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High-energy milling as a method for obtaining tetragonal form of PbO

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ABSTRACT

Purpose: The aim of this work was to verify the usefulness of high-energy milling, using electromagnetic mill, as a method for obtaining tetragonal (red) form of PbO, alternative to standard methods.
Design/methodology/approach: Experiments were held to compare samples of the yellow form of PbO after milling in electromagnetic mill with the ones milled in high-energy planetary ball mill as a function of grinding medium (sticks or balls) to powder mass ratio, milling duration and instrumental conditions.
Findings: Quantitative X-ray diffraction and analysis of granulation of mill products were applied. The characteristics of structural transitions of studied powder depending on milling conditions were defined.
Practical implications: Utilization of electromagnetic mills was found to be suitable for milling of PbO. The speed and unit price of this process assure competitiveness of the method to standard methods. Tested method of high-energy milling assures possibility to supply, in certain conditions, good product. Obtained product may be used for manufacturing of minium.
Originality/value: Optimum conditions of milling process and milling limitations were determined. Suggestions regarding optimization of mill construction were presented.
Keywords: Technological devices and equipment; High-energy milling; Lead oxides; X-ray phase analysis; Phase transformation

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1. Introduction

The aim of this work was to verify the usefulness of high-energy milling in electromagnetic mills as a method for obtaining red form of PbO and estimate cost-effectiveness of such milling.

On an industrial scale lead oxide PbO is obtained by oxidation of sprayed liquid metal particles in air. The process is conducted in a temperature range from 500 to 550°C. These values are higher than the temperature of phase transition from high-temperature orthorhombic (yellow) β-PbO phase into low-temperature tetragonal (red) α-PbO form, equal to 489°C [1]. As a result of rapid quenching, the obtained oxide is almost entirely composed of supercooled yellow form of PbO. This oxide is a raw material in manufacturing processes of other lead compounds, especially minium Pb_3O_4. Since manufacturing of minium from the red PbO is more effective, it is purposeful to optimize process of transformation of PbO form β into α form taking into account its duration and energy necessary for the transition to occur.

However, the industrial practice indicates that even very slow quenching of PbO does not lead to phase transition, contrary to mechanical interaction, i.e. grinding [2], which appears to be a very effective factor inducing the transition. High-energy milling appears very useful tool to obtain materials exhibiting unusual advantages [3-8]. The authors' research indicates that high-energy milling proved to be a very effective method of modification of hydrogen storage materials' structure [9]. Hence, the concept of investigation of grinding the yellow PbO powder in ultra-high energy mills, such as electromagnetic mills, is justified.

2. Experiment description

2.1. The principles of electromagnetic milling

The operation of electromagnetic mill is based on intentional formation of rotating magnetic field inside the mill, in order to force the grinding media to move [10]. It is, in a sense, a reversal of construction principles of electric engine, in which stator creates a constant field and the rotation of rotor is induced by cyclic conversion of its poles. In an electromagnetic mill the "rotor" are the grinding media spinning around a steel pipe placed between mill windings which create rotating magnetic field of required parameters.

Until recently, electromagnetic mills were less known and rarely used, because of their low efficiency which caused high losses in inductor windings [11, 12]. The research carried out by Sosiński [10] has laid foundations for constructing highly efficient electromagnetic mills. Implementation of the modern design assumptions enabled constructing at Czestochowa University of Technology an experimental mill with great possibilities and low energy consumption during work [13]. Its abilities have been utilized in different industrial applications [14-19]. This type of mill, in contrast to classical ball or roll mills, does not require movement of massive grinding media. The active surface of standard grinding media is relatively small in comparison with their mass, and the absorbed energy is used mostly for other purposes than material grinding - i.e. for transporting material between balls. The situation is opposite to grinding media used in electromagnetic mill, where ferromagnetic sticks made of low-carbon steel could be used. As initially calculated by authors of work [15], costs of investment and operation of electromagnetic mill would be a few times lower than that of ball mill of comparable yield. Also the harmfulness of electromagnetic mill for environment is many times lower which is connected to incomparably lower level of emitted noise. It is, therefore, purposeful to investigate the use of electromagnetic mill also in the case where grinding is not only supposed to grind used material but most of all to provide propellant energy for phase transition.

