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MECA-CLAY: ACTIVATED CLAY WITHOUT CALCINATION

thyssenkrupp Polysius has launched Polysius® meca-clay, a technology that enables the industrial scale mechano-chemical activation of clays, without calcination or process emissions.

Limestone and clay are some of the most common materials in the world. Clays have the advantage over limestone in that they are alumino-silicates that do not produce any CO_2 emissions during calcination. As the processing temperatures for clays (750-850°C) are significantly lower compared to the cement clinkering process (1450°C), CO_2 emissions can be reduced by up to 40% compared to a standard CEM I type cement when using calcined clays in an LC3 type cement. Calcined or activated clays can therefore make an important contribution on the way to CO_2-neutral cements. However, they do also pose challenges:

1. Activation energy is achieved thermally, most commonly from fossil fuels, which emit CO_2;
2. Necessary secondary measures to reduce emissions (CO_2, NO_x, SO_x etc.) complicate plant design and increase both capex and opex;
3. The use of AFR is subject to technical limits;
4. Calcination requires clays with suitable kaolinite content (usually ≥40%), deposits of which do not match demand location or size;
5. The use of calcined clays can lead to other issues, for example increased water demand in concrete.

Figure 1: polysius® charger (agitator bead mill) for the mechano-chemical activation of clays.

The concept

Investigations conducted jointly by SCHWENK Zement and thyssenkrupp Polysius have shown that activated clay can also be produced at industrial scales by mechano-chemical treatment. SCHWENK Zement's experience with mechano-chemistry is based on the production of Celitement, an alternative and innovative hydraulic binder. thyssenkrupp Polysius is a pioneer in the field of clay activation, with its first industrial reference starting to produce calcined clay at a CIMPOR cement plant in Cameroon in October 2023.

The history

Mechano-chemical processes were described as early as 1882 by Matthew Carey Lea.[1] As early as 1966, Heinicke provided an overview of the reactions investigated.[2] New research results have been published by Tole et al.[3]

Mechano-chemistry goes beyond classical grinding. Classical ultrafine grinding, also known as the Rittinger stage, is only the first of a total of three steps in mechano-chemistry. Once a material-specific particle size limit has been reached, further comminution is no longer possible. Instead, the particles are plastically deformed by the input of further energy. This second phase is when activation of the material takes place.

At the same time, the changes also lead to an initial aggregation of the fine particles. In this stage, the specific surface area reaches a maximum. The newly-formed surface area formed by the destruction of the crystalline lattice structure (recognisable by the increasing degree of amorphisation), and the reduction of the surface area due to the formation of agglomerates are balanced.

In the third step, the specific surface area decreases as the formation of stable agglomerates predominates. This is an extremely important step in the process, particularly for the use of clays in cement. It is also important to mention that crystal water and/or hydroxyl groups are not - or are only slightly - expelled during the mechano-chemical activation. Instead, xero-gels or interlayer water form. This is a clear difference from calcination.

meca-clay does not change the laws of thermodynamics. During calcination, structural and chemical changes in the clay minerals are caused by thermal energy. However, with meca-clay the changes occur through mechanically induced energy. The result is an increase in the Gibbs free energy and an activation of the clay minerals.

Until now, activation effects could only be achieved with laboratory equipment such as planetary ball mills or vibrational disc mills. These needed extremely long milling times of several hours, or even days. However, thyssenkrupp Polysius has now launched Polysius® meca-clay, a technology that enables mechano-chemical activation of clays on an industrial scale. This is realised by an energy density 10 times higher than a normal ball mill, achieved within the Polysius® charger: a high-energy agitator bead mill (Figure 1).

The performance

To demonstrate the full potential of mechano-chemical activation, a lean clay material with a low amount of 1:1 clay components was selected. The material also contained a significant portion of quartz and dolomite. The activation process was monitored by X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF). The degree of activation can be controlled by the energy supplied. During the process, all clay components, as well as the dolomite, were amorphised and activated. In the sample produced with medium energy most of the clay was already activated, suggesting that high energy treatment might not be necessary for this specific clay. Depending on the amount and type of clay even lower activation energies might be sufficient.

