https://doi.org/10.32604/zkg.2025.01.02

From sugar coated dragées to tablets: experiments on the way to a new grinding aid for XRF and XRD applications in cement plants

Jasmin Holzer, Aurelija Sugzdaite, Thomas Rüther and Michael Enders
thyssenkrupp Polysius GmbH, Beckum/Germany

ABSTRACT: Grinding aids are mandatory for powder grinding for automated pressed tablets preparation for improved comminution, self-cleaning, stability of pressed tablets and analytical quality (XRF, XRD). Polysius Mahlhilfe (MH1) was frequently used until the long-time manufacturer stopped production in 2019. Within short time thyssenkrupp Polysius developed a substitute based on cellulose and wax (Polysius Grinding Aid (MH2)). In most cases this new development was perceived well. However, some laboratories experienced less stability of pressed tablets, increased dust formation and difficult XRD quantification of amorphous constituents. The feedback motivated thyssenkrupp Polysius to open a second development cycle with the focus on improved tablet stability and reliable XRD quantification of amorphous materials in XRD. Polysius reached all tasks with a new high resin grinding aid. The challenging production of tablets from sticky resin process was supported by experts in tablet manufacturing. The new product Polysius Mahlhilfe MH^3 performed best in all tests even above the original Polysius Mahlhilfe (MH1). Polysius Mahlhilfe MH^3 will be the new standard.

1 Introduction

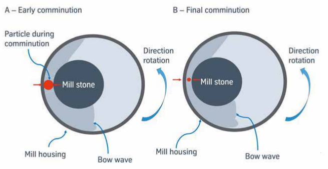
Pressed tablets are the preferred samples for process control in cement, ceramics, and mining [Potts, 1992]. In many plants pressed tablets are prepared semi- to fully automated in combined grinding and pressing machines with minimum sample handling efforts at a small footprint [Enders, 2003]. XRD and XRF analyses require finely ground powders, homogenous and stable pressed samples for accurate and reliable results. In a typical setup ≈12 g of sample are ground and pressed into a 51 mm steel ring. The benefits of pressed tablets versus fused bead analysis are a single sample preparation for both, XRF and XRD, the ease of sample preparation and low specific cost per sample [Enders, 2017].

In this paper we compare the performance of three grinding aids for pressed tablet sample preparation based on resin, cellulose and wax. This test procedures can also be used to verify and optimize sample preparation procedures for varied materials.

1.1 Pressed tablet preparation and the role of grinding aids

Grinding of brittle and dry materials for pressed tablet samples is often conducted in lab disc mills. Lab disc mills grind by the parallel eccentric movement of the mill housing and the centrifugal movement of the grinding stone inside the mill housing (Fig. 1). Grinding is driven by rotational and centrifugal forces at the interface between the mill housing and the mill stone. Grinding aids are lenticular or rounded tablets which can be handled by automated dosing units. Grinding aids are needed to disperse the material inside the mill, to improve comminution, to ease automatic cleaning, and to improve de-aeration during sample pressing.

The task of sample grinding is creating enough particles for a representative analysis (see section 1.2). During the first seconds of grinding unground material is crushed by impact. Very soon, the preground powder forms a grinding bed at the interface between mill stone and mill housing. The unground material suffers pressure between mill housing and the mill stone and attrition below the mill stone. Comminution occurs inside the grinding bed at the smallest distance between mill stone and mill housing (Fig. 1). Particles larger than the thickness of the grinding bed suffer double sided pressure between mill stone and mill housing (Fig. 1A). Brittle particles fracture into



1 Sketch of lab disc mill grinding. (A) Conditions at the beginning of grinding with coarse particle grinding. (B) Conditions when final fineness is reached

