INVESTIGATION ABOUT THE EFFECT OF CHEMICAL GRINDING AIDS ON CEMENT MILLING AND SEPARATION EFFICIENCY

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ABSTRACT

Cement manufacturing involves a grinding process of clinker, gypsum and secondary mineral additions, usually carried out in ball or vertical roller mills. Efficiency of grinding (in terms of energy actually used to increase cement fineness over total energy) is usually very low and reported to be in the range 10-30%. Due to increasing interest in energy savings and high fineness cement production, it is mandatory a better understanding of physico-chemical processes involved. Chemical grinding aids are organic compounds used as process additives during cement grinding that allow to increase milling efficiency. Their mechanism of action (that may involve the formation of a monomolecular organic layer on cement surface or the neutralization of electrostatic forces) is not totally clear. The effect of grinding aids is particularly evident in closed circuit grinding systems, in which a specific device (the separator or classifier) separates coarse particles from fines fractions. The addition of suitable chemical additives normally improves the efficiency of separation by reducing agglomeration and modifying the behavior of material processed by separator. In this paper an investigation on the morphology of cement particles ground in a typical ball mill with and without chemical grinding aids is described. Results are discussed considering the evaluation of separator and mill efficiency as well as physico-mechanical properties of cements.

INTRODUCTION

Manufacturing process of Portland cement is standardised and widely described in several publications [1]. Raw materials (usually limestone and clays) are quarried, then properly blended and ground in order to prepare the so-called raw mix. This is used as feeding for the pre-heater tower and kiln, where silica and lime (with alumina/iron oxides used as flux) react in a high temperature process to form the calcium silicates that compose the Portland clinker.

Clinker is then finely ground together with gypsum and secondary mineral additions (such as limestone, fly ash, granulated blast furnace slag, natural or artificial pozzolans) in order to obtain the well known grey powder usually referred to as Portland cement, used by millions of construction workers as hydraulic binder in concrete, mortars, screeds, grouts and many others masonry applications.

Cement manufacturing is a typical heavy industry process characterized by a high energy demand, in forms of fossil fuels and electrical energy. It has been reported [1] that energy consumption of a modern plant is close to 115 kWh per ton of cement produced. In 2012, 3.6 billions ton of cement were produced globally [2], thus more than 0.4 TWh energy were consumed.

Among main operations in cement manufacturing, finish grinding is reported to be the most expensive in terms of energy, especially nowadays, when high performances required by modern concrete pose the need of high fineness cements. Up to 40% (depending on the grinding system used) of the aforementioned 115 kWh/t are used to increase specific surface of cement. It has to be pointed out that efficiency of grinding process is very low: only 10% to 30% of the total energy spent for grinding is actually used to increase specific surface [1]. Thus, in 2012, 0.16 TWh energy were used worldwide to reduce clinker and mineral additions to a fine powder and the biggest part of this energy was wasted, mainly in form of heat and noise.

In the light of this, it is evident that energy (and cost) reduction in cement industry has always been the main driving force for innovation, even before recent concerns about greenhouse gases emissions and global warming. The use of grinding aids plays a key role in increasing grinding efficiency: nowadays, it is nearly impossible to manufacture cements with high fineness requirements without using chemical grinding aids.

Grinding aids are organic compounds (used as process additives during cement grinding) that allow to increase milling efficiency. They are usually sprayed in the mill, or added on the clinker conveyed in the grinding stage. Their macroscopic effect is the reduction of cement coating on grinding media and mill lining and the improvement of hourly mill production and cement fineness. Using a suitable grinding aid, it is possible to manufacture more cement at higher fineness, hence reducing the kWh/t. Their mechanism of action is still unclear, but it is believed to involve the formation of a monomolecular organic layer on cement surface or the neutralization of electrostatic forces formed during breakage of clinker minerals.

In this paper we present a study on the effect of chemical grinding aids during cement grinding. Cement samples produced with and without grinding aid are compared in terms of performances and milling efficiency. Microscopy techniques are used to confirm and understand the reasons for the variations in grinding efficiency and for the improvement of cement performances promoted by the use of additive.

It is interesting to point out that this investigation is not a lab simulation: all cement samples were collected on site, during normal industrial production of a common cement. To our knowledge, this is the first time that this type of investigation is performed on a modern cement.

GRINDING OF CEMENT

Closed circuit grinding: mill and separator

The most common equipment for cement grinding is a ball mill, a horizontal tubular mill partially filled with steel balls of proper dimensions and rotating on its horizontal axis (figure 1). Clinker/gypsum/additions fed move through the mill (thanks to combined action of rotation and air stream) and are ground by impact between the balls (figure 2).

The material exiting the mill is conveyed to a device called "separator" or "classifier" and divided in "coarse" and "fine" fractions. The coarse fraction (separator reject) is sent back to mill entry for further grinding. Fine fraction is sent to storage as finished cement. This is the typical arrangement of the so called "close circuit grinding", as described in figure 3.

Cement grinding is a continuous process: the clinker/gypsum/additions blend is continuously fed at mill entry and extracted as fine fraction from separator. The mass of material sent back to the mill as coarse fraction can be several times the fresh feed, depending on the fineness required and separator type. For modern cements production, the mass of material moving through the mill/separator combined system (usually referred to as "circulating load") accounts for several hundreds of tons per hour.

For the purposes of the cement industry, the classification (separation of fine and coarse fractions) of the ground material is based on the size of particles. Modern high efficiency separators include a rotating cage composed of several radial "blades". Materials is conveyed through an air stream around the rotating cage. The combination of air flow and rotation speed of the cage allows only particles having a diameter lower than a specific "cut size" to pass through the cage and to be sent to fines, while bigger particles are sent back to mill as separator reject (figure 4). Fine adjustments of cut size are possible by operating on air flow and rotation speed of the cage.

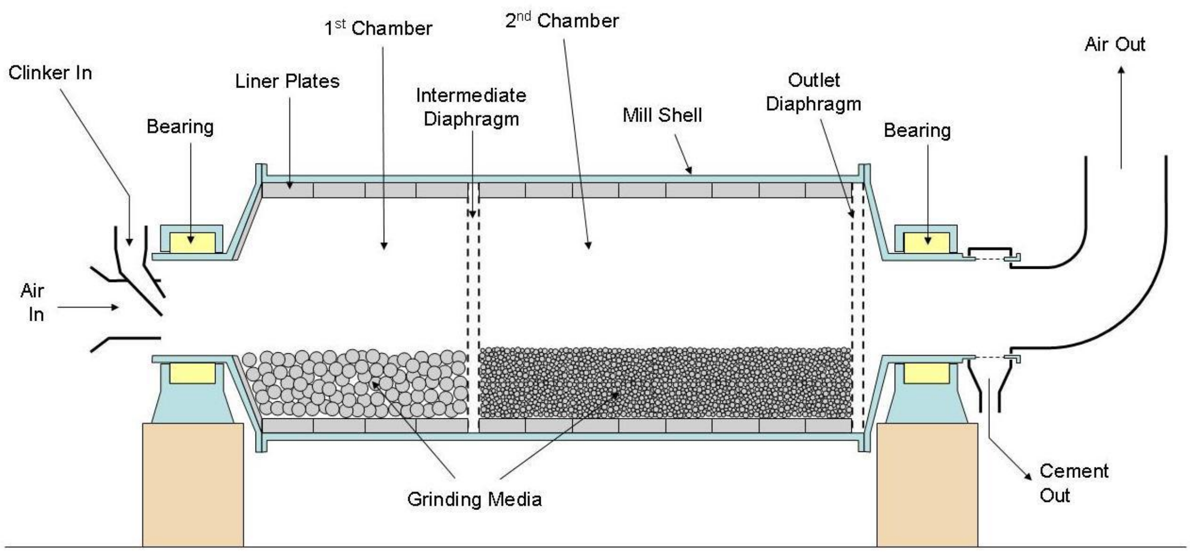

Fig. 1: Typical description of a ball mill [3].

