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CHEMICAL AND PHYSICAL PROPERTIES OF GROUND MAGNESITE ROCK AS MAGNESIUM MANURE

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Summary

According to valid STN, the semi-product is understood as a suitable manure containing magnesium and calcium after ejecting fraction above 0,5 mm. In average, the semi-products and raw materials in question contain 86,64 % $MgCO_3$ a 8,30 % $CaCO_3$, that responds to 46,46 % MgO and 4,65 % CaO. It is also suitable for alternative agriculture, where is required sufficient contents of magnesium in matured products. The decisive portion of magnesium is bound in carbonates, magnesium in silicate forms complements it. The product has got a relative high contents of manganese of 1643,68 $mg.kg^{-1}$, however the mobilisable contents of it represents only 0,3%. Also other controlled micro-elements (Cu, Zn, Co) are appeared in forms not suitable for vegetables.

Keywords: magnesite manure, magnesium, calcium, grain composition, heavy metals, trace elements

Introduction

Magnesium is ranked as a basic nutriment of vegetal and animal organisms. Vegetables contain it bound in chlorophyll, animals in various body organs, in bones, blood serum etc.
The question of magnesium insufficiency and the effect of it on agriculture products yield reducing was searched by many authors (FECENKO, 1995; HOLOBRADÝ et all.1975; NEUBERG et all.1995; MATULA et all.,1996; RUŽICKA, 1996;BAIER,1996;VANEK,1996). What concerns of the nutrition of vegetables with magnesium, the authors specify the following contents of exchange cations in soil as "optimal": 60 % Ca, 10 % Mg, 20 % H a 5 % K. For sorptive saturated soils (muck, brown soil, black soils and fluvial soils), the contents of calcium mostly exceeds 65%, and the contents of magnesium is in contrary less than 10%.
Generally, the average contents of magnesium in vegetal dry residue is given as 0,2 % and 80 μmol.g-1. From countries with high intensification are given more and more references on the symptoms of vegetal starvation not only on sand soils, but also on heavy soils (FECENKO 1986).

Materials and methods

For valuation of grain composition, chemical characteristics, contain of accesible nutrients, biological influential microelements, heavy metals (risky elements) and value of pH the samples were acquired from intermediate products in plant SMZ Jelšava, a.s. The samples were acquired from 10 various places to stored tumble of deposited waste from magnesit production. In samples were analysed chemical and physical properties.

Raw material and semi-products of SMZ Jelšava a.s.

The subject of our interests comprises the basic raw materials and semi-products of the magnesite factory of Jelšava, which are of carbonate type, and exploitable for nutrition of vegetables with magnesium as well as for soil de-acidification, however the problem is not still not resolved on the level of experimental and practical exploitation.
Classification of grain composition according to exploitation of semi-products and raw materials as magnesite, magnesite-calcareous and calcareous-magnesite manure.
With magnesite, magnesite-calcareous manure, their grain composition is taken as their determining physical property. According to valid STN, the size of particles is figured in mm, by residue on sieve, or fall through the sieve of specified mesh.

The results of grain assessment (granulometry) of ten samples taken from the stack of semi-products and raw materials deposited in the area of the factory are given in table No.1.
We express the size of particles in millimetres through a residue on the sieve in a size interval above 3 mm and under 0.05 mm in the following fractions:
No.1 > 3 mm; No.2 > 2 mm; No.3 > 1 mm; No.4 > 0,5 mm; No.6 > 0,05 mm; No.7 < 0,05 mm
The results of sieve analyses are referred in weight % as arithmetic average, average deviation and standard deviation. Following the results obtained, the size of the grains of the analysed semi-products and raw materials above 3 mm represents an average value of 4,68 % of their total weight. However, this value is strongly impacted by the size of the particles of the sample No.7 that comprises also grains above 3 mm, the ratio of which is more times higher than the ratios of other nine samples. In fact, such size of the grains of the classified materials is practically agrochemical indifferent, and therefore we assume such ratio as not suitable what concerns of agrochemical application. The next fraction of grains above 2 mm represents 10,59 %. The fraction less than 2 mm and above 1 mm represents 9,45 % particle ratio. Within the fourth

fraction we specified an average of 24,79 % of particles of a size under 1 mm and above 0,5 mm. The lowest percentage particle ratio of the referred size was within the sample No.7, namely 16,73 %. With other samples, the particle ratio of the

