High Performance Cements and Advanced Ordinary Portland Cement Manufacturing by HEM- Refinement and Activation

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Abstract

Ordinary Portland Cement (OPC) is the material most widely used in construction industry all over the world and therefore consumed in super large volume. This causes general interest in improving this product with respect to materials properties. Compared to the raw material cost, the manufacturing cost is energy intensive and therefore cement industry has been and is interested in improvements in the efficiency of their milling operation and their rotary kilns.

If High Energy Milling (HEM) is applied for the grinding of cement, this can lead to substantial refinement (< 2 µm) and mechanically activation of the powder particles that in conventional material exhibit a particle size in the order of 50 µm.

Earlier work and preliminary studies have shown that this can result in a faster setting time, a faster curing time and in increased mechanical properties. Due to the far shorter grinding process at far higher energy efficiency, due to an expected reduced firing temperature in the processing and finally due to an expected significant saving in production space for the grinding step, an economically advanced manufacturing process of cement seems to be offered by HEM.

Due to a tremendous refinement into submicron range at high active surface, the material can result into a super fast setting cement (SFC ≈ 3 min) where this feature being available for repair-work of concrete constructions would also lead to an advanced product application which would be the first appliance imagined for short term range. Later this maybe spread out by reduced construction dimensions and faster building due to increased mechanical properties.

The key question if HEM is available and can be scaled up for this kind of super large volume application can be carefully answered positively since the high kinetic semi-continuously processing route based on a carrier-gas in compression mode has been introduced.

The present paper reviews the preliminary studies, explains the novel technique and suggests the route into commercial application. Particular attention is paid to wear results with an applied Si_3N_4-grinding unit where no substantial wear was found after 4000 h of operation.

1. Introduction

Since ancient times, cement has been used as binder material to form concrete structures. Today, Ordinary Portland Cement (OPC) is a super large volume product with thousands of monthly produced tons all over the world. OPC has a particle size distribution (PSD) where 90 % of total particles correspond to 50 µm, disclosing an onset setting time of 2 to 3 hours. Depending on its chemical composition OPC might attain 320 kg^f/cm^2 of compressive strength after 28 days curing. The conventional firing temperature is today about 1450°C.

In this paper we suggest to apply High Energy Milling (HEM) as an innovative processing technique for the commercial production of superfine High Performance Portland Cement (HPPC) in short term range. As an almost natural consequence, then in long term range, this technique should be applied also for the manufacturing of OPC at lower energy consumption and then at finer structure as well.

HEM leads to a significant refinement of the cement particle size. The here reviewed preliminary studies [1-2] had lead to an average submicron particle size which seems economically realistic. Compared to the conventional OPC which may have an average particle size in the order of 50 µm, cement mortar made out using refined cement can end up with larger strength, faster setting time and faster curing time.
Additionally, since HEM is based on the collision of grinding media rather than shear and friction effects of the same in low kinetic conventional ballmilling, this process results in a significantly higher efficiency related to the total energy consumption [3].
It is further shown, that the tremendously larger and high active surface of the HEM-refined powder which is also related to solid state reactions during HEM, leads to significantly lower firing temperatures as well as to a super fast setting time (< 3 min) of the cement.

Previously reported work conducted on slightly refined cement has reveled that its compression strength might be increased by micron-size refining of cement particles [4]. In other work it was stated that refining cement leads to a number of drawbacks, such as strength retrogression, unusually fast setting features, and a large demand for water by the refined cement which dramatically reduces its compressive strength [5-6].

Based on the HEM-refined superfine cement and following the ASTM C109 norm as close as possible, a number of cement pastes have been produced using special sand as well as a water-reducing agent. Results verify that using proper additives and refined-clinker (RK) leads to a substantial increase on the material compressive strength, as compared to the typical strength of OPC. For an intermediate comparison to the state of the art, a mixture maintaining the total amount of each concrete ingredients as stated by the standards of RK, HPPC by HEM and other ingredients have been made and this material did undergo high early-strengths in the order of 320 kg/cm^2 (first day) and over 1100 kg/cm^2 after 28 days curing [2].

In result, next to a significant improvement of the mechanical properties of concrete, this technique also seems to offer a high potential in becoming a revolution for the conventional processing route of OPC since due to refinement and activation, setting time and firing temperature might substantially be improved. Thus, a promising safe of energy in the manufacturing process as well as cost in construction time and dimension supports the here given attempt, too.
Later this might even become interesting for tile-production where the firing temperature for the base-plate is equal to the one of cement but the melting temperature of the glaze-coating is significantly lower at around 450-600°C. Energy consumption in this industry is also a determining factor in the manufacturing costs [7].

The present paper reviews the preliminary work that has been done and proposes and explains the route to achieve commercial appliance in large volume.

2. High Energy Milling, technique and application

High Energy Milling (HEM) is one of the High Kinetic Processing techniques (HKP) which covers HEM, Mechanical Alloying (MA) and Reactive Milling (RM).
Mechanical Alloying (MA) is maybe the most historical one and has been described as a process where powder particles are treated by repeated deformation, fracture and cold welding by highly energetic collisions of grinding media in a milling process [8-9]. By this technique it is possible to synthesize new materials with new properties that cannot be created by conventional route e.g. due to a not present thermal equilibrium or immiscibility of their components. By structural design, important materials properties can be influenced (e.g. nanocrystalline, amorphous).

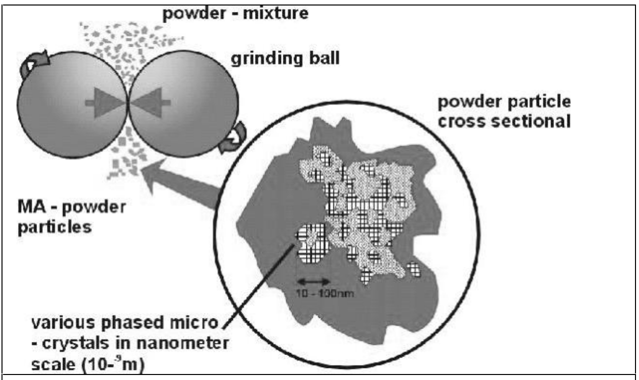

Figure 1: schematic of the collision as the main event of energy transfer

High energy milling (HEM) and reactive milling (RM) are performed by the same processing principle where the variation is in general based on the target of the processing, the transformation effect by the kinetic energy and the starting materials.