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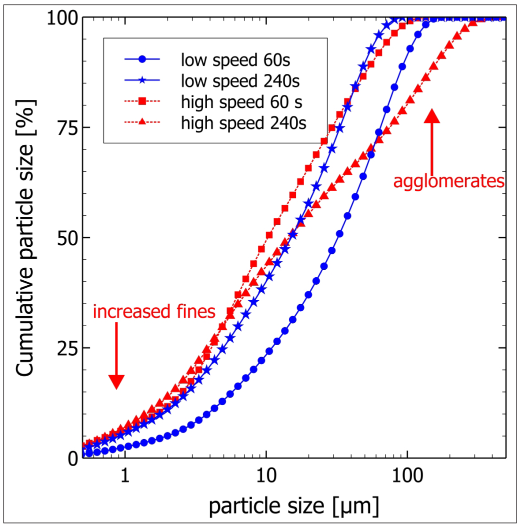
multiple smaller particles while soft minerals might shear along cleavage planes to form platelets. Later, when main pressure is absorbed by the grinding bed only, particles smaller than the grinding bed may be fractured by the confining pressure inside the grinding bed. The comminution process ends when no further comminution is achieved under given conditions. Within the grinding bed particles harder to grind and with a less pronounced cleavage remain coarser compared to soft particles. Grinding aids disperse the powder in the mill. A better dispersion decreases the thickness of grinding bed for a better comminution. Further comminution effects are reached by rotation speed.

Moist materials and samples containing clays may stick to the walls of the mill housing and mill stone and they might form agglomerates. Both effects reduce the force working on single particles. Materials sticking in the mill and agglomeration counteract comminution. The better dispersion of the powder in the mill by grinding aids reduces stickiness and agglomerate formation and improves self-cleaning of the mill.

Fig. 2 highlights the agglomeration effect with a clinker sample ground without grinding aids. With increasing grinding energy by speed and time, the fines content increases. However, at high grinding speed also new coarse particles form by agglomeration as seen in an overall wider and bimodal particle size distribution. Grinding aids support separation of individual particles to reach a desired comminution without significant agglomeration.

For XRD analyses grinding forces must be controlled to reach on one side enough particles for sufficient statistics but also to avoid critical effects in the XRD pattern like spottiness (weak statistics) or amorphization (loss of the crystal structure) [Enders 2005, Schmidt 2024].



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2 Clinker ground without grinding aid at different grinding energies (by speed, time). The overall particle size of a clinker sample decreases and the fines content increases. At high grinding speed agglomeration is apparent from newly formed coarse particles

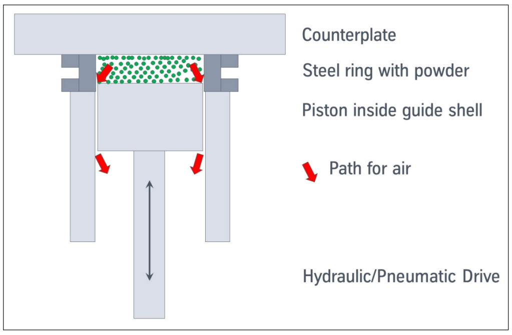
During grinding, platelets or needle shaped particles may form by shear or cleavage. After transport by gravitation from the mill into the press these particles will align in the powderous mill product by shape (large plane, longest plane). This parallel alignment of the platelets and needles in the powder sample is called preferred orientation. Preferred orientation causes modified peak intensities in the X-ray diffraction pattern. Within limits preferred orientation is corrected by Rietveld software packages. XRF analyses are usually not critically affected by preferred orientation.

Grinding aids are also important for pressing the powder into the steel ring. Inside the press the air confined in the powder must be removed from the volume between counter-plate and piston to reach compaction. The sample surface at the counter- plate is compacted first and it becomes airtight. The remaining air in the sample can leave the closed volume along voids inside the guide shell (Fig. 3). If the air is removed incompletely it is compressed with the powder. When the piston is retracted, this excess air starts to decompress. Decompression may damage mainly the lower sample surfaces by lamination along compressed air rich layers in the powder tablet [e.g., Mazel & Tchoreloff 2022]. Once the surfaces are disturbed, the pressed tablets may suffer erosion during automated de-dusting by compressed air (Fig. 4). Occasionally pressed tablets are lost completely. Brittle and hard materials with a steep particle distribution (clinker, GBFS, sand) are more critical for the lamination effect.

