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Original Research

Economic Evaluation of Thermal and Mechanical Activation Energies in Plaster Production

Muhammed Şener[a,*], Turan Uysal[b,**], Murat Erdemoğlu[c,***]

[a] Turgut Özal University, Hekimhan Vocational School, Department of Civil, Malatya, TÜRKIYE
[b] Gümüşhane University, Faculty of Engineering and Natural Sciences, Department of Mining Engineering, Gümüşhane, TÜRKIYE
[c] İnönü University, Faculty of Engineering, Department of Mining Engineering, Malatya, TÜRKIYE

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A B S T R A C T

Plaster is among the most needed raw materials in the world. In this study, thermal activation provided by calcination and mechanical activation methods provided by intensive milling in the plaster production process were evaluated in terms of activation energy. In this context, the energies of laboratory-scale thermal and mechanical activation processes were calculated and these activation methods were evaluated economically and the ideal activation methods were determined. Although the mechanical activation method creates additional investment and operating costs, it reduces the calcination temperature by 13 °C, thus provides lower energy costs. Addition of a mechanical activator mill before thermal activation in plaster production as a more economical and more environmentally friendly method was proposed.

Keywords: *Plaster, Thermal Activation, Mechanical Activation, Energy Cost.*

Introduction

Gypsum ($CaSO_4.2H_2O$) is a naturally occurring calcium sulphate mineral containing two moles of water in its crystal structure. When pure, it contains 79.1% calcium sulphate and 20.9% water. According to the mineralogical formula $CaSO_4.2H_2O$, when gypsum, which contains approximately 21% water, is heated, 15% of this water is removed (Eq. 1). Thus, hemihydrate ($CaSO_4.1/2H_2O$), also known as plaster, containing 0.5 moles of water is obtained. If the hemihydrate continues to be heated, it loses all the water in its structure and turns into anhydrite (Eq. 2).

$$CaSO_4.2H_2O(\text{Gypsum}) \xrightarrow{\text{Calcination (160-170°C)}} CaSO_4.{}^1/_2\,H_2O(\text{Plaster}) + {}^3/_2\,H_2O \quad (1)$$

$$CaSO_4.{}^1/_2\,H_2O\,(Plaster) \xrightarrow{\text{Calcination (250°C)}} CaSO_4(Anhydrite) + {}^1/_2\,H_2O \quad (2)$$

Depending on the properties of gypsum ore (pure gypsum, natural gypsum, gypsum grade, component type, etc.) and calcination conditions, the calcination temperature varies. The conversion temperatures of gypsum to hemihydrate are in the range of 100-120 °C, which is the temperature at which gypsum starts to lose mass; 160-180 °C, which is the temperature at which the transition from hemihydrate to anhydrite starts, and 180-250 °C, which is the temperature at which it no longer loses mass (Putnis et al., 1990; Hudson-Lamb et al., 1996). The production of plaster used in the construction sector is generally carried out by rotary kiln or vertical kiln. The flow chart of the process including a rotary kiln is given in Figure 1. Simply, plaster is obtained by heating in such a way that 15% of the water contained in the gypsum is evaporated and milling the plaster before packaging.

Mechanical activation (MA) is defined as an "increase" in the reactivity of a solid whose chemical structure remains unchanged throughout the milling process, during which mechanical energy transfer takes place. During MA, the particle size of the mineral is reduced by milling, while defects in the crystal structure are formed depending on the mechanical energy density (Baláž and Achimovičová, 2006). Thus, fresh, clean surfaces and semi-stable species are formed (Boldyrev, 1986; Sekulic et al., 1999). In the case of mechanical activation, the mineral will then behave more actively during a metallurgical process such as calcination (Uysal

* Corresponding author: muhammed.sener@ozal.edu.tr • https://orcid.org/0000-0002-7567-4654
** turanuysal@gumushane.edu.tr • https://orcid.org/0000-0003-1643-6725
*** murat.erdemoglu@inonu.edu.tr • https://orcid.org/0000-0003-2922-7965

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et al., 2016; Erdemoğlu et al., 2020; Aydoğmuş et al., 2023) sintering (Uysal et al., 2015; Birinci et al., 2017; Alyousif et al., 2023a) or leaching (Erdemoğlu et al., 2017; Uysal, 2018), which will reduce the temperature or increase the speed of the process. Recovery as a result of this mechanical activation can be realized at lower energy costs than thermal activation (Alyousif et al., 2023b). Even if thermal activation (TA) can be achieved at lower temperatures, it may result in less energy costs in the calcination process. It is also known that in the plants where mechanical activation is applied, reactions take place in shorter times, using simpler and cheaper reactors or furnaces (Erdemoğlu et al., 2018; Barry et al., 2019). The only modification to the present plant is the installation of a high-energy transfer mill before the kiln.