2.2. Grinding conditions

Usefulness of electromagnetic mill was analyzed through grinding of yellow form of PbO. A commercial PbO powder of purity over 98.8% was used. Experiments were held with a maximum possible power load of mill of this construction that is 230 V × 120 A. Low-carbon steel sticks of ϕ 1.0 mm × 10 mm dimensions of total mass of 375 g were used as grinding media. Mass of ground powder was equal to 63, 125, 250, 375, 500 and 750 g and the grinding media to powder mass ratio was about 6:1, 3:1, 1.5:1, 1:1, 0.75:1, and 0.5:1, respectively. These initial values slightly increased as a result of collecting the samples for analysis after assumed milling times. To minimize changes of the ratio of grinding media to powder, small samples were collected, of mass about 1-1.5 g, sufficient to perform basic analyses.

Milling chamber was a steel pipe with steel grinding media. During the tests they were heated rapidly. After more than 2.5 minutes of milling, the temperature inside the chamber was exceeding 100°C and the cooling water was boiling on the chamber walls. Therefore, series of shorter milling times of about 2 minutes were applied, and after each milling step the chamber was cooled from outside with a stream of cold water. Samples for analyses were collected after total milling times forming a geometric series and equal to 2, 4, 8, 15 and, in one case, 30 minutes.

In order to compare the results of milling in electromagnetic mill with results of milling in classical mill, tests of grinding of the same material in high-energy laboratory planetary ball mill PM-400 from Retsch company, were performed. A 350 ml container was used to mill batches of 50 g of PbO with speed of 200 or 300 rpm. Using the full rated power of the mill's engine of 1500 W, it was theoretically possible to mill at one go up to 100 g of powder with 400 rpm mill speed. Steel balls of diameter of 10 mm and total mass of 350 g were used for milling.

Three tests of milling in a ball mill were made. The first one took 30 minutes in total, speed of the mill was 200 rpm, and samples were collected after 2, 4, 8, 15 and 30 minutes of milling. The second and third testes were held for speed of 300 rpm, and samples were collected after 30 minutes and 1, 2, 4 and 8 hours of milling. During the first and second tests of milling of PbO powder dry conditions were adopted, while during third one - PbO was milled in a protective environment of acetone.

2.3. Analytical methods

Collected samples were examined with quantitative X-ray phase analysis, and chosen samples also with chemical analysis, granulation analysis and density measurements.

Phase analysis was made with X-ray diffractometer XRD7 with Co Kα radiation. Identification of phases was made based on the data from JCPDS-ICDD catalogues [20]. Quantitative content of samples was determined with Rietveld method by SIROQUANT™ software with database enriched by own diffraction patterns.

Analysis of granulation was made with wet method, in a water suspension, using Fritsch Particle Sizer Analysette 22 NanoTec. Density measurements of samples were made with AccuPyc 1330 from Micrometrics.

3. Experimental results

Starting material contained a little amount of phases other than yellow PbO form, with only 2.1% of red form of PbO. X-ray phase analysis showed that the content of yellow form of PbO decreased during milling, in favour of the red PbO form, however with a slight dependence on the adopted milling conditions. These changes are evidenced in Figures 1-3 and collected in Tables 1 and 2.

Very weak diffraction lines of metallic lead and minium were visible in diffraction patterns of initial material and material after milling. However, the intensities of the lines decreased, probably because of broadening resulting from mechanical treatment.

Large milling times have brought increase of α-PbO line intensities together with an upcoming of alkaline lead carbonate lines. The amount of these new phases has sometimes reached even few tens of percent, after long milling in ball mill without a protective environment of acetone (Fig. 4 and Table 3).