Table 1 Grain composition of semi-products and raw-materials

Sample No.	(1) >3 mm	(2) >2 mm	(3) >1 mm	(4) >0,5 mm	(5) >0,1 mm	(6) >0,05 mm	(7) <0,05 mm
1	2,42	9,13	8,69	23,58	52,79	3,23	0,16
2	5,68	8,08	9,63	24,12	49,85	2,44	0,20
3	2,25	9,44	12,26	30,93	43,40	1,52	0,20
4	3,23	6,15	8,88	23,25	55,91	2,35	0,23
5	5,65	8,45	10,11	21,88	50,18	3,35	0,38
6	2,78	12,28	8,3	22,85	50,78	2,72	0,29
7	14,22	12,78	7,32	16,73	45,20	3,44	0,31
8	4,01	12,48	14,94	31,51	36,79	0,24	0,03
9	3,86	12,16	6,34	26,10	49,17	2,20	0,17
10	2,71	15,04	7,98	26,93	45,01	2,10	0,23
Average	4,68	10,59	9,45	24,79	47,91	2,36	0,22
Average deviation	2,30	2,31	2,52	3,26	4,25	0,68	0,07
Standard deviation	3,39	2,85	3,26	4,13	5,16	0,91	0,09

referred sizes was significantly higher. The highest percentage, for all samples, was determined in the interval of sizes under 0,5 mm and above 0,1 mm. The average percentage ratio represents 47,91 % , with minimum of 36,79 % and maximum of 55,91 %. The rest is represented by very fine grains under 0,1 mm that create 3,36 % with minimal differences in individual samples, but under 0,05 mm we determined a ratio of 0,22 %.
The interpretation of the given specification of fractions is that 74,27 % ratio of grains is contained in an interval of sizes under 1 mm, while the grains of a size above 1 mm represent 22,73 %. In our case it means a requirement for separation of the fraction above 0,5 mm.
In the case of hard limestone and dolomite limestone dominate such opinions that particles above 0,5 mm are of low agrochemical efficiency, and grains above 1 mm are classified as not efficient at all. The referred is to be fully applied also for the materials containing magnesium and calcium, analysed by us.
Classification of the effective constituents contents of semi-products and raw materials:
Beside the granularity, the next decisive feature of magnesite, magnesite-calcareous and calcareous manure is the contents of efficient constituent. It means at first the contents of magnesium acting as a nutriment, the way of its bound that determines solubility and agrochemical efficiency also.
Technical requirements for the quality of calcareous and magnesite manure according to valid STN prescribe that minimally 65 % of carbonate forms should be represented by $CaCO_3$ – $MgCO_3$ and maximal humidity of 1 %. A calcareous-magnesite manure according to STN 721210 with magnesium in carbonate form have the contents of $MgCO_3$ in dolomite limestones 4,6 – 22,9 %, in limestone dolomites 22,9 – 41,2 % and in dolomites 41,2 – 45,7 %.
Sample withdrawal for chemical analysis of the semi-products and products of SMZ Jelšava a.s. was executed according to STN 721210 as stated for calcareous and magnesite-calcareous manure produced from natural rocks by grinding exclusively.

Methodical procedures of chemical analyses

pH/H_2O: in suspension (20 g of fine soil sift through 2 mm sieve) prepared from fine soil and distilled water 1:2,5, and measured by electrometer method.
pH/KCl: in a suspension of fine soil and 1 M KCl in a ratio of 1:2,5, and measured by electrometer method.
Assessable Mg: 10 g of fine soil + 100 ml 0,05 $CaCl_2$ shake for one hour in a horizontal shaker, Mg in filtrate will be determined by atom absorption spectroscopy method (AAS).
Heavy metals total contents: mineralization by dry procedure and subsequent lixiviaton with HNO_3. Determination of Cd, Pb, Cr, Ni by AAS method and Hg on a single-purpose analyser TMA 254.
Microelements Cu, Zn, Mn, Co: mineralization by dry procedure and their determination by AAS method.

Results of chemical analysis

The average chemical composition of the semi-products and raw materials of SMZ Jelšava a.s. is given in Table 2.

Table 2 Average chemical composition of the semi-products and raw materials

Determined constituents	%
MgO	40,46
CaO	4,65
$MgCO_3$	84,64
$CaCO_3$	8,30
SiO_2	1,90
R_2O_3 (Fe_2O_3 + Al_2O_3)	4,71
MnO	0,22
Loss through heat	50,22
Humidity	0,042

Following the table, the classified semi-products and raw materials contain 84,64 % $MgCO_3$ a 8,30 % $CaCO_3$ in average at an average humidity of 0,042 %. It represents 40,46 % MgO and 4,65 % CaO in average. For comparison, MgO contents within the magnesite manure of sulphate forms that are most spread (soluble forms) are as follows: kieserit (crystal) 27 % MgO, kieserit (granules) 25 % MgO, bitter salt 16,2 % MgO. This applies not only for intensive agriculture production where magnesium deficit prevails (more magnesium is taken from soil than added therein), but also for alternative agriculture where the goal is production of products with sufficient magnesium contents that is not replaceable.
According to the results we can conclude that the determining portion of magnesium and calcium is bound in carbonate forms as proved by average 50,22 % loss through heat. Magnesium along with other elements presented in silicate form is a complement of the composition of the classified materials. It is documented by the magnesium content as well as SiO_2 contents of 1,90 % in average.
In table No.3 are given the results of the classification of the chemical composition variability of samples taken on ten various places of the deposited materials in question.

