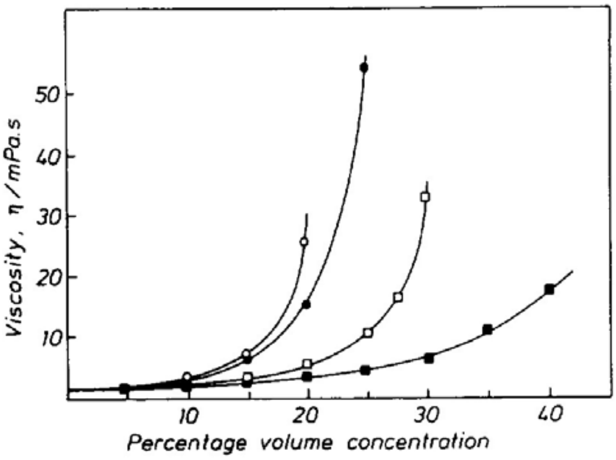


Figure 1: Dependency of the viscosity of differently shaped particles in water on concentration at a shear rate of 300/s (from Barnes et al., 1996) ■ spheres, □ grains, ● plates, ○ rods.

Bergström (1996) found that deviation from a spherical shape always lead to higher viscosity, it can also result in other effects, for example: rod shaped particles can cause shear-thickening.

2.3 Limestone's effect on cement hydration

From a chemical point of view, limestone filler does not have pozzolanic properties, but it reacts with the aluminate phases of cement to form an calcium monocarboaluminate hydrate with no significant changes on the strength of blended cement (Bonavetti 1992, 2003)

Nehdi (2000) asked the question: Although there is abundant literature suggesting the nucleation mechanism as the primary cause for the microfiller acceleration of the early age hydration, there is a certain confusion as to what is nucleating: C-S-H or portlandite (calcium hydroxide, CH) or both, and in what sequence?

Soroka and Stern (1977) state that limestone filler act as the crystallisation nucleus for the precipitation of calcium hydrate (CH). Bonavetti et al. (2003) also hold that view, i.e., that the main effects of limestone filler are of physical nature, it causes a better packing of the cement paste, disperses the cement grains and acts as the crystallisation nucleus for the precipitation of CH.

Ramachandran and Zhang (1986) suggested that calcite not only accelerates the hydration of C_3S, but that a certain percentage of calcite is consumed before the first 24 hours in this process. They explained the increased hydration rate by the nucleation of C-S-H around calcite particles, which would incorporate a part of the calcite in some kind of composite. They supported this idea by 24 hours SEM micrographs illustrating the growth of C-S-H around calcite grains.

Kjellsen and Lagerblad (1995) argued that the acceleration of the hydration is initiated during the induction period, before any notable long-range nucleation of C-S-H can be expected. The acceleratory effect of limestone fillers may be due to precipitation of hydrates on the particles. The surface of calcite may provide beneficial substrates for CH precipitation implying that CH probably will precipitate on theses minerals, which in turn will lower the Ca^{2+} ion concentration in the pore solution. This can lead to the observed increased hydration rate, therefore they questioned the above mentioned explanation.

Nehdi and Mindess ( ) argued that in the presence of calcite removal of calcium ions from the cement-water solution the hydration would start earlier, and would enhance further dissolution of calcium ions. They thought that calcite particles would partially dissolve in the limestone cement water system, providing extra Ca^{2+} ions and thus modifying the kinetics of the hydration reactions. Because of the low solubility of calcite in alkaline systems this theory does not seem to be thermodynamically plausible. They investigated this aspect by comparing he effect of limestone filler and hydrated lime powder, the hydrated lime is much more soluble in water than limestone powder and would provide many more Ca^{2+} ions in the solution, thus further increasing the hydration rate. No severe losses of workability were observed. Therefore, the effect of dissolution of Ca^{2+} ions may not have a major effect on the rheological problems associated with some carbonate fillers.

2.4 Z-potential of limestone

Limestone has a positive (low) zeta-potential in deionised water (Johansen et al., 1992). Limestone has a negative zeta potential in synthetic pore solution (Moosberg-Bustnes et al., 2003x). The resulting zeta-potential from titration of a limestone filler in synthetic pore solution, with a polycarboxylate type of superplasticizer is shown in Figure 2. The plateau can be estimated with the adsorption maximum of the superplasticizer on the limestone particle surfaces (Flatt et al., 1997). The zeta potential obtained at maximum adsorption is –11.4 and the adsorption is 5 mg/g, which is close to cements values. Since the absolute value of the zeta-potential of limestone is low and approximately the same as cement's, there may be a risk of agglomeration if not a superplasticizer is used.

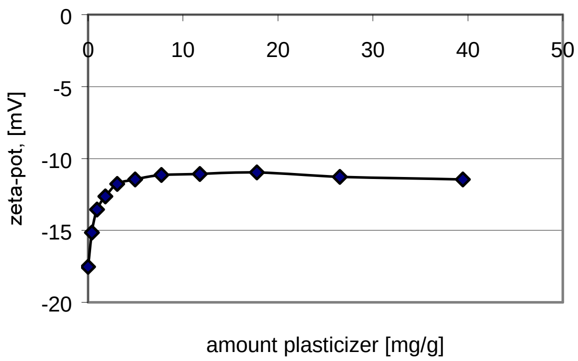


Figure 2: The zeta-potential as a function of the amount of plasticizer added to the solution (Moosberg-Bustnes et al., 2003).

3 Experimental

3.1 Material

Limestone fillers with the same origin but varying particle size distributions were collected, as well as materials with approximately the same particle size distribution but different origins or metamorphose level. The number of fillers tested in this study is 8 (Table 1). Two types of Portland cement are used for the experiments, they are designated CEM I 42.5 BV/SR/LA ("anläggningscement" = cement for civil engineering structures) and CEM II/A-LL 42.R ("byggcement" = cement for housing). They have approximately the same chemical composition but the particle size distribution varies (Table 2).

In order to examine the effect of the limestone fillers' particle size distribution on cement paste rheology, strength and particle packing, two series of fillers were made. A few kilos of the limestone filler L25 were divided into three different fractions, 0-16, 16-63 and 63-125 µm with hydro-cyclones.

Base filler, the limestone filler L25, was gradually replaced with 0-16 and 16-63 µm fraction, respectively, and the desired properties of the resulting cement pastes were examined. The replacement levels were 10, 30, 50 and 70 percent.

Table 1: Limestone fillers used in the study

Name	Genesis	Age	Mine/plant
L15	Sedimentary limestone	70 million years old	Ignaberga
L20	Sedimentary limestone	450 million years old	Orsa
L25/L40	Crystalline limestone	Metamorf limestone, 1.8-2 milliard years old	Forsby/Köping
P8/80	Crystalline, calcite		Pargas
P5/100	Crystalline, calcite		Pargas
K250	Sedimentary limestone	400 million years old	Boda/Kullsberg
G250	Crystalline limestone	1900 million years old	Gåsgruvan

Table 2: Chemical composition, weight percent, and particle size distribution of the used cements (Cementa, 2003)

Chem. cont.	Anläggningscement CEMI 42.5BV/SR/LA %	Byggcement CEMII/A-LL42.R %	Particle size µm	Anl. cement Acc. %	Byggcement Acc. %
CaO	64.8	63.7	125	100	100
SiO_2	22.3	19,6	63	100	99.9
Al_2O_3	3.4	3.6	32	79.6	82.9
Fe_2O_3	4.3	2.8	15	52.4	61.9
MgO	0.8	2.7	8	35.7	43.8
Na_2O	0.1	0.23	5	26.8	33.4
K_2O	0.6	0.92	3	19.5	23.6
SO_3	2.4	3.5	2	14.3	16.9
Cl	0.015	0.04	1	6.3	8.0

3.2 Scanning electron microscopy analyses

A Philips 515 Scanning electron microscopy (SEM) has been used to investigate the limestone fillers particle shape, their f-shape, and to obtain pictures (micrographs) of the by-product particles surfaces.

3.2.1 Particle shape

Micrographs of the limestone filler particles were taken with scanning electron microscopy to enable evaluation of the three-dimensional particle shape, particle surface textures and pores, if any.

3.2.2 F-shape

Image analysis (computer analysis of digital SEM images) was used to define the parameter F-shape of the limestone fillers, which is an aspect ratio of the shortest versus the longest diameter of a particle. At least 400 particles in each sample were measured. Persson (1996) describes the procedure. Spherical particles have an F-shape value of 1, and cubical particles 0.71. The image analysis study makes it possible to describe the particle shapes of the filler materials.

3.3 Particle size distribution and specific surface area

The particle size distributions of the materials were determined by laser diffraction analysis (SILAS) and the specific surface areas were analysed by the producers. The BET-method was used, although some limestone fillers also were analysed with the Blaine-method.

3.4 Calorimetry

Isothermal calorimetric measurements were performed on cement/limestone filler mixtures in order to see how the limestone fillers particle size distributions and different origins affect the cement hydration. The cement used for the calorimetric experiments was a Portland cement (CEM I 42.5 BV/SR/LA) and the w/s-rate kept at 0.40. The limestone filler was mixed into the cement pastes by 20 weight percent. The heat development was measured for 24 hours, four minutes elapsed between the addition of the water to the cement/filler mixture and the placement of the paste in the calorimeter. The first heat peak, the wetting peak, was thus discarded. The calorimeter has an accuracy of ± 5 percent. The analyses were performed twice, with excellent repeatability.

3.5 Determination of water/powder ratio for zero flow - β_p

Determination of the filler/cement mixtures water demand, i.e., the influence of addition of filler materials on the flowability of the cement paste was investigated. Two different cement types were used in the experiments to evaluate the effect of the cement type on the filler materials.

The water/powder ratio for zero flow (β_p) is determined in the paste, with the chosen filler/cement proportions of 15, 30 and 45 volume percent filler. Flow cone tests with water/powder ratios by volume of, e.g., 1.1, 1.2, 1.3 and 1.4 were performed with the selected powder compositions. The measurements were performed three times for each powder mixture. The results are plotted in xy-diagram, with relative slump versus water/powder ratio. The point of intersection with the y-axis (water/powder ratio) is designated the β_p value. The method is in accordance with EFNARC's specifications (EFNARC). The slope of the regression line represents the materials sensitivity of increased water content. Lower values indicate greater sensitivity to increasing water content.

In order to determine the β_p value for each limestone filler and mixture, straight-line regression analyses were made on the resulting values for each mixture. The β_p values and the corresponding filler amount could then be plotted in a diagram.