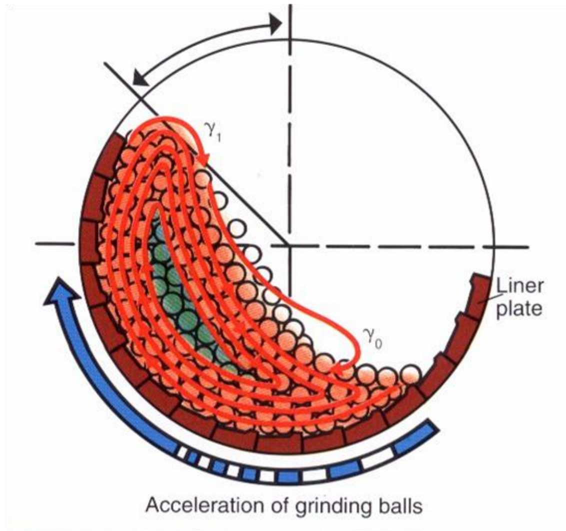

Fig. 2: Rotation of mill and movement of grinding media.

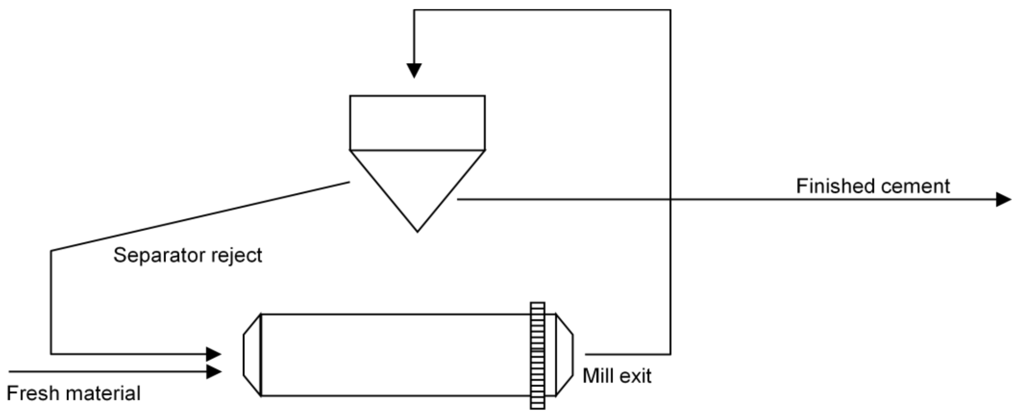

Fig. 3: Closed circuit grinding.

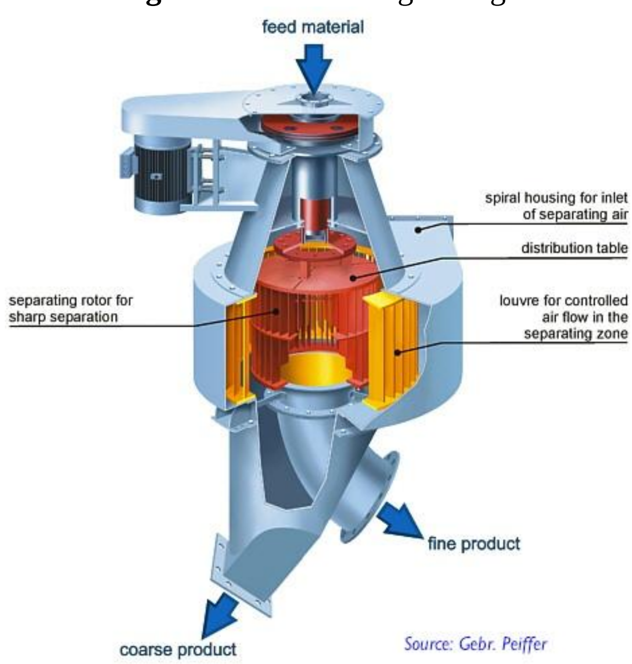

Fig. 4: High efficiency separator [4].

Efficiency of separator: the Tromp curve

An ideal separator would give a perfect classification: all particles having dimensions below the cut size would be sent to finished stream, all particles above cut size would finish in reject. Actually, in real separators it is not possible (neither desirable) to reach perfect division at cut size. Electrostatic forces promote the formation of agglomerates of fine particles that are treated as particles of larger size. In a similar way, small particles that coat coarse ones are sent back in reject stream.

The calculation of the so-called Tromp curve is a typical approach for evaluating the efficiency of a separator. The Tromp value represents the percent of the material in each individual size fraction that is recovered into the reject stream. It can be expressed as the ratio of the coarse fraction mass to the feed fraction mass:

$$T(x) = R \cdot f_R(x) / A \cdot f_A(x)$$

Where:

- $T(x)$ is the Tromp value (dimensionless, or expressed as %) for particles having diameter x (usually in microns).
- R is the mass flow (in t/h) of the reject stream from separator.
- A is the mass flow (in t/h) of the feeding stream at separator.
- $f_R(x)$ is the fraction of particles having diameter x in the reject stream.
- $f_A(x)$ is the fraction of particles having diameter x in the feeding stream.

When plotted in a logarithmic diagram with particle diameters in x axis, it is possible to draw the Tromp curve, that allows to qualitatively evaluate the separation process. Detailed descriptions of the Tromp curve approach are available in literature [5, 6].

Effect of grinding aids on closed circuit cement grinding

As introduced before, grinding aids are sprayed in the mill, or added on the clinker, with dosages usually ranging from 100-200 g up to 2-3 kg per ton of cement. Once a grinding aid is added during cement manufacturing, the main effect is the reduction of separator reject: more material is sent to finished stream and the circulating load is decreased. Hence, the grinding circuit could afford a higher mass of materials and a combination of the following actions can be taken:

- Increase in fresh material: optimisation of the circulating load is obtained by increasing the clinker/gypsum/additions feed. This allows to increase the mill hourly production (usually improvement are in the range 5-20%).

- Increase in separator speed: higher circulating load is obtained by increasing the mass of material in the reject stream. This allows to modify the cement particle size distribution, thus obtaining a finer and better performing cement.

Grinding aids act at two levels: in the mill, with the reduction of cement coating on grinding media and mill lining, and in the separator, with the improvement of classification process. Detailed description of the use of grinding aids in cement industry is reported elsewhere [7].