The different procedures can be described as High Kinetic Processing (HKP) where the collision of the grinding media is the main event of kinetic energy transfer from the milling tools into the powder [8-9]. Fig. 1 shows the schematic of the collision. The basic equation (1) describes the relation between the kinetic energy (E_{kin}) and the mass m and the velocity v of a single ball:

$$E_{kin} = \frac{1}{2} m v^2 \tag{1}$$

It is clearly seen that the maximum relative velocity of the grinding media is the most determining factor contributing to the kinetic energy.
A typical example of practical importance that demonstrates the effects that are inherent in Figure 1 has been described in detail [10] in the system:

$$24\ Ti + Al_{11}Nb \rightarrow Ti_{24}Al_{11}Nb$$

In this work the influence of the milling parameters have been evaluated and basically the processing route of Cycle Operation for CMB-materials [11] had been invented. By this technique, the problematic agglomeration and sticking behavior of the, in this case, Ti-Al-based material in a dry milling process could be significantly reduced which did lead to an increase of the powder yield from < 4 % to 80 %. Later on similar effects were found in the Ti-Ni-system [12] and in the processing of a number of ductile metal flakes [13-14]. In 1999, Kim et al. investigated the difference of Cycle Operation and Constant Operation in the Fe-Co-system and found tremendous effects on particle- and in particular crystallite-size reduction [15].
If the here described processing method is applied for particle and /or crystallite size reduction or particle deformation (e.g. flakes) in single systems, this route is described as HEM. The goal can be to receive a special particle geometry e.g. for rapid and large-scale production of ductile metal-flakes in dry process without solvents and less energy e.g. for paint-pigments, conductive pastes and anti-corrosives [16-17]. On the contrary rapid particle size reduction of brittle solids like Enamels or Glass Fluxes has recently been introduced as a new application field [18-19].
The definition of RM is suitable if during milling a chemical reaction is wanted and observed.
By this route, a dispersion of ultra-fine (nano-scaled) crystals and/or a homogeneous dispersion of transformed phases in a matrix can be achieved [20].
A typical example of practical importance here has been demonstrated in the Ag-Sn-system [21]:

$$Ag_3Sn + 2\ Ag_2O \rightarrow 7\ Ag + SnO_2$$

Due to the CMB-behavior of this ductile system, again the processing has to be performed by applying Cycle Operation. With respect to the starting materials (e.g. Ag_2O instead of Ag), RM in this kind of principle can show economical advantage. Often these processes are environmentally benign as they avoid wastes e.g. in solid state synthesis where organic solid-solid reactions and others can rapidly proceed without any wastes and in the absence of solvents [22-23].

3. Equipment

Industrial mills of different types are in practical use. Vibration-mills have to move the mass of the milling chamber. This limits their sizes and they are hard to run in normal environments which is also

valid for simple (drum-)ball-mills with a rotating vessel. The efficiency related to the total energy impact of these types is known to be less than 5 % [24-25].
Jet-mills use large streams of energy intensive air or inert gas which very much limits their economical use and cannot supply solid state reactions for the cement application since the piece-mass of the single accelerated particles would be too small. Bead-mills, horizontally or vertically, do not exhibit a significant kinetic impact, planetary ball-mills [26] and shaker-mills [27] are limited to laboratory size. The most suitable choice are therefore high energy horizontal rotor-mills that can be operated in dry processing at high relative velocity of the grinding media (up to 14 m s^{-1}) that cannot be reached by the other types (up to 5 m s^{-1}) and which are mostly the referees in chapter 2 for process and application.
Furthermore these high energy mills can be operated in batch, continuous and semi-continuous operation mode using carrier gas in de- and compression mode where the last mentioned is expected to be of substantial importance for the large volume manufacturing of cement.

4. Preliminary Studies (in laboratory scale and batch operation)

4.1 Ordinary Portland Cement

For the preliminary studies, OPC supplied by Grupo Cementos de Chihuahua (GCC), Mexico was used as the starting material for the refinement tests by HEM. A typical raw-composition of GCC-cement, as released from the milling operation is given in table 1. The typical particle size distribution (PSD) of the GCC-cement is given in table 2.

average raw-composition of GCC-cement, as released from the milling operation									
component	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	SO_3	Na_2O	other
mass%	64.2	21.8	4.1	3.3	1.4	0.61	2.5	0.15	bal.

Table 1: average raw-composition of GCC-cement, as released from the milling operation

typical particle size distribution (PSD) analysis of GCC-cement										
fraction [%]	10	20	30	40	50	60	70	80	90	100
size [µm]	2.5	5.1	7.2	10	15	20	28	34	49	85

Table 2: typical particle size distribution (PSD) analysis of GCC-cement

4.2 High Energy Milling process in batch operation (preliminary studies)

For the preliminary studies, a laboratory scale high energy mill (Simoloyer CM01-2l) was used.

In order to test the wear-resistance of recently available ceramic grinding units that are based on Si_3N_4, a grinding unit W01-2lm-SiN has been used, where the vessel is lined inside with Si_3N_4-plates and the rotor is built up by restorable Si_3N_4-bulk-blades.
Figure 2 shows a horizontal high energy mill with 2 L chamber volume, which can be operated on a table next to the process controlling computer. It runs with water cooling at rotation frequencies up to 1800 rpm.

Figure 2: 2-L horizontal high energy ball-mill (Simoloyer CM01-2l) with vacuum and inert-gas loading, operation and unloading.

Figure 3a shows the disassembled grinding unit (flange, rotor, vessel and blind-lid) and figure 3b the draingratings and in the center the side-adapter:

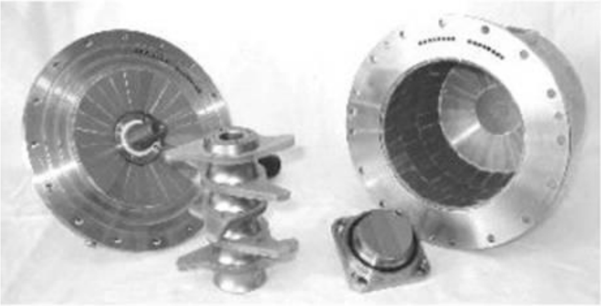

Figure 3a: disassembled grinding unit W01-2lm-SiN (flange, rotor, vessel & blind-lid

Figure 3b: draingratings As-01-2l-SiN, As-G1-2l-SiN and side adapter RKDN01-SiN (center)

With respect to the ceramic milling tools, the rotational speed of the mill was chosen not to exceed 900 rpm. It was further decided to operate the cooling system because of the temperature limitation of the bonding of the ceramic to the stainless steel base parts.

In the preliminary studies, 3 main parameters have been investigated. The processing time has been varied between 30 and 150 minutes at different powder/ball weight ratios from 1:20 to 1:40. This was additionally performed under varied rotational speed from 500 to 900 rpm and in another test-series, Cycle Operation had been applied which means during processing, the rotational speed of the rotor is changed in a special frequency in the range from here 500-900 rpm which has been proven to tremendously increase the powder yield of materials that tend to stick and agglomerate under MM to the milling tools and to each other [10-13].

analyzed parameters during the processing of GCC-cement powder			
parameter	processing time [min]	powder/ball weight ratio	rotational speed [rpm]
variation	30, 60, 90, 120 and 150	1:20, 1:30, 1:40	500, 750, 900 and 900/500*

Table 3: varied parameters at the processing of GCC-cement powder

The detailed parameter variation is given in table 3 and the used Operation Cycle for the test-series at 900/500* rpm is given in figure 5 and the corresponding Discharging Cycle 500/900** in figure 6.