Table 3 Classification of chemical composition variability

Sample	Determined constituents					
	MgO	CaO	SiO_2	R_2O_3	Humidity	Loss through heat
1	40,49	3,96	1,66	4,33	0,015	49,90
2	40,75	4,11	2,68	4,38	0,015	49,95
3	40,40	3,52	2,14	4,38	0,055	49,93
4	41,51	4,01	2,13	4,38	0,075	50,36
5	40,55	4,74	1,31	6,22	0,065	50,44
6	41,40	4,85	2,43	3,80	0,005	50,25
7	39,37	5,74	2,14	5,81	0,055	50,50
8	40,54	5,06	1,34	5,47	0,065	50,09
9	39,04	5,71	1,16	4,46	0,015	50,35
10	40,49	4,83	1,98	4,49	0,050	50,45
Average	40,46	4,65	1,90	4,71	0,042	50,22
Aver.deviation	0,508	0,602	0,42	0,55	-	-
Stan. deviation	0,726	0,708	0,48	0,67	-	-

Table 4 Active reaction (pH/H_20), exchange reaction and (pH/KCl) and CS module

Sample	pH/H_2O	pH/KCl	CaO:SiO_2
1	7,89	8,99	2,38
2	7,91	9,33	1,53
3	8,09	9,13	1,67
4	7,11	9,31	1,88
5	7,87	9,38	3,61
6	8,23	9,36	1,99
7	8,84	9,63	2,68
8	8,37	9,44	3,77
9	7,97	9,33	4,92
10	8,35	9,35	2,43
Average	8,16	9,33	2,68
Aver.deviation	0,23	0,11	-
Stan. deviation	0,29	0,16	-

Results given in table No.3 imply that MgO contents varies about an average of 40,46 % with a variational interval from R_{min} 39,04 to R_{max} 41,51 %, with average variation of 0,5081 and standard variation of 0,7264. The variability of CaO contents is similar, and varies about an average of 4,65 % with practically balanced values of average deviation as it is with MgO. The value of losses through heat is also balanced acknowledging that we are dealing with carbonate forms of magnesium and calcium.

In comparison to a neutralising activity standard represented by calcium carbonate (figured as 1,00), the activity of magnesium carbonate that create decisive part of classified materials is figured as 1,19 (HOLOBRADÝ and BUJNOVSKÝ 1977).
In table No.4 are given results of assesment of pH/H_20 (active reaction) and pH/KCl (exchange reaction), as well as CS module (calcium silicate modul).
The obtained results imply that the average value of pH/H_20 is 8,16 and pH/KCl 9,33. It is reasoned by different solubility of magnesium and calcium in used solutants.
The CS module expresses CaO : SiO_2 ratio, and depends on the solubility of the semi-products and raw materials. If the module is greater than 2, the matter is calcium magnesite, if less than 2, silicon magnesite. According to table No.4, for this case is the average value of CS module figured as 2,68, that means the matter is calcium magnesite.
In table No.5 we refer the total contents of some foreign (risky) elements and biologically significant microelements.
With calcium, magnesium-calcium manure and magnesite manure it means cadmium, chrome, lead and mercury. Arsine isn't controlled in carbonate forms of manure.
Following the results given in table No.5, all specified elements are bellow maximally allowed values (NPM). For cadmium it means 0,729 $mg.kg^{-1}$ against NPM of 1,5 $mg.kg^{-1}$. The average contents of total chrome is 6,31 $mg.kg^{-1}$ against 50 $mg.kg^{-1}$. The average contents of lead in the specified materials is 8,17 $mg.kg^{-1}$ against NPM of 30 $mg.kg^{-1}$. The mercury average is 0,0124 $mg.kg^{-1}$ against NPM of 0,5 $mg.kg^{-1}$.

Table 5 Total contents of foreign (risky) elements and biological microelements

Sample	Chemical elements									
	Ni	Cr	Pb	Cd	Hg	Zn	Cu	Co	Fe	Mn
1	6,13	7,28	13,59	1,469	0,0248	11,49	6,05	6,23	25389,8	1673,74
2	5,44	7,82	7,38	0,718	0,0113	8,18	4,39	5,51	25483,9	1630,86
3	5,35	5,66	7,09	0,639	0,0110	10,13	4,20	5,61	25480,7	1634,56
4	5,80	5,00	8,80	0,650	0,0188	7,60	4,45	6,29	25479,8	1649,77
5	6,26	7,13	7,70	0,610	0,0103	5,60	5,40	6,54	24594	1674,75
6	5,38	5,95	8,01	0,741	0,0102	10,81	4,65	5,49	25090,1	1627,75
7	6,11	6,63	7,10	0,540	0,0117	6,30	4,60	6,18	24067,6	1599,32
8	5,31	5,91	7,11	0,541	0,0084	5,61	4,05	5,36	21782,9	1632,16
9	5,49	3,84	7,11	0,660	0,0081	6,19	3,65	5,56	23896,0	1633,33
10	5,88	7,87	7,80	0,720	0,0092	12,20	4,00	5,83	25172,5	1680,57
Average	5,72	6,31	8,17	0,729	0,0120	8,41	4,54	5,86	24643,8	1643,68
Average deviation	0,32	1,04	1,21	0,150	-	2,20	0,50	0,36	846,78	-
Standard deviation	0,35	1,22	1,88	0,255	-	2,42	0,67	0,39	1105,38	-

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