EXPERIMENTAL

Sampling during industrial grinding

The following sampling protocol was followed, during industrial production of a typical limestone blended cement (CEM II/A-LL 42.5 R according to EN 197-1 [8], mass composition: 80% clinker, 5% gypsum, 15% limestone), produced with ball mill equipped with high efficiency separator:

- In steady state and stable conditions of the main parameters controlling the milling operations, cement streams around separator (alimentation, reject and fines) were sampled. A specific grinding aid (MA.P.E./S520, grinding aid and performance enhancer based on alkanolamines blend and inorganic accelerator, manufactured by Mapei) was added during grinding (dosage: 2 kg per ton cement). All the cement samples can be considered containing grinding aid.

- Grinding aid addition was stopped: the mill/separator could not afford anymore the same circulating load and fresh feed guaranteed by the chemical additive, thus the mill was allowed to stabilise on a new level of grinding parameters.

- After 4 hours grinding, considering the circulating load, the cement could be considered free from grinding aid. Thus, in steady state and stable conditions of main parameters (but without the addition of grinding aid) the same cement streams were sampled.

- Cement samples collected were tested for main physico-mechanical parameters (compressive strengths, air-jet residuals, Blaine specific surface, mortar compressive strengths), particle size distribution and powder morphology.

Analytical procedures and test method

Compressive strengths developed by cements in mortar were evaluated according to EN 196-1 [9], Blaine specific surfaces according to EN 196-6 [10] and air-jet residual were tested with Hosokawa Alpine air jet sieving model 200 LS-N (pressure drop: 4750±250 Pa, sieving time: 6 minutes). The reproducibility of the aforementioned tests (expressed as % standard deviation over average) can be considered as follows: compressive strengths: ±5%, Blaine: ±1.3%, air-jet residual: ±3%).
The particle size distribution were obtained by dry laser scattering analysis using a Coulter LS 13 320 Series Laser Diffraction Particle Size Analyzers (using the Mie model, with real and imaginary refractive index respectively 1.6 and 0.1).
Cement powder morphology of each separator stream was observed by FEI QuantaFEG-250 (Environmental Scanning Electron Microscope, equipped with a Field Emission Gun). The field emission gun allowed to obtain a much higher brilliance of the electronic source than the one of an ordinary tungsten gun.
Samples were prepared simply by dipping a conductive adhesive sample holder in cement and gently shaking, in order to eliminate material in excess. Images were collected working in low vacuum mode using a back scattered detector.

RESULTS AND DISCUSSION

Mechanical performances of cements

In table 1, data referring to mill output and fineness of cement produced with and without grinding aid are summarized, while in table 2 details of compressive strengths at early and late ages are reported.

The effect of chemical additive is evident: when added, there are remarkable benefits in mill hourly production and cement fineness (higher Blaine specific surface and lower air jet residuals). Compressive strengths are improved at all ages, particularly at early curing time. This is the sum of improved fineness and chemical effect of additive on cement hydration.

To be noticed that highest hourly production and improved fineness and strengths have been reached with the same mill power absorption in kW. Hence, by addition of grinding aid a better cement was manufactured with reduced specific energy consumption in kWh/t.

	Mill output	**Blaine**	**32 µm air jet residual**
CEM II/A-LL 42.5 R blank	109 t/h	389 m^2/kg	20.7 %
CEM II/A-LL 42.5 R with MA.P.E./S520	115 t/h	411 m^2/kg	17.9 %

Table 1: mill output and fineness data.

	24 hours	**2 days**	**7 days**	**28 days**
CEM II/A-LL 42.5 R blank	9.1	20.0	34.5	47.2
CEM II/A-LL 42.5 R with MA.P.E./S520	12.4	24.8	38.3	47.6

Table 2: mortar compressive strengths of finished cement samples. Data are expressed in MPa.

Tromp curve determination and grinding efficiency

Figure 5 shows particle size distribution of cement streams around separator (alimentation, reject and fines) as evaluated with laser scattering analysis. Separator divides alimentation stream in fine and coarse fractions, whose finenesses are respectively higher and lower than alimentation, as correctly represented in figure 5.

Particle size distributions of alimentation, fines and reject streams produced with and without grinding aids were used to calculate Tromp curve, represented in figure 6 (blank cement) and figure 7 (cement with MA.P.E./S), while in table 3 some of the most relevant Tromp curve parameters are reported. Graphs in figures 6 and 7 are expressed as double logarithmic. A simple linear regression on both sides of Tromp curve was used to fit the data and calculate the minimum of the curve (where straight lines intersect) that allows to obtain main parameters such as bypass and acuity.

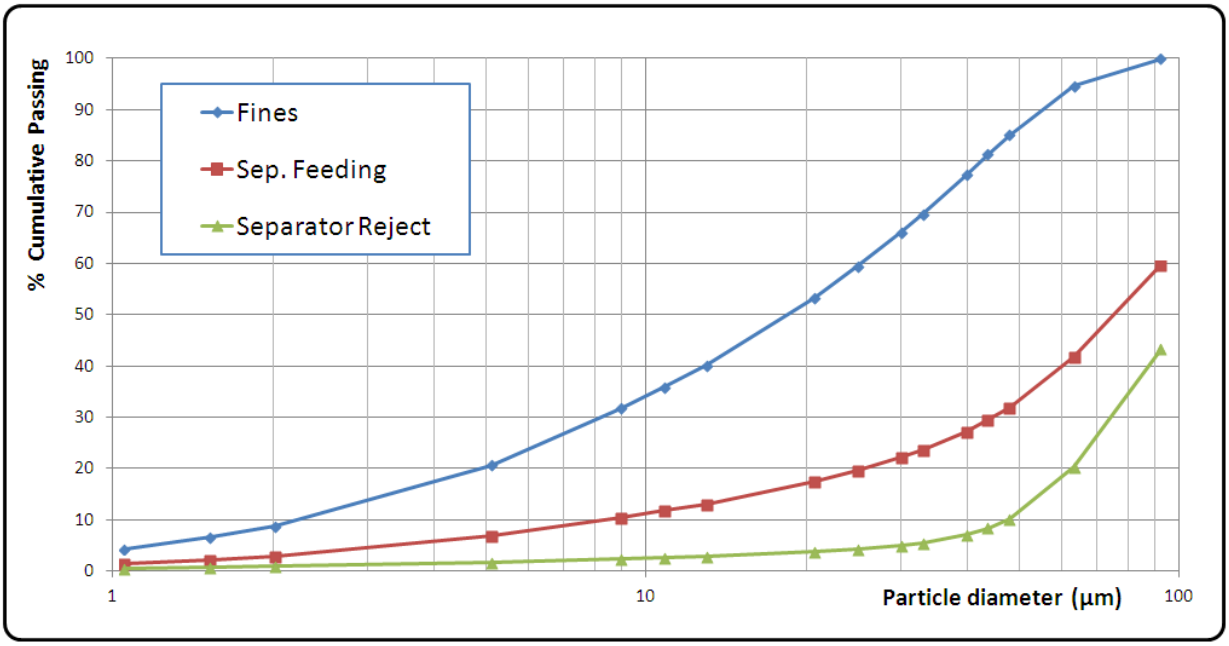

Figure 5: particle size distribution of cement streams around separator.