Finally, the constituents of the grinding aid shall function as a glue to provide stability and reduce dust on the surfaces of the pressed tablet to avoid contamination of the analyzers. Common grinding aid dosage is 5-15 % where the lower numbers are for raw meal, kiln feed, and cements and the higher numbers are for clinker, GBFS and composite cements.

1.2 Analytical requirements of sample preparation

A homogenous powder is prerequisite for a representative XRF analysis. Primary polychromatic X-rays of a Rh tube penetrate the pressed tablet.



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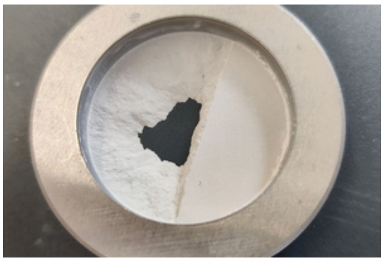
3 During pressing, air confined in the powder can leave the compartment through voids between piston and guide shell. Compaction starts at the interface to the counter-plate



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4 **Lower surface of a pressed tablet first broken by lamination after incomplete de-aeration during pressing and eroded by compressed air**

The limiting factor in X-ray analyses is not the initial polychromatic radiation but the maximum depth from where secondary fluorescence radiation of light elements can escape to the vacuum and further to the detector [Potts, 1992]. X-ray radiation of light elements like Si, Al, Mg and Na is less intense but strongly absorbed. In their case only a small volume close to the sample surface contributes to the signal (Fig. 5). For a correct analysis, the composition of the upper 20-30 µm of the sample must be homogenous and representative for the bulk sample. This returns, that the maximum particle size in the sample must be less than 30 µm.

Cu-Ka radiation for XRD penetrates the upper 5% of the sample (200 µm) and scattered X-rays can emerge from this depth in the sample (Fig. 5). Only at small scattering angles long pathways inside the sample suffer absorption causing asymmetric peak shapes in XRD patterns [e.g., Enders, ZKG 2005]. Particle size effects are less critical in XRD as Cu-Ka radiation covers a rather large volume of the sample.

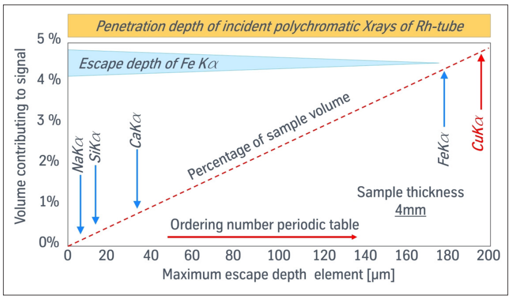
Grinding aids should not contain elements of interest in the unknown sample to avoid misinterpretation. They should be made from light elements to reduce absorption and grinding aids should not add intensity to diffraction peaks of phases present in the sample.

2 Materials and Methods

2.1 Test materials and equipment

Tests with grinding aid samples were conducted with a kiln feed from a German cement plant. This high quartz kiln feed has been used for fine grinding tests and lab mill improvement for two decades. XRD experiments were conducted with CEM IIIA from the thyssenkrupp Polysius stores.

A polab®APM$_{plus}$ combined mill and press was applied for sample grinding and pressing. A Panalytical Zetium at tk Polysius lab was utilized for chemical analyses. For readability reasons the XRF results are reported as (virtual, non-calibrated) weight percentage obtained with a generic calibration line. XRD diffraction patterns were recorded with a Bruker D8 Endeavor diffractometer with a Lynxeye detector.