The performance of the mechano-chemically activated clay was assessed in comparison to the calcined variant using different methods. The Reactivity Test by Isothermal Calorimetry (also known as the R^3 test) allows the characterisation

LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	P_2O_5	TiO_2	Cl^-	Mn_2O_3
12.0	58.7	15.5	7.7	7.1	6.7	0.3	3.3	0.3	0.2	0.8	0.0	0.2

Table 1: Loss of ignition and oxide composition of the raw clay as determined by X-Ray Fluorescence analysis.

Table 2: Mineralogic composition of the raw clay and activated clays as determined by X-Ray Diffractometry.

XRD (%)	Raw Clay	meca-clay			Calcined Clay
		Low Energy	Medium Energy	High Energy	
Amorphous	19	34	54	68	42
Kaolinite	6	5	2	0	0
Muscovite/Illite	20	14	7	3	18
Chlorite	11	3	1	0	3
Montmorillonite	2	2	1	0	2
Quartz	26	28	27	26	29
Calcite	1	1	0	0	0
Dolomite	15	13	8	3	0
Lime and Periclase	0	0	0	0	6

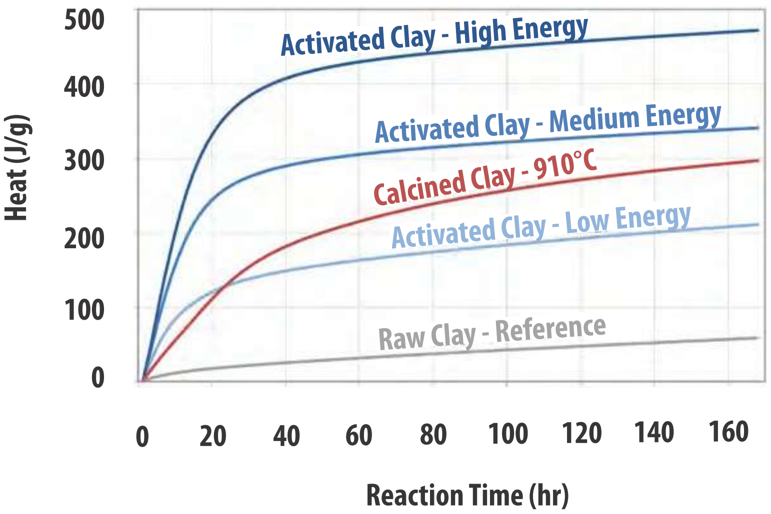


Figure 2: Reactivity Test for SCMs acc. to ASTM C1897-20, Isothermal Calorimetry; Activated clay with low/medium/high energy input compared with calcined clay and raw clay (dried and milled).

and evaluation of pozzolanic materials and SCMs regarding their potential as a main component in cement. Depending on the energy input during activation, clays can be produced in a wide range of reactivity (Figure 2). Heat is released more quickly than with calcined clay and the reaction kinetics are higher.

The Strength Activation Index (SAI) represents the relative compressive strengths compared to a CEM I 52.5 N (Figure 3). It becomes clear that with low to medium energy input during activation, the same performance is achieved as in the calcined material. With maximum activation energy, an SAI of 120% can even be achieved after 28 days.

Particle size and particle shape were examined using electron microscopy. Comparative SEM images of calcined and activated clay clearly show significant differences in microstructure (Figure 4). The calcined clay exhibits a typical plate-like and layered morphology, similar to raw clay but with a deformed structure due to thermal treatment. In the activated clay, there are no longer any recognisable clay-like structures. It mainly consists of rounded agglomerates of much smaller primary particles, and the clay structure is completely deformed. This explains some advantages of the activated material, including lower water demand.