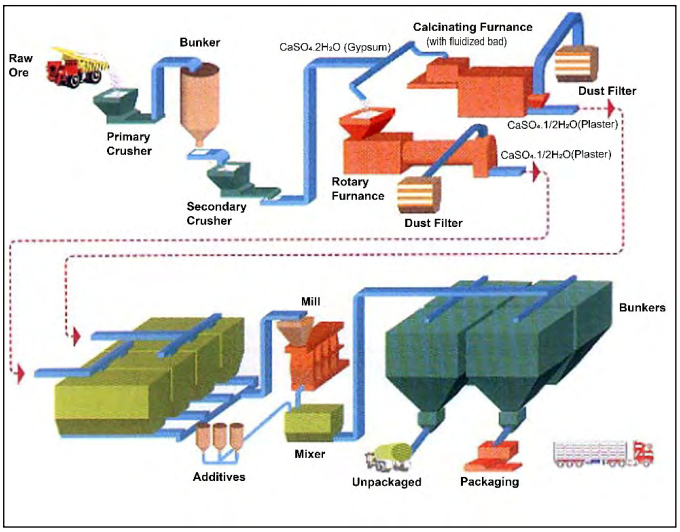

Figure 1. General flow chart of plaster production

Although there are many studies on plaster production, there is not enough work in the literature on the activation energy calculation, which has a significant effect on the economics of the production process. In this study, thermal and mechanical activation energy calculation was carried out in order to contribute to the research on plaster production with lower costs. With MA, gypsum formation temperature decreases and energy cost decreases. With this reduced energy cost, it was calculated how many years the initial investment cost required for MA can be amortised and evaluated economically. The activation energy spent per unit quantity was evaluated and the appropriate activation method was determined.

2. Materials and Methods

2.1. Material

The gypsum used for the experimental studies was obtained from Arslanlı Alçı A.Ş. (Elazığ, Türkiye) plaster plant. The ore used in the experiments is a massive natural alabaster gypsum ore with a CaO content of 32.45%. The chemical analysis results of this gypsum ore are given in Table 1 and XRD analysis results are given in Figure 2. According to the CaO and loss on fire values in Table 1, the $CaSO_4.2H_2O$ content of the ore was determined to be approximately 99.0%. According to XRD results, the ore consists of gypsum and anhydrite.

Table 1. Chemical content of the gypsum ore sample (Şener, 2012)

CaO	SO_3	SiO_2	MgO	Cl	LOI*
32.45	44.49	0.2	0.004	0.41	20.63

**LOI: Loss on ignition (1000 °C)*

2.2. Method

Representative samples of ore with an average particle size of 20 cm were taken from the plant stockpile by sampling. The samples were crushed in a jaw crusher and then ground to a particle size of -2 mm in a ceramic ball mill. This milling was performed under dry conditions. Samples (1 kg) were ground in the ceramic mill at 200 rpm for 5 min. The ore with -2 mm particle size was intensively milled to provide mechanical activation. Intensive milling operations were carried out using Fritsch Pulverisette 6 mono mill model planetary ball mill. In the air-cooled mill, a 250 cm^3 bowl made of hard metal tungsten carbide (WC) and and 10 mm diameter 50 pieces balls made of the same material with the bowl were used. Protherm PLF120/5 model muffle furnace and 15 ml porcelain crucibles were used for calcination of the intensively milled samples. A Setaram LabSys 60 model TG-DSC device was used to observe the thermal behavior of the intensive milled gypsum. The measurements were carried out in an argon atmosphere at a heating rate of 10 °C/min in a platinum crucible. The crystal structures of the powders subjected to intensive milling were examined by X-ray diffraction analysis performed using a Rigaku brand RadB model device in a Cu-Kα (λ = 1.5405 Å) radiation environment at a scanning speed of 2 min^{-1} and at diffraction angles varying between 5-80°.

