

Purification of magnesite from harmful materials with Mg  $(NO_3)_2$  application-prevention of the pollution of environment

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Selver HODA<sup>1</sup>, Islam FEJZA<sup>2</sup>, Shefqet RASHANI<sup>2</sup>, Sabri AVDULLAHI<sup>2</sup>, Eflorim HAJRA<sup>2</sup>

<sup>1</sup>XIM-Strezoci, Dardanë, <sup>2</sup>University of Prishtina- Faculty of Mining and Metallurgy, Prishtina-Kosova

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Abstract: In this article it is researched the issue of possibility of magnesite valorisation with application of thermodynamic and kinetic methods in dissolution process for purification of magnesite from calcium with help of magnesite nitrate influencing in this way evidently in preventing of the pollution of environment (earth and water). For this reason it is realised a wide spectrum of experimental granulometric researches, chemical, difractometric (XRD) and termodifferentiate analyses (DTA) in magnesite of "Strezoci" - Kosova. Massive magnesite is selected for detailed analyses that have a high content of calcium minerals, while it has few other impurity contents. With experimental researches is verified that the dissolubility reaction of calcium oxide is a very complex process and it is dependant from temperature, granule size in solid phase, reagents concentration and rapport of phases. Depending on the condition for the development of experiments, dissolubility of calcium oxide in process was: after 5 min. 65-83% solubility, while after 1h 88-95% solubility. The up to now method of magnesite treatment (without treatment of its sub products) influenced evidently in the pollution of environment, while the method we used in this article offers a possibility of prevention of the pollution of environment with treatment of other sub products with help of magnesite nitrate.

**Keywords**: magnesite deposits, calcium oxide, solubility, purification, pollution, magnesite treatment.

#### Introduction

Magnesite (MgCO<sub>3</sub>) is the main mineral for the gain of magnesite that is applied in many industry branches as: for production of sinter magnesite and of bricks with very high flame-resistance, of steel, cement, limestone *etc*. With decarbonisation process from magnesite (Hoda, 1983) is gained also the "caustic" magnesite oxide that it is used as charger in the industry of paper, tyre and plastic gauges, then for the production of guanos *etc*.

Magnesite deposits are mainly located in the medium and less development countries as in: Austria, Slovakia, Greece, Turkey, China, Australia *etc*. In lack of sufficient natural resources of magnesite the countries with high industrial development as USA, Japan and Great Britain developed the methods for the artificially gain of magnesite oxide based on limestone, or dolomites with water or from salt dissolution (that contains ion of Mg<sup>++</sup>). However the applied methods for the enrichment of magnesite because of their untreated subproducts influenced evidently until now in the pollution of environment. The method we applied eliminates all up to now defects.

According to genesis, magnesite deposits in Kosova (Jankovic, 1969; Fejza, 2004) belong to two types:

- 1. Hydrothermal magnesite of vein type-created by dismounting of serpentinite under the influence of thermal water. Deposits of this type are Goleshi (Lypjan) and Dubovc (Vushtrri) deposits.
- 2. Magnesites with sedimentary origin—created by hot or cold dissolution connected with carbonate rocks mainly with dolomites. Deposits of this type in Kosova are in locality of Strezovc (Dardanë).

<sup>&</sup>lt;sup>1</sup>Corresponding: E-mail: islamfejza@gmail.com; Tel. + 377 44 260649

In this article of methods' application, we have researched the magnesites of sedimentary type of Sterzovci treating the conductor impurities of magnesite as are: calcite, quartz, iron and aluminium oxide etc. Since in sedimentary deposits in conduction of magnesite is calcium minerals, then this is characterised with high content of dolomite and calcite, whereas with relatively tolerated content of silicon, aluminium and iron. Dolomite's impurity is spread between pure magnesite parts with concrete form, but in many cases it is also mixed in a very compound manner in crypto crystals or stratified manner in magnesite's sediments. Three main magnesite types are noticed at Strezoc (Jelenkovic, 1985): massive magnesite, brecciated magnesite and banded magnesite.

Impurities in magnesite have negative influence and cause environmental pollution in production and use of sinter magnesite and basic bricks with high flame-resistance; hereupon we dedicated a great consideration to the treatment of these impurities with prevention of environment pollution. Negative influence of calcium minerals, during the processing of magnesite is expressed through the formation of calcium oxide in the so-called "free" form if other oxides are not present also (oxide of silicon, iron etc.) in sufficient quantity that with it to form respective components.