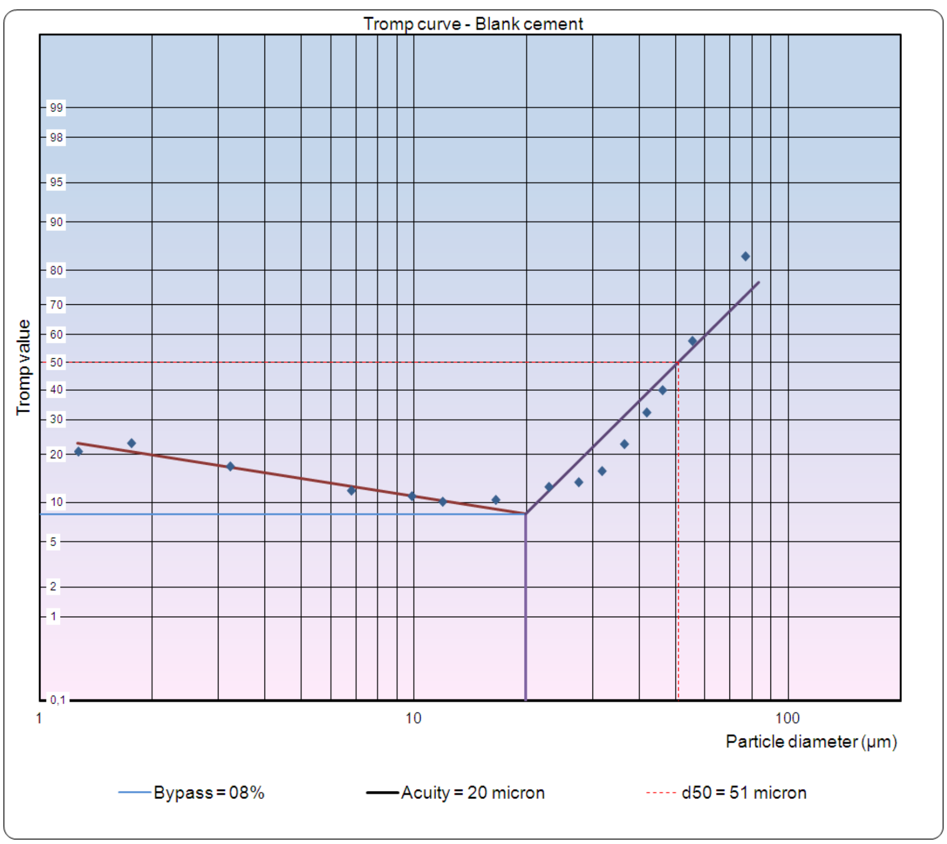

Figure 6: Tromp curve, cement ground without grinding aid.

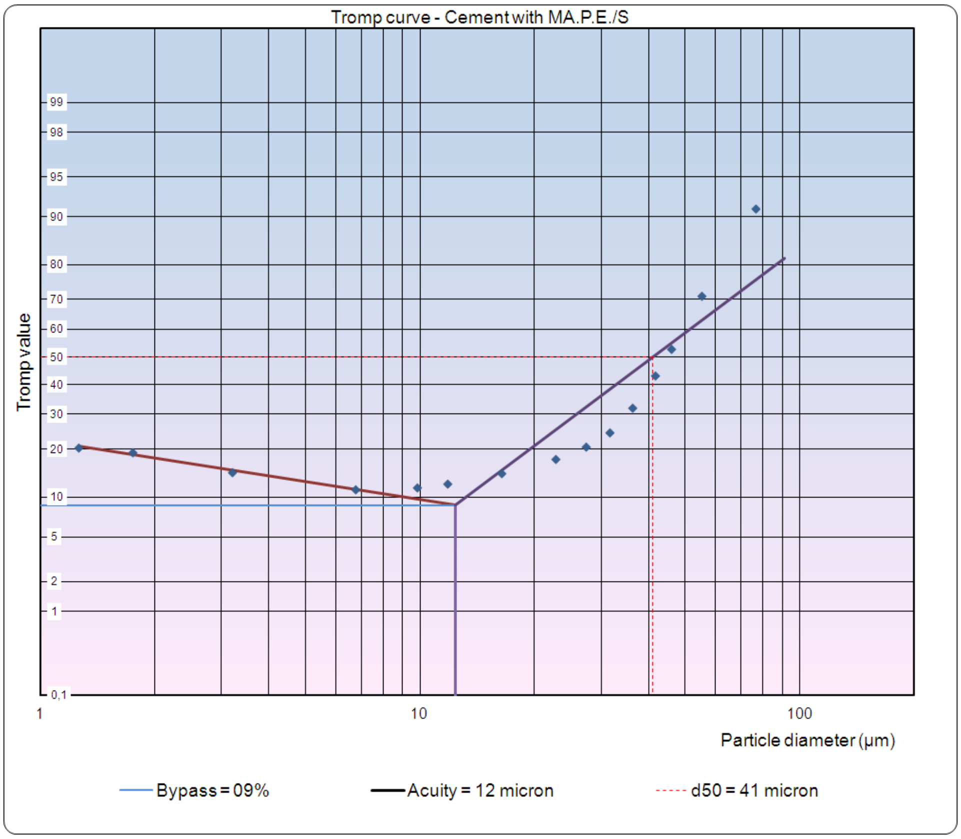

Figure 7: Tromp curve, cement ground with MA.P.E./S.

	Circuit coefficient (A/F)	**Bypass**	**Acuity (D-limit)**	**Cut size (d50)**
CEM II/A-LL 42.5 R blank	2.63	8.2 %	20 µm	51 µm
CEM II/A-LL 42.5 R with MA.P.E./S520	3.33	8.7 %	12 µm	41 µm

Table 3: main parameters evaluated through Tromp curve.

Circuit coefficient is expressed as ratio of separator feeding mass stream A (fresh feed + reject) to fines mass stream F (both are expressed in t/h).
The bypass value defines the portion of the material that bypasses the classification process: some part of the alimentation is sent to coarse stream, regardless of the particle dimensions. The bypass corresponds to the ordinate of the minimum in the Tromp curve.
The acuity (or D-Limit) is the corresponding abscissa of the minimum in the Tromp curve. It represents the maximum particle dimension that can be processed by the separator: below the D-limit (on the left side of the Tromp curve) the percent of fines in the reject start to increase, thus there is no selective separation.
The cut size (or d50) is the particle dimension where Tromp value is 50%, thus particles having an equal chance of passing into either the reject or fines.

When grinding aid is added, a general improvement of separator performances can be noticed:

- Bypass remains stable, notwithstanding a higher circuit coefficient (with increased mill output): separator can process a higher mass of material without decreasing efficiency.

- D-limit is reduced to 20 µm. Without grinding aid particles below 20 µm can not be processed properly, while when grinding aid is added the separator is able to classify particles down to 12 µm.

- Cut size is reduced to 41 µm. Without grinding aid only particles above 51 µm have higher probability to be sent to reject, while with grinding aid this limit is lowered to 41 µm.

