Journal of Chemical Technology and Metallurgy, 60, 4, 2025, 679-684

PRODUCTION OF BARIUM SULFATE WITH CONSIDERABLY IMPROVED WHITENESS THROUGH CALCINATION OF BARITE RECOVERED FROM WASTE MATERIAL

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Received 28 November 2024
Accepted 19 April 2025
DOI: 10.59957/jctm.v60.i4.2025.17

ABSTRACT

The study presents calcination of barite recovered from gangue stored in a tailings dam located in Bulgaria with the aim to product $BaSO_4$ with improved whiteness. The calcination was carried out in a rotary kiln at 1150°C under air. Samples from three batches of barite with different particle size, namely 40 µm, 20 µm and 6 µm, were processed and the colour and brightness value of the product was measured. The residence time of the material in the kiln, respectively in the heated zone, was also determined. The results show that the brightness of the barite recovered from the gangue could be improved by 4 - 20 units through calcination.

Keywords: barite processing, whitening, calcination, titanium dioxide alternatives.

INTRODUCTION

The non-metallic mineral barite is characterized by high whiteness and density like that of the titanium dioxide, hence it is shown as a material that could replace TiO_2 in many areas of industrial application [1]. The raw barite contains coloured impurities, mostly Fe_2O_3, carbonate minerals or organics compounds, which usually require a chemical agent to be removed. For bleaching minerals of industrial interest most widely employed are sodium hypochlorite, sulfur dioxide, and sodium dithionite. Other techniques use conventional mineral acid as H_2SO_4 or HCl [2, 3]. Biotechnological techniques have been also developed. Groudev et al. [4], Toro et al. [5] and Strasser et al. [6] proposed microbial leaching methods for iron removal under environmentally safety conditions. However, these methods have been seen to be less effective as chemical bleaching, which may be due to the smearing of iron impurities on particle surface [7].

Deniz and Gueler report whitening of barite ore through magnetic separation and bleaching whereby the brightness index of the barite was increased from 68.05 % to 90.12 % [7]. The patent application CN102616824B describes a method for producing an ultrafine high-whiteness active barite powder through oxidation leaching reaction [8]. Salem and Osgouei report reduction of barite at different particle size in presence and absence of 5 % Na_2CO_3 or 5 % $Fe(NO_3)_3$, whereby a considerable reduction of the isokinetic temperature was achieved when using sodium carbonate as a catalyst. In the mentioned study the effect of the reduction process on the barite whiteness has been not evaluated [9].

To the best of our knowledge, no research results have been reported on the possibility of using calcination, as a chemical agent-free method, for whitening of barite, moreover the barite used in this study was not recovered from ore, rather by processing of waste product stored in the tailings dam at a metallurgical plant.

In the presented work samples from three batches of barite with different particle size, namely 40 µm (sample 1), 20 µm (sample 2) and 6 µm (sample 3), were processed through calcination and the colour and brightness value of the product were measured. The residence time of the material in the kiln respective in the heated zone was also determined.

EXPERIMENTAL

The barite used for this investigation was recovered from the gangue through flotation. Some parameters of the kiln are presented in Table 1.

Fig. 1 presents schematic the rotary kiln process.

The chemical composition of the samples was analysed by X-ray fluorescence technique (S2 Puma 2 Bruker). The particle size was measured using laser particle sizer (Fritsch Analysette 22) and the colour and brightness index were determined spectrophotometric meeting the ISO 2470 standard [10]. Gravimetric analysis method was applied to determine the bulk density of the raw barite.

Table 1. Technical Parameters of the used kiln.

Kiln/Plant	IDC
Material of rotary kiln tube	2.4851 (Inconel Alloy 601)
Heating	Indirect, electric, 3 heating zones
Dimensions (diameter x length; heated tube)	0.1 m x 1.0 m
Throughput (Raw material), depending on material properties	0.1 - 2 kg h^{-1}
used	1 - 2 kg h^{-1}
Temperature range	100 - 1400 °C
Exhaust cleaning	Post combustion