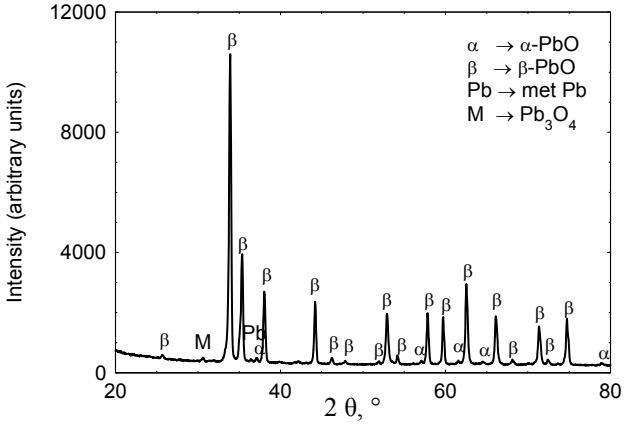

Fig. 1. X-ray diffraction patterns of initial powder

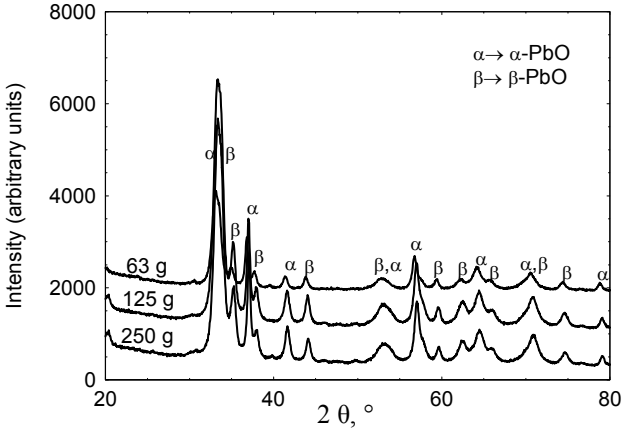

Fig. 2. X-ray diffraction patterns of the powders milled for 15 min. in electromagnetic mill, depending on the mass of the batch. Well-dried chamber mill

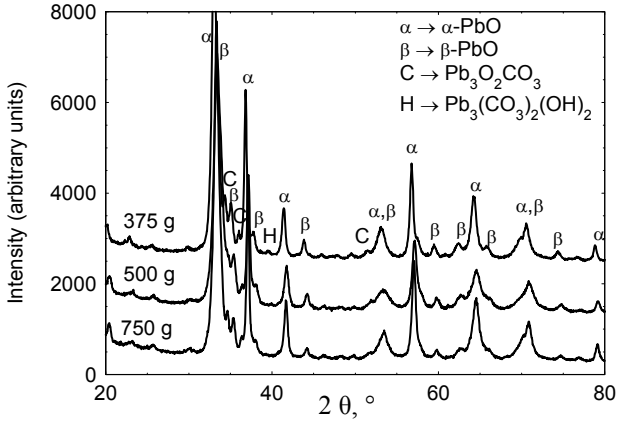

Fig. 3. X-ray diffraction patterns of the powders milled for 15 min. in electromagnetic mill, depending on the mass of the batch. Wet chamber mill

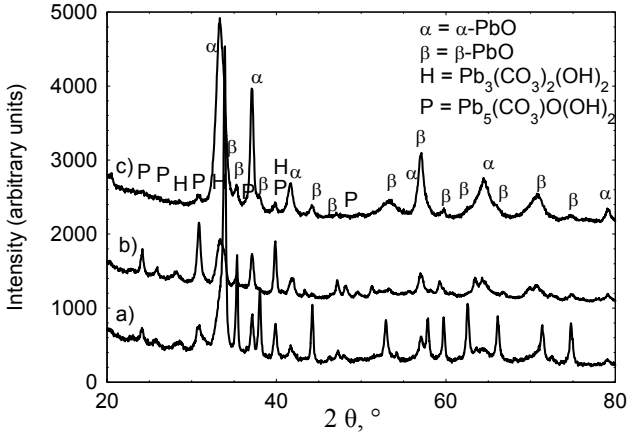

Fig. 4. X-ray diffraction patterns of the powders milled for 30 min in ball mill. a) 200 rpm, b) 300 rpm, c) 300 rpm in acetone

The less efficient process has been also noticed for some samples milled in electromagnetic mill (Fig. 3). It was not present in samples of masses equal to 63, 125 and 250 g. In case of samples of 375, 500 and 750 g weight the content of alkaline lead carbonate inside milled material was reaching a few percent and more. This could be related to the fact that before milling samples of weight of 375, 500 and 750 g, the milling chamber had been washed with water. Despite the later cleaning with alcohol and careful drying, some of the water could still have been present in the chamber. This could be the same cause for formation of alkaline lead carbonate in ball mill. In all, such behaviour indicates a very high absorptivity of CO_2 and moisture from the air of PbO which had initially very small grains and strongly developed surface.

The fragmentation additionally increased as a result of intensive milling, which is evidenced in Table 4. Figures 5-7 show, respectively, granulation distribution in initial material (Fig. 5), in material after 8 hours of milling in ball mill (Fig. 6) and typical composition for a material milled in electromagnetic mill (Fig. 7).