Morphology of powder
The reasons for improved grinding/separation efficiency when grinding aid is added can easily be understood by comparing the morphology of ground cement, as highlighted by ESEM-FEG images.
Figure 8 and 9 show the cement in separator alimentation stream without and with grinding aid. In absence of additive, the material tends to agglomerate: fine particles are found in clusters, together with coarse particles. Clusters of fine particles are likely to be considered as coarse particles, and preferentially sent in reject stream, thus lowering efficiency of separation process. In presence of additive on the other hand fine particles are uniformly dispersed. Hence, separator receives a stream of material in which cement particles are already partially separated.
Figure 10 and 11 (500x magnification) better clarifies the difference. In figure 10 (cement ground without additive) several clusters can be noticed (labelled with yellow arrows). It is also evident the coating of coarse particles with fines (labelled with red arrow). Fine particles stuck on a coarser one are not classified as fines, but are likely to be treated as a unique coarse particle and sent to reject stream. This is another reason for poor separator efficiency.
In figure 11 (cement ground with additive) fine particles are uniformly dispersed, rather than agglomerated, thus they are correctly recognized and selectively directed in fines stream.
Figures 12 and 13 show the cement in separator reject stream, with and without grinding aid. When additive is present (figure 13) reject material appears to be globally coarser, in comparison to cement without additive (figure 12). This is a consequence of improved separation process: higher efficiency classification shall promote lack of fine particles in reject stream, thus increasing the average size of reject.
Higher magnification microphotographs (500x, figure 14 and 15) show, as expected, fine particles coating on larger ones in reject, when grinding aid is not used (labelled with red arrow in figure 14). The addition of grinding aid generally reduces the coating, leaving coarse particles “free” from the fines mistakenly sent to reject (figure 15).
Figure 16 and 17 show details of cement particles surfaces giving more evidence to the fines fractions agglomeration.

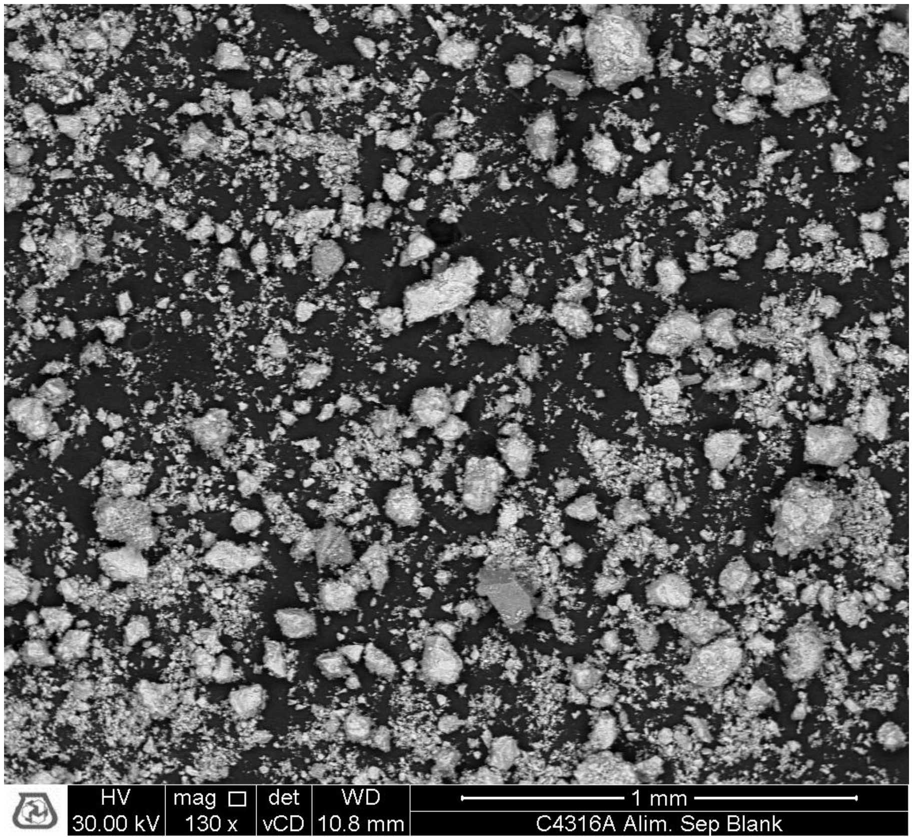

Figure 8: Morphology of cement in separator feed, without grinding aid.

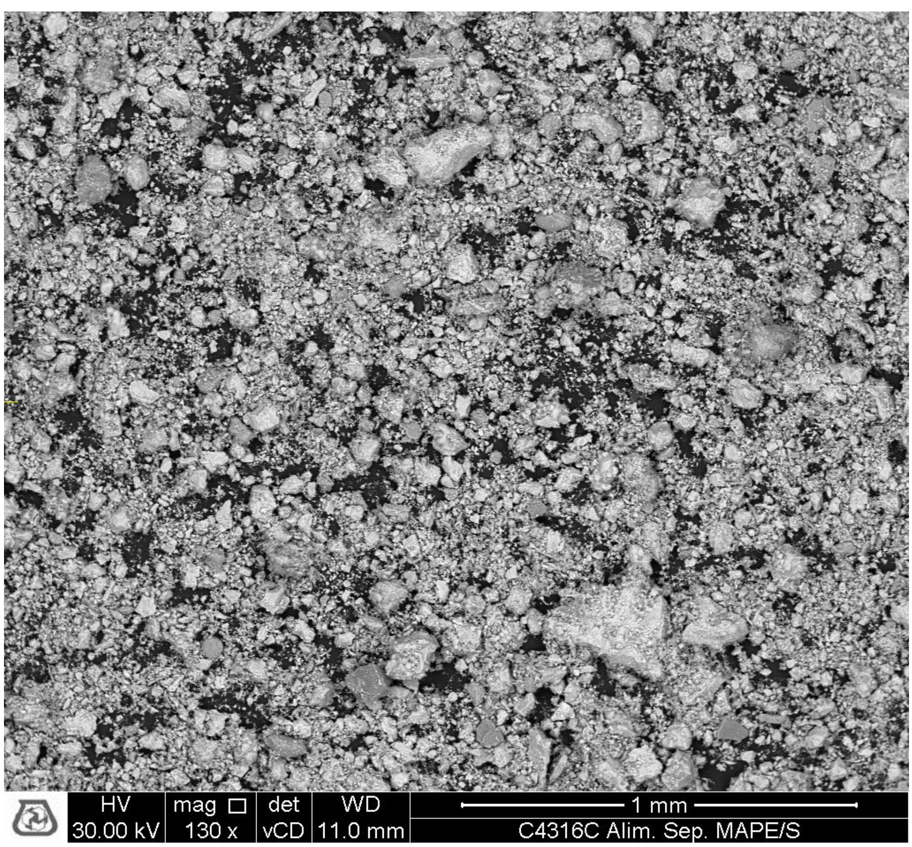

Figure 9: Morphology of cement in separator feed, with grinding aid.