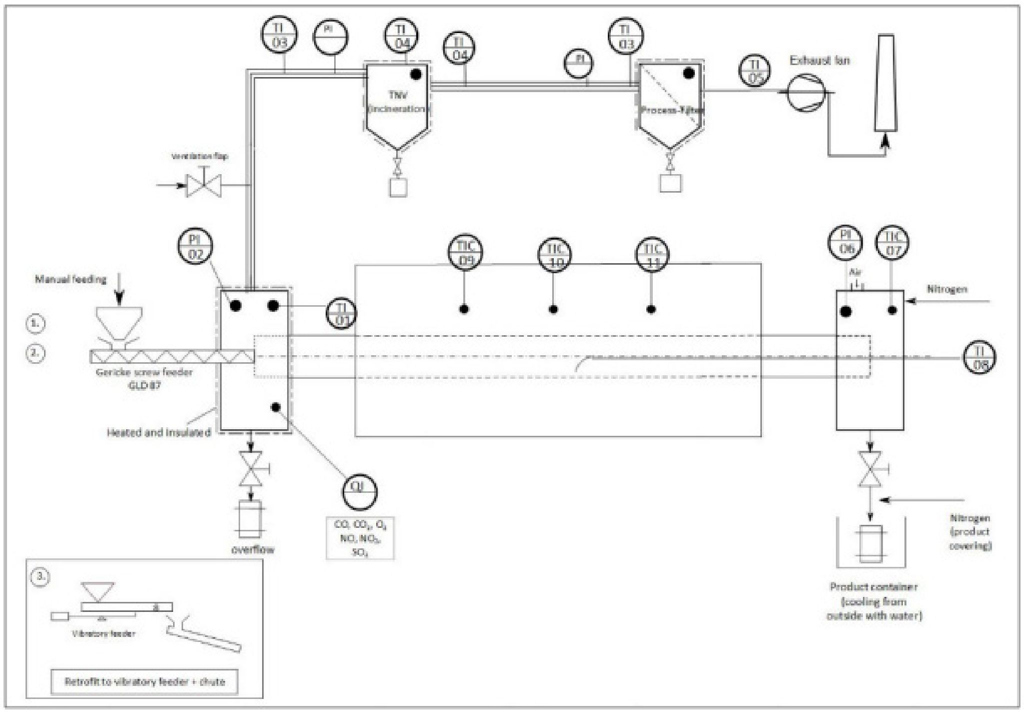

Fig. 1. Scheme of the rotary kiln process.

RESULTS AND DISCUSSION

In Table 2 is presented the chemical composition, the particle size, the bulk density and the brightness index of the barite used.

The barite calcination was carried out in a rotary kiln whereby the temperature was set at 1150°C and kept equal over the time. Knockers at the kiln inlet side were used to prevent adhesion of the product at the inner tube wall. The time needed for the pre-run product (VL) was taken at least as twice of the dwell time. The time for product collection under steady state conditions (VP) was at least 1.5 - 2 times of the dwell time. During the barite calcination, small amounts of sulfur dioxide (SO_2) were produced. We assume that $BaSO_4$ was reduced by organic material still present in the raw material. This hypothesis is supported by the observed increase in CO and CO_2 concentration at the maximum of SO_2 evolution. Fig. 2 shows the SO_2 concentration over the time. It is remarkable that the concentration and probably the amount of SO_2 increases as the particle size of the raw material decreases (40 µm → 20 µm → 6 µm). The production of sulfur dioxide during the barite calcination requires further investigation and analyses to avoid or minimize this adverse effect.

Table 2. Chemical composition, particle size, bulk density and brightness of the barite used.

Parameter	Barite 40 µm (sample 1)	Barite 20 µm (sample 2)	Barite 6 µm (sample 3)
Content $BaSO_4$, %	96.00	96.00	96.00
Content $SrSO_4$, %	1.646	1.307	1.270
Content Fe_2O_3, %	1.020	1.270	1.407
Content MnO, %	0.430	0.430	0.450
Content SiO_2, %	0.510	0.530	0.500
Content CaO, %	0.190	0.190	0.180
Content MgO, %	0.040	0.040	0.040
Content Al_2O_3, %	0.100	0.100	0.100
Content Zn, %	0.003	0.002	0.003
Content Pb, %	0.040	0.040	0.041
Content Cu, %	0.010	0.011	0.010
Particle size, µm	< 40	< 20	< 6
Bulk density, kg/dm^3	2.2	2.2	2.2
Brightness, ISO 2470	64.6	74.8	61.8

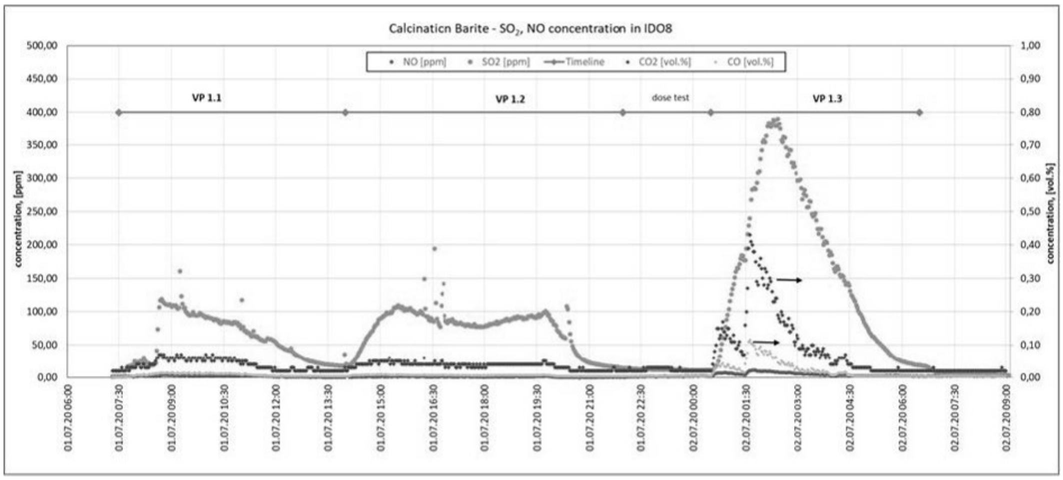

Fig. 2. Exhaust gas analysis during the barite calcination.