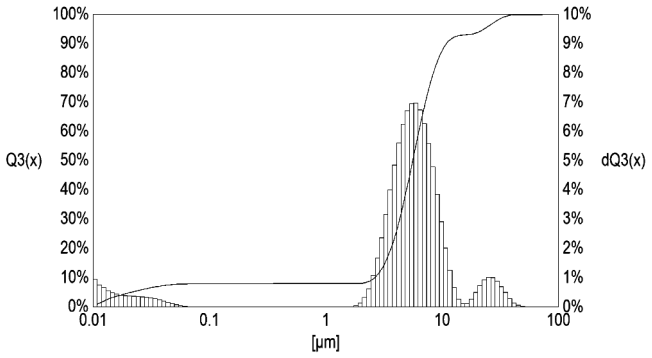

Fig. 5. Granulation distribution in initial PbO powder

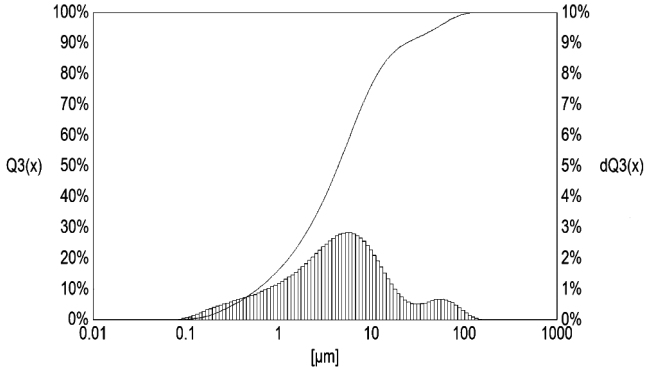

Fig. 6. Granulation distribution in the powder milled in ball mill, 300 rpm/8 h

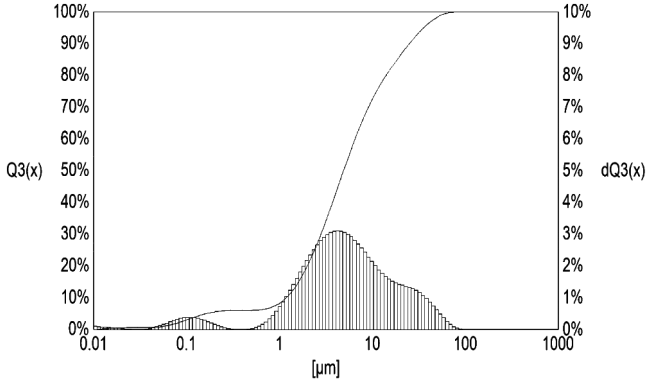

Fig. 7. Granulation distribution in the powder (batch III) after 15 min of milling in electromagnetic mill

In material ground in electromagnetic mill two fractions are present - a fraction with particle diameter fluently ranging from 1 to 100 µm and a fraction of particles of diameter of about 0.1 µm. The small particle fraction is not present in material milled in ball mill.

High-energy milling is also a reason for high density of lattice defects. It is evidenced through broadening of diffraction lines and decrease of milled material's density caused by increase in defect density, which is equivalent to increase in internal energy of milled powder. This density is underestimated in relation to density expected from quantitative phase composition and theoretically calculated densities of constituent phases (Table 5). This is mostly the effect of presence of crystal structure defects - dislocations, stresses and pores introduced with very intensive milling.

In general, during high-energy milling in electromagnetic mill in the presence of water the growth of unexpected phases, mostly alkaline lead carbonates, must be taken into account when planning industrial conditions of milling.

Additional undesired impurity is iron (Table 6), which is introduced into the material during intense milling from rather soft grinding media that are rubbing off. The rubbing off the grinding material is the weaker, the lower is the grinding media to powder mass ratio, and is present in all studied cases. It also requires taking into account in a future industrial practice.

4. Discussion of results

Effectiveness of milling process, in the sense of obtaining the desired amount of red form of PbO, is similar for all samples. Initially the effectiveness of the process is noticeably lower when the mass of milled powder is small. This is probably due to high grinding media to powder mass ratio. Therefore, during milling process the grinding media hit mostly each other rather than the PbO particles. However, after 8 to 15 minutes these differences nearly vanish. For lower ratios, that is for powder mass of 375 g, 500 g and 750 g, this effectiveness seems to be even slightly higher. It is likely that a similar relationship exists also for a little larger powder masses.