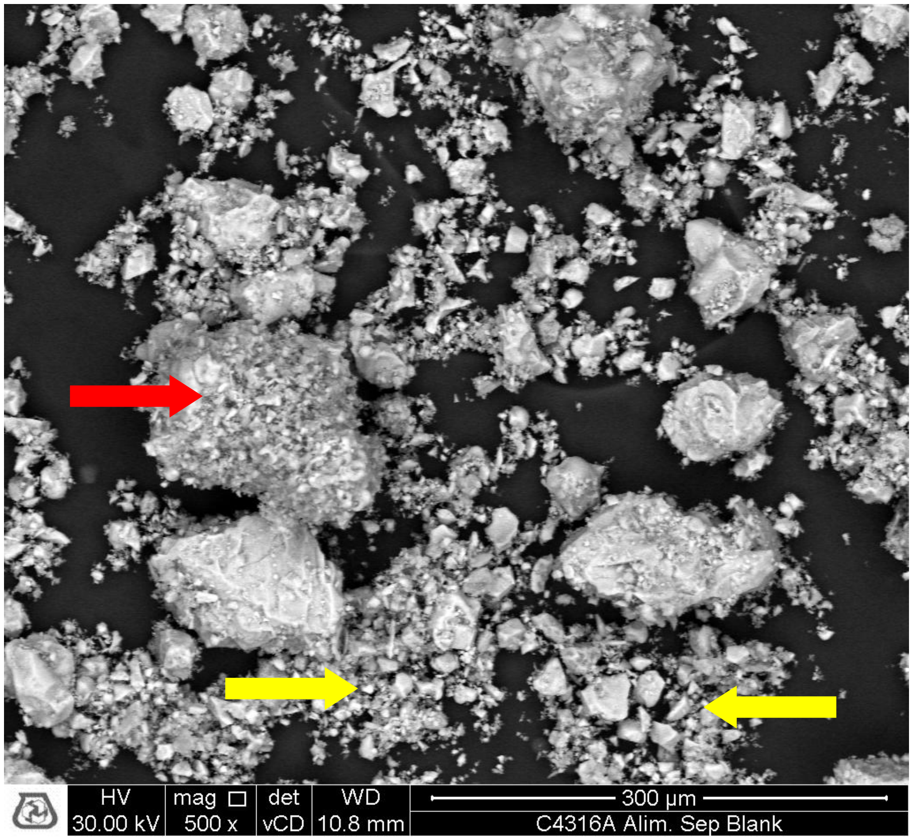

Figure 10: Morphology of cement in separator feed, without grinding aid.

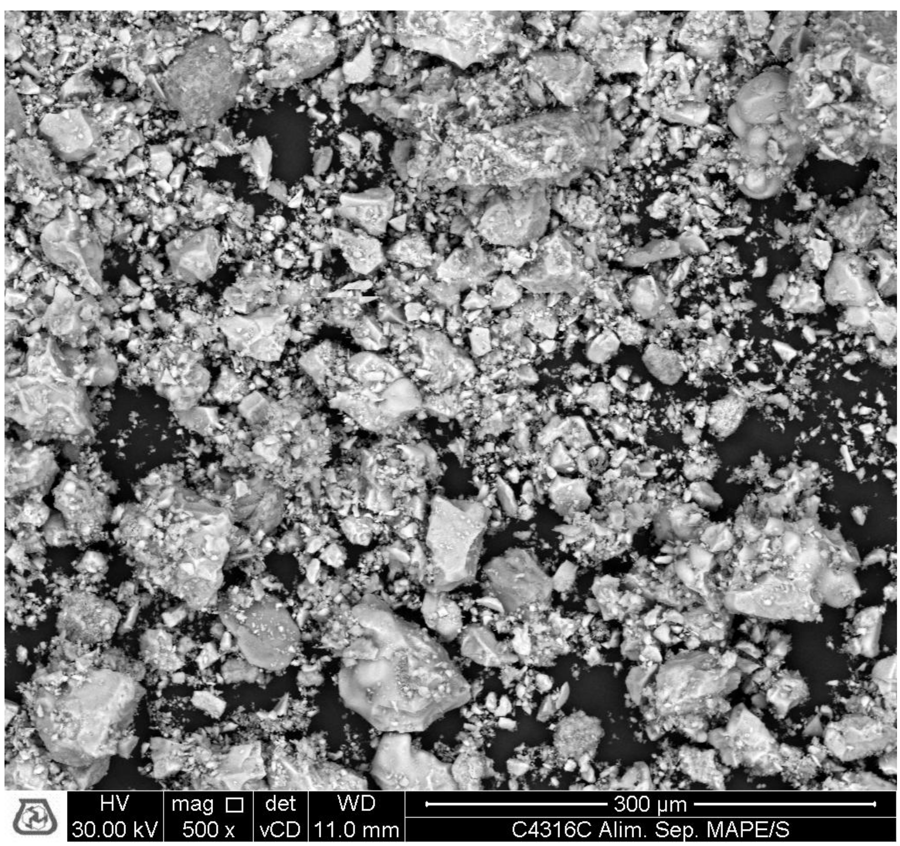

Figure 11: Morphology of cement in separator feed, with grinding aid.

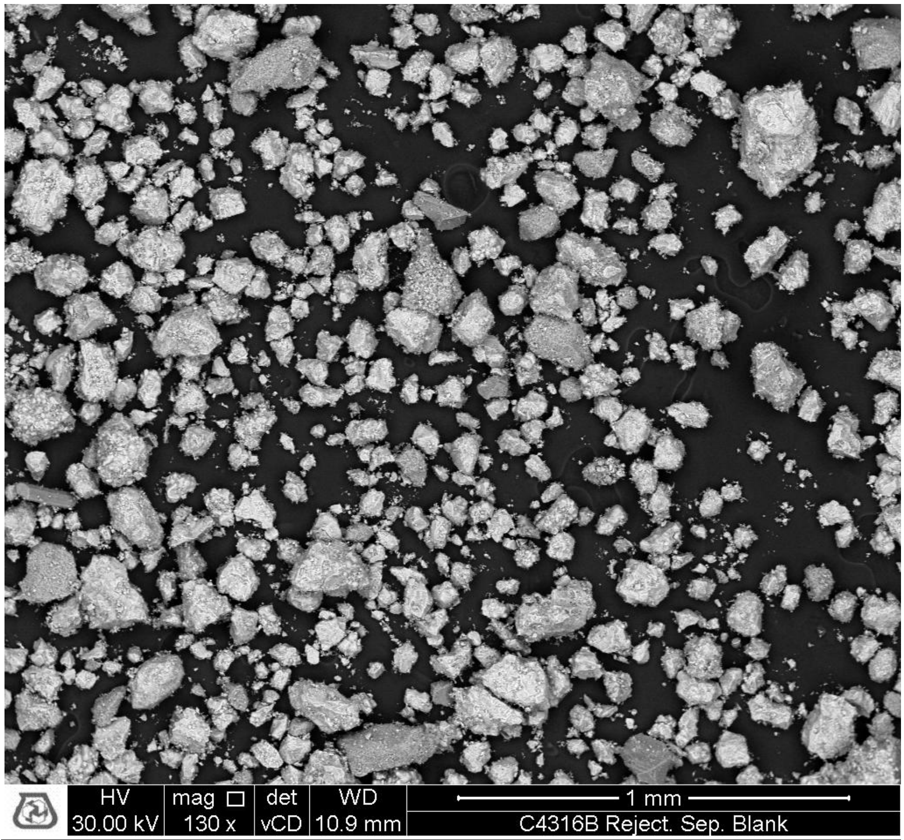

Figure 12: Morphology of cement in separator reject, without grinding aid.