3.6 Rheological measurements

Water/cement-ratio, plasticizer, cement and the amount of filler added to the cement paste were kept constant to isolate the effect of the size distribution of the filler material. The recipe for the cement paste, calculated on a paste volume of 0.35 dm^3, is 169.4 g limestone filler, 390.6 g cement, 154.9 g water and 1.6 g Chemflux prefab, a plasticizer functioning as a dispergator. The measurements were performed twice, two different cement types were used in the experiments, CEM I 42.5 BV/SR/LA and CEM II/A-LL 42.5 R.

The viscosimeter used for rheology measurements is a HAAKE Rotovisco CV20. The sensor system consists of concentric cylinders with the outer cylinder (the cup) from an original HAAKE sensor system, ZA30. A new inner cylinder (bob) differs from the original bob in diameter and surface structure providing a gap between the inner and outer cylinder of 2.58 mm, and is serrated with grooves, 0.5 x 0.5 mm wide and deep to prevent any slip-surface occurring. Using a Hobart laboratory scale mixer, the mixing sequence is as follows: All dry materials are mixed for 10 seconds. The water is poured slowly into the beaker while mixing the fine mortar for 30 seconds. The superplasticizer is added. The fine mortar containing all ingredients is mixed 1 minute by hand, then 1 minute by machine. The last sequence is repeated once. Billberg (1999) describes the whole procedure in detail. The shear sequence is shown in Figure 3. The linear Bingham model is used to describe the flow (Barnes 1996).

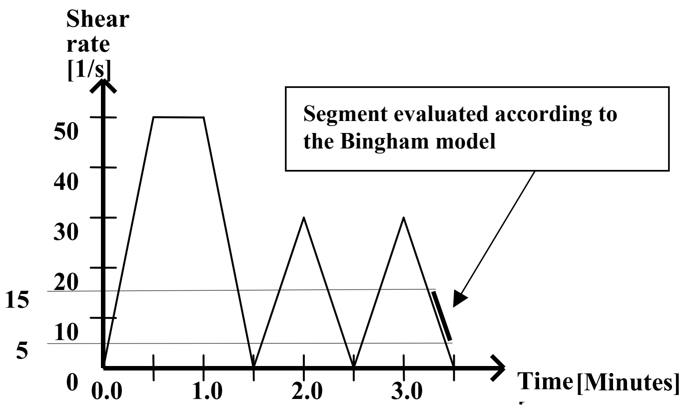


Figure 3: The shear sequence used in the experiments. The Bingham model is used on the third down curve of the shear sequence. The model states that when material shear stress exceeds the material's yield stress the material starts to flow. The relationship between the shear rate and the shear stress is linear and the slope defines the plastic viscosity (Billberg, 1999).

The characteristics of the three up- and down curves of the shear sequence also indicate whether any particle segregation occurs, as indicated when the measured shear stress increases for every up- and down curve, for particles during shearing sink to the bottom of the cup resulting in a vertical concentration gradient of particles. The sediment layer eventually reaches the bob, which records higher and higher torque.

3.7 Strength

In order to examine the effect of the different limestone fillers on cement pastes' compressive strength the cement pastes were immediately poured into 4 x 4x 16 cm^3 moulds after the rheological measurements were finished. The prisms were cured for 24 hours before demoulding, and then stored in 100 RH, 20 °C. The compressive strength was measured on three samples of each cement/limestone paste after 7 and 28 days. The same procedure was used for the cement pastes in the replacement experiments.

3.8 Particle packing

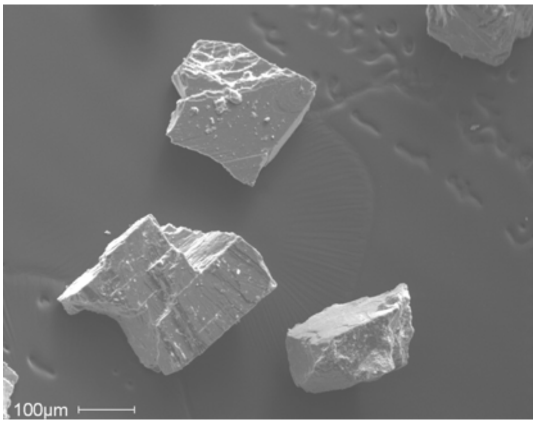
The particle packing of the replacement series was calculated with software developed by the Nordic project "Concrete mix design" (Gram, 2003). The model, CPM (Compressible packing model), used in the computer software to calculating the linear packing density (LPDM) is developed by Larrard (1999).

4 Results

4.1 Material: Particle nature and texture

Scanning electron microscopy was used to investigate the particle surfaces and shapes. Micrographs of the limestone filler were taken in order to facilitate comparison between the crystalline and sedimentary materials.

G250 is a crystalline limestone with distinct fractures and smooth surface texture (Figures 4 and 5). K250 is a sedimentary limestone, the grains consists of a fine crystalline mass and they lack the typical rhomboedric crystal shape, the texture is uneven (Figures 6 and 7).



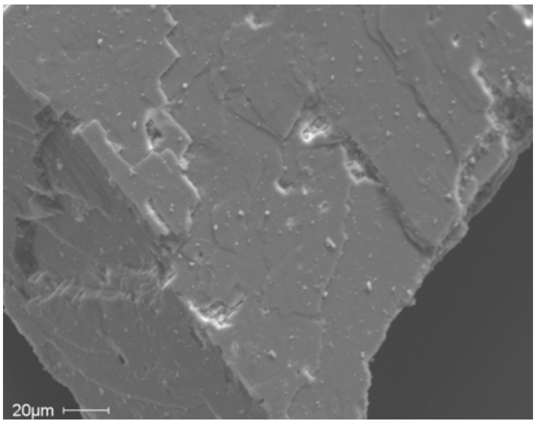


Figure 4 and 5: Limestone filler G250

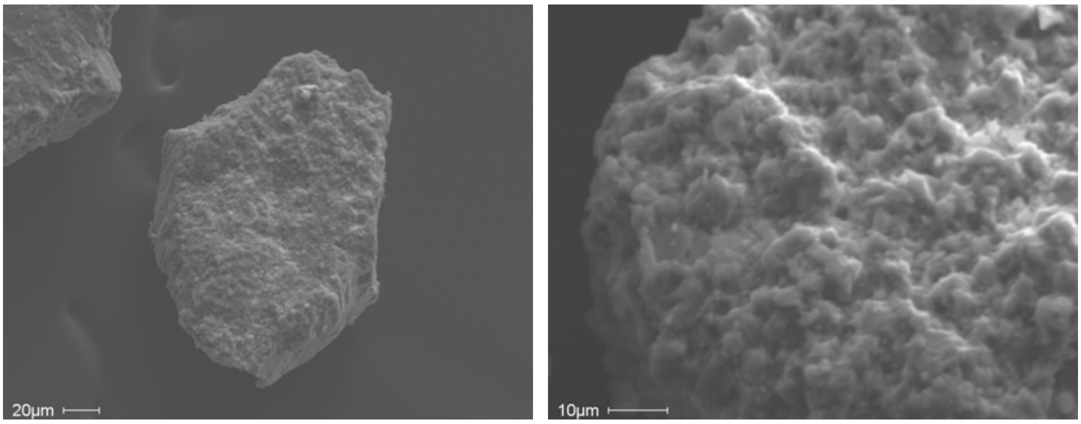


Figure 6 and 7: Limestone filler K250

L25 and L40 are crystalline limestone fillers of the same origin, they have the same particle shape and texture but different particle size distributions. The crystal shape can clearly be seen, although, there are some grains with a rounder appearance (Figures 8 and 9).

L15 is a filler material that is made of a young sedimentary limestone. It is composed of fine-grained crystalline material and it is also possible to see remains/parts of fossils in it (Figures 10 and 11).

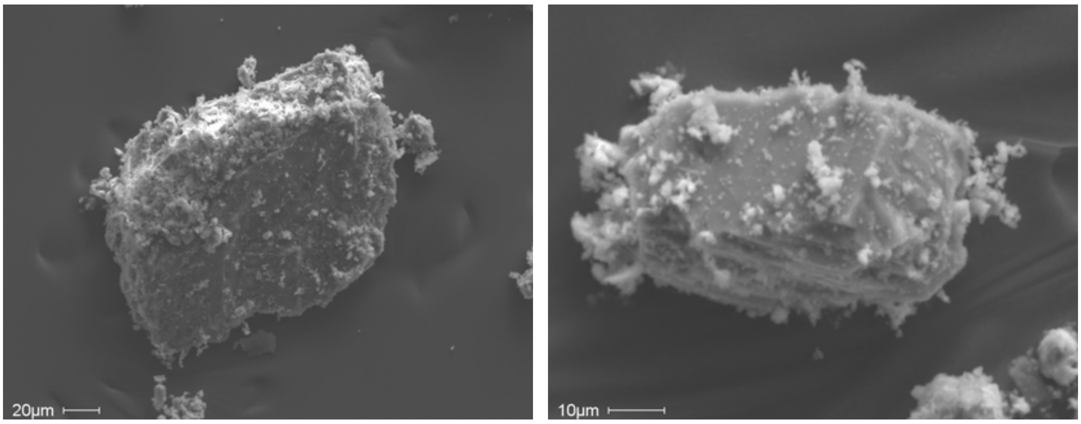


Figure 8 and 9: Limestone filler L25 and L40

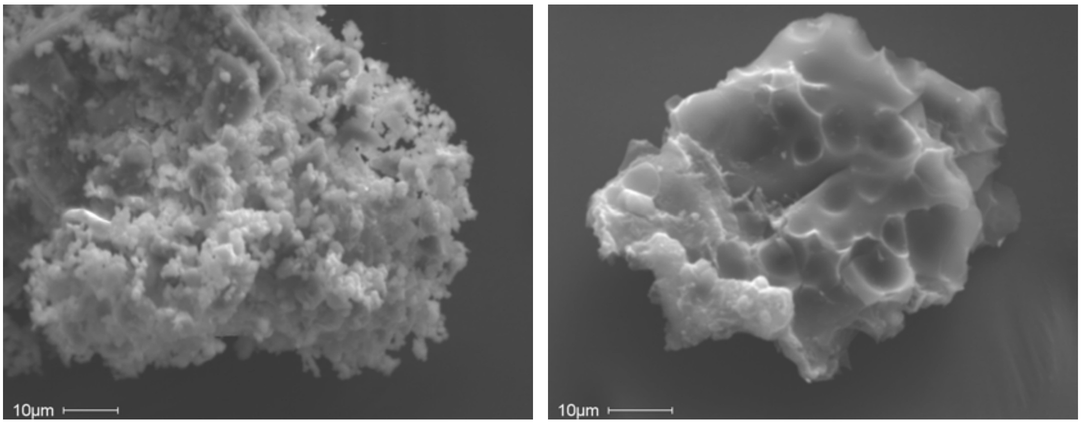
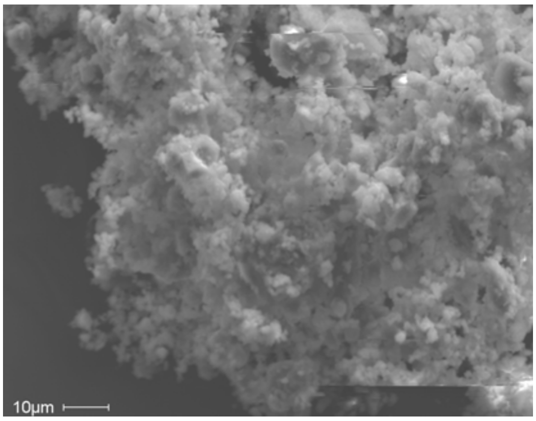