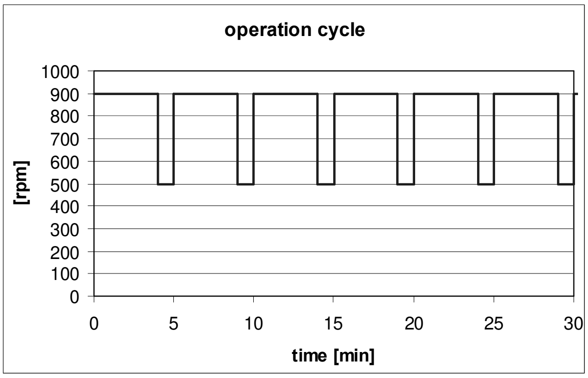

*Figure 5: Operation Cycle 900/500**

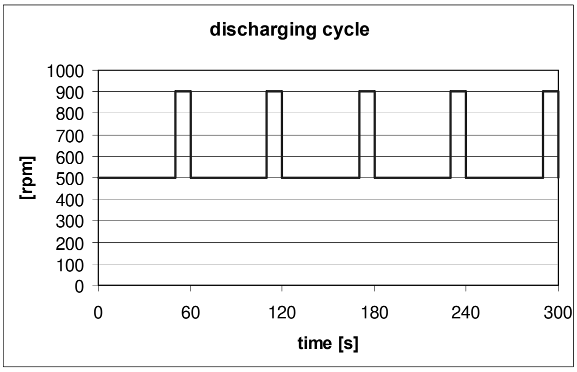

*Figure 6: Discharging Cycle 500/900***

The processing was done under air, which means no air-lock, no evacuation or flooding with inert-gas was used and the vessel was kept at RT by the cooling systems. The detailed base-parameters of the processing schedules are given in table 4:

base parameters for the processing of GCC-cement powder	
milling device	Simoloyer CM01, 2.7 kW
operating software	Maltoz 3.1
grinding unit	W01-2lm-SiN (2 liter, water-cooled, Si_3N_4 lining / bulk)
grinding media	Zirconia, fully stabilized (YTZ), 5 mm, 2.3 kg
PCA (lubricant)	drops of propylene-glycol
starting powder	GCC-cement powder
starting powder load	varied at 57.5, 76.6 and 115 g
powder/ball weight ratio	1:20, 1:30 and 1:40 varied
atmosphere	no, operation, charging and discharging under air
HEM time I - V	30, 60, 90, 120 and 150 min varied
Operation Cycle	900/500 rpm - 4/1 min
Discharging Cycle	500/900 rpm - 50/10 s
average discharging time	5-10 min
milling temperature	< 25 °C (vessel inside by Maltoz)
discharging/separation	draingrating As-01-2l-SiN
average powder yield	close to 100 %

Table 4: base parameters for the processing of GCC-cement powder

For loading the starting powder for a single test, first the grinding unit is set into charging/operation position which means the main-port P01 is on top. Then the powder is loaded through the open main-port. For operation, the main-port is closed with the blind-lid. After processing, for discharging, the blind-lid is replaced by the draingrating As-01-2l-SiN with an adapted powder container. Then the grinding unit with the adapted container is turned into discharging position, which means the main-port is in bottom position. Then the discharging operation is started and the powder is transferred into the powder container where the grinding media remains in the grinding chamber.

4.3 Characterization and Specimen-Code (preliminary studies)

The as-received (initial) and the as milled powders were characterized by laser diffraction (PSD), XRD, BET and optical microscopy.
The particle size measurement was carried out with a Malvern Mastersize 2000 device and for X-ray diffraction we applied a Siemens Diffractometer D 5000 using monochromatic Cu-Kα radiation. The BET-surface area of the powders was analyzed with a sorption/desorption commercial Quantachrome device, and for optical microscopy an Olympus microscope AX70 model was used, optical pictures were taken with a JVC-TK1270 video set. Compressive tests were carried out using a 50-C-21H4 universal testing machine. The American standards for cements were used along this research work for all samples, i.e., using 5x5x5 cm large specimens (ASTM 109/C).

For the definition of the quite large number of up to 60 different powder-charges, where some have been disregarded corresponding to received results, a code as given in table 5 was used to determine each powder charge:

specimen-code for determining the different powder charges of processed GCC-cement powder			
parameter	processing time [min]	powder/ball weight ratio	rotational speed [rpm]
example	60	1:40	500
code	m60	40	500
full code	m60-40-500		

Table 5: specimen-code for the different powder charges of processed GCC-cement powder

The wear of the milling tools was determined by visual observation and measurement of the blade diameter.

4.4 Results (of preliminary studies)

Figure 7 gives the x-ray diffraction patterns of the as received (OPC) cement and of the refined cement (Milled HPPC) where the investigated powder refers to the charge m60-40-500.
After the HEM-process, most of the peaks appear very much shortened and broadened verifying structure refinement.

