MECHANO-CHEMICAL MODIFICATION OF SIDERITE ORE IN WET STIRRED BALL MILL

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ABSTRACT. Mechano-chemical activation of siderite ore from Kremikovci deposit was observed on this study. Siderite ore from Kremikovci deposit is characteristic with high manganese content (1:4 - Mn:Fe) in crystal structure of mineral siderite. Intensive milling of siderite for different periods of time 30, 60, 90 and 120 minutes was observed in presence of activator CaO (5, 10 and 15 g/ton). The milled ore samples were feed to low intensity magnetic separation and characterized by using X-ray powder diffractometry, Thermal gravimetric analyses and ICP. Obtained results show evidence of mechanical activation upon intensive milling of the siderite and formation of new highly magnetic minerals and phases like magnetite and maghemite.

МЕХАНО-ХИМИЧНА АКТИВАЦИЯ НА СИДЕРИТОВА РУДА С МОКРО СМИЛАНЕ В АГИТАЦИОННА ТОПКОВА МЕЛНИЦА

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РЕЗЮМЕ. Сидеритовата руда от Кремиковското находище се характеризира с високо съдържание на манган (Mn:Fe=1:4), който се съдържа в кристалната структура на минерала сидерит. Целта на настоящето изследване е механо-химичната активация на сидеритовата руда от това находище. Изследвано е интензивното смилане на сидерита при различна продължителност на смилането – 30, 60, 90 и 120 min и при наличието на активатор CaO (5, 10 и 15g/t). Смляната руда се подава на ниско интензивна магнитна сепарация и се изследва на прахова рентгенова дифрактометрия, термо-гравиметричен анализ и ICP. Получените резултати показват наличието на механична активация, в следствие на интензивното смилане на сидерита и образуването на нови силно магнитни минерали и фази като магнетит и магхемит.

Introduction

Siderite is one of the important iron minerals used for production of steel, filler in drilling industries, adsorbent in chemical industry, and so on. Such industrial applications require high quality products and fine dispersed siderite. Mechano-activated surface modification is a modification method of utilizing mechano-chemical effect during ultrafine grinding.

Mechanical activation of minerals by intensive milling is an innovative method which improves the efficiency of mineral processing operations and metallurgical processes. Mechano-chemical effect is a physical and mechanical change on the near surface region, where the solids come into contact with each other under mechanical forces. In this paper, we reported that the results of investigation of the feasibility of mechanochemical activation of siderite with calcium oxide by wet stirred ball mill. During mechanical activation, the crystal structure of a mineral is usually disordered and generation of defects or other metastable forms can be registered. It has been reported that the application of high energy mills like planetary mills and vibratory mills allows a dramatic change of the structure and surface properties of solids to be induced (M. Erdemoğlu,Y. Ding and M. Ghadiri Intensive Milling of Siderite, 2010).

Materials and Methods

The experimental sample was taken of horizon 460 m from Kremikovci deposit. Siderite ore was crushed down to 2 mm. Its main chemical compositions is represented in the Table 1.

Table 1.
Chemical composition of siderite ore

Al_2O_3	CaO	Fe_2O_3	K_2O
1,16	4,46	33,19	0,17
Na_2O	P_2O_5	SO_3	SiO_2
0,05	0,03	1,99	15,33
MgO	MnO	TiO_2	3H
5,64	6,31	0,04	28,86

The size distribution of sample was given in Table 2.

For surface modification reagent was used calcium oxide. In the experiments, distilled water was used. Laboratory modification tests were carried out in a stirred ball mill.

The grinding medium is steel balls with diameters 1.0–1.2, 1.8–2.0 and 2.8–3.0 mm. In the experimental tests were made at pH7-8, 50% pulp density.