Figure 10 and 11: Limestone filler L15



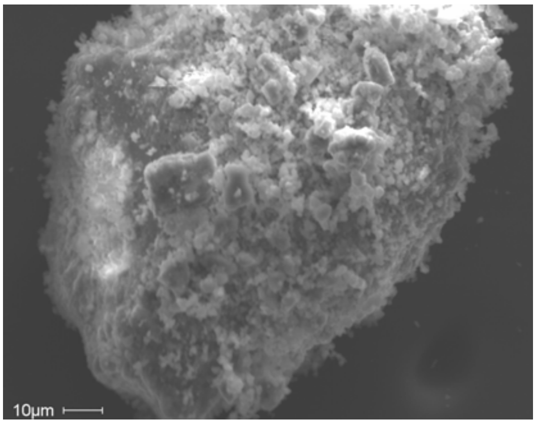
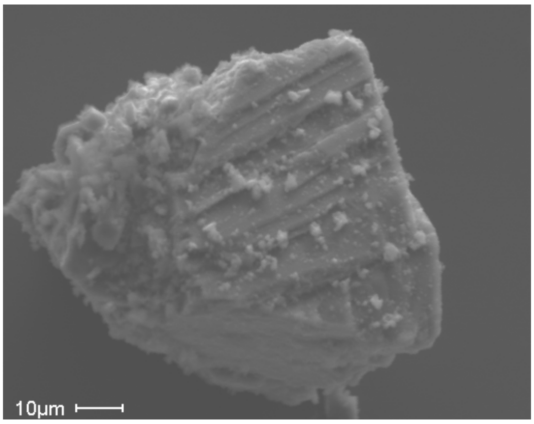


Figure 12 and 13: Limestone filler L20

The L20 limestone (Figure 12 and 13) is sedimentary although it is older than L15, it is fine-grained crystalline with an uneven surface texture.

Parfill8/80 and 5/100 are crystalline limestone of almost pure $CaCO_3$. The crystal shape is clearly rhomboedrical and the surface texture smooth (Figure 14 and 15).



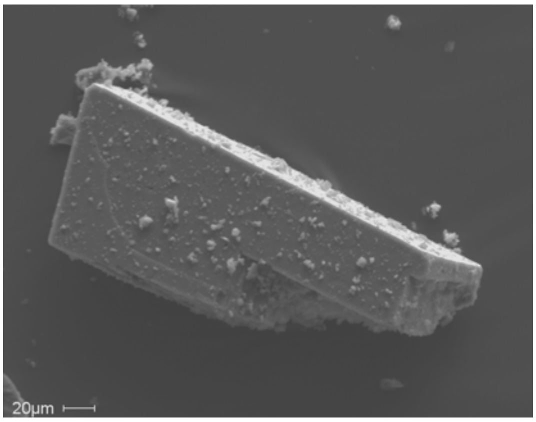


Figure 14 and 15: Limestone filler Parfil 8/80 and 5/100

4.2 Particle size distribution

The crystalline and sedimentary limestone fillers were chosen to complement each other's particle size distributions (Figure 16).

L25, L20 and IG have similar particle size distribution, L20 differs in the upper part of the distribution and IG in the lower part of the curve. L25 and L40 have the same origin but they have different particle size distributions.

G250 and K250 are fillers with approximately the same particle size distribution. Moreover G250 and L40 have the same particle size distributions, with only a slight difference in the upper part of the curve.

Parfil 8/80 and 5/100 are of the same origin but with different particle size distributions.

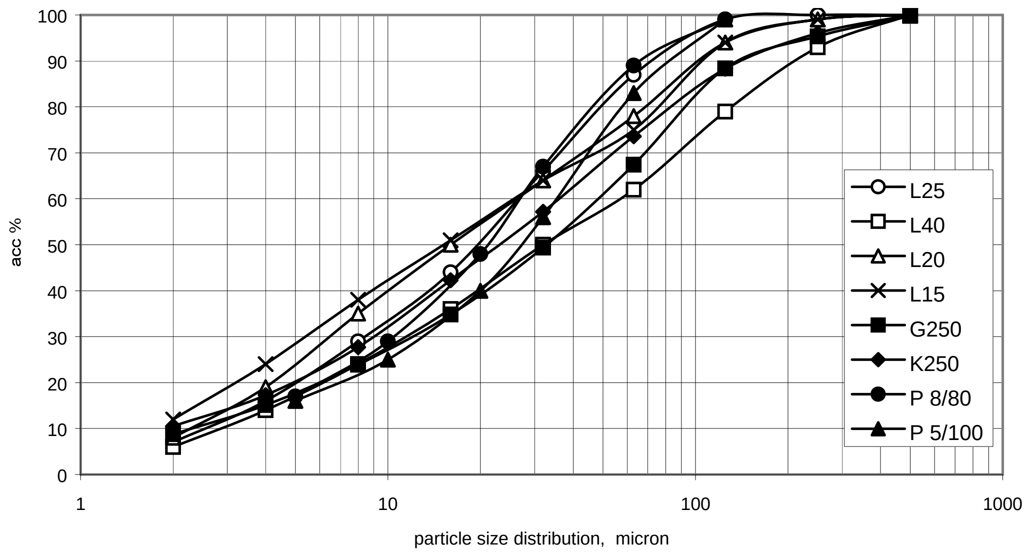


Figure 16: Particle size distribution of the fillers

4.3 Specific surface area and density

The specific surface area is measure with the BET-method and the density with helium pycnometer, by respective producer (Table 3). The specific surface area varies, the coarser materials have lower surface area than the fine particulate.

Table 3: The specific surface area and density of the used limestone filler, measured by the producers.

Material	BET m^2/kg	Blaine m^2/kg	Density kg/dm^3
L25	1338	474	2.76
L40	1188	332	2.76
L20	1775	489	2.71
L15	1760	577	2.83
8/80	-	340	2.71
5/100	-	260	2.71
K250	900	-	2.7
G250	630	-	2.7

4.4 F-shape

K250 has the lowest F-shape, L20 the highest. This means that L20 has the roundest shape and K250 the most angular one. All the other limestone fillers have F-shapes that are similar to each other, and the curves are located between K250 and L20 (Figure 17).

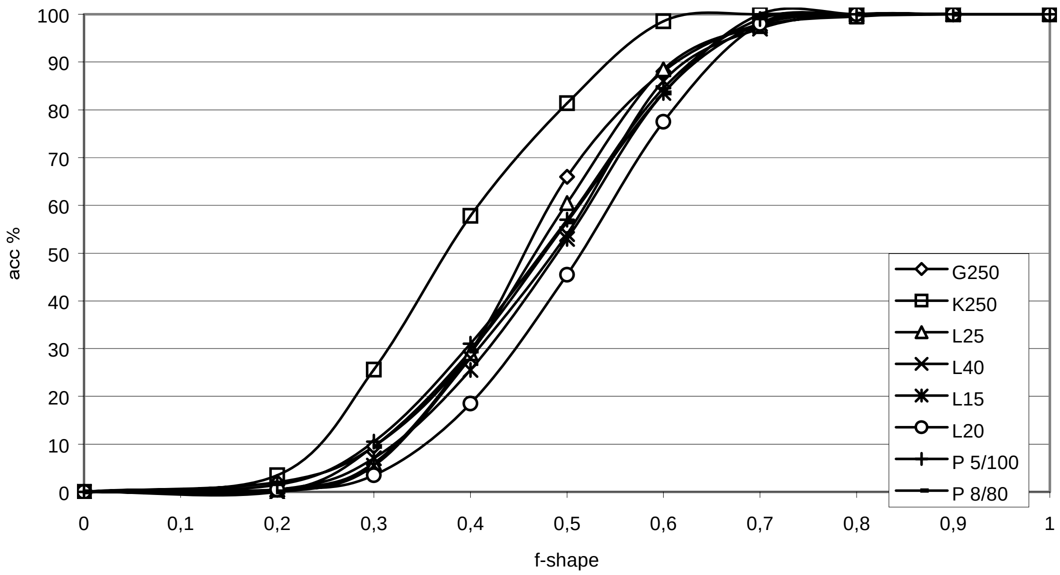


Figure 17: The limestone fillers F-shape, analysed with SEM.

4.5 Calorimetry

Addition of limestone filler to cement paste changes the heat development. The finer limestone particles the higher total heat developed. Figures 18-21 show the total heat development of the investigated limestone fillers.

Figure 18 shows that the cement paste containing L25 has a higher total heat developed than the one that contain L40. This is probably due to L25's higher amount of fine particles and finer particle size distribution. Comparison between cement pastes containing L40, K250 and G250, respectively, which are limestone fillers with approximately the same particle size distribution, show that addition of the sedimentary limestone, K250, caused a slightly higher total heat than the other two, that that are crystalline and have similar total heat development curves (Figure 19). The two cement pastes with addition of the two limestone fillers 8-80 and 5-100 have the same total heat after 24 hours (Figure 20). Comparison shows that there is a slight difference between the values from 2 to 15 hours, the filler 8-80 gives rise to a slightly accelerated heat. This can probably be explained with the material's slightly finer particle size distribution. Figure 21 shows that the total heat developed by the cement pastes containing L25 and L20 are the same, L15 gives rise to a slightly lower total heat.

However, the differences in total heat developed for the various filler materials are small and may not affect the hardened cement paste's properties at all.