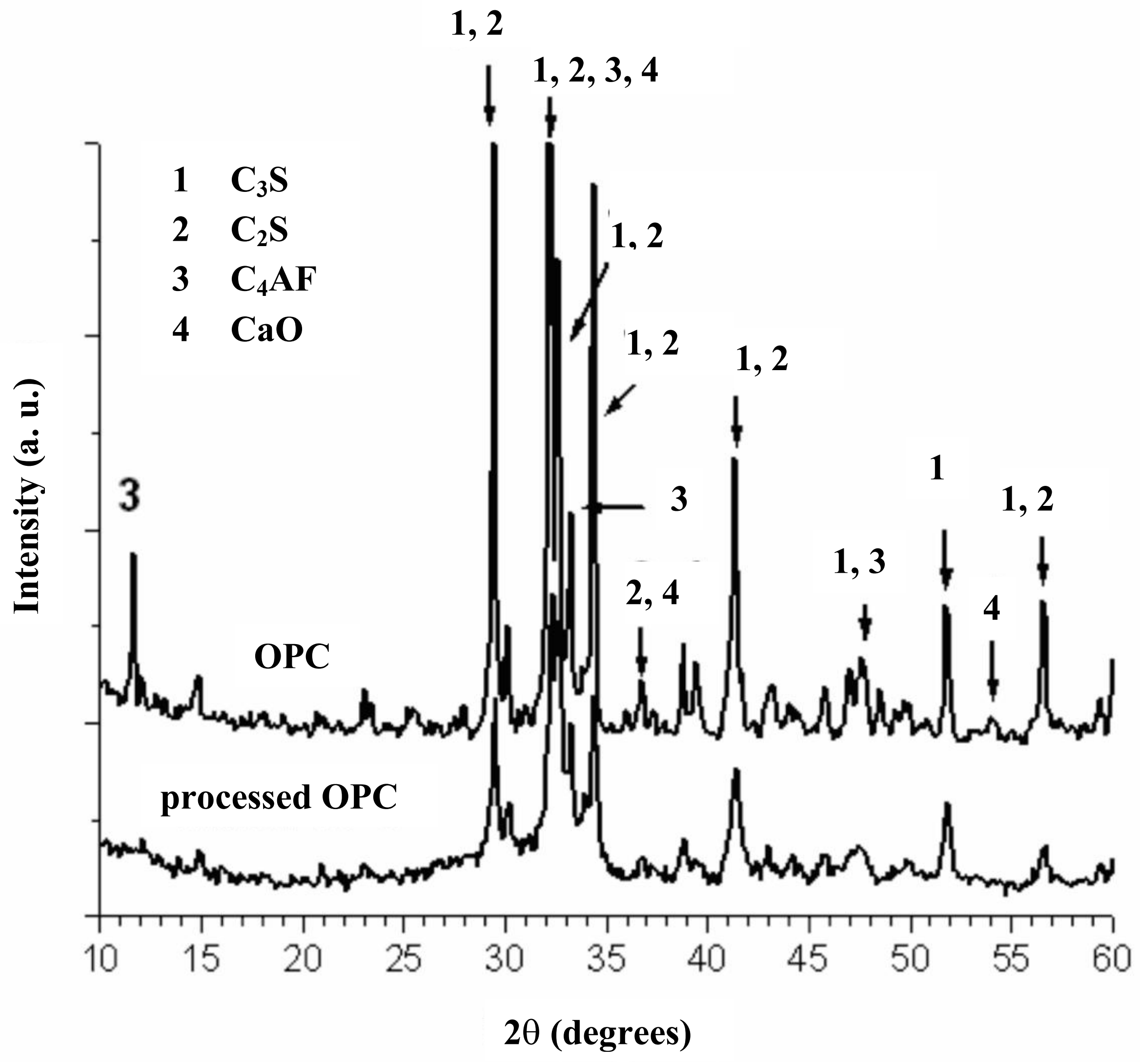

Figure 7: XRD-patterns of GCC-cement powder (OPC) and of processed powder m60-40-500

Most interesting is here, that next to refinement a number of solid state reactions [28] seem to proceed which is caused by the kinetic energy impact. E.g. in case of the quartz (SiO_2) given at 21.8 wt% and forming an infinite covalent crystal lattice, fragmentation of Si-O bonds leads to completely unsaturated freshly cleaved faces with free ▒Si˙ and ˙O-Si▒ surface radicals and other highly reactive species. They represent a local plasma which tends to be saturated immediately and leads to tribochemistry effects [22-23].

Figure 8 gives the particle size distribution of selected results.
The finest powder at most economical parameters is represented by the test m30-20-500. This is in so far surprising, as this powder is achieved after the shortest applied processing time at lowest applied rotational speed and at lowest applied powder/ball weight ratio but does belong to the finest achieved powders in total. In other words, here the lowest applied kinetic results into one of the finest achieved powders. This can only mean, that the general attempt of the processing schedule was to long and gives the expectation, that here a rapid particle size reduction of the naturally brittle solids leads to

very fine powder after much shorter time and that this fine powder leads to a dumping effect for the kinetic impact (acts like a liquid in the dry process) [18-19] which is a general problem in the batch process. Further processing time of further increase of kinetic by increased velocity (rpm) or by increases ball/powder weight ratio does then not lead to further significant particle size reduction.

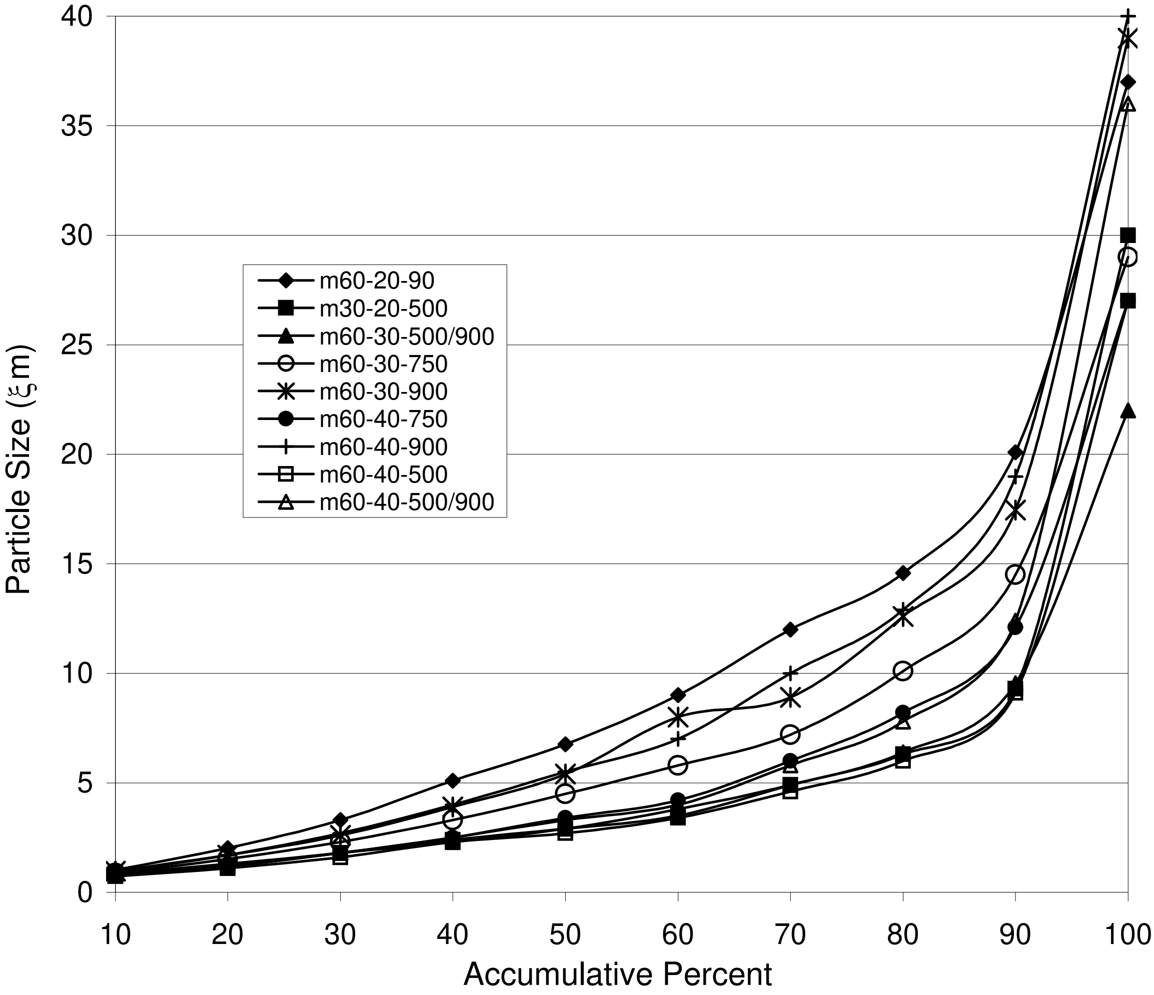

Figure 8: particle size distribution of processed GCC-cement powders

As far as we can observe here a slight increase of the of the particle size with the processing time, this leads to the assumption of agglomeration of the fine particles in an "over-milled" stage.