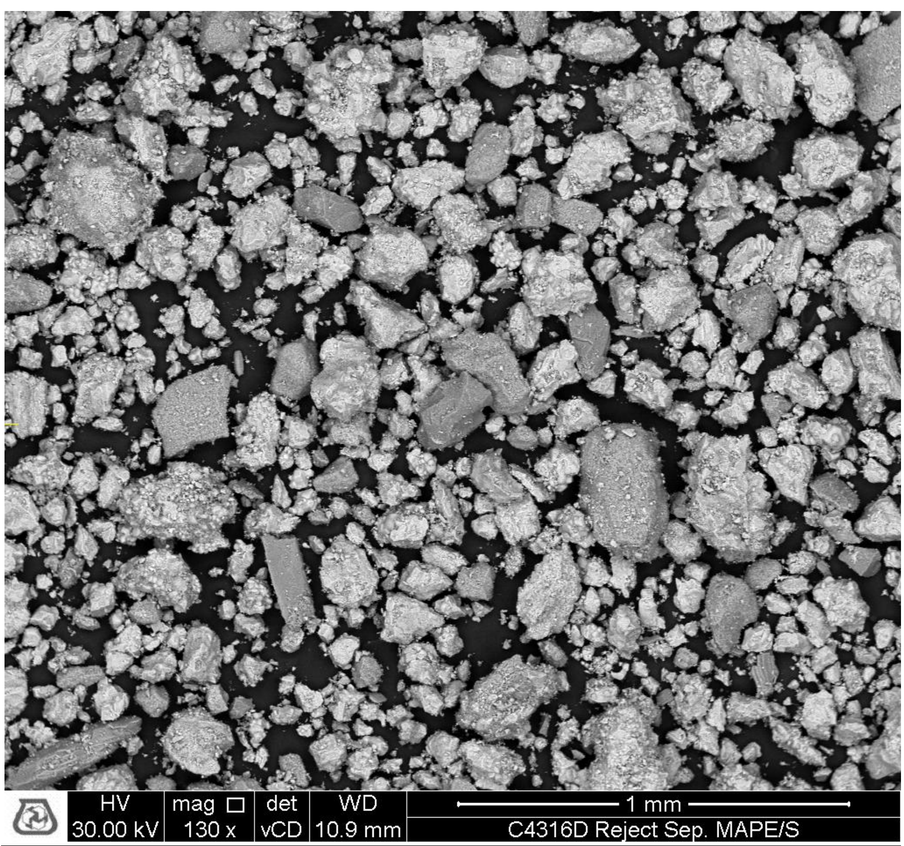

Figure 13: Morphology of cement in separator reject, with grinding aid.

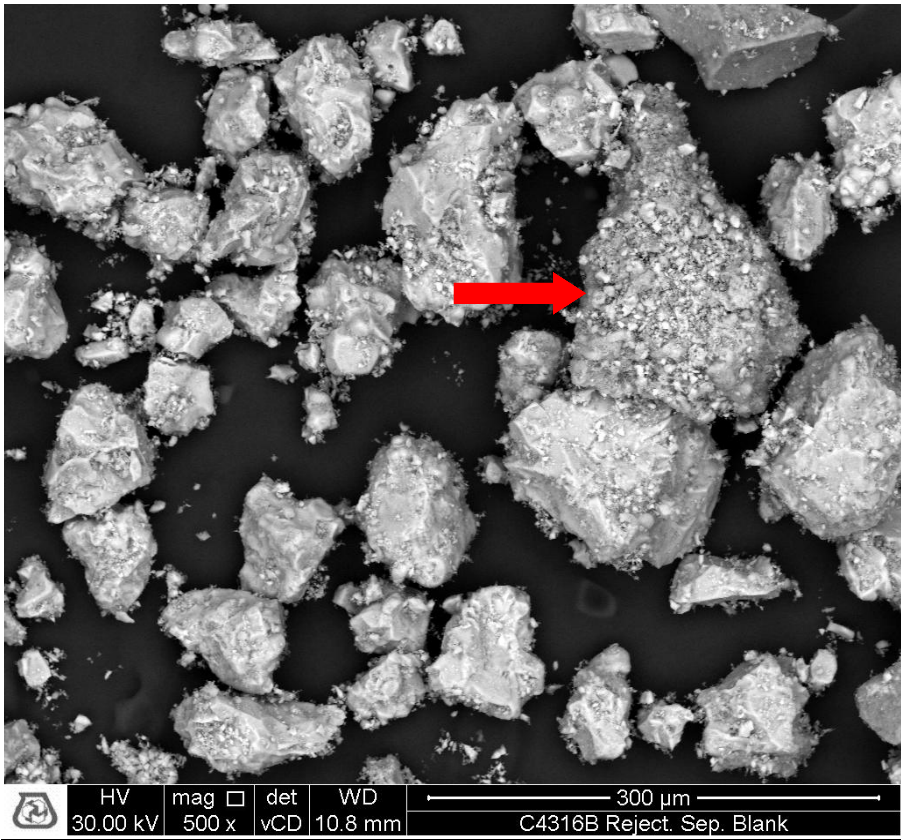

Figure 14: Morphology of cement in separator reject, without grinding aid.