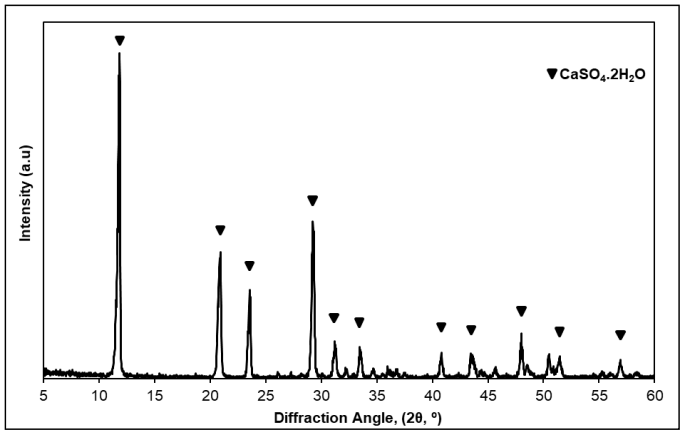

Figure 2. XRD pattern of the gypsum ore sample

The ball-to-ore ratio by weight was 10 and the mill rotation speed was 300 rpm, as recommended by Şener (2014). In the calculation of activation energies, the specific milling energy per unit amount of ore was calculated using Eq. 3 (Pourghahramani and Forssberg, 2007; Balăz, 2008) and the specific heat energy was calculated using Eq. 4.

$$SE = (m_B/m_S) * a * n * t_M * D \quad (3)$$

Where, m_B is mass of milling media (balls) (kg), m_S is mass of ore to be milled (kg), a is theoretical acceleration of the balls (26.41 m/s^2 for the planetary mill used), n is mill rotation speed (1/s), t_M is milling time (s) and D is mill diameter (m). In this formula, the specific energy unit is kJ/kg and kWh is converted (1 kJ: $2{,}78*10^{-4}$ kWh).

$$Q = m * C_p * \Delta T \quad (4)$$

Where m is the mass in kg, Cp is the heat capacity at constant pressure and ΔT is the difference between the initial ambient and final temperature. The Cp of gypsum was calculated as the sum of the specific heat and mass fraction of each of the chemical elements of gypsum and estimated as 1.090 kJ/kg.K (Engineering toolbox, 2003; Evans, 2016). In both activation methods, sample masses were taken as 1 kg due to the close feed amounts.

3. Results and Discussion

3.1. Particle Size Distribution

Table 2 shows variations of selected cut point particle size values with increasing milling time. Milling, as expected, not only decreased the particle size, but also increased the amount of fine particles in the powders. Milling up to 15 min significantly shifted the size distribution to finer sizes, however milling for longer times as much as 18 and 20 min shifted the distribution relatively coarse sizes again. The particle size of unmilled gypsum is minus 2 mm, milling 15 min decreased the cut point d_{90} from 710.29 µm to 38.56 µm. But, prolonged milling for 18 and 20 min increased it to 52.81 and 75.90 µm, respectively. Some coarse particles of long milled powders are not primary but formed by coating of secondary fines or aggregation.

Table 2. Variation of cut point particle size with increasing milling time.

Milling time (minute)	Particle Size (µm)		
	d_{90}	d_{50}	d_{10}
0	710.29	250.27	53.46
5	104.31	34.19	2.45
10	63.02	9.16	1.48
15	38.56	5.74	1.34
18	52.81	5.38	1.08
20	75.90	15.04	1.51

3.2. Energy Consumption

The thermal behaviour of gypsum samples was investigated by thermal analysis methods and the thermal analysis (TG) curve is given in Figure 3. TG and DTA curves of the 15 minutes milled sample are given in Figure 4.

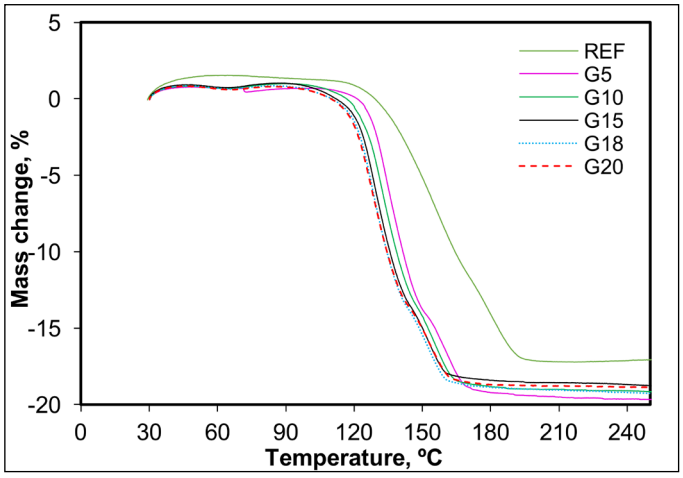

Figure 3. TG curves of unmilled (REF) and prolonged milled gypsum samples (G5: 5 minutes, G10: 10 minutes, G15: 15 minutes, G18: 18 minutes, G20: 20 minutes) (Şener and Erdemoğlu, 2014)