What is further interesting, is the observation, that the finest powder in total, which means the finest 100 % value, is achieved when Cycle Operation is applied (test m60-30-900/500). This might be explained by the known effect of this processing route to avoid dead-layers in the process, where particles could be "hidden" resulting into less or non-processed particles after discharging. A further hint to this can be seen in figure 9b where among the very fine processed powder a few (<10 µm) mediums sized particles and one large particle is observed.

In general figures 9a and b show optical micrographs of the as received and of the processed powder with the code m60-40-500. Impressively the difference in microstructure and morphology is presented here. The non-refined cement appears as a very heterogeneous material with a huge number of large sized particles in the order of 30-60 µm and some very large particles in the order of 100-120 µm.
On the contrary, the refined cement shows a much more homogeneous microstructure at very small particle size (D50 is given at about 2 µm by PSD) with a few (<10 µm) mediums sized particles below 20 µm size and one large particle in the order of 100 µm. The BET-surface area was found to be 15 m^2/g.

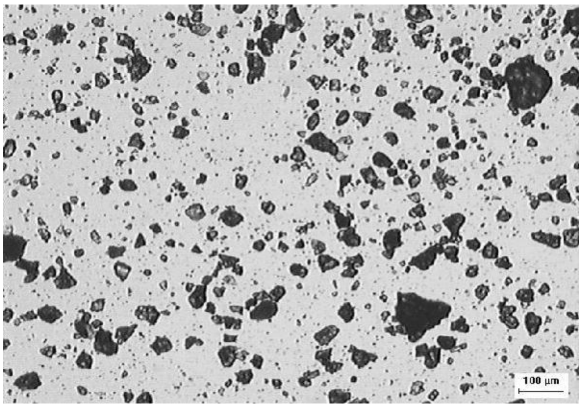

Figure 9a: optical micrograph of GCC-OPC cement powder (as received)

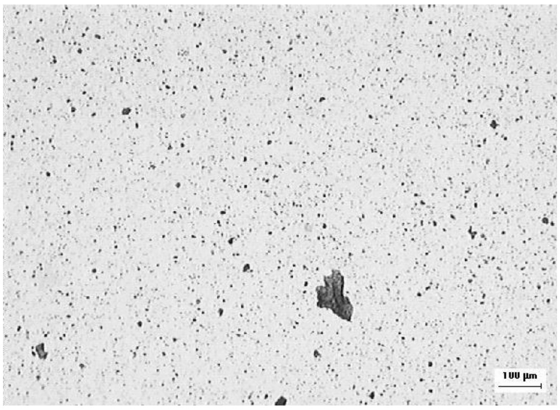

Figure 9b: optical micrograph of GCC-HPPC cement powder (processed under the code m60-40-500)

As a demonstration of the chemical and physical behavior of studied cements, using both materials shown in figures 9a-b, very fluid mortar-cement pastes were carefully prepared and the two little sculptures, as given in figure 10 were molded applying no pressure.

Here, impressively the filling capability of finer grade cement for the expansion into fine and complex structures compared to the one of conventional material is shown. The setting time of the fine graded high performance material was 2-3 minutes only.

In particular these properties can be of major importance for the future advanced repair of cracks and hollow spheres of concrete constructions like bridges or dams.

Figure 10: sculptures made by conventional OPC (left) and by refined HPPC (right).

In order to compare the strength of the High Performance Portland Cement (HPPC) by HEM-refinement, samples were tested using a universal testing machine 50-C-21H4 shown in figure 11 at a compressive rate of 900 N/s. Tests were applied after 1, 3, 7 and 28 days, results are given in fig. 12:

Figure 11: universal testing machine for HPPC specimens' strength evaluation

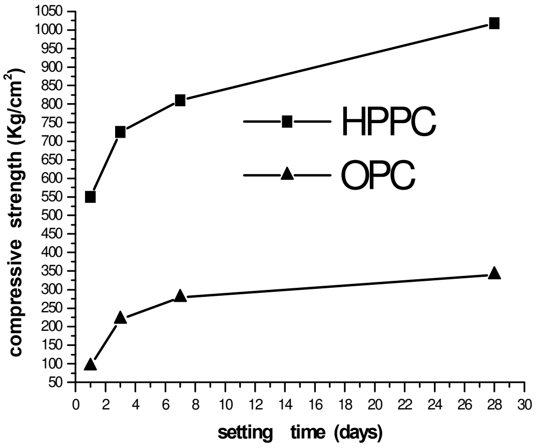

Figure 12: compressive strength results of HPPC as compared to OPC

The compressive strength results of conventional OPC from around 94 kg^f/cm^2 after the first day to 320 kg^f/cm^2 after 28 days curing do agree well with typical expected values as reported by the C-109 ASTM standards.

The HPPC-material achieves a compressive strength of 550 kg^f/cm^2 after the first day and of 1018 kg^f/cm^2 after 28 days.

In comparison, the refined and activated HPPC achieves a very high early strength where already after 1 day the strength is about 70 % higher than the strength of the conventional material after 28 days.

After 28 days, the strength of the HPPC is more than 3 times higher than the corresponding value of the conventional material.

Finally we checked the wear of the milling tools which is important to be estimated in early stage since in case of success, extremely huge production numbers must be considered. The results are in so far surprising and impressive at the same time.

Figures 13-16 shows pictures taken in CIMAV from the disassembled grinding unit after in total 4000 hours of operation with a grinding media load of 2300 g and an OPC-powder load varying between 115-230 g at rotational speeds varying between 500 and 900 rpm.

