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SERPENTINE WASTE MILLING

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Serpentine heaps in the surroundings of Dobšina are a long-life ecological problem of the city and at the same time a suitable raw material for production of $MgCl_2$ and SiO_2. In the technological scheme of chemical processing the milling operation it has an important role. In this context the milling rate is an important parameter for creation of the technological scheme and suggestion of industrial equipment.

Key words: *serpentine waste, milling, technological scheme, $MgCl_2$, SiO_2*

Mljevenje otpadnog serpentinita. Serpentinitne hrpe u okolici Dobšine su dugotrajan ekološki problem grada, no i istovremeno pogodna sirovina za proizvodnju $MgCl_2$ i SiO_2. Operacija mljevenja ima važnu ulogu u tehnološkoj shemi kemijskog procesa. Pri tom je za stvaranje tehnološke sheme i prijedlog industrijske opreme brzina mljevenja važan parametar.

Ključne riječi: *serpentinit otpadni, mljevenje, tehnološka shema, magnezijev klorid, silicijev dioksid*

INTRODUCTION

The results of one part of research involving hydrometallurgical procedure of obtaining two types of material from secondary raw serpentine summarises this paper: $MgCl_2$ and high-purity SiO_2 that SiO_2 content is from 95 to 98 %. Such materials find in wide variety of the fields: $MgCl_2$ is raw material for Magnesium production, SiO_2 find possible uses for electronics industry, for silicon production, for quartz glass etc. The technological line consists of two separate parts that includes physical processing of the raw material, that is describes in this article and chemical production of SiO_2 and $MgCl_2$ [1].

The paper is oriented to particularity of serpentine milling that is optimal for obtaining of SiO_2 and $MgCl_2$. Numerical simulation of kinetic study in serpentine milling has the great practical importance, because it enables determination between the delay time of material in the mill and elimination unfavourable influence of fine grains in the batch.

Partial information on SiO_2 and $MgCl_2$ production from serpentine waste heap in Dobšiná has already been published [1]. The basic precondition for serpentine leaching is grinding of material to fraction 0 - 0,25 mm.

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Milling of raw material is a universal technological operation characterised by high energy consumption and low effectiveness of its usage.

Processes at the milling can be evaluated from different points of view, e.g. physically-mechanical, dynamical, statistical, energy, etc. [2 - 4]. One of them is the kinetic aspect of milling [5]. The process of milling as to the speed can be simulated from the position of analogy with chemical reactions or according to semi-empiric or empiric equations, according to integral-derivative or matrix models. In spite of progress in the field of designing industrial milling units it is based on empiric basics and phenomenological effects.

HISTORY AND BASICS OF MILLING KINETICS STUDY

Since the first using of industrial cylindrical mills (1876) in general the milling speed is proportional to the amount of larger particles in the particular moment in the mill. Similarly to the chemical reactions decrease of amount of larger particles in the mill is proportional to its amount at the beginning of the time period and the following equation is valid

$$\frac{dR}{d\tau} = -k \cdot R^n \quad (1)$$

which for $n = 1$ is according to C. Mitag (1928) and A. I. Zagustin (1935) [6].

Solution of the differential equation is

$$R(\tau)=R(0)\cdot \mathrm{e}^{-k\tau} \tag{2}$$

which is often used in the following form

$$R(\tau)=k\cdot \mathrm{e}^{-m\tau} \tag{2a}$$

in the case when $n = 0$, it is a reaction of zero place value, which is suitable for milling kinetics description in rod mills.

$$R(\tau)=R(0)-k\tau \tag{3}$$

For $n \neq 1$ a general solution of equation (1) is

$$R^{(1-n)}(\tau)=R^{(1-n)}(0)-(1-n)\cdot k\tau \tag{4}$$

The meaning of symbols is the following:

$R(\tau)$, $R(0)$ - rest on sieve of selected mesh in time τ and at the beginning,
k - speed constant of milling,
n - reaction place value,
τ - time.

To the category of semi-empiric equations belongs the equation, which was presented by V. V.