Table 2.
Grain size distribution of crushed down to – 2mm siderite sample

Fractions		Yield		Summary yield
(mm)	(mm)	(g)	(%)	(%)
	+2	411,88	44,29	44,29
-2	+1,6	71,66	7,71	52
-1,6	+1,0	96,49	10,38	62,38
-1,0	+0,8	27,82	2,99	65,37
-0,8	+0,5	85,63	9,21	74,58
-0,5	+0,25	51,27	5,51	80,09
-0,25	+0,16	36,24	3,9	83,99
-0,16	+0,071	38,39	4,13	88,12
-0,071		110,62	11,9	100
Raw ore		930	100	

After contact time, the aqueous phase was separated from the sample by filtration, washed with distilled water and, the obtained products were dried at 105 °C. The effect of surface modification was evaluated by magnetic separation test which represented the ratio of the magnetic product to the overall weight of the sample after they are mixed in water and stirred vigorously. The samples were characterized with TGA measurement and ICP analyses. The weight loss was calculated from thermogravimetry-differential thermal analysis (TGA) curves. The effect of milling time on the particle size distribution is given in Fig.1.

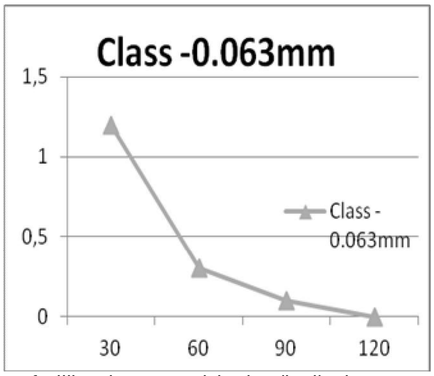

Fig. 1. Effect of milling time on particle size distribution

As mentioned before, size of the unmilled siderite is almost 100% minus 2 mm. After 30 and 60 min of milling affected the particle size class -0.063 mm to 1.2 and 0.3%. Distribution to a large extent so that, in the case of 90 min of milling time, all of the particles are almost finer than -0.063 mm. However, 90min of milling resulted in an 100% under -0.063 mm. Change of particle size distribution was not significant for longer milling times, however particle sizes determined for 90 and 120 min of milling were still higher than those for 30 and 60 min of milling.

Results and Discussion

Modification experiments were carried out according to the full factorial design of experiments. The variables studied were the effect of modifier reagent dosage, stirring velocity, modification time, sample and mill ball mass ratio and ball filling volume ratio. The final sample was characterized by TGA measurements. The weight loss was calculated from thermogravimetry-differential thermal analysis (TGA) curves. TGA analysis results gave in the Fig. 3, for siderite ore samples,respectively. In the other word, mechano-activated surface modification is very effect method for siderite magnetic properties modification.

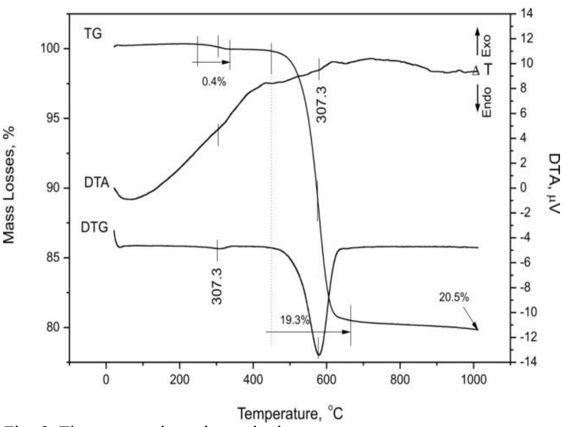

Fig. 2. Thermogravimetric analysis

In figure 2 DTA analyses show weight loss at 590°C.

Thermal analysis can provide great information on the decomposition, reduction and oxidation, phase changes, and structural changes of substances, and could be used to determine the effects of mechanical activation on the reactivity of the minerals and its relationship with structural changes during activation. Experimental tests were provided on 120 minutes time for grinding and 10, 15, and 20 grams. Tested sample was 330 grams of raw siderite ore. After grinding magnetic separation was done on slimes. Results of magnetic separation are presented in Tables 4, 5, 6, 7, 8 and 9.