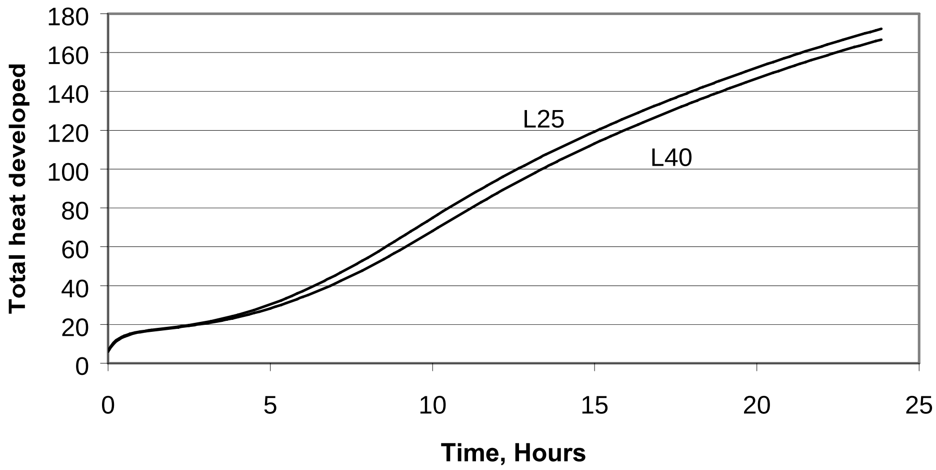


Figure 18: The total heat, mW/g cement, developed for cement pastes that contain limestone fillers L25 and L40.

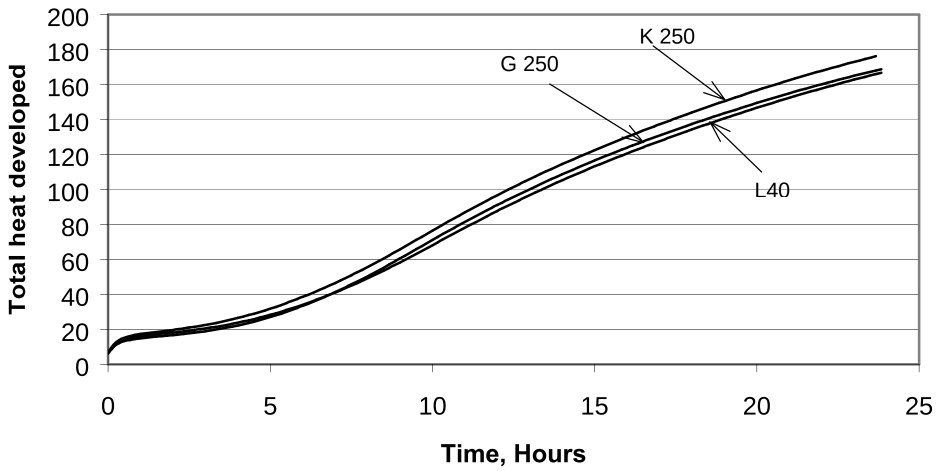


Figure 19: The total heat, mW/g cement, developed for cement pastes that contain limestone fillers L40, K250 and G250.

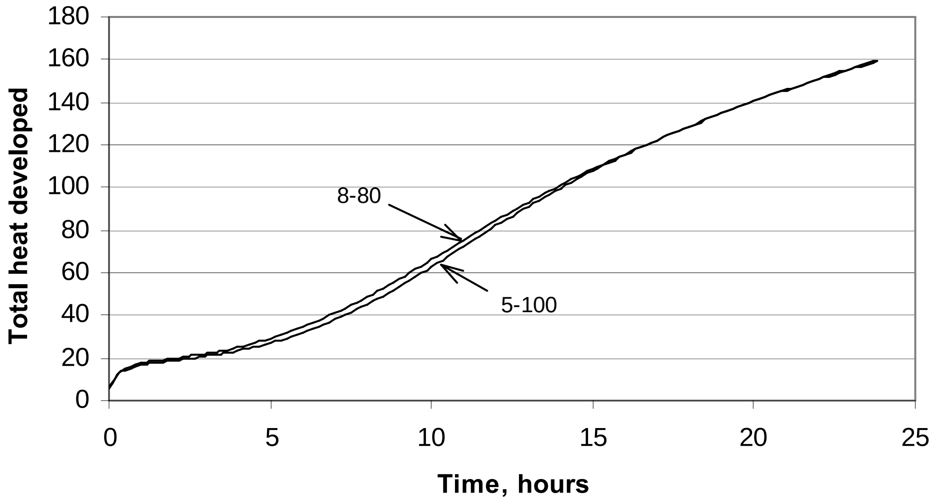


Figure 20: The total heat, mW/g cement, developed for cement pastes that contain limestone fillers Parfil 8/80 and Parfil 5/100.

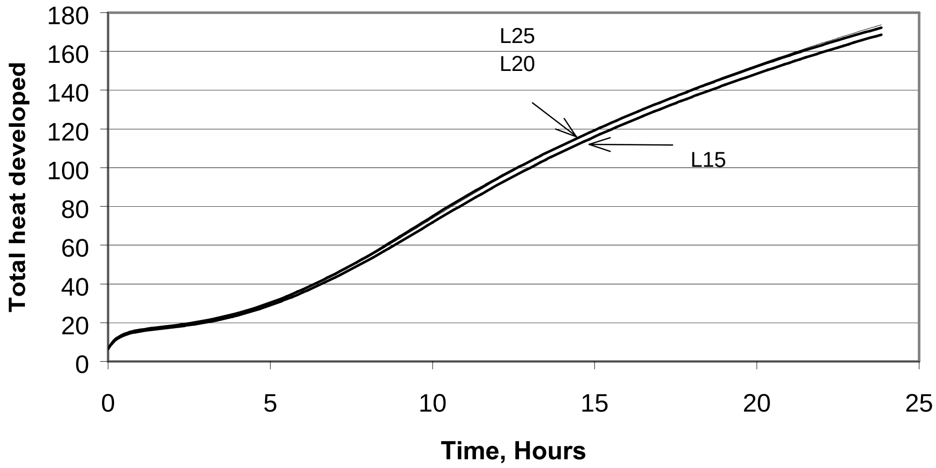


Figure 21: The total heat, mW/g cement, developed for cement pastes that contain fillers L20, L15 and L25.

4.6 Beta-p

The β_p measurements show that increased amounts of filler decrease the water/powder-ratio that gives zero flow, see Figures 22. The measurements show that the fine particulate materials have higher β_p–values than the ones with a coarser particle size distribution. The measurements were made with two types of cement, and the results/trends were the same for both types. However, the "anläggningscement" (*CEM I 42.5 BV/SR/LA)* had lower β_p-values, this is due to the coarser particle size distribution of the cement and thus of the whole system. A weak tendency of separation could be seen in the cement pastes that contained the coarser materials when the water/powder ratio was raised.

Comparison of materials that have approximately the same particle size distribution but different origin, i.e., sedimentary or crystalline limestone fillers, show that the water demand changes with the origin – the sedimentary material appears to have a higher water demand, this is probably due to the more uneven surface texture. Some of the sedimentary materials have particles that consist of fine crystalline material that form a three-dimensional network where water can be caught.

The slope of the regression line between the four w/p-ratios was used to determine β_p, i.e., the sensitivity for water changes. Higher values indicate lower sensitivity. Figure 23 shows that the fine particulate limestone fillers have lower sensitivity for water changes than the coarser ones. G250 is noticeably more sensitive than K250 and L40, even though they have approximately the same particle size distribution. L25 and L20 are the limestone filler that have the lowest sensitivity, and L15 has a slightly higher.

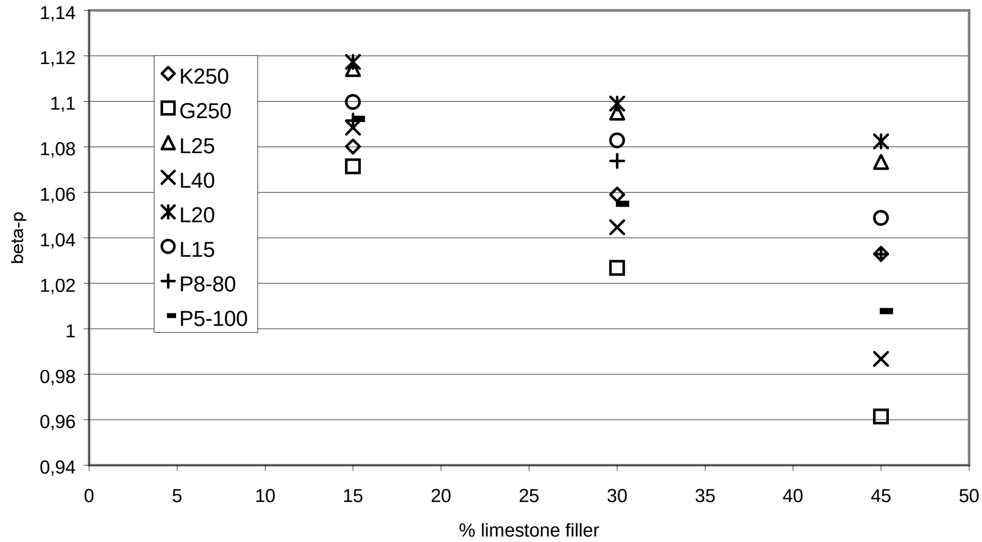


Figure 22: β_p values for the investigated limestone fillers mixed with CEM II/A-LL 42.R ("byggcement") as a function of percentage limestone filler in the cement/filler mix.

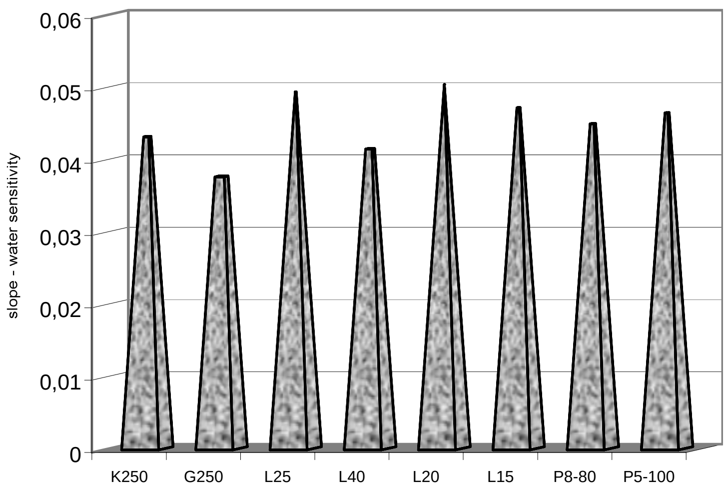


Figure 23: The sensitivity for water changes, i.e., the slope of the regression line between the four w/p-ratios used to determine β_p for the cement pastes that contain 45 percent of the limestone fillers, respectively.