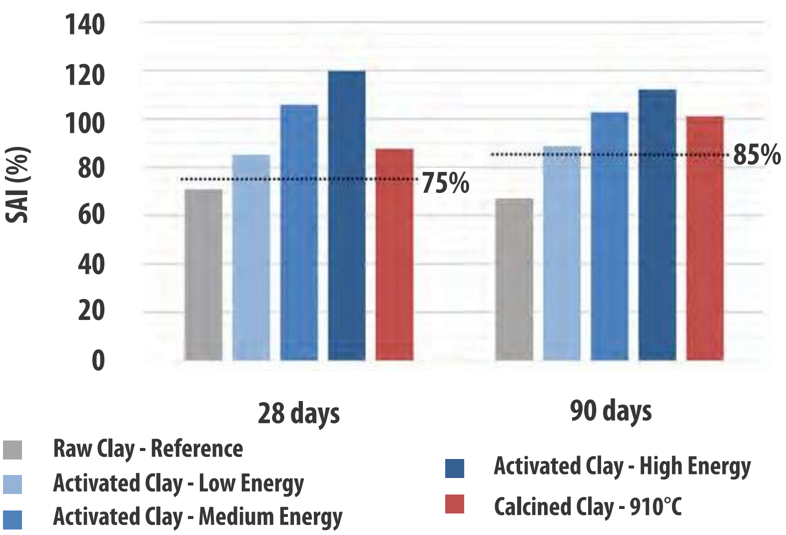


Figure 3: Strength Activation Index (SAI) acc. to DIN EN 450-1, binder composition: 75% CEM I 52.5 N + 25% clay, required SAI after 28 days ≥ 75% and after 90 days ≥ 85%; Activated clay with low/medium/high energy input compared with calcined clay and raw clay (dried and milled).

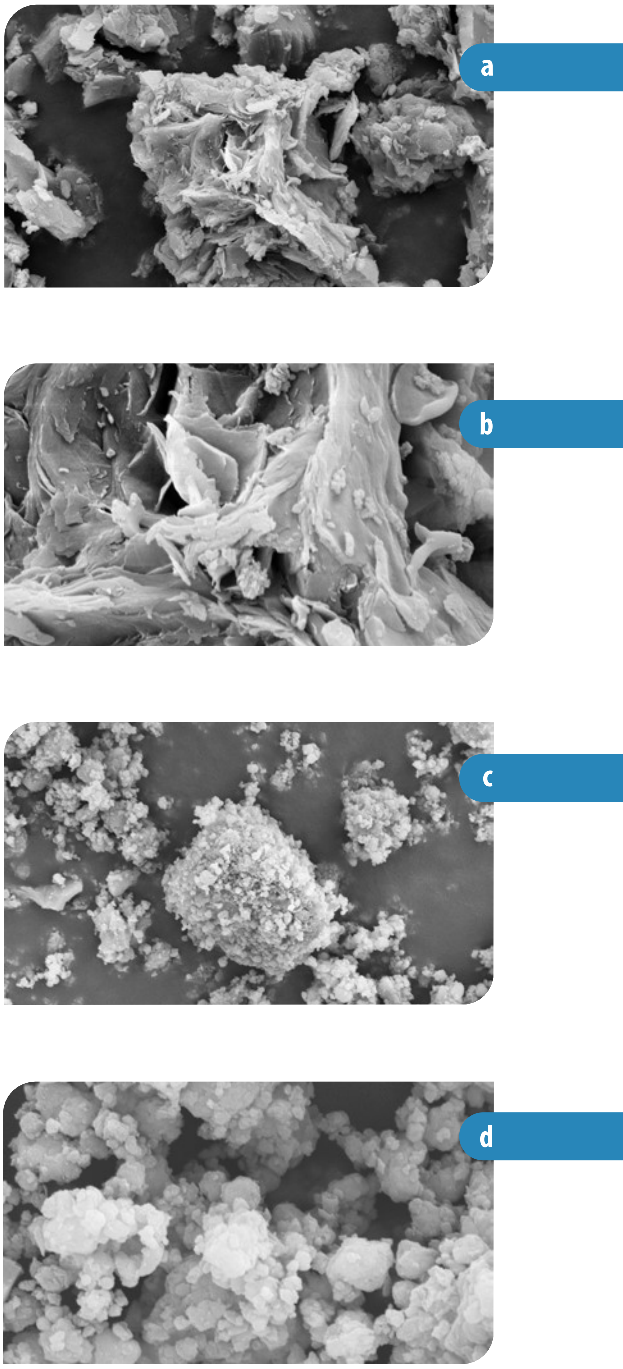
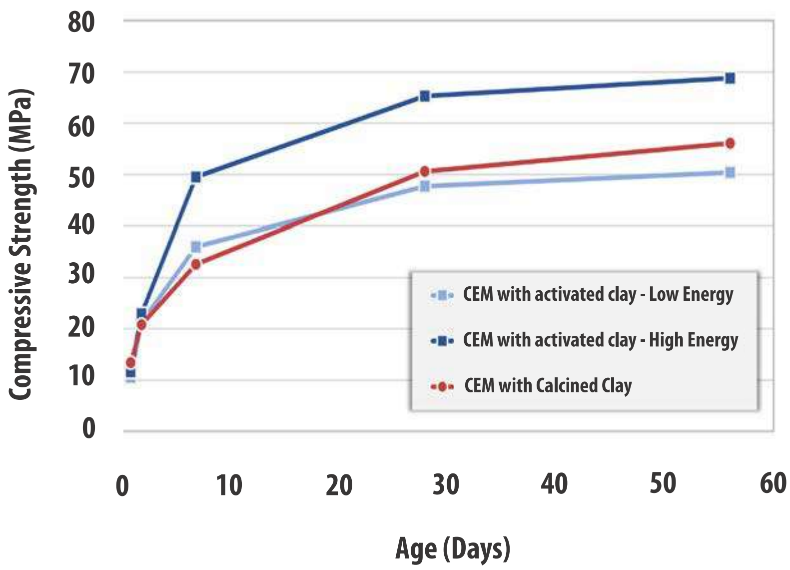