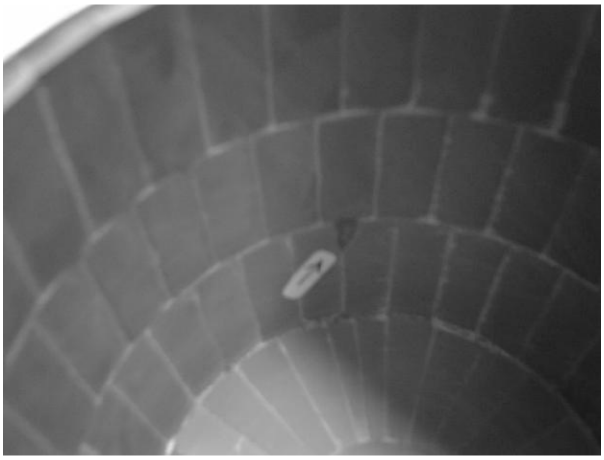

Figure 13: one of two cracks in the lining plates, both appeared in cylinder-lining

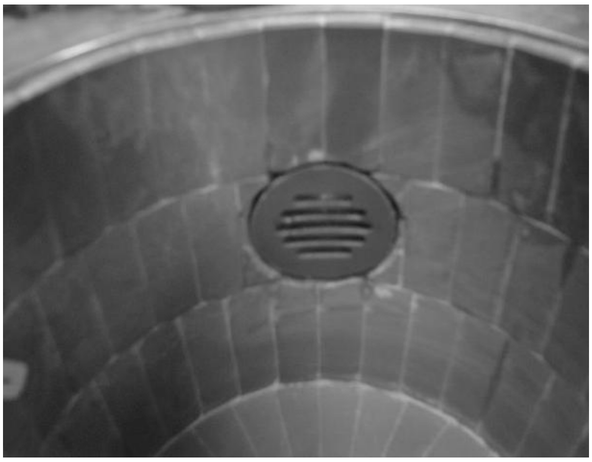

Figure 14: circle-edge of P01 acts as a dead-zone which should be improved

In detail figure 13 shows the inner Si_3N_4-lining of the vessel where in total (all components) 2 cracked plates have been found. One of these cracks is in the area of the given picture and is marked with an arrow. In both cases, no fracture of the plates did fall off which means the cracks are not considered as being problematic, in particular not after that long milling operation at relatively high kinetic.

Figure 14 shows the inner view of the main-port P01 with the assembled draingrating As-01-2l-SiN where it can be seen, that the border of the vessel-lining causes in so far problems, as the not well defined circle-edge can act as a dead-zone in the process. This should be improved by using a 2- or 4-piece form-part for the lining, where then the circle-edge would be preformed when producing the Si_3N_4-lining plates.

Figure 15 shows the draingrating As-01-2l-SiN. One of the center-edges was broken and had to be repaired. The edges are considered to be too weak for the kinetic impact during discharging, in particular when Cycle Operation is used since then at least for short time periods, high kinetic impact is exposed. This matter should be subject of dimensional improvement (thickness of lining or width of center-edges).

Figure 15: broken center-edge of draingrating, dimensional improvement is recommended

Figure 16: no damage on the rotor-blades, wear surprisingly low, diameter loss less than 2 mm (after 4000 h !)

Figure 16 shows flange and rotor. No cracks or damage could be noticed in the flange-lining and most surprisingly, no damage or cracks could be found at the Si_3N_4-bulk rotor-blades as well.
The diameter of the blades has been measured and a diameter-loss of less than 2 mm has been determined. This is a surprisingly very good result and it should be pointed out, that the given total processing time of 4000 hours would refer e.g. to a 24-h-operation for a period of more than 5 months.

The YTZ grinding media did not show significant diameter-loss as well.

4.5 Conclusions (of preliminary studies)

In conclusion, the preliminary studies do show, that HEM/RM is capable to refine and activate OPC which then results into a High Performance Cement with very interesting properties such as high early strength higher than the final strength of conventional material and 3 times higher strengths after 28 days.

There seems to be a good chance to produce far better material at lower cost.

As far as the refinement-operation by HEM is concerned, the results lead obviously to the assumption, that the set processing times have been too long and that the batch operation procedure might be suitable to show up attempts in laboratory scale, but not in large scale production and not for optimum processing results.
Here, the semi-continuously route using a carrier-gas in compression mode has to be considered because simultaneously to the appearance of fine fraction, this fine fraction is extracted from the grinding process and therefore can not any longer dump the kinetic of the impact during HEM. This technique will be discussed in the following chapter.

5. Major goal: continuous HEM-process

Since OPC is a super large volume product based on relatively cheap raw materials, the manufacturing costs play the major role in the total product costs. The main operation steps in the manufacturing process are grinding of the raw-materials and the firing of the compound.

Figure 17: huge drum(ball)mill at Interceramic in Chihuahua, Mexico

The grinding process today is done in huge drum(ball)mills in a low-kinetic batch process. Figure 17 shows such a huge mill that can exceed the dimensions of a 2-floor building easily. The firing step is done in even bigger rotary kilns at temperatures around 1150°C. In fact in the literature we found a statement, that most of the total electric energy used in the world is consumed by milling devices producing cement [29] which probably should include the kilns.

If an advanced processing/grinding technique could reduce both, the energy consumption in the milling operation as well as the one during the heat treatment (firing) due to reduced temperature caused by high active large surface after finer milling, this might lead to a significant cost reduction of the entire manufacturing process.

Since the preliminary studies also end with the conclusion, that the used batch operation should not be considered for mass production, another technique shall be considered, which here most obviously must be the continuous process, first because of naturally larger throughput (if applicable) and second in this case because of expected far better parameters (faster process, finer particles) where the last expectation is based on experience in rapid particle size of enamels and glass-fluxes [18-19].
The process principle and a mass-production attempt for cement are explained in the following chapters.

5.1 semi-continuously processing

The semi-continuous operation procedure can be divided into two principles, the one using depression and the one using compression. The difference describes a different use of carrier-gas where in depression mode the gas system is open and suction is used to carry powder particles out of the grinding chamber into a cyclone. In compression mode, the carrier-gas is cycled in a closed gas-circuit which may also be divided into a primary and secondary circuit. In both cases, the Simoloyer is continuously fed with starting material and continuously processed material is discharged. Important issues here are the control of the amount of powder in the grinding chamber and the separation res. classification of the product out of the gas-flow.

5.2 semi-continuously processing in depression mode

Experience in depression mode is already available in industrial production of ductile metal flakes [16-17]. Figure 18 shows a picture of the HEM-devise in such a process where the cyclones are located in the second floor and can therefore not be seen on this picture.

However, it must be noticed that the production rates in this application can not be compared to the numbers that would be applicable in the cement-world.

The entire unit is based on a load cell which is connected to a control unit that also controls the automatic feeder for the starting powder and in this case another one for a PCA. A fan is initiating depression through 2 cyclones that are connected with the grinding chamber where the first one separates to heavy particles and returns the separated fraction into the Simoloyer (high energy mill), the second one then separates product and gas.