4.7 Rheology

Figure 24 and 25 show the yield stress as a function of the plastic viscosity for the examined cement/limestone pastes. See Appendix III for more details.

The relative order of the limestone containing cement pastes is the same for both cement types, although the magnitude of the investigated parameters differs. The coarser materials, L40, G250 and K250 forms two "groups", where the crystalline fillers L40 and G 250 gives rise to approximately the same yield stress and plastic viscosity, whereas the cement paste containing the sedimentary limestone K250 have higher values. The results obtained for the finer material are not consistent with the results from analysis of the coarser filler. Cement pastes containing the two sedimentary limestone fillers L20 and L15 have the highest and the lowest values respectively, while the cement paste containing L25 has values that lay half way between the others.

The crystalline fillers Parfil 8/80 and Parfil 5/100 have approximately the same yield stress but the viscosity differs. Comparison of the crystalline L25 and L40 shows that the L25, which have a finer particle size distribution, has higher yield stress and plastic viscosity.

The yield stress values obtained from the combination of L20 and "byggcement" are close to the upper limit of the instruments range of measurement. It is though clear that L20 is the limestone filler that has the most pronounced effect on the measured rheological parameters. Comparison with the mixture of L20 and "anläggningscement" shows that the rheological values are the highest in this series of combinations as well.

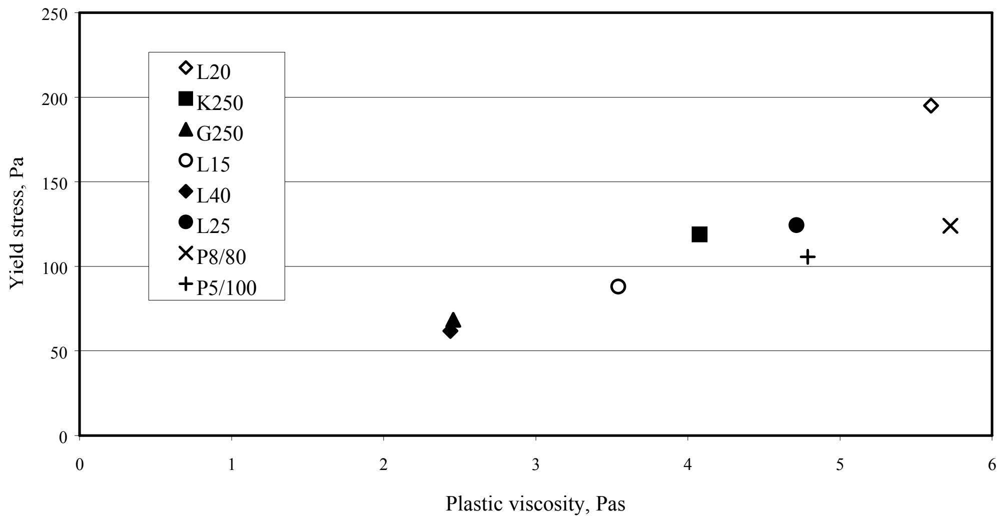


Figure 24: Yield stress versus plastic viscosity, the rheology for cement paste with respective limestone filler and CEM II/A-LL 42.5 R ("Byggcement"). NB! The value obtained for the cement paste containing L20 is close to the instrument's upper limit of the measurement range.

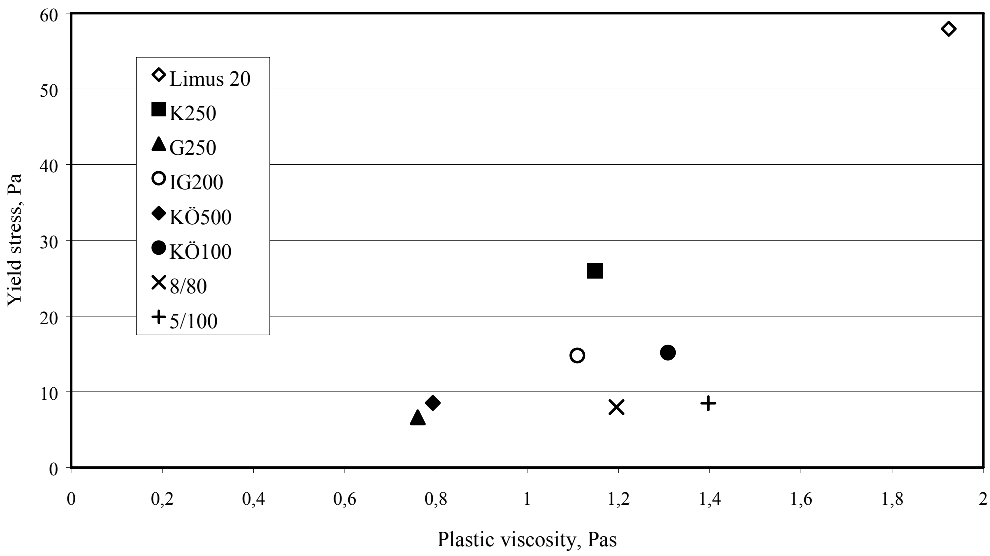


Figure 25: Yield stress versus plastic viscosity, the rheology for cement paste with respective limestone filler and CEM I 42.5 BV/SR/LA ("Anläggningscement").

4.8 Strength

The compressive strength for the various limestone fillers was measured after 7 and 28 days, see Table 4. The strength is almost the same for all measured cement pastes of a certain age. It is not possible to distinguish the various fillers' effect on strength from each other in this analysis.

Table 4: Compressive strength (MPa), mean values of three measurements, for cement pastes containing limestone filler.

	7 days Strength, MPa	28 days Strength, MPa
L25	47.3	56.4
L40	46.7	55.9
L15	47.1	56.6
L20	47.3	56.2
G 250	46.1	56.3
K 250	46.9	56.2
Parfil 8/80	47.4	57.0
Parfil 5/100	47.3	56.2

4.9 Replacement of base filler with 0-16 and 16-63 micron fraction.
4.9.1 Particle size distribution of limestone filler mixtures

The Figures 26 and 27 show the particle size distribution curves where the base filler, L25, has been replaced with 10, 30, 50 and 70 percent of the size fraction 0-16 µm and 16-63 µm, respectively.

Replacement of the base filler with the 0-16 µm fraction has a larger impact on the particle size distribution of the mixture than the replacement with the 16-63 µm fraction has.

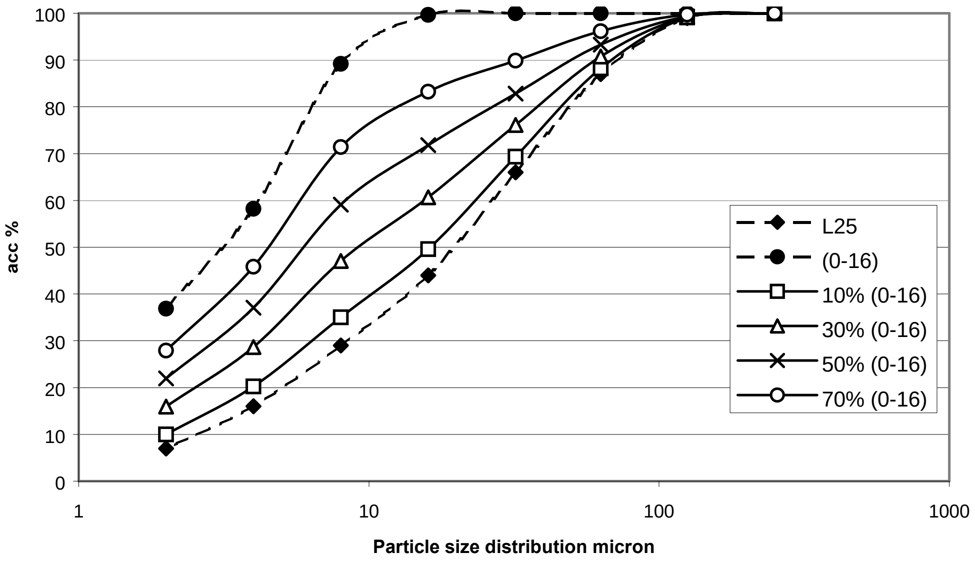


Figure 26: The diagram shosw the particle size distribution curves where the base filler, L25, has been replaced with 10, 30, 50 and 70 percent of the size fraction 0-16 µm. The particle size distribution curves for L25 and the limestone filler fraction 0-16 µm are shown in the diagram.

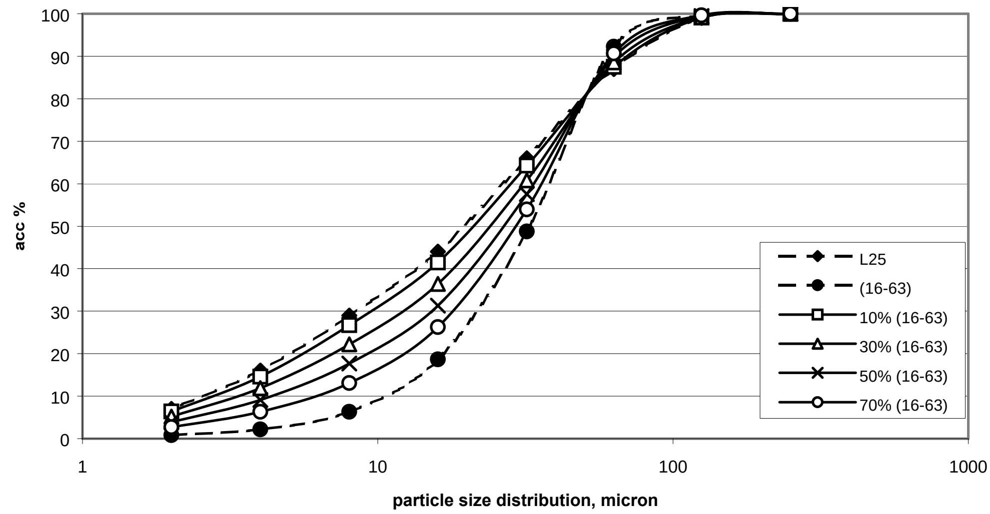


Figure 27: The diagram shows the particle size distribution curves where the base filler, L25, has been replaced with 10, 30, 50 and 70 percent of the size fraction 16-63 µm. The particle size distribution curves for L25, the limestone filler fraction 16-63 µm are shown in the diagram.

4.9.2 Particle size distribution of limestone filler mixtures and cement

The Figures 28 and 29 show the particle size distribution curves of the limestone filler mixes and cement.