Figure 4: Scanning Electron Microscopy (SEM) of calcined and activated clays:
a) Calcined clay - 910°C, afterwards VRM milled; magnification 5000 (image width 22.9µm).
b) Calcined clay - 910°C, afterwards VRM milled; magnification 20,000 (image width 5.7µm).
c) Activated clay - medium energy input; magnification 5000 (image width 22.9µm).
d) Activated clay - medium energy input; magnification 20,000 (image width 5.7µm).

Figure 5: Concrete compressive strength acc. to EN 12390-3.
Concrete mixture design: 320kg cement, 160kg water, gravel A/B 16, PCE 1.1-1.4%.
Cement design: 55% CEM I 52.5 R, 25% activated/calcined clay, 19% limestone, 1% anhydrite.



For the first time, mechano-chemical activation of clay was conducted on a pilot plant scale, with about 10t material produced. Consequently, concrete tests were conducted with the formulation of a CEM II/C-M (P/Q-LL). The performance of the material was impressive (Figure 5).

The chances

It is clear that the mechano-chemical activation of clays represents a complementary alternative to calcination, especially for the activation of lean clays. Depending on the availability and price of electricity, mechano-chemically activated clays can be economically produced, ready to be used as SCMs, e.g. in LC3 type cements. Taking scale-up effects into account, the specific energy consumption for mechano-chemical activation is likely to be in the same range as for thermal activation. The main advantages of meca-clay are:

1. The activation works with any clay, meaning that e.g. illitic 2:1 clays or calcareous clays can be effectively activated as well;

2. Comminution (grinding) and activation takes place in a single process and plant;

3. The scalable meca-clay process is modular and flexible;

4. Thanks to a patented method, meca-clay enables easy colour control of the activated clays;

5. Exhaust gas purification is not necessary;

6. The activation process is fully electrified. There is no need for fossil fuels;

7. The polysius® charger: renewable energy can be stored like in a battery - depending on the activation energy introduced and the degree of activation;

8. Lower water demand and higher early strength compared to calcined clay.

After successfully proving the feasibility of this technology, both partners have already agreed on taking the next crucial step: Together with thyssenkrupp Polysius, SCHWENK Zement has decided to build a demonstration plant for the production of activated clay using meca-clay technology at the Allmendingen plant in southern Germany (Figure 6).

References

1. Carey Lea, M.; *'Disruption of the Silver Haloid Molecule by Mechanical Force,' American Journal of Science,* 1892, pp. 527-531, 1892. **2.** Heinicke, G.; in *'Grundlagen der Tribochemie,'* Berlin, Akademie-Verlag, 1967, pp. 179-189. **3.** Tole, I. et. al., *"Mechanochemical activation of natural clay minerals: an alternative to produce sustainable cementitious binders - review", Minerology and Petrology,* 2019, 113: 449-46.

Figure 6: Demo-scale plant at SCHWENK Zement's Allmendingen plant.