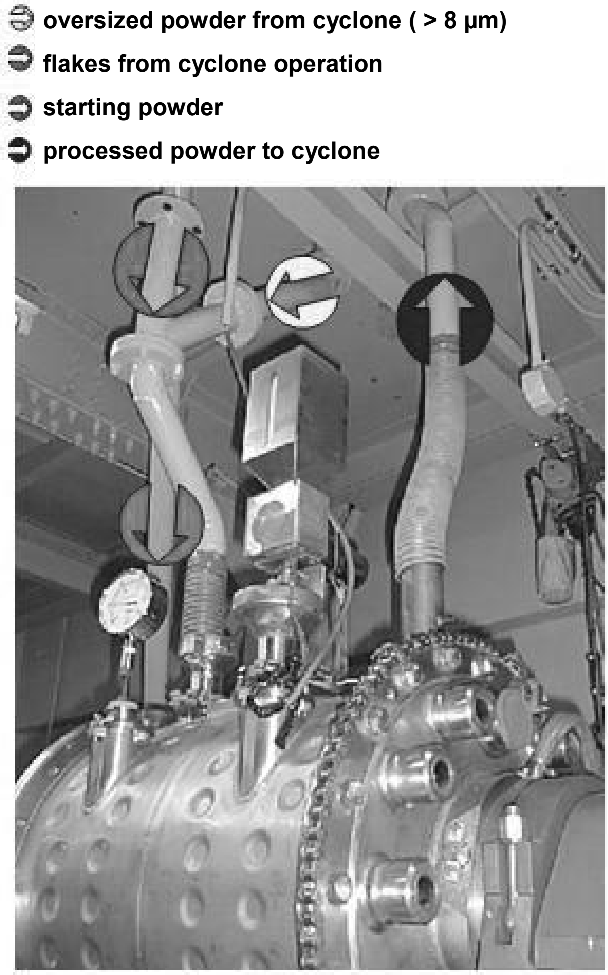

Figure 18: Simoloyer CM100-s1 in semi-continuous configuration in depression mode (picture: Fukuda, Japan)

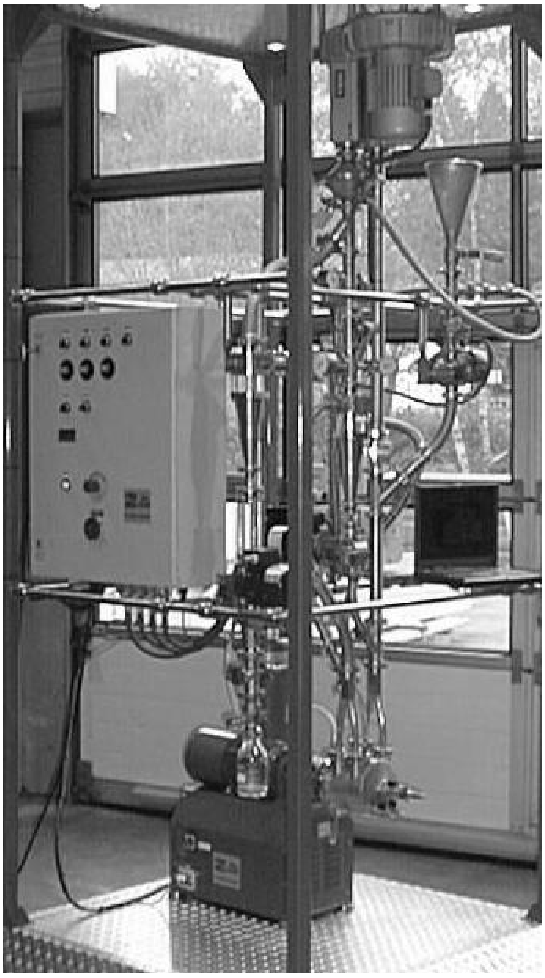

Figure 19: VS01a (Simoloyer CM01-2ls1,pilot plant in compression mode, picture: Zoz, Germany)

5.3 semi-continuously processing in compression mode

For the here discussed cement-application, for a number of reasons, the second mentioned principle, the semi-continuous processing based on compression mode is considered. Experience in this is based long term project work in rapid particle size reduction of enamels [18-19, 30] where one of the pilot-plants is shown in figure 19 which is based on the laboratory scale Simoloyer CM01.

Figure 20 shows the corresponding scale-up to a CM100-Simoloyer in compression mode.

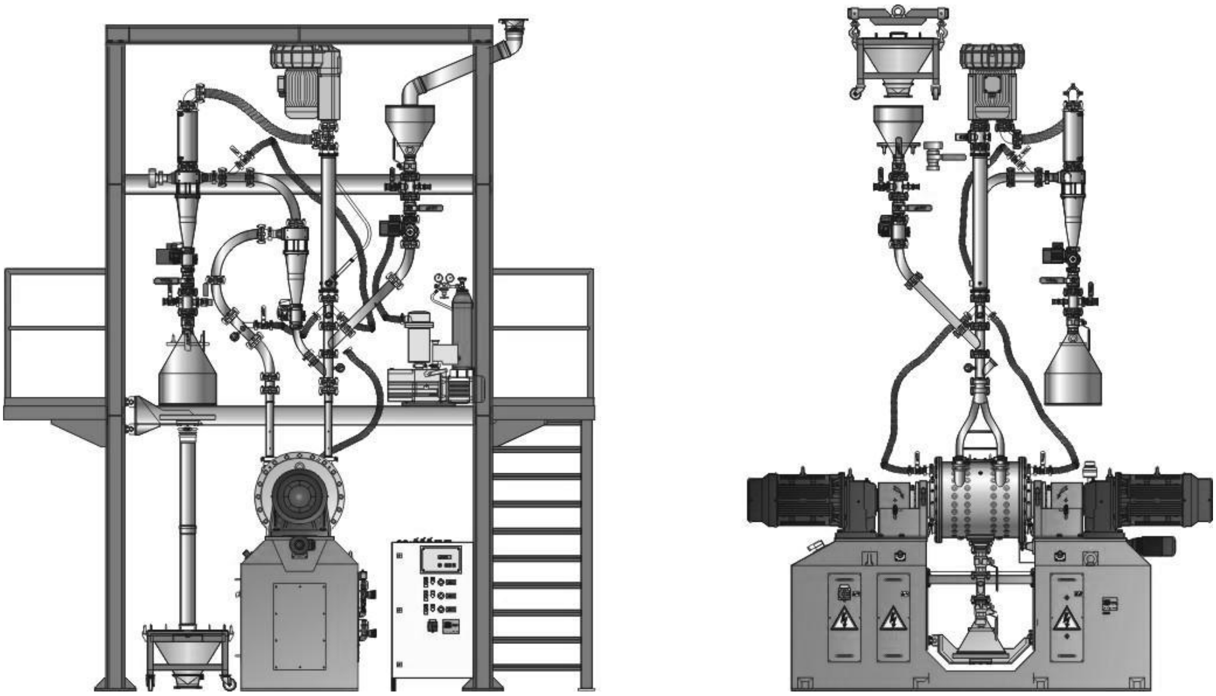

Figure 20: Simoloyer CM100-s1 in semi-continuous configuration (compression mode)

This unit is suggested to be used for the continuously refinement of OPC in large volume and is based on the experience of the earlier and smaller pilot-plants VS01a and VS20a based on CM01 and CM20 scale respectively [18-19].