The analytical results of the product samples from the 3 baches are summarized in Table 3. The brightness of the calcinated barite depends obviously on the particle size of the raw material. The highest increase was achieved with the finest material (sample 3) as raw material. From Table 2 it is seen that the concentration of Fe_2O_3 and Pb is higher for sample 3 as for the other two samples studied, since sample 3 exhibits as raw material lower brightness index (Table 3) in comparison to sample 1 and 2.

Fig. 3 compares the raw and the calcinated barite (sample 1) in terms of brightness. The product is noticeable lighter and whiter.

The residence time of the material in the rotary kiln, respectively in the heated zone, was determined by measuring the product rate vs. time at start up (Fig.4).

The time is equal to the average residence time in the kiln when the product rate is constant. From this, the residence time in the heated zone can be calculated according to Eq. (1):

$$\mathrm{t_{0,heated}} = \mathrm{t_{0,tube}} \frac{\mathrm{l_{heated}}}{\mathrm{l_{tube}}} \qquad (1)$$

where $t_{0,heated}$ is the residence time in the heated zone, $t_{0,tube}$ is the residence time in the kiln tube, l_{heated} is the length of the heated zone and l_{tube} is the length of

Table 3. Measured colour values and brightness index of the raw material (RM), the pre-run product (VL), the product collected under steady state conditions (VP) and of the tail product (NL).

Material	Sample	Colour			Brightness
		L*	a*	b*	ISO-2470-1
Barite 40 µm	RM	86.5	0.8	4.1	64.6
	VL	89.4	0.8	2.9	71.1
	VP	91.1	0.6	3.2	75.2
	NL	91.0	0.5	3.4	72.8
Barite 20 µm	RM	88.7	0.7	3.5	74.8
	VL	92.7	0.1	4.1	70.0
	VP	93.3	0.1	4.4	78.0
	NL	93.3	-0.1	4.4	79.2
Barite 6 µm	RM	85.1	1.1	4.3	61.8
	VL	94.6	0.5	3.5	82.6
	VP	94.6	0.5	3.6	82.7
	NL	91.9	0.2	6.1	74.3

Fig. 3. Comparison of brightness; left: raw barite with particle size 40 µm, right: the same barite after calcination.

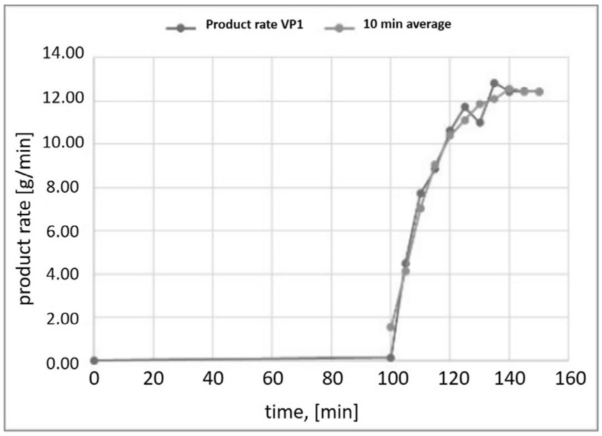

Fig. 4. Determination of residence time: Product rate vs. time of VP Barite 40 μm.

Table 4. Residence time value obtained by measuring the product rate vs. time at start up.

Sample	Barite 40 μm, VP
residence time (kiln tube)	140 min
residence time (heated zone)	62.2 min

the kiln tube. In Table 4 is given the so determined residence time for the sample containing barite with particle size 40 μm. The value is in good agreement with the theoretical calculated residence time Eq. (2) of 60 min in the heated zone.

$$\bar{\tau} = \frac{L\sin\xi}{2\pi r n \phi} \qquad (2)$$

where $\bar{\tau}$ is the residence time, L - the length of the kiln tube, n - rotation speed, ϕ - kiln inclination and ξ - dynamic angle of repose [11].

CONCLUSIONS

A chemical agent-free and cost efficiency method for production of barite with increased whiteness has been proposed. Raw barite recovered through flotation from waste product stored in the tailings dam of a metallurgical plant has been processed by calcination in a rotary kiln, whereby the brightness of the product has been improved by 4 - 20 units in comparison to the raw material.

Acknowledgments

This study is funded by the European Union-NextGenerationEU, through the National Recovery and Resilience Plan of the Republic of Bulgaria, project № BG-RRP-2.004-0002, "BiOrgaMCT".

Authors' contributions: *I. M.: Conceptualization, Methodology, Investigation, Supervision, Manuscript Review and Editing, Funding acquisition; A. S.: Data curation, Writing - original draft; B. Y.: Methodology, Investigation. R. G.: Methodology, Investigation.*

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