Tovarov and V. P. Romadin after many milling experiments as

$$\frac{\mathrm{d}R}{\mathrm{d}\tau}=-k\cdot m\cdot R\cdot \tau^{m-1} \tag{5}$$

The solution of this equation is

$$R(\tau)=R(0)\cdot \mathrm{e}^{-k\tau^{m}} \tag{6}$$

or in the form of common logarithm it is

$$R(\tau)=R(0)\cdot 10^{-k\tau^{m}} \tag{6a}$$

which was used more often in the past [3].

The parameter m - characterises the change of milling speed with the time. The possibility of material milling is changing by time [6] and for different granularity classes is always different. Equations (6) or (6a) describe the milling process in spherical mills for particle size 5 - 90 % [7].

Different modifications of these equations were developed and created at the same time. S. F. Šinkorenko (1977) considers the most suitable milling kinetics model for milling different types of iron ores from Krivoj Rog the modified equation of V. V. Tovarov

$$R(\tau)=R(0)\mathrm{e}^{-k[\tau\cdot\ln(\tau+1)]} \tag{7}$$

A big advantage of these equations is the simplicity, relatively problem less gaining of data and the possibility of their graphic evaluation. By linearization of equations (1) - (7) it is possible to estimate the parameters k, n and m.

A big disadvantage is that the equations do not enable creating of a milling model or designing of a milling unit without further complementary data.

An interesting phenomenon in the field of milling are the famous energy models of crushing known as the theories of P. Rittinger, V. L. Kirpičov, F. Kick and F. C. Bond [2, 8, 9].

The theory of Bond was used in practice, because it enables suggestion of industrial milling machineries according to the milling experiments. Its big disadvantage is relatively broad milling experiments, which can be simplified by suggestions of various authors [10].

EXPERIMENTAL PROCEDURE

The following parameters were studied at milling of serpentine waste under particular conditions in a laboratory mill with diameter D = 316 mm (26,4 l):

- rate of new particle size class (NPSC) creation / $g\cdot s^{-1}$,
- energy consumption for creating a unit amount of particle size class 0 - 0,25 mm - NPSC.

At milling experiments it was necessary to take into account the conditions that arise:

- from requirements considered for the input fraction to the leaching reactor, minimum 96 % of 0 - 0,25 mm fraction,
- from required suspension density 1510 $kg\cdot m^{-3}$, R = 1,85.

Considering the aim of research work, which is determination of milling conditions and project of milling technological method, it was necessary to:

- verify the influence of selected factors on rate of NPSC creation 0 - 0,25 mm,
- verify the milling of batch with different content of fraction 0 - 0,25 mm.

For research needs following types of mill batch were used:

P - original batch with fraction 0 - 1 mm containing 58,9 % of fine fraction,
A - batch with fraction 0 - 1 mm containing 31,0 % of fine fraction,

B - batch with fraction 0 - 1 mm containing 15,0 % of fine fraction.

In practice spherical mill always works in closed cycle with hydraulic sorter when milling in wet medium. When the hydraulic sorter is operated in the function of control sorting as well as pre-sorting, the mill batch can be of similar composition as the B type batch at a relatively good sorting efficiency. At a low sorting efficiency the A type batch is considered.

From technological conditions it is necessary to mention that steel spheres weighing 20000 g with diameter 20, 30 and 40 mm were used for milling.

Milling experiments verifiably confirmed the following facts [11]:

- suspension dilution $R = m_w/m$ expressed by weight proportion of liquid m_w and solid phase m has no significant influence on milling speed in the range R = 1,67 - 3,0,
- granularity of batch, especially the content of particle size class 0 - 0,25 mm, has an underlying influence on milling speed,
- mill rotation in the range φ = 64 - 93 % significantly influences the creation of NPSC 0 - 0,25 mm at milling.

Table 1. **Counted parameters of equations (2), (6) and (7)**
Tablica 1. **Izračunati parametri jednadžbi (2), (6) i (7)**

Batch type	Parameter	Equation (2) $R(\tau) = k \cdot e^{-m\tau}$	Equation (6) $R(\tau) = R(0) \cdot e^{-k\tau^m}$	Equation (7) $R(\tau) = R(0) \cdot e^{-k[\tau + \ln(\tau+1)]}$
Type P	ln k	-	–2,3321	–2,3099
	k	1328,3	0,0971	0,0993
	m	–0,1456	1,0928	0,7890
	R^2	0,9973	1,0382	0,9990
Type A	ln k	-	–2,2582	–2,2451
	k	1952,8	0,1045	0,1059
	m	–0,0527	0,7778	0,5624
	R^2	0,9865	1,0009	0,9996
Type B	ln k	-	–2,1427	–2,1280
	k	2397,4	0,1173	0,1191
	m	–0,0656	0,8123	0,5870
	R^2	0,9900	0,9959	0,9955