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5 **Maximum escape depth for X-rays from a compacted powder sample (modified from Potts 1992)**

2.2 Grinding aid samples

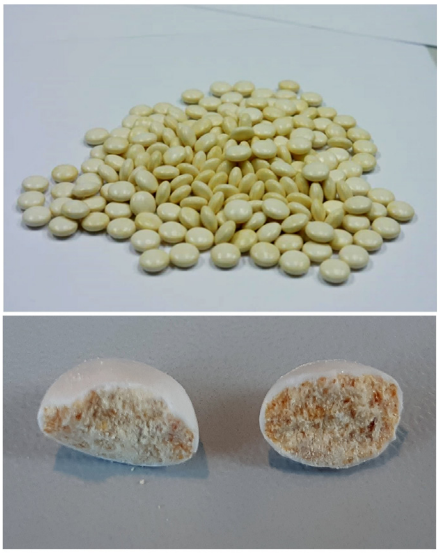
Polysius Mahlhilfe (MH1) has been the standard grinding aid in the cement industry. MH1 is made from a resin core stabilized with cellulose and covered with sugar (dragee) to improve the handling in automated dosing (Fig. 6). In 2019 the supplier of Polysius Mahlhilfe (MH1) discontinued the supply to comply with new regulations for pharmaceutical production sites. The complicated production process could not be transferred to a new site due to the need for experienced personnel and equipment.

Polysius grinding aid (MH2) was developed to maintain continuous supply of the market. The new formulation relied on well-known grinding aid constituents like cellulose and wax [Potts, 1992]. Resin was added as a minor modifier.

After market introduction MH2 performed well in many labs, however, the feedback was heterogeneous. Some labs observed increased dust formation, less stable tablets, and an increased number of lost samples (often clinker and high GBFS cements). Some users tried to achieve stability by overdosing MH2 grinding aids leading to even worse pressed tablets. Finally, the quantification of amorphous cement constituents (e.g., GBFS, pozzolan, fly ash) in composite cements with the hkl-phase became difficult. In most cases the loss of stability could be attributed to incomplete de-aeration during pressing. This opened space for the implementation of practical solutions like a slower movement of the piston and increased pressure holding time to give for de-aeration.

Overall, the market feedback did not satisfy thyssenkrupp Polysius and it was decided to restart the development program for a new grinding aid (Polysius Mahlhilfe MH3). The targets were defined as follows:

- Comminution with high XRF intensities in raw meal analyses like MH1
- Sugar free tablets to improve XRD work by eliminating sucrose
- Low wax and cellulose content to avoid diffuse scattering and lamination
- Accurate XRF and XRD results with none to minimum adaptions of MH1 recipes
- Strong stability of pressed tablets and good handling properties in automated dosing



6 **Polysius Mahlhilfe (MH1). Tablet core is made from a cellulose resin mix. After, the sugar coating is added in a second process**

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During the research thyssenkrupp Polysius development team took advice from experts in tablet manufacturing to solve the difficult task to bring sticky resin into well shaped and homogenous tablets. The complete development was supervised by analytical and physical testing of the pressed tablets.

3 Experiments for grinding aid testing

The grinding aid development applied standard tests for assessment and optimization of pressed tablet preparation in automated cement plant laboratories:

- Finding the correct grinding energy for raw meal,
- Repeatability
- Confirming sample stability and
- Avoid contamination and artifacts in XRF and XRD results

3.1 Composition of grinding aids

Cellulose is used as a binder in tablets in many industries (pharmaceuticals, food, grinding aids). Cellulose is available in different grades (e.g., particle size, crystallinity). Each grade has specific effects on grinding processes and the XRD pattern.

Sticky components like wax and resin are the glue for the powder in the pressed tablet. During the experiment with MH2 it became apparent, that waxes have a strong impact on pressed tablets strength, while natural resins are tolerant. Natural resin has good comminution effect and self-cleaning properties during grinding, and resin contributes to strong pressed tablets. Furthermore, in XRD analysis the natural resin shows a flat amorphous hump in a low 2°Theta range, without effects on the quantification of GBFS or other amorphous components.