"Free" calcium oxide hydrates intensively by absorbing humidity from environment, during that it increases the volume of flame-resistance materials, where it comes also to their decomposition and the pollution of environment.

From technological aspect (Spasic et al., 1972) purification of magnesite can be done in two forms:

- 1. with selective removal of some conductive impurities from magnesite and,
- 2. with separate of magnesite, respectively of magnesite's ion from impurities.

Purification of magnesite from calcium in industrial dimension is not realised in any country of the world, but only the magnesite with content added with calcium minerals usually mixes with magnesite which contains great quantity in silicon minerals after which it is realised their common sinteration, most frequently while adding specified quantity of iron oxide to this mixture, to enable the formation of calcium components resistance to hydratisation.

In these cases, it is understandable that the product of low quality is gained and with limited possibilities' of usage (e.g. the mass for the floor of Siemens-Martini ovens or production of bricks for the nucleus of thermo-accumulated heaters). From distinction of the existing practice, the results of purification of magnesite with dissolution method of calcium oxide with the help of magnesite nitrate solution are presented within this project.

## Methods and Methodology

Method contains these operations:

- -calcinations of magnesite, (the sample is prepared with granulation from 10 mm),
- -crush and hydratisation of calcified magnetise (the sample must be crushed in powdery manner),
- -the process of calcium dissolution from weak dissoluble calcium hydroxide in well dissoluble calcium nitrate with the help of magnesite nitrate solution according to reaction:

$$Ca(OH)_2 + Mg(NO_3)_2 = Ca(NO_3)_2 + Mg(OH)_2$$

During reaction, in sediment the magnesite hydroxide is divided, while calcium nitrate is divided in dissolution.

-The separate of calcium nitrate dissolution by decantation and filtration, washing the sediment with distillate water. In this manner it is gained the magnesite hydroxide in the product form with low content of calcium and calcium nitrate in dissolution as sub-product. The pollution of environment is not caused during these processes or they are just in the allowed limits. From the calcium nitrate dissolution is gained calcium crystal-hydrate Ca (NO<sub>3</sub>)<sub>2</sub> 4 H<sub>2</sub>O, that it can be used as guanos in agriculture. If it is wanted the powdery production of magnesite oxide, then it is required to apply also the operation of:

- -Baking of filtering dough of magnesite hydroxide and powdery magnesite oxide it is gained in this manner, that has a wide use in different part of industry: as charger in the industry of paper, tyre and plastic gauges, and as raw material in production of "Sorrel" cement etc. In the end, if we want that from magnesite oxide to gain the sinter magnesite production it is required to apply also two operation of:
- -briquetting of (powdery) magnesite oxide and,
- -sintering of magnesite oxide from briquette form.

Since each abovementioned operation has special importance for the successful magnesium purification from calcium minerals, but for the specified reasons the efficiency of process excessively depends on successful development of dissolution reaction (which means that also other operations to be correctly realised), for these reasons the dissolution process will be researched in particular manner.

# Thermodynamics of Reactions Development

Is the reaction of calcium hydroxide dissolution available with the help of calcium nitrate solution, by thermodynamics aspect (Rashani, 1985) in which direction the reaction will be developed, and with what probability is assessed based on calculation values of Gibbs potential (isobar potential) and constant of balance, below the standard conditions. For reaction:

$$Ca(OH)_2 + Mg(NO_3)_2 = Ca(NO_3)_2 + Mg(OH)_2$$

The change of Gibbs potential below the standard conditions would have been:

$$\Delta G_T^O = (\sum v_i \Delta G_T^O)_P - (\sum v_i \Delta G_T^O)_R$$

$$\Delta G_T^O = (\Delta G^O_{Ca(NO_3)_2} + \Delta G^O_{Mg(OH)_2}) - (\Delta G^O_{Ca(OH)_2} + \Delta G^O_{Mg(NO_3)_2})$$

$$\Delta G_T^O = (-744.00 - 834.27) - (-898.40 - 591.28) = -88.28 \ KJ / mol$$

$$\Delta G_T^O = -88.280 \ KJ / mol$$

Since the relatively high negative value for Gibbs potential is gained, in standard conditions, we can conclude that the process of dissolution reaction will be developed spontaneously from left to right.