It is clear that the combinations with the finer filler (Figure 28) have a larger impact on the particle size distribution of the cement paste than the coarser filler (Figure 29) mixes. The amount of fines, accumulated percent at 10 µm particle size, increases with 15 percent when the replacement level goes from 0 to 70 percent. The decrease of the accumulated percent, at 10 µm particle size, for the coarser material is only 5 percent.

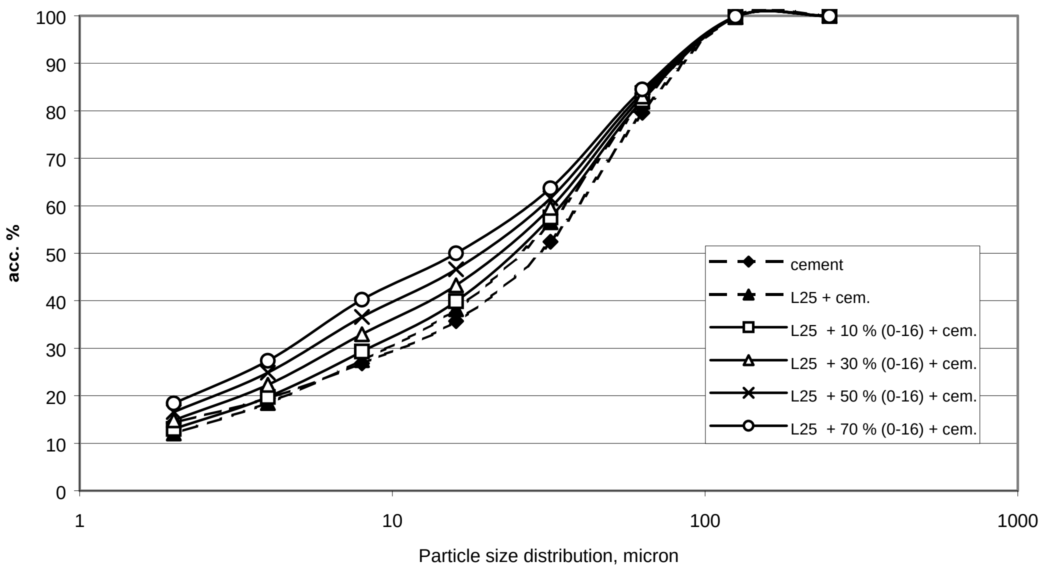


Figure 28: The diagram shows the particle size distributions for the limestone filler /cement mixes where the base filler is replaced by a 0-16 µm fraction. The particle size distribution curve of pure cement is included.

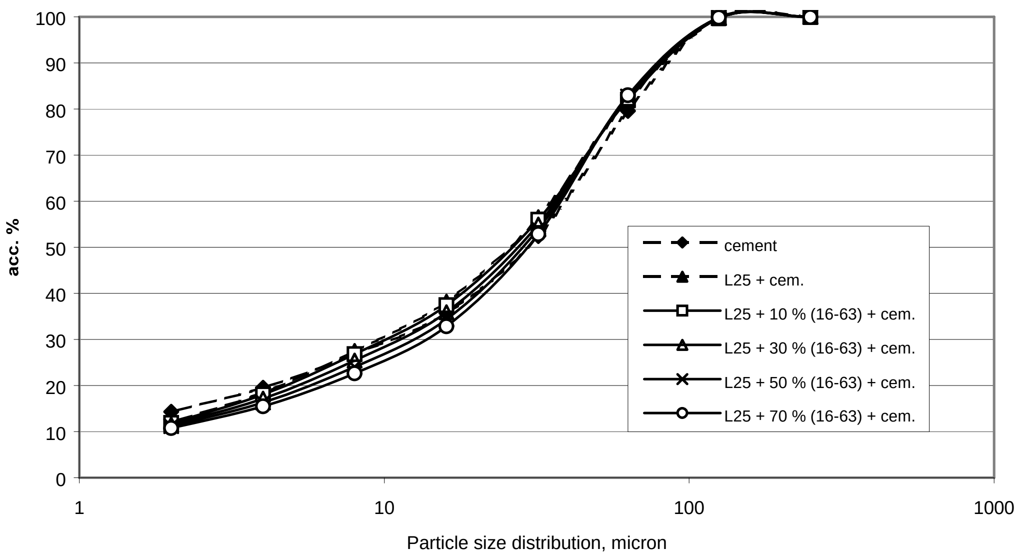


Figure 29: The diagram shows the particle size distributions for the limestone filler/cement mixes where the base filler is replaced by a 16-63 µm fraction. The particle size distribution curve of pure cement is included.

4.9.3 Rheology of replacement series

The yield stress increases with increasing replacement levels for the finer material (Figure 30). The series of cement pastes where the coarser limestone filler replaces the base filler has a slightly decreasing yield stress.

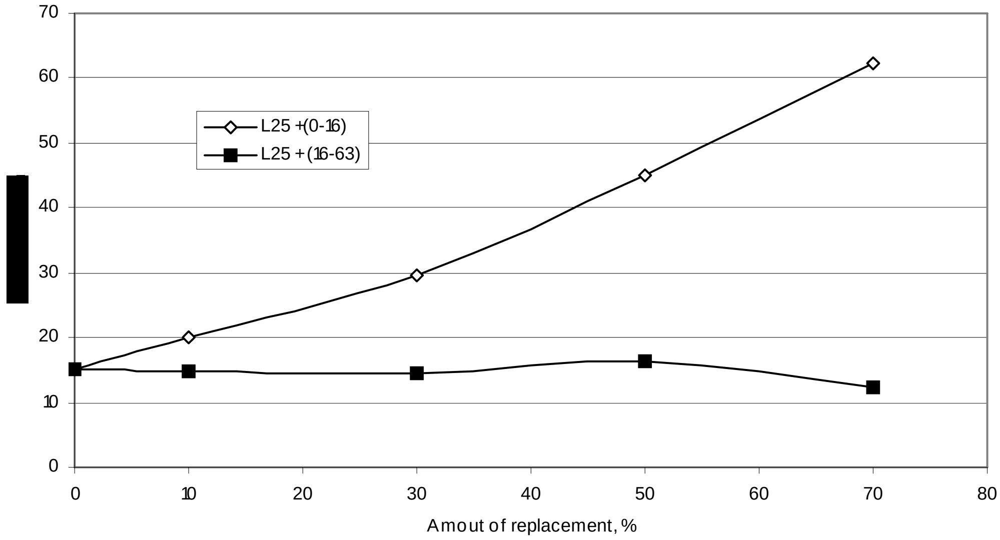


Figure 30: The diagram shows the yield stress of cement paste as a function of the amount of replaced base filler, the replacement has been made with the 0-16 µm and the 16-63 µm fraction, respectively.

The plastic viscosity is slightly increasing for both replacement series (Figure 31).

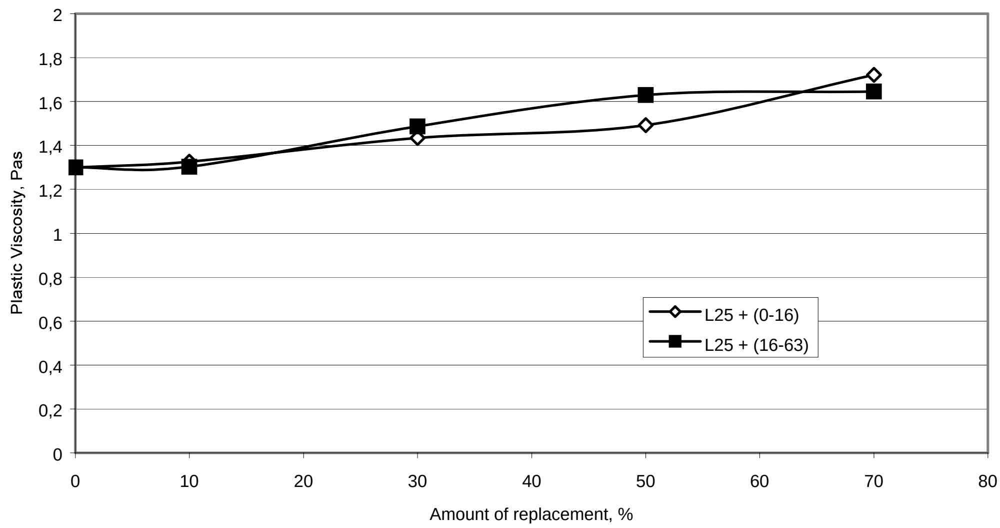


Figure 31: The diagram shows the viscosity of cement paste as a function of the amount of replaced base filler, the replacement has been made with the 0-16 µm and the 16-63 µm fraction, respectively.

Examples of the flow curves for cement pastes are shown in Figures 32 and 33. All curves are shown in Appendix I and II. The curves obtained for cement paste containing base filler (L25) and filler where parts are replaced with the 0-16 µm fraction indicate that they are stable and that no separation takes place. The flow curves for the cement pastes containing filler where parts are replaced with the coarser 16-63 µm fraction show, however, that there is a tendency to separation.

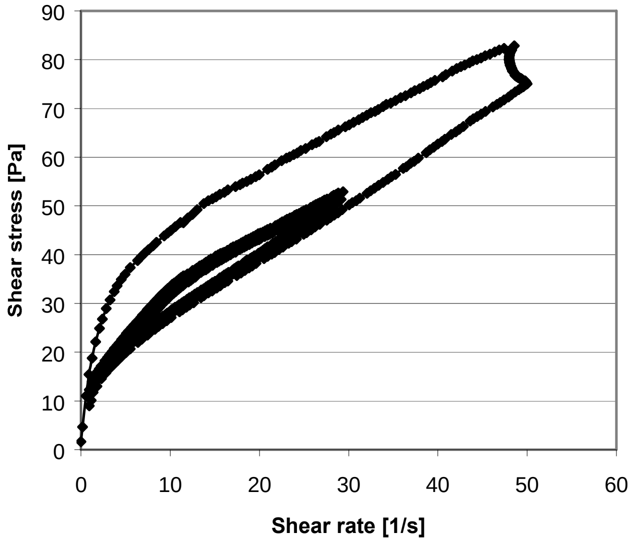


Figure 32: Flow-curve showing the cement paste containing the base-filler

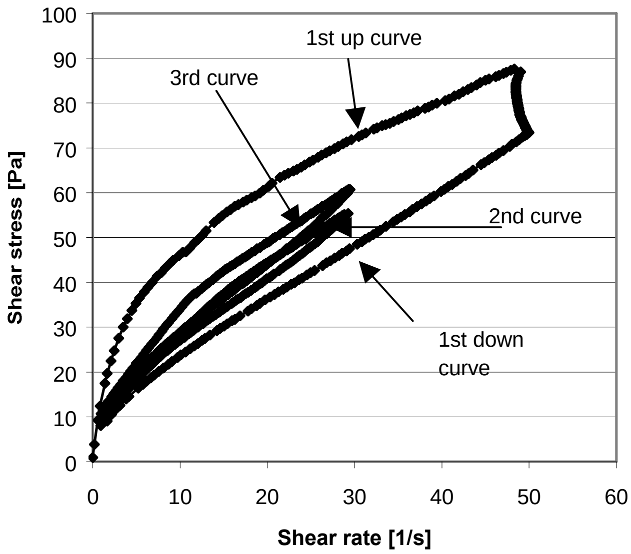


Figure 33: Flow-curve showing the limestone filler/cement mix where the base filler is replaced with 70 percent with the 16-63 µm fraction. The separation is indicated by the increasing shear stress for each loop, i.e., the position of the down curves changes upwards in the diagram with each loop. The shear stress increases due to increasing particle concentration in the lower part of the sample holder, thus a higher resistance against rotation.