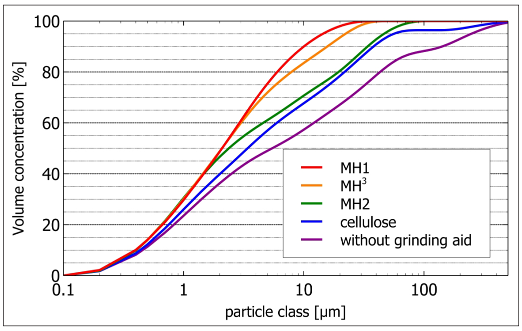
Other materials sometimes used in pressed tablet sample preparation are boric and salicylic acid.

3.2 Finding the correct grinding energy for raw meals

On first sight the effect of different grinding aids on comminution and agglomeration can be analysed by particle sizing the mill product from fine grinding (Fig. 7). The best comminution effect is reached by resin-based grinding aids MH1 and MH^3. Cellulose-wax based MH2 and pure cellulose produce less fine powder; however, cellulose grinding aids perform better than running samples without a grinding aid. Samples ground with pure cellulose or grinding aids with high cellulose content or without grinding aid show a bimodal distribution with an increased coarse particle content which is evidence for agglomeration. The fines fixed in agglomerates cannot be resolved by particle sizing.

The better way to identify sufficient grinding for raw meals is a grindability test by varying grinding time at a given grinding energy and analysing the samples by XRF (Fig. 8). During grinding and subsequent XRF analyses the virtual SiO_2 content (i.e., X-ray intensity) increases with grinding time. This increased SiO_2 value is a measure for better homogenization of the top 20-30 µm of the sample (see Fig. 5). The correct grinding time is picked where the slope of the curve decreases changes from steep to flat in the range from 180 – 240 s (see box in Fig. 8). After 240 s grinding the SiO_2 signal indicates no or only minor additional gain of fineness. This almost flat slope marks the final achievable fineness under the given conditions (rotation speed).

The highest SiO_2 values corresponding to the best comminution are found for the sugar coated MH1 and for MH^3 just beyond 200s grinding time (Fig. 8). The parallel shift of MH^3 to higher values compared to MH1 is due to a slightly lower weight



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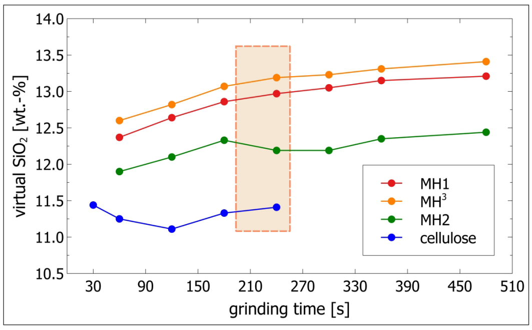
7 **Particle size distribution of kiln feed samples ground for 180s in a polab APMplus with different grinding aids. High resin-based grinding aids MH1 and MH3 produce fine powders and no agglomeration. Agglomeration is apparent for samples with MH2, pure cellulose and samples ground without grinding aid**



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8 Grinding time experiments for different grinding aids. The highest SiO_2 intensities (i.e., the best comminution) are reached with resin-based grinding aids

of the grinding aid tablets relative to MH1 leading to less dilution of the sample. Grinding with MH2 is less efficient as seen by the overall lower SiO_2 values. Pure cellulose does not contribute to grinding of raw meal at all. The grinding time at the change of the slope is similar for all grinding aids.

This test with grinding time variation only works for cement raw meals. Clinker and cement or rock samples may show minor changes; but the signals are not useful for grinding energy optimization.