Another possible reason for this increase was the presence of a little amount of water in batches IV-VI during milling. It had been experimentally proven [2] that a presence of up to a few percent of water in the milled material facilitates the transformation of yellow PbO into red one. Wet milling is also one of the reasons for high amount of α-PbO in the powder milled in ball mill in acetone. Nevertheless, such intense milling as in electromagnetic mill causes the water to boil and evaporate. A side effect of the process is formation of alkaline lead carbonates at the expense of the proper transformation, which makes milling in the presence of water unfavourable.

On the other hand because of the intense milling not only the duration of the process is shorter but also one obtains a product of highly defected structure and, as a result, of increased energy. Similarly, as described in the papers by Nowosielski [7] and Adamiak [8], it is evidenced through a considerable increase in the width of diffraction lines and decrease in the milled powder's density due to increase in density of lattice defects. In the case of milling in electromagnetic mill that decrease is even much larger than when using ball mill, and increase in amount of finest grain fractions is faster (Figures 6 and 7). Increase in lattice defects is conducive to increasing the reactivity of the product, as a rule. Therefore, it is found to be a profitable result of grinding in electromagnetic mill.

Table 1.
Results of quantitative phase analysis of PbO samples ground in electromagnetic mill for 15 minutes depending on the mass of milled powder, % mass.

Material (batch & mass of the milled powder)	initial powder	batch I - 63 g	batch II -125 g	batch III - 250 g	batch IV - 375 g	batch V -500 g	batch VI - 750 g	ball mill, 200 rpm
Litharge α-PbO (red)	2.1	77.1	78.2	78.9	77.4	76.5	78.7	7.8
Massicot β-PbO (yellow)	96.8	22.9	21.8	21.1	11.6	8.2	7.9	69.5
Minium Pb_3O_4	0.7	-	-	-	-	-	-	-
Pb metallic	0.4	-	-	-	-	-	-	-
$Pb_3O_2CO_3$	-	-	-	-	11.0	15.3	13.4	-
$Pb_5(CO_3)_3O(OH)_2$		-	-	-	-	-	-	15.8
$Pb_3(CO_3)_2(OH)_2$	-	-	-	-	-	-	-	6.9

Table 2.
Results of quantitative phase analysis of PbO samples ground in electromagnetic mill. The amount of red PbO phase in the milled powder depending on duration and milling conditions, mass %.

Material	batch I - 63 g	batch II - 125 g	batch III - 250 g	batch IV - 375 g	batch V - 500 g	batch VI - 750 g	ball mill, 200 rpm	ball mill, 300 rpm	ball mill, 300 rpm + acetone
2 min.	63.0	62.8	62.3	63.9	62.2	59.4	3.9		
4 min.	68.7	69.1	70.5	71.3	73.2	72.1	5.6		
8 min.	73.8	73.2	75.5	78.8	79.6	81.6	6.9		
15 min.	77.1	78.2	78.9	77.4	76.5	78.7	7.8		
30 min.		83.9		75.5			8.9	37.1	83.1
2 h								34.2	84.5
8 h								31.6	82.9

Table 3.
Total amount of alkaline lead carbonates* in the milled powder depending on duration and milling conditions, mass %.

Material	batch I - 63 g	batch II - 125 g	batch III - 250 g	batch IV - 375 g	batch V - 500 g	batch VI - 750 g	ball mill, 200 rpm	ball mill, 300 rpm	ball mill, 300 rpm + acetone
2 min.	-	-	-	1.7	3.4	3.0	9.7		
4 min.	-	-	-	4.9	6.6	5.5	14.1		
8 min.	-	-	-	7.5	9.4	9.0	18.7		
15 min.	-	-	-	11.0	15.3	13.4	22.7		
30 min.		-		14.8			24.1	51.4	5.1
2 h								57.1	7.0
8 h								61.7	10.3

*)Powder milled in electromagnetic mill contained mostly $Pb_3O_2(CO_3)$ and powder milled in ball mill - mostly $Pb_5(CO_3)_3O(OH)_2$ and $Pb_3(CO_3)_2(OH)_2$

Table 4.
Granulation parameters of material of various quantities milled for 15 minutes (sample in ball mill - for 8 hours).

Material	initial	63 g	125 g	250 g	375 g	500 g	750 g	ball mill, 300 rpm
Modal diameter, μm	5.69	4.59	4.09	4.00	3.35	3.36	3.33	5.71
Median diameter, μm	5.60	5.66	5.64	4.89	4.65	4.39	4.15	4.37

Table 5.
The density of material of various quantities milled for 15 minutes (sample in ball mill - for 8 hours).