4.9.4 Strength of cement/limestone filler prisms – replacement series

The measurements of the compressive strength after 7 and 28 days show a weak positive trend for the cement pastes when the filler becomes gradually finer (Table 5). Likewise, the strength is constant for the cement pastes where the filler becomes gradually coarser. The significance of these trends is, however, low since the difference between the samples that contains 10 and 70 percent of the fine materials is only 0.7 MPa, and the accuracy of the method is 0.9 MPa. There is, though, one fact that indicates that this trend is accurate – the increase in strength is consistent for all samples.

Table 5: Compressive strength (MPa), mean values of three measurements, for cement pastes containing limestone filler. Parts of the base filler has been replaced with the fractions 0-16 and 16-63 μm, respectively,

Replacement Level	Strength, MPa Replacement (0-16) μm	Strength, MPa Replacement (16-63) μm
10 %	47,2	47,2
30 %	47,3	47.3
50 %	47,8	47.1
70 %	47.9	47.2

4.9.5 Particle packing – replacement series

The calculations of the filler/cement systems particle packing show that the series of replacement with finer material obtain increasing particle packing with increasing fineness of the particle system (Table 6). The coarser the materials in the the second series get the lower the degree of particle packing is obtained.

Table 6: The calculated particle packing of the two replacement series.

	Particle packing	
Replacement level	(0-16) μm	(16-63) μm
10 %	0.666	0.670
30 %	0.673	0.670
50 %	0.682	0.668
70 %	0.689	0.660

5 Discussion

5.1 Limestone fillers' with different origins

L20 have the highest F-shape, i.e., it is the limestone filler with the most spherical particles, IG has the next highest Ff-shape. Their particle size distributions, densities and specific surface areas are almost the same, however, their effect on cement paste rheology differs. The SEM investigation of the materials showed that they both have uneven surface texture and that the surfaces are covered with small limestone particles. Both fillers contain particles that consist of fine-grained crystals. L25 contains some remains of fossils. L25 is a crystalline limestone filler with a slightly lower F-shape than L20 and L15, the crystal shape can be seen and the surfaces of the grains are fairly smooth and clean. The particle shape is slightly larger, which is consistent with the smaller specific surface area.

L40 and G250 are crystalline limestone fillers with similar particle size distributions, the difference is in the coarser part of the distribution curve - L40 contain a bit more of coarse particles. Both have smooth surface textures and lower specific surface areas than the finer filler materials. K 250 has the same particle size distribution but it is a sedimentary limestone filler, there is no typical calcite crystals and the surface texture is uneven. The yield stress and the plastic viscosity of cement paste containing K250 is higher than for cement pastes containing the crystalline materials. The cement pastes that contain L40 and G250 obtain the same rheological results.

The crystalline filler Parfil 8/80 contain more fine particles than Parfil 5/100, which correlates to their specific surface areas. The fillers have smooth surfaces and all the particles are crystalline. They have approximately the same yield stress but the viscosity differs when they are mixed into cement paste.

The measurement of total developed heat from the cement pastes containing the various limestone fillers indicates that the particle size distribution affects the amount of heat evolved. Coarser material in cement paste give rise to a lower total heat than the finer material of the same origin. Addition of the the younger, 70 miljon years old, of the two fine particulate sedimentary limestone fillers to cement paste, give rise to a lower total heat than the other, which is 450 miljon years old. L20 and the crystalline L25 have almost the same total heat developed after 25 hours. The cement paste containing the two coarse crystalline fillers show approximately the same heat development, however, the cement paste containing the sedimentary coarse filler has a higher total heat.

The rheological measurements show that crystalline limestone fillers effect on rheological parameters differs from the sedimentary limestone fillers, even though they have the same particle size distribution. Fillers that have the same origin but different particle size distributions will, when mixed into cement paste, affect the rheology in different ways. The finer the material is the more it will increase the yield stress and plastic viscosity.

The β_p measurements show that if materials with the same origin but different particle size distributions are compared, the filler that contains the highest amounts of fine particles will have the highest water demand and also higher yield stress and viscosity. The material with the coarser particle size distribution have lower β_p values for all amounts of filler, this means that the material is more sensitive for water changes – coarser material need less water to moisten the surfaces. The result from the β_p measurements appears to correlate well with the viscosity and yield stress values.

Comparison of materials that have approximately the same particle size distribution but different origin, i.e., sedimentary or crystalline limestone fillers, show that the water demand changes with the origin – the sedimentary material appears to have a higher water demand, this is probably due to the more uneven surface texture. Some of the sedimentary materials have particles that consist of fine crystalline material that form a three-dimensional network where water can be caught.

Addition of the various limestone fillers to cement pastes appears to have a minor effect on the compressive strength after 7 and 28 days.

The F-shape of the particles in this investigation appears to have no effect on β_p, strength or rheology. L20 is the material with roundest particles, but also the one that gives rise to the highest plastic viscosity and yield stress.

5.2 Replacement series

Comparison of the two replacement series show that the changes in the particle size distributions are more pronounced for the filler consisting of a finer material. This leads to the conclusion that this material must show more pronounced trends in the examined properties when the replacement levels 0 to 70 percent are examined. Likewise, the coarser material must have weaker trends due to the smaller difference between the particle size distributions for the respective replacement level.

The yield stress increases with increasing amounts of fines, this can be expected since the volume of the particles are the same but the actual number of particles increases. Increasing amounts of fine material will reduce the free water in the paste. The added amount of super plasticizer is the same for all cement pastes, due to the increasing amounts of fine material in these experiments there will be less and less free admixture in the water. This will lead to a higher yield stress. The measurement of the plastic viscosity shows a slightly increasing trend, this can be explained by the same theory as for the yield stress.

The yield stress measured for the cement pastes that contained filler material that gradually become coarser shows a slightly negative trend. This can be explained by the fact that the total particle system becomes coarser and thus more water and admixture are free in the matrix. The slightly positive trend of the plastic viscosity is not consistent with the theory. However, the flow curves give an indication of the reason for this anomaly, the material seems to segregate. Segregation (sedimentaion) of the material, will according to Barnes et al. (1996), result in an increase in the measured viscosity.

The calculations of the filler/cement systems' particle packing show that the series of replacement with finer material obtain increasing particle packing with increasing fineness of the particle system. The coarser the second series get the lower the degree of particle packing is obtained. The compressive strength of the cement pastes containing the limestone filler mixes appears to show a correlation to the particle packing, the better packing grade the better strength.

6 Conclusions

- The β_p measurements show clearly that increased amounts of filler decreases the water/powder ratio that gives zero flow, and that the filler with finer particle size have higher values than the coarser ones, i.e., they are less sensitive for water changes.
- The β_p measurements appear to correlate well with the rheological measurements.
- The F-shape of the particles in this investigation appears to have no effect on β_p, strength or rheology.
- The particle size distribution of the added limestone filler affects the cement pastes total developed heat. The sedimentary (younger materials with less metamorphose grade)

appears to affect the heat development, although this investigation did not answer the question of how they affect the cement hydration.

- Increasing amount of fines in the filler material will increase the grade of particle packing, as well as it appears to increase the compressive strength and the viscosity and yield stress of the cement paste. However, when the amount of coarse particles is increased in a particle system the strength, viscosity and yield stress decrease.