We have done the calculation of Gibbs potential also for temperatures: 313 K; 328 K and 343

K, to verify this ascertainment.

We had these values from calculations:  $\Delta G^0_{313K}$ = -88.422  $\pm$  5.694 KJ mol<sup>-1</sup>,  $\Delta G^0_{328K}$  = -88.558  $\pm$  5.772 KJ mol<sup>-1</sup> and  $\Delta G^0_{343K}$  = -88.694 ±5.85 KJ mol<sup>-1</sup>

Constant of balance of this reaction under normal conditions would have the value:

$$\ln K_p = -\frac{\Delta G_T^o}{RT} = -(-\frac{88.280}{8.3 \cdot 298}) = 35.69$$

$$K_p = 3.1676 \cdot 10^{15}$$

Because of the most completed researches the calculations are done also for the constant of balance for temperatures: 313 K, 328 K and 343 K, and results are:

$$Kp_{313 \text{ K}} = 6.048 \cdot 10^{14}$$
;  $Kp_{328 \text{ K}} = 1.34 \cdot 10^{14}$  and  $Kp_{343 \text{ K}} = 3.39 \cdot 10^{13}$ .

Since according to calculations, the constant of balance pronouncedly distinguishes from one, this reaction can be considered as irrevocable and it testifies that it is possible the full transition of reaction in products.

For this purpose it will have been very reasonable to calculate also the thermal effect of dissolution reaction from enthalpy according to equation:

$$\Delta H_{T}^{O} = (\sum v_{i} \Delta H_{T}^{O})_{P} - (\sum v_{i} \Delta H_{T}^{O})_{R}$$

$$\Delta H_{T}^{O} = (\Delta H_{T Ca(NO_{3})_{2}}^{O} + \Delta H_{T Mg(OH)_{2}}^{O}) - (\Delta H_{T Ca(OH)_{2}}^{O} + \Delta H_{T Mg(NO_{3})_{2}}^{O})$$

$$\Delta H_{T}^{O} = (-939.39 \pm 1.21 - 925.28 \pm 0.84) - (-985.78 \pm 1.05 - 793.31 \pm 0.96)$$

$$\Delta H_{T}^{O} = -85.58 \pm 4.06 \, KJ / mol$$

Since thermal effect in standard conditions would have been:

$$\Delta Q^{o} = -\Delta H_{T}^{o} = 85.58 \pm 4.06 \, KJ \, / \, mol \, ,$$

Due to which comes out the positive value and the reaction of dissolution is exothermic. Also this value is a very important indicator because from this process of exothermal reaction will come till a considerable increase of temperature in reactive mixture that it influences positively in the velocity of reaction's development and with more intensity it will be manifested in the dissolution with great concentrations.

### Methodology of experiments realisation

Experiments are realised according to these methods:

-Magnesite sample is crushed in powdery form (in sufficient quantity that from it is gained 200 g caustic from burning of magnesite), and it is sent for burning in oven in temperature from  $950\,^{\circ}$ C, with duration of 5 hours.

-This caustic quantity gained of 200g, is subject to the hydratisation process with relative quantity of distillated water in temperatures determined in conformity with work's schedule for special experiments, mixing intensively in duration of 30 minutes (200g Mg(NO<sub>3</sub>)<sub>2</sub> per kg.

-In the same time, in determine temperatures it is also prepared magnesite nitrate dissolution, in other dish, it is prepared with 20% magnesite nitrate dissolution (200g Mg(NO<sub>3</sub>)<sub>2</sub> per kilogram of dissolution), softening with distilled water until 400g of mass, in temperature 20°C.

-The respective weighed rapport between solid – liquid stages is achieved with the mixture of caustic suspension gained from the burning of magnesite, with magnesite nitrate dissolutions in determinate temperatures.

-Reactive suspension gained in this manner, is intensively mixed by mixer with adjustment of rotation numbers. Samples in volume quantity of 20 ml are taken with help of pipette from this suspension in definite time intervals of 5, 10, 20, 30 and 60 minutes, which are filtered under vacuum in too short duration (until 10 sec.), rinsing with water with quantity which is