Material	initial	63 g	125 g	250 g	375 g	500 g	750 g	ball mill, 300 rpm
Measured density, g/cm^3	9.613	9.072	9.136	9.139	8.903	8.883	8.956	7.860
Calculated density*, g/cm^3	9.636	9.421	9.417	9.415	9.328	9.197	9.219	7.948
The difference, %	-0.24	-3.70	-2.99	-2.94	-3.83	-3.41	-2.85	-1.10

*) Weighted average of the densities of crystalline phases present in respective sample, calculated based on atomic masses and crystal cell parameters (data from JCPDS-ICDD [20]) and quantitative content shown in Tables 1 and 2

Table 6.
Iron content in samples after milling for 15 minutes in electromagnetic mill (sample in ball mill - for 8 hours).

Material	initial	63 g	125 g	250 g	375 g	500 g	750 g	ball mill, 300 rpm
Fe content, mass %	0.001	0.95	0.42	0.13	0.10	0.06	0.04	0.02

However, none of the processes have given the effectiveness of 90% or more, and the time of 15 minutes and even 30 minutes of milling, even in an electromagnetic mill, appears to be still too short. Rough estimates indicate that this process should be held for an hour or a little longer.

What is more, it is essential to solve a problem of overheating of milling chamber during milling for a time longer than an hour. In case of electromagnetic mills for milling PbO at industrial scale, it would be difficult to stop the process every 2-3 minutes, not to allow overheating the milling chamber which would be harmless not only for the equipment but also for the speed of transition from yellow to red form of PbO. It is, therefore, necessary to develop a running system of cooling of the chamber, which will not interrupt the interaction of the magnetic field with the grinding media.

Another factor that negatively influences the product quality is rubbing off of grinding media during milling. Even with the grinding media to powder mass ratio was equal 0.5:1, the amount of iron present in the milled powder was largely enhanced in relation to the initial material, already after 15 minutes of milling. It is as well a factor difficult to eliminate in the process of electromagnetic milling, where for proper work it is necessary for the grinding media to be made of ferromagnetic material. Therefore, they cannot be replaced with grinding media which are more resistant to rubbing off, i.e. made of WC or ZrO_2 but, at most with media made of more hard steel.

5. Final remarks and conclusions

The most essential factor in selection of the technology for industry is the factor of economy. It decides about the purpose of further investigation, or the lack of it, in order to improve the procedure of production of red PbO form using electromagnetic mills.

Considering the ratio of mass of obtained red PbO form to used energy, it can be deducted that the optimal conditions of milling are conditions with maximum usage of milling chamber which is equivalent to milling of maximum mass of PbO, even larger than 750 g. Even such a high mass did not trigger essential suppression of movement of the grinding media in the rotating magnetic field and the decrease in milling effectiveness did not occur, which has been confirmed by results of analyses. A decrease in effectiveness of the transformation process, expected when even more mass of PbO is milled, will be at least partially compensated by an increase in the amount of obtained red PbO form.

With full use of power of the planetary ball mill, it has a power load of 15 W per gram of milled powder. According to the experimental conditions defined in chapter 2.2, the data for electromagnetic mill are equal to 2.76 kW per 750 g powder, which gives a power load of 3.7 W/g. Hence, the calculated costs, obtained for electromagnetic mill, are four times lower than that

for a ball mill. Application of electromagnetic mill, therefore, appears to be very price competitive even with the same process duration in which the same amount of α-PbO is created.

However, according to data in Table 2, the same amount of red PbO in the milled powder could be obtained after much longer milling time in classical mill than in electromagnetic mill with well-dried chamber mill. Therefore, the unit of energy usage should be significantly smaller when using electromagnetic mill. The unit cost of α-PbO production should in that case be also significantly smaller, even taking into account necessary adaptation of the mill to provide a continuous work without danger of overheating and to obtain conditions required to produce a powder sufficiently pure.

Taking into consideration factors connected to production time, especially the cost of labour, the proportions become even more beneficial, than those calculated from estimated power use. Despite the stated critical remarks, it is, therefore, purposeful to continue the investigation and improvement of the procedure of lead oxide milling in electromagnetic mill in order to possibly develop a price competitive production of red form of PbO. Based on the previous effects of works there are great expectations of implementation in industry of other technologies using high-energy and highly efficient electromagnetic mills of similar construction to the one that has been tested.

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