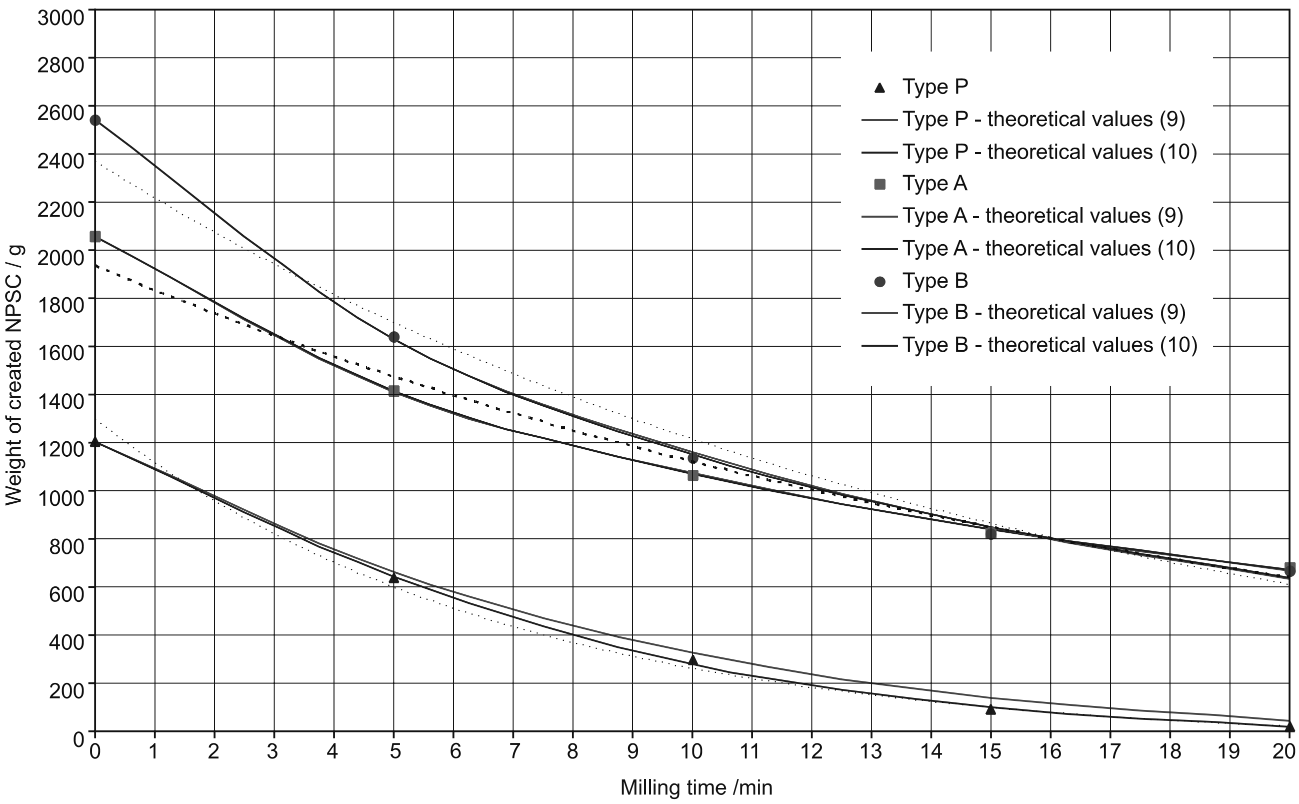

Figure 1. **Kinetics of serpentine raw material milling. The approximating function (2) is presented in the form of thin lines not introduced in the legend. Parameters of functions (6) and (7) were calculated using the method of least squares regression analysis**
Slika 1. **Kinetika mljevenja serpentinitne sirovine. Aproksimacijska funkcija (2) prikazana je u obliku tanke linije koja nije navedena u legendi. Parametri funkcija (6) i (7) izračunati su metodom najmanjih kvadrata**

Monitoring of newly created class at experiments was realised in 5 minute intervals. It was always milled for a particular time: 5, 10, 15 and 20 minutes (weight of batch: 3000 g; suspension dilution: R = 1,67). After milling experiment the whole volume of sample 3000 g material + water was analysed for particle size distribution on sieves.