According to the results showed in Figure 3, with the increase in milling time, the conversion temperatures of gypsum to hemihydrate and hemihydrate to anhydrite decreased. It was observed that the transformations shifted to lower temperature regions. In thermal analysis, one reason for the shift of the mass loss temperature value to lower temperature regions is the reduction of the particle size of the gypsum exposed to calcination. However, since the gypsum sample was also prepared by milling for thermal analysis, it was assumed that the effect of particle size on the decrease in conversion temperatures can be neglected. Results similar to these results obtained as a result of thermal analyses were also determined by various researchers. In a study by Lou et al. (2011), the dehydration behaviour of artificially produced gypsum was investigated with the help of TG and DSC analyses. In this study, the temperature at which gypsum starts to lose mass is shown in the range of 110-115 °C; the temperature at which the transition from hemihydrate to anhydride starts is 160-165 °C and the temperature at which it starts not to lose mass is 175-185 °C.

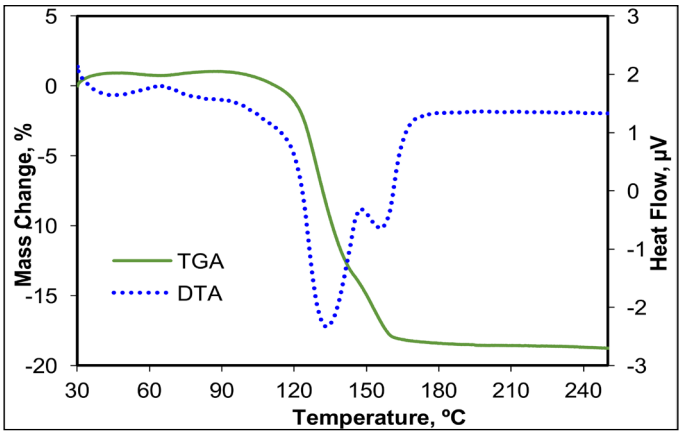

Figure 4. TG and DTA curves of the sample milled for 15 minutes

When the curves in Figure 4 are analyzed, it was determined that the initial temperature of conversion of the sample milled for 15 minutes to hemihydrate was 99.1 ºC, the initial temperature of conversion from hemihydrate to anhydrite was 140.9 ºC and the mass loss ended at 157.4 ºC. When the specific milling and heat energy values were evaluated together, the optimum milling time was determined as 15 minutes (Figure 5). Therefore, the TG and DTA curves of the sample milled for 15 minutes were taken into consideration and the specific milling and heat energy changes depending on the milling time are given in Figure 5. The initial temperature values of conversion of gypsum milled and calcined at different times to gypsum and anhydrite are given in Table 3, and the specific milling, heat energy values and costs are given in Table 4. The specific heat energy (kWh/ton) value was calculated depending on the temperature required for gypsum conversion.

Table 3. Initial temperature values for conversion of gypsum milled and calcined at different times to plaster and anhydrite

Milling time, minute	0	5	10	15	18	20
Initial temperature for conversion to plaster, °C	112.8	109.2	107.3	99.7	100.2	103.4
Initial temperature for conversion to anhydrite, °C	166.6	145.9	144.1	140.9	140.1	137.9

In Table 3, it was observed that the initial temperature of gypsum to plaster transformation decreases until 15 minutes of milling time and increases slightly after 15 minutes. The increase after 15 minutes of milling was thought to be due to the decrease in intensive milling efficiency with agglomeration. This was also observed in the specific heat energy value given in Figure 5. When these two data were evaluated together, the optimum milling time was determined as 15 minutes as indicated by the dashed line in

Figure 5. With 15 minutes of milling, the initial temperature of conversion from gypsum to plaster decreased by 13.15 ºC and the initial temperature of conversion to anhydrite decreased by 25.7 ºC.

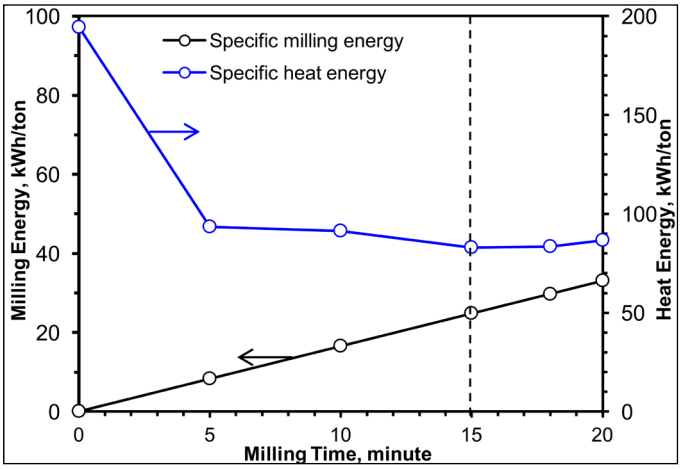

Figure 5. Variation of specific milling energy and heat energy with respect to milling time