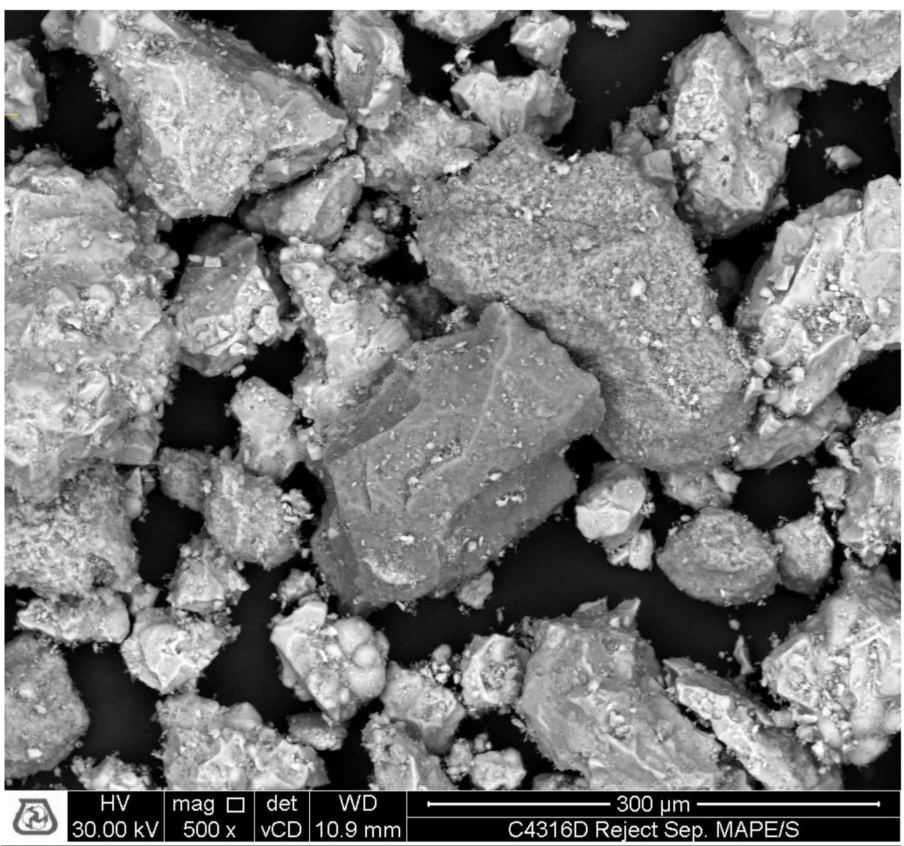

Figure 15: Morphology of cement in separator reject, with grinding aid.

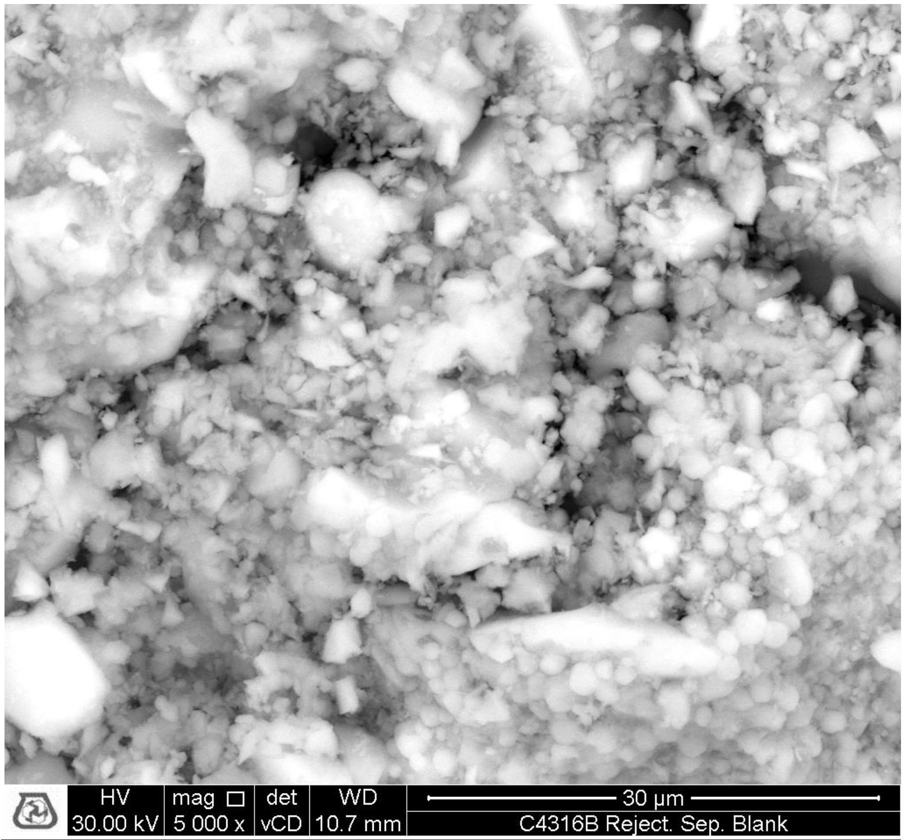

Figure 16: Morphology of cement in separator reject, without grinding aid. Detail.

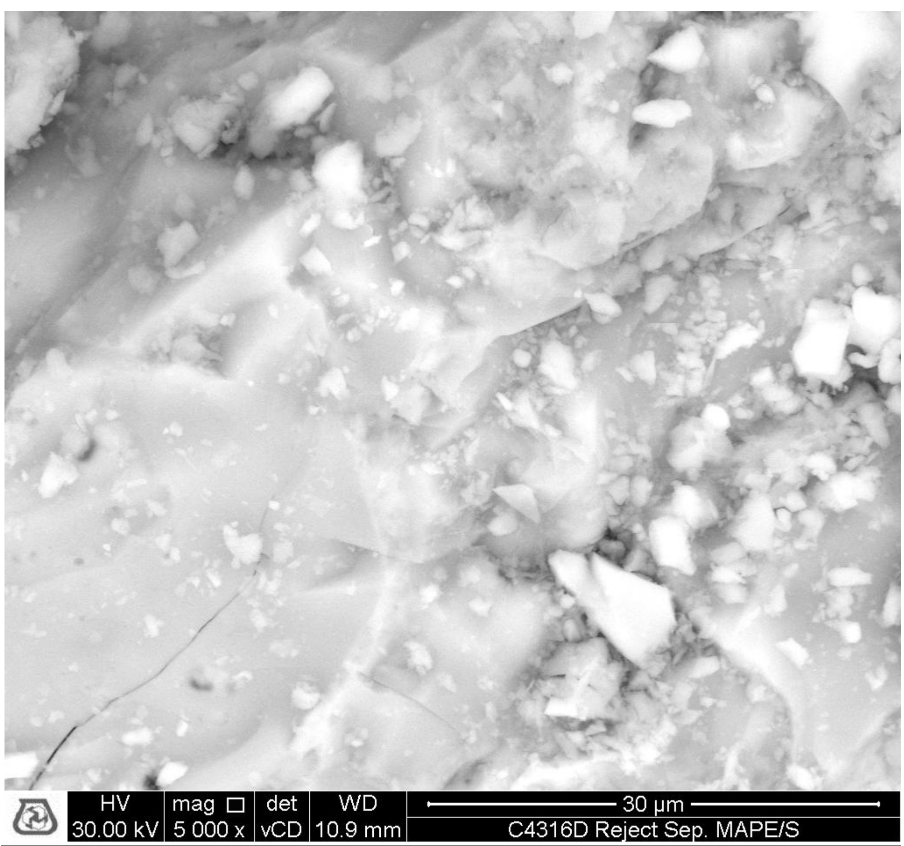

Figure 17: Morphology of cement in separator reject, with grinding aid. Detail.

CONCLUSIONS

The cement grinding process has been reviewed with particular attention to the effect of chemical grinding additives. During industrial production of a typical blended cement, samples of material streams around separator were collected and carefully analyzed. The cement ground with MA.P.E./S (a commercially available grinding aid and performance enhancer based on alkanolamines blend and inorganic accelerator) shows better performances in terms of fineness and mechanical strengths.

The separator efficiency (as described using Tromp curve approach) results enhanced, allowing higher mass of material to be treated.

The reasons for the reported better efficiency of separation process are clearly pointed out thanks to a morphological analysis with scanning electronic microscope. A comparison of cement ground with and without additive shows that in presence of grinding aid the cement particles are generally better dispersed and the tendency of fines to agglomerate in clusters and to coat coarse particles is remarkably reduced. Hence, the separator receives materials "pre-classified", with improvement of the whole classification.

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