3.3 Repeatability test

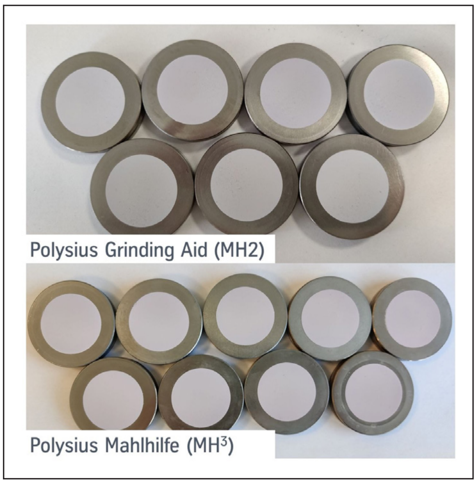
Once the correct grinding energies are found in terms of speed and grinding time, at least ten repeats of kiln feed samples are prepared with the given conditions to quantify the combined error of the sample preparation and the spectrometer. As expected, MH^3 shows the highest absolute SiO_2 readings and the lowest LSF (lime saturation) (Tab. 1). The repeatability of sample preparation is exceptionally good for all grinding aids as seen by the low standard deviation in the range from 0.04 to 0.05 for SiO_2. However, MH^3 reaches the highest intensity which returns to the best analytical resolution and detection.

If repeatability tests are conducted for clinker grinding, the sample must be pre-homogenized to maximum particle size <1000 µm. Repeatability tests with coarse clinker samples can be affected by inhomogeneities in clinker.

3.4 Stability of the tablets

Pressed tablets must be stable and dust free to avoid contamination and pollution of the vacuum pump of the spectrometer (Fig. 9). Pressed tablets prepared with MH1 and MH^3 always produce stable and dust free samples, unless grinding aid dosage is low.

Pressed tablets produced with MH2 grinding are less stable and sometimes dusty (Fig. 4). Both observations can be attributed to the cellulose content which may cause expansion after pressing the samples. Cellulose limits the de-aeration of the sample (Fig. 3). The samples appear stable at first sight; however, once the surface of the pressed tablet is broken it can also be eroded by compressed air during automated tablet cleaning (Fig. 4). Broken surfaces cannot be handled by suction devices for sample transport in analyzers.



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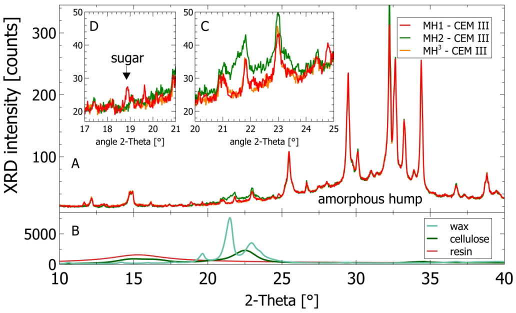
9 Examples of pressed tablets prepared with MH2 and MH³ grinding aids

3.5 XRD results

Another deficiency of MH2 grinding aids became apparent during Rietveld quantification of cements with a considerable amorphous composite material like CEM IIIA. The quantification of non-crystalline (amorphous) components in XRD requires a hklphase. For an accurate quantification of the amorphous composite content a diffraction signal of the grinding aid must not contribute to the amorphous hump; otherwise, the hkl model fails.

Fig. 10 shows the diffraction patterns of CEM III prepared with different grinding aids. It is obvious, that in most areas the patterns produced with different grinding aids overlap. This is an indication for a good and repeatable sample preparation with all grinding aid samples.

However, in the region from 21-24° 2-Theta, grinding aid MH2 shows an increased diffraction (Fig. 10A) which can be tracked back to wax and cellulose (Fig. 10B, Fig. 10C). The overlap of the



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10 (A) Diffraction pattern of a CEM IIIA high Gbfs cement. (B) Diffraction pattern of cellulose, wax, and resin. Diffuse scatter of resin occurs at lower angles than cellulose and wax. (C) Enlargement of the critical area, where cellulose and wax overlap with the amorphous hump of the Gbfs content. (D) Sugar peak of the sample ground with MH1

Table 1 **Repeatability test to confirm the accuracy of sample preparation for different grinding aids**

MH1	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	LSF
Average	12.98	3.00	1.70	42.35	0.90	103.40
Min.	12.91	2.98	1.66	42.30	0.88	102.90
Max.	13.02	3.01	1.72	42.41	0.90	104.10
Std	0.04	0.01	0.02	0.04	0.01	0.36