The results of milling experiments are presented in Figure 1. in the form of integral data and the differential data are presented in Figure 2.

Counted parameters of kinetic equations are introduced in Table 1.

According to the value of deterioration coefficient, except for one case, the equations describe adequately the empiric data and it is possible to use them for prediction of amount of created NPSC at different milling times. The following equation can be used for counting the amount of created NPSC, considering fraction 0 - 0,25 mm:

$$D(\tau)+R(\tau)=R(0) \qquad (8)$$

$D(\tau)$ - amount of created NPSC 0 - 0,25 mm [g]
$R(0)$ - amount of rough particle size class (0,25 - 1 mm) at the beginning of milling, τ = 0.

RESULTS AND DISCUSSION

Presented results of milling experiments represent broad information potential that is possible to use for design of industrial milling cycle. Briefly they can be presented as follows:

- rate of creation of NPSC, according to Figure 1. and 2., decreases with time and the energy consumption increases;
- rate of creation of NPSC is influenced by the content of fine grains in the batch. With growing amount of fraction 0 - 0,25 mm the rate decreases in batch B > A > P;
- with increasing delay time of raw material in the mill the energy consumption increases hugely, Figure 2. With growing content of fine grains in the mill elimination of kinetic energy of the milling spheres occurs;
- energy consumption for creation of unit amount of fine fraction after longer milling time is extremely high;
- energy consumption widely influences the efficiency of mechanical transfer of torque from electric motor to the mill, therefore the measured values allow relative evaluation of milling efficiency and they are not suitable for determination of absolute energy consumption.