Table 4. *Specific milling and heat energy value and costs of samples milled at different times*

Milling time, minute	0	5	10	15	18	20
Specific milling energy (kWh/ton)	-	8,26	16,52	24,78	29,74	33,04
Specific heat energy, (kWh/ton)	194,24	93,43	91,36	82,86	83,47	86,58
Milling energy cost, TL	-	33,33	66,66	99,99	120,00	133,32
Heat energy cost, TL	783,77	376,97	368,64	334,33	336,80	349,34

The average electricity consumption cost per kWh of the enterprises located in Türkiye in January 2024 is 4.035 Turkish Liras (Energy Agency, 2024) and this price was taken as a source in the calculations. While the initial temperature of conversion of unmilled gypsum to plaster is 112.8 ºC, the calcination temperature decreases as the milling time increases (Table 3). The initial temperature of conversion to plaster decreased by 13 ºC with 15 minutes milling and the initial temperature of conversion to anhydrite decreased by 25.7 ºC. When the energy consumption and energy cost values per ton were analyzed, 194.24 kwh/ton energy is required for complete calcination of unmilled gypsum, while this energy requirement is 107.64 kwh/ton with 15 minutes milling, which was the sum of milling energy and heat energy (Table 5). For more than 15 minutes of milling, specific energy values largely decreased.

Table 5. *Energy consumption and energy cost values per ton of gypsum*

Cost	TA	MA + TA
Energy Consumption, kWh/ton	194.20	107.64
Energy Cost, Turkish Liras	783.77	434.32

With the addition of the mechanical activator mill before calcination in plaster production per ton, the calcination temperature required for plaster production was lowered by 13.15 °C. The energy saving resulting from this temperature reduction was 349.45 TL per ton.

4. Conclusions

In this study, TA and MA circuits used in the production of plaster, which has an intensive use today, were evaluated economically. From the economic analysis, it was determined that the MA circuit is generally efficient and the addition of mechanical activator mills to the plaster production circuit before calcination as suggested in Figure 6 is a more economical and environmentally friendly method with less energy consumption. Considering the global energy crisis in recent years, it was evaluated that the MA+TA circuit will be a more profitable investment. Since it is thought that the correlation of the data obtained with the equipment used in the laboratory scale with the data to be obtained in industrial plants will be very low, no evaluation has been made regarding how long the initial investment cost of the mechanical activator mill will be covered during the calculations. This study was a reference in terms of energy efficiency and cost analysis stages, which are the most important steps of feasibility studies to be carried out for a gypsum production plant to be established on an industrial scale.

The need for ultrafine materials in the industry will continue to grow in the future. Consequently, the use of mechanical activator mills in industry is expected to continue to grow. The use of mechanical activator mills in many different processes on an industrial scale is already available in literature. When evaluating plaster production, it is predicted that activator mills will be used in this sector in the near future because they are economical and environmentally friendly.

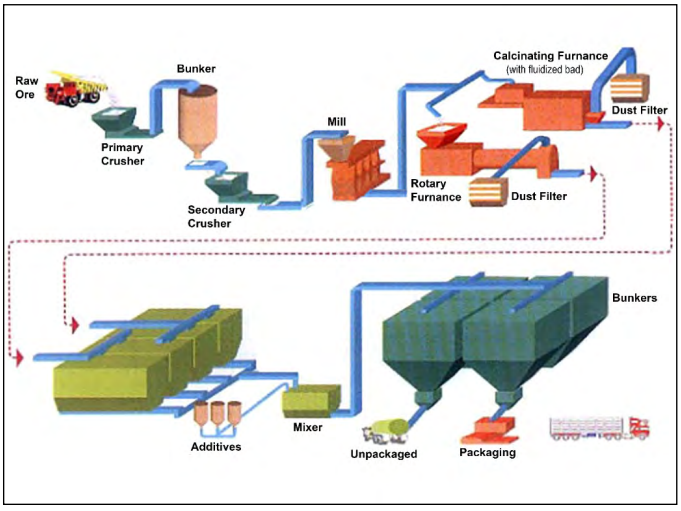

Figure 6. Proposed flow chart for plaster production

Acknowledgement

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