MH2	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	LSF
Average	12.15	2.88	1.62	42.67	0.88	110.90
Min.	12.06	2.86	1.61	42.60	0.87	110.00
Max.	12.23	2.90	1.63	42.71	0.88	111.70
Std	0.06	0.01	0.01	0.04	0.00	0.55

MH3	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	LSF
Average	13.11	3.04	1.70	42.45	0.91	102.60
Min.	13.06	3.02	1.69	42.40	0.91	102.20
Max.	13.16	3.05	1.71	42.49	0.91	102.90
Std	0.04	0.01	0.01	0.03	0.00	0.26

amorphous peak with scatter from wax and cellulose corrupts a correct quantification. Quantification is still possible, but it requires work with individual samples.

In contrast, the diffuse scatter of resin as a major component of MH1 and MH^3 occurs at smaller angles. The signal of resin does not interfere with the amorphous hump of GBFS and no critical effects for quantification are found.

The new grinding formulation of MH^3 also allowed to remove the sugar coating (Fig. 10A, Fig. 10D) and the sugar signal in diffraction can now be ignored which further improves accuracy.

4 Conclusion

Tk Polysius Mahlhilfe (MH1) has been the premium grinding aid in the cement industry for many years. Very unexpected the supply of MH1 ended in 2019.

The development of the wax-based grinding aid ended in a working solution (Polysius grinding aid (MH2)) fulfilling the requirements in many cases. Deficiencies of MH2 sometimes observed included low tablet stability, dust formation and complicated Rietveld quantification of cement with amorphous materials as a major constituent. For users successfully working with MH2 no changes are required and MH2 will be supplied in future. MH2 should be used with attention when quantification of amorphous composites is of interest.

The feedback on MH2 triggered the latest development (Polysius Mahlhilfe MH^3) with Polysius Mahlhilfe (MH1) as the benchmark. The new formulation returned to high resin and minimum cellulose content which gave strong pressed tablets without diffuse diffraction overlapping with amorphous composite cement constituents. Polysius Mahlhilfe MH^3 performs better than the phased out MH1:

- » Comminution with high XRF intensities in raw meal analyses similar to MH1. Higher intensities are achieved due to lower dilution of sample material (slightly less weight)
- » Sugar free grinding aids to improve XRD work for crystalline and non-crystalline phases. No extra phase in the sample
- » New tablet coating without effects XRD and XRF to prevent dust formation and to optimize tablet handling in dosing unit
- » XRD intensities higher than other products in the market
- » No wax and minimum cellulose content to avoid diffraction overlapping the amorphous hump
- » Accurate XRF and XRD results with little adaptions of MH1 sample preparation recipes
- » Increased analytical quality to improve product quality of the process

The test of three grinding aids confirms the superior performance of Polysius Mahlhilfe MH^3. MH^3 is now the recommended grinding aid for application in lab automation systems (further information: thyssenkrupp Polysius Guidebook for sample preparation is available on request).

REFERENCES

[1] Enders, M (2003): Röntgenbeugungsanalyse in der Laborautomatisation: Neue Anforderungen an die Probenpräparation. - ZKG International 56 (2003): 64-62

[2] Enders, M (2005).: Sample preparation for quantitative X-ray diffraction in cement plants: sources of errors and solutions. - ZKG International 58 (4): 28-37

[3] Enders M (2017): Sample preparation for XRF and XRD revisited: pressed tablets, fused beads, and mineralogical effects. - AXSCem 2017, 03-05 May 2017, Karlsruhe/Germany

[4] Mazel V. & Tchoreloff P. (2022): Lamination of Pharmaceutical Tablets: Classification and Influence of Process Parameters. - J Pharmaceutical Sciences 111(2022): 1480-1485

[5] Potts, P.J. (1992): A handbook of silicate rock analyses. - Springer New York, NY, 622p, doi.org/10.1007/978-1-4615-3270-5 Schmidt R. (2024): Optimizing and Controlling Sample Preparation. - 7th AXS CEM March 19th – 21st 2024, Ettlingen/Germany