In general, the Simoloyer is equipped with a closed gas circuit where the side channel turbine on top blows the gas at high velocity through a heat-exchanger, then the carrier-gas picks up the starting material at the injection unit and goes into the grinding chamber at 2 tangentional ports. On the other side of the unit, the multiphase flow leaves the chamber via 2 more tangentional ports and goes into the first cyclone which has a return path into the chamber. In line after the first cyclone the classified multiphase-flow is separated in the second cyclone and the final material is collected in a container that is adapted with and automatic air-lock. Before the carrier-gas is returned into the turbine, it has to pass a filter-unit that automatically returns filtered dust into the second cyclone. In order to classify the multiphase-flow at the first cyclone, the gas system is equipped with various by-pass units which allow to adjust different velocities in each of the cyclones, the grinding chamber and the piping.

With respect to application, the main criteria is the remaining time. Up to now, this principle can only be realized for those processes that require in batch operation a processing time in the range of several minutes e.g. rapid particle size reduction of enamels [18-19]. Due to the effect, that the fine fraction of particles is continuously, which means here also immediately discharged out of the vessel, the dumping effect of this fraction (like liquid) is terminated and consequently the kinetic of the system is increased tremendously. Additionally it is important to understand, that in case of treating large brittle particles in up to several mm-scale by collisions of grinding media at high kinetic, these particles will collapse not just into two pieces but into a number of pieces of different size and finally with a size distribution. This means that also a very fine fraction is present right away. For the today's understanding, this all together leads then to the found extremely short processing times in continuously mode in the range of several seconds for these materials-systems which is expected to be also valid for the cement-system.

For the refinement of OPC, this suggests additionally, that the starting material should probably not be the already ground cement powder in a range of 50 µm. Economically it appears more interesting to use much coarser material in the order of 4-10 mm which then maybe produced only by crushing and not by grinding which finally means the today existing milling step in the previously mentioned huge drummills could be skipped.

Since the preliminary studies did show a potential, that achievable processing times will be below 30 min and since the experience in the glass-systems did show a cut of processing time of factor 10-50, this seems to open a good chance to achieve final processing times in the range of 1-3 minutes which could then be estimated to a production rate of several tons per day with a single CM100-system as given in figure 19. If we then take into account, that Simoloyer-systems are available up to 900 liters size with the potential of further enlargement, then this technique seems to offer the application for the here discussed super large volume product. In any case and from this point of view it will be far capable to produce smaller volumes of High Performance Cement in the range of 10-100 to/day.

6. future work and target

6.1 next steps

In the next step it will be important, to prove that the here described laboratory scale knowledge and potential can be scaled up to an industrial scale. For this it will first be necessary to set up the semi-continuously operation in compression mode where for this we suggest a CM20-scale (VS20*) which is a device with a grinding chamber capacity of 20 liters and has been calculated to be suitable for an initial small-scale production of > 720 kg / day based on a 20 h / day [31]. Thus being obeyed as a notable production rate already, the CM20-plant could still be operated in a laboratory which is necessary in order to investigate ideal processing parameters and to introduce technical improvements based on the feedback from online testing.

In the second step, the achieved knowledge and experience from the CM20-scale pilot plant should be further scaled up to the CM100-size with a grinding chamber capacity of 100 liters which has been calculated to be suitable for an initial medium-scale production of > 3.6 to / day based on a 20 h / day [31].

It is important to notice, that the calculated yield data for both systems is based on the achieved data from the preliminary studies that have obviously been processed at far too long processing times and at quite medium kinetic capability of the systems. In fact and compared to the maximum relative velocity (MRV) of the grinding media, the Simoloyer-device can be operated up to 4x faster than it has been used in this studies. Therefore the further general improvement of the processing parameters will be a major part in the first mentioned step (CM20-base) which then can give a different view for the given yield data.

Finally, the scale up to the CM100-size could be considered as the achievement of success for this project goal since then any further increase of production rate seems to be relatively easy by further increasing the size of the applied devices (up to 900 liter volume today) and by just increasing the number of devices.

6.2 application of the project-result/goal

The short-term application of the project-goal is to produce HPC and take advantage of it’s accelerated curing time and at the same time substantially increased mechanical properties. This would be e.g. an ideal application in repairing bridges and dams by injection technique where in particular under-water repair conditions would tremendously benefit from the new materials’ properties.

For these particular applications, today some high-performance materials usually based on polymer and polymer water management are available at costs from $US 700,00-1.000,00/to. A careful full-cost calculation in the production order of 10 tons per day leads to a value of around $US 600,00/to for the HPPC [31] which promises even if disregarding superior properties an immediate acceptance on the market.

Here it must be pointed out, that the calculated cost level for the HPPC is based on the operation of pilot plants, which means after the achieved project goal, these cost are expected to be substantially decreased.

In mid-term application, the increased mechanical properties shall potentially be used for key-units in construction and building in order to safe limited and cost-intensive space. This can e.g. be pillows of shifted mass-transportation like highway or monorail. Any successful introduction here will directly depend on decreased product cost by increased production rates, where this seems quite possible since the today’s standard cost of OPC can be estimated to about $US 60.00/to and a good share of this is related to the energy cost of the heat treatment step [31].

In long-term range, it might even be possible to replace entirely the conventional manufacturing technique of OPC and gradually reduce the firing temperature by refinement with higher activation and then meet the key-points at maximum mechanical properties, accelerated curing time and producing cost reduction by energy saving. In this case the mark-line of product market cost based on the average $US 60,00 per ton of OPC today will be about $US 100,00 /to which would mean that an expected 100 % increase of compressive strength (to be on the very safe side) might lead to a general material volume saving of at least 30 % equivalent to about $US 20,00 /to already and another $US 20,00 /to would be to be benefited by reduced labor- and construction cost and building time at least.

7. Conclusions, Acknowledgement & References

Conclusions

It has been proved, that HEM of OPC can lead to substantial property improvements.
It has further been proved, that the semi-continuously HEM-route using carrier-gas in compression mode can offer a manufacturing process in super-large volume capability for brittle solids.
These two general findings must be combined in a project with cement industry to introduce HEM as an innovative processing technique for the commercial production of superfine High Performance Portland Cement (HPPC) as well as later for the manufacturing of OPC at lower energy consumption and then at finer microstructure as well.
This is finally the suggestion of this work in order to achieve:

a) a better product

- ➢ by reducing the particle size and activating the surface of OPC which can lead to:
- a faster setting time
- a faster curing time and
- substantially increased mechanical properties

b) an economically advanced process

- ➢ by a far shorter grinding process at far higher energy efficiency
- ➢ by reduced firing temperature in the processing
- ➢ by reducing the production space for the grinding step

c) an advanced product application

- ➢ by availability of super fast setting cement for repair-work
- ➢ by reduced construction dimensions and faster building

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(a)
development of a Ceramic-Simoloyer, a high kinetic processing device to perform
Mechanical Alloying, High Energy Milling and Reactive Milling at high kinetic energy impact
applying ceramic processing tools, project no. TPW 9403-858-02/02-642-214
(b)
continuously and monitored flake-production by HEM with aerodynamic
separation & classification and rapid particle size reduction of brittle solids
(aux. target, enamel) project no. TIP 001-0102-0016

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