7 Acknowledgement

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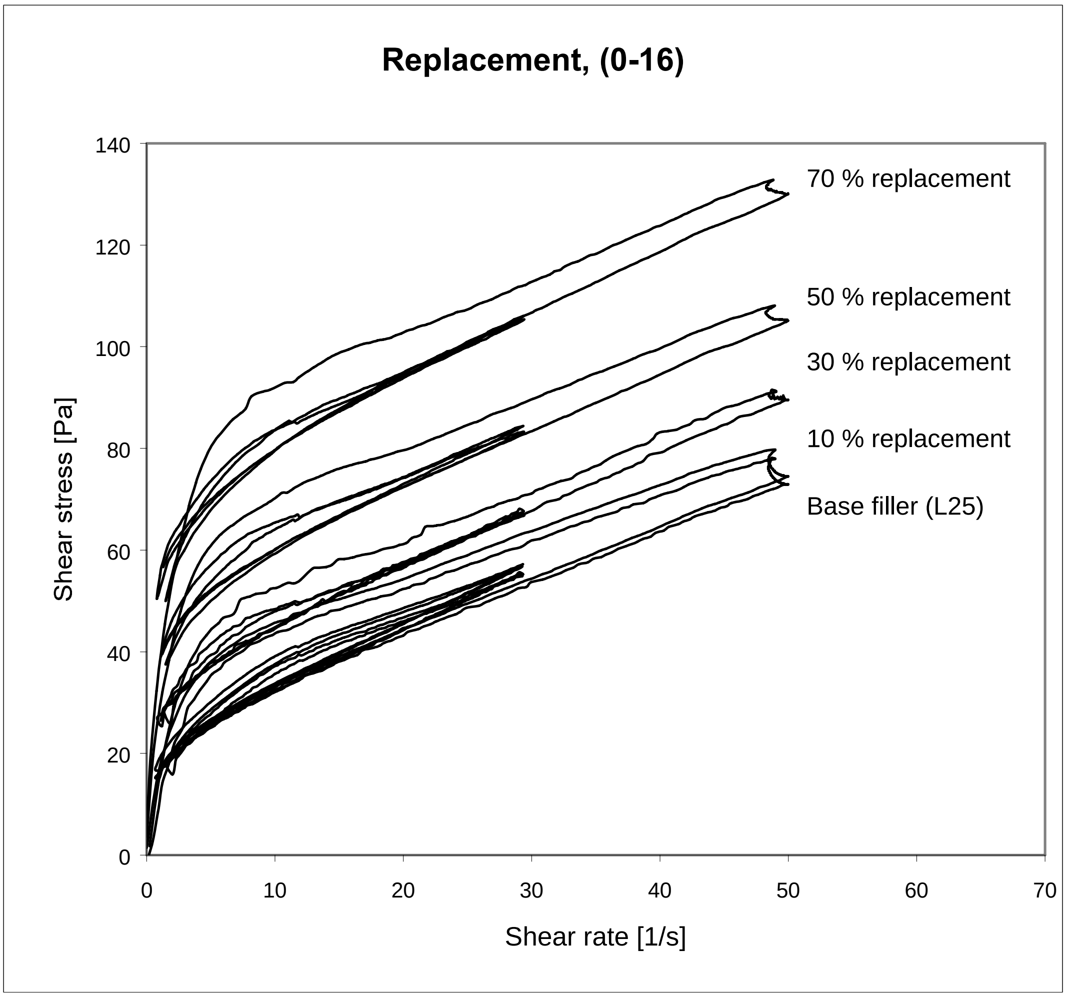
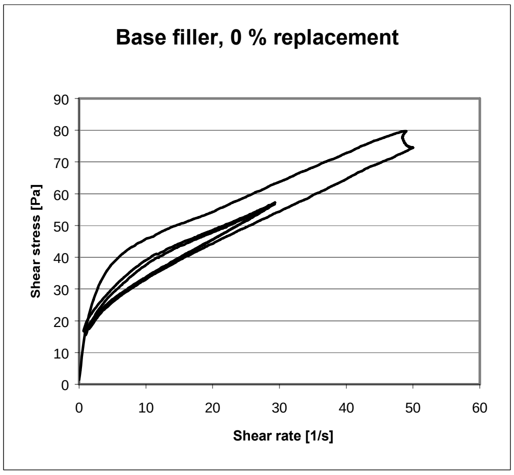
Appendix 1

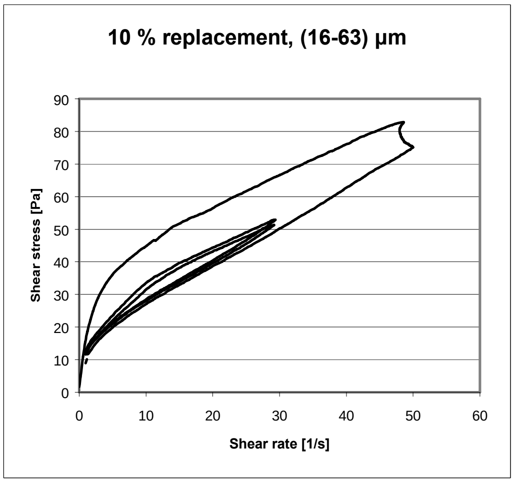
Flow curves, the shear stress as a function of shear rate, for cement pastes containing the base filler and the filler where parts been replaced with the (0-16) μm fraction.

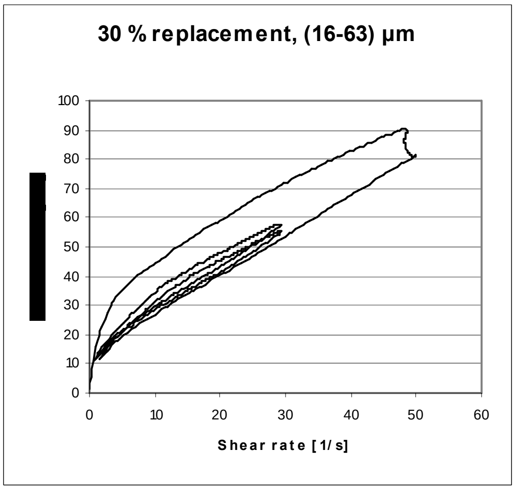


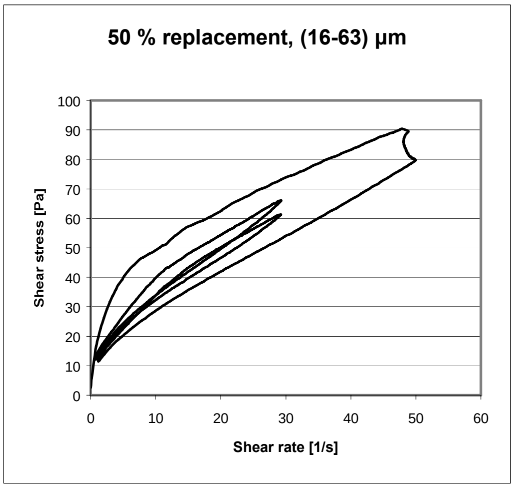
Appendix II

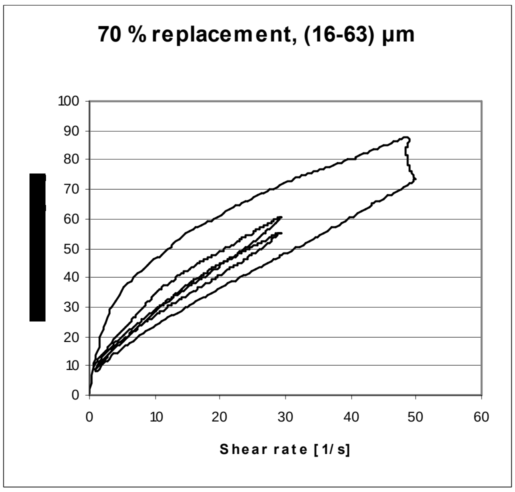
Flow curves, the shear stress as a function of shear rate, for cement pastes containing the base filler and the filler where parts been replaced with the (16-63) µm fraction. The curves are shown in separate diagram since they otherwise would overlap and make it impossible to distinguish any details.











Appendix III

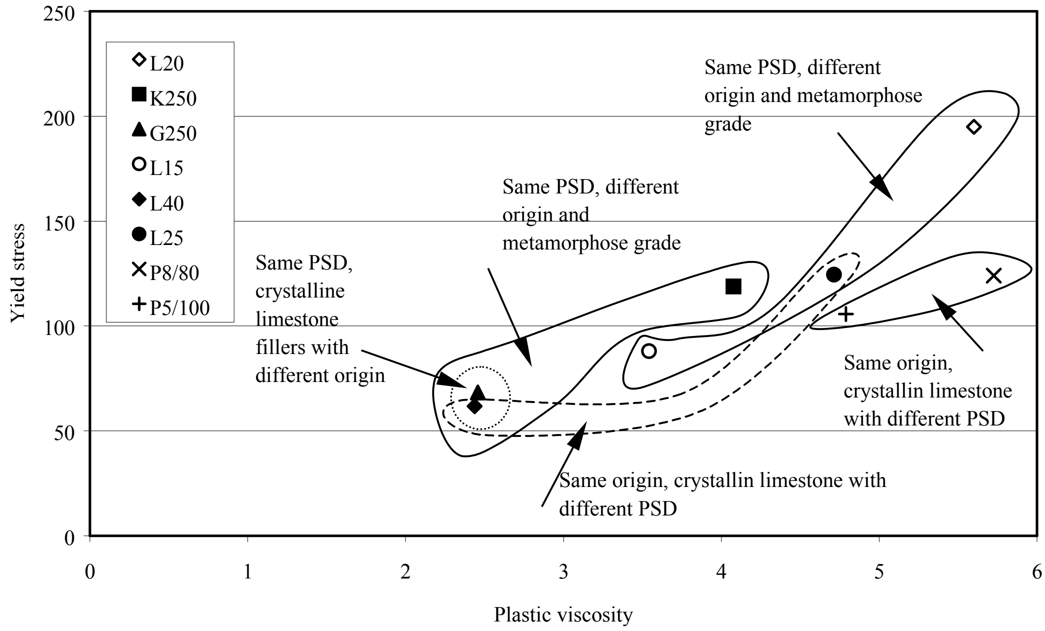


Figure 1: Rheological measurements of cement paste with the different limestone fillers. The cement used is a CEM II/A-LL 42.5 R ("byggcement")

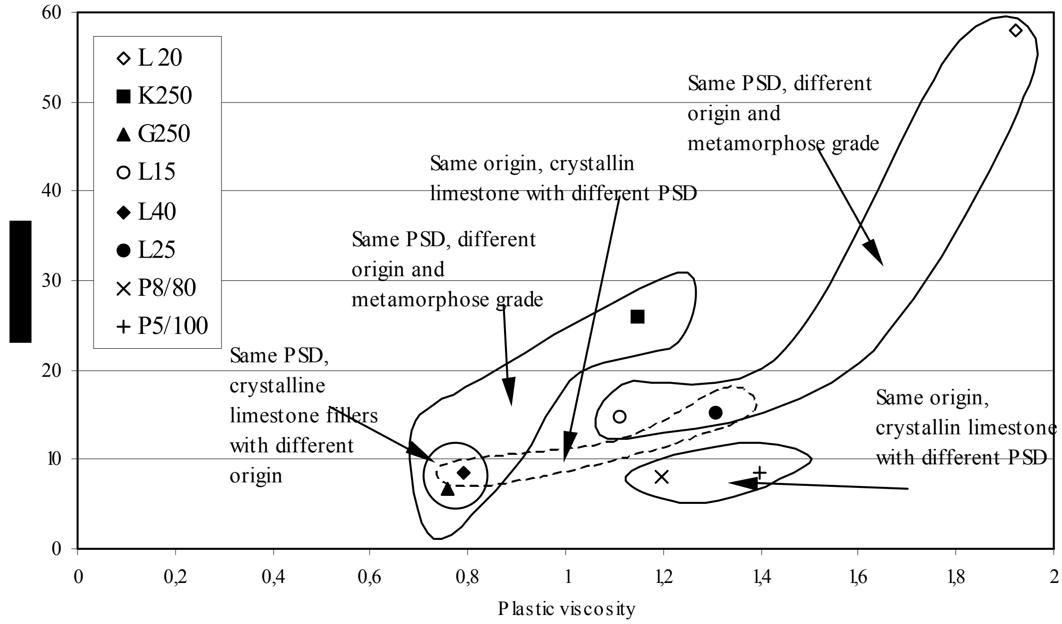


Figure 2: Rheological measurements of cement paste with the different limestone fillers. The cement used is a CEM I 42.5 BV/SR/LA ("anlöggningscement")