Table 3.
Chemical analyses of siderite after grinding time 30 minutes and 5 grams CaO. Raw ore after grinding

Al_2O_3	BaO	CaO	Fe_2O_3
0,86	7,09	2,23	34,88
Na_2O	P_2O_5	SO_3	SiO_2
0,05	0,03	3,89	13,43
K_2O	MgO	MnO	TiO_2
0,13	4,37	7,15	0,03
3H			
22,78			

Table 4.
Magnetic product after grinding 120 minutes and 5 grams CaO

Al_2O_3	BaO	CaO	Fe_2O_3
0,55	4,47	3,18	38,31
Na_2O	P_2O_5	SO_3	SiO_2
0,06	0,02	2,16	6,82
K_2O	MgO	MnO	TiO_2
0,2	2,78	8,67	0,04
3H			
21,06			

Table 5.
Non magnetic product after grinding 120 minutes and 5 grams CaO

Al_2O_3	BaO	CaO	Fe_2O_3
0,93	7,77	3,16	29,31
Na_2O	P_2O_5	SO_3	SiO_2
0,05	0,03	3,76	15,82
K_2O	MgO	MnO	TiO_2
0,11	4,82	6,77	0,05
3H			
22,3			

Table 6.
Recovery of the products

Sample	grams	Recovery of Fe,%
Magnetic product	20	21,96
Non-magnetic product	80	78,04
Raw ore	100	100

From table 6 is obvious presence of highly magnetic phases and minerals recovered from low intensity magnetic separation. Intensity on the surface of magnetic drum of the separator is 0.13-0.14T.

Table 7.
Magnetic product after grinding 120 minutes and 10 grams CaO

Al_2O_3	BaO	CaO	Fe_2O_3
0,45	2,1	5,18	39,31
Na_2O	P_2O_5	SO_3	SiO_2
0,05	0,03	0,96	7,21
K_2O	MgO	MnO	TiO_2
0,05	1,8	7,85	0,05
3H			
21,42			

Table 8.
Non magnetic product after grinding 120 minutes and 10 grams CaO

Al_2O_3	BaO	CaO	Fe_2O_3
1,01	8,93	11,3	27,31
Na_2O	P_2O_5	SO_3	SiO_2
0,05	0,03	4,35	16,45
K_2O	MgO	MnO	TiO_2
0,15	5,32	6,87	0,03
3H			
20,52			

Table 9.
Recovery of the products

Sample	grams	Recovery of Fe,%
Magnetic product	27	30,42
Non-magnetic product	73	69,58
Raw ore	100	100

Table 10.
Magnetic product after grinding 120 minutes and 15 grams CaO

Al_2O_3	BaO	CaO	Fe_2O_3
1,22	4,11	6,18	40,91
Na_2O	P_2O_5	SO_3	SiO_2
0,05	0,03	2,72	5,75
K_2O	MgO	MnO	TiO_2
0,2	1,61	8,95	0,03
3H			
19,2			

Table 11.
Non magnetic product after grinding 120 minutes and 15 grams CaO

Al_2O_3	BaO	CaO	Fe_2O_3
3,92	8,33	12,18	32,41
Na_2O	P_2O_5	SO_3	SiO_2
0,06	0,04	4,14	16,56
K_2O	MgO	MnO	TiO_2
0,12	5,31	6,17	0,05
3H			
22,9			

Table 12.
Recovery of the products

Sample	grams	Recovery of Fe,%
Magnetic product	27	34
Non-magnetic product	73	66
Raw ore	100	100

Results from provided experiments represents recovery of 34% from sample of 100 gr. grinded for 120 minutes in addition of 15 grams of CaO for activation of siderite raw ore. Newly formed magnetic minerals (magnetite, maghemite) are attracted to magnetic separator with low intensity of magnetic field. This simple activation could reduce costs for traditional beneficiation followed grinding. The received slimes could easily enriched with WHIMS(wet high intensity magnetic separation) or traditional calcination reducing temperature for decarbonisation.

Conclusion

From energy saving points of view, activation of siderite with CaO will decrease the calcination temperature. Result of milling can be considered as an important issue. Simple, low cost utilization technology may be developed for existing siderite processing operations.

We have succeeded in preparing active and super-fine siderite particles with calcium oxide.

The results obtained from the experiments indicated that mechano-chemical surface modification of siderite in wet stirred ball mill is very effect method for decomposition of siderite and formation of new high magnetic minerals and phases. This technology could be used as a substitution of traditional calcinations of siderite ore.

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