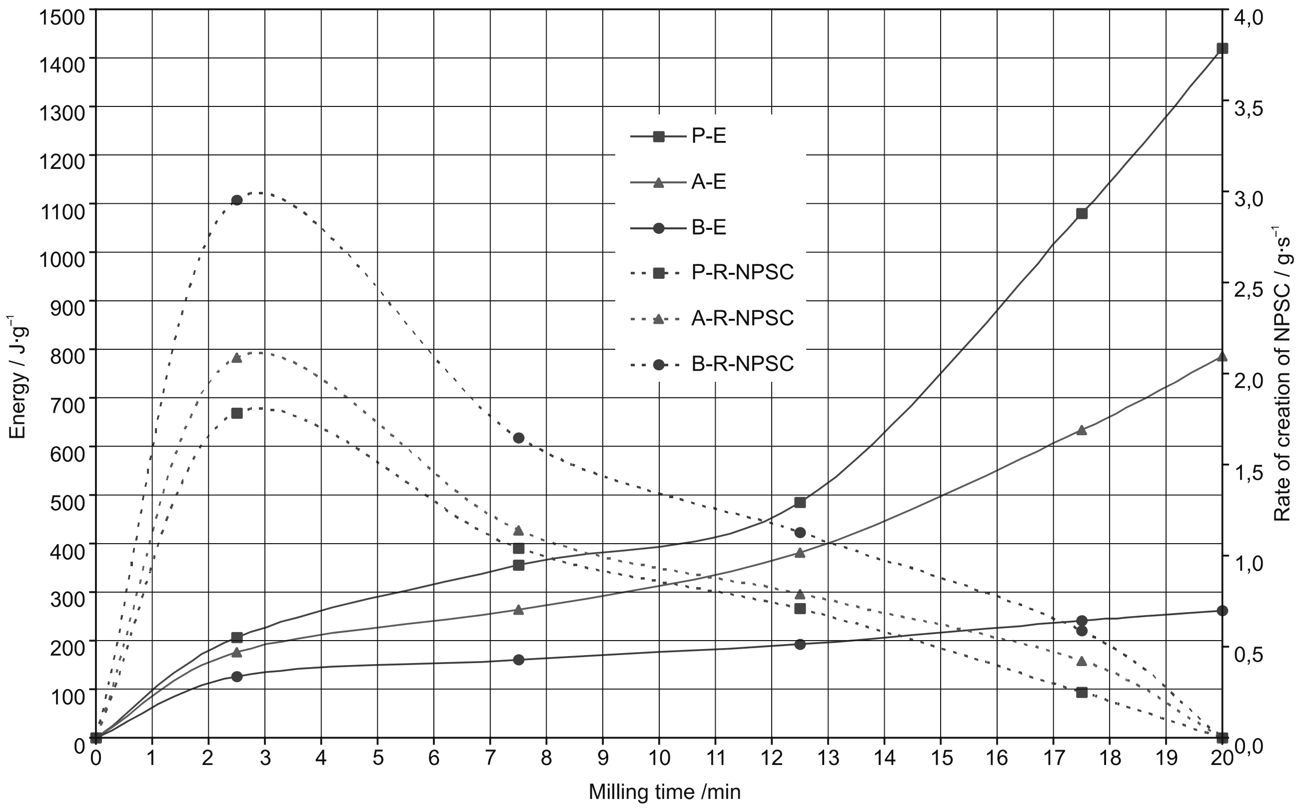

Figure 2. **Differential data of milling kinetics, rate of creation of NPSC / g·s^{1} and energy consumption for its creation / J·g^{1}**
Slika 2. **Diferencijalni podaci kinetike mljevenja, brzina stvaranja NPSC / g·s^{1} i potrošena energija stvaranja / J·g^{1}**

CONCLUSIONS

Milling of serpentine waste provides important information that can be used for designing of mill in preparatory project. Anyway in the designs of milling cycle it is necessary to

- reduce the delay time of material in the mill,
- eliminate unfavourable influence of fine grains in the batch,
- solve optimisation analysis: granularity of the batch - mill rotation speed - energy consumption - amount of created NPSC by simulation program.

For regulation of milling technological knot it is necessary to create a dynamic model: mill - hydraulic sorter or hydraulic sorter - mill - hydraulic sorter.

REFERENCES

[1] A. Pietriková, M. Búgel, M. Golja: Preparation of SiO_2 powder through leaching of serpentine, Metalurgija 43 (2004) 4, 299 - 304.
[2] M. Brozek, W. Maczka, T. Tumidajski: Modele matematyczne procesów rozdrabniania, UWND AGH Krakow 1995.
[3] F. Jusko: Štúdium kinetiky mletia rúd a jej význam v úpravníckej praxi. Kandidátska dizertačná práca, Kremnica 1965.
[4] K. Trybalski: Analiza wlasciwosci dynamicznych procesów ukladów technologicznych przerobki surowców mineralnych, UWND AGH Krakow 1999.
[5] N. Magdalinovič, I. Budič, N. Čalič, R. Tomanec: Kinetika mlevenja (Kinetics of Grinding), Univerzite u Beogradu, TF Bor, 1994.
[6] V. A. Perov, V. J. Brand: Mletí rúd, SNTL Praha 1953.
[7] S. F. Šinkorenko: Technologia izmeľčenija rud černych metallov, Nedra Moskva 1984, 543.
[8] F. Jusko: Niekoľko poznámok k tretej teórii F. C. Bonda a jej aplikovateľnosti pre prevádzkové podmienky. Zb. Vedecká banícka konferencia, sekcia úpravnícka, Košice 1967, pp. 54-67.
[9] Spravočnik po obogaščeniju rud. Podgotoviteľnyje procesy. Nedra Moskva 1982.
[10] B. Tora: Wybranie metody badania podatnošči na mielenje. Inžynieria mineralna-zeszyt specjalny 3/2003.
[11] M. Leško, M. Búgel, A. Pietriková, T. Bakalár: Transformácia výsledkov mletia serpentinitového odpadu z laboratórnych na prevádzkové podmienky. Zb. Odpady 2004, pp. 13 - 16.
[12] M. Leško, M. Búgel, T. Bakalár, A. Pietriková: Kinetics of serpentine waste milling. Zb. 9th Conference on Environment and Mineral Processing, Part II, Ostrava 2005, pp. 335 - 338.
[13] A. J. Lynch: Cikly droblenija i izmeľčenija, Nedra Moskva 1981.
[14] S. F. Šinkorenko: Novyje uravnenija kinetiki izmeľčenija, Fiziko-mechaničeskije problemy razrabotki poleznych iskopajemych (1977) 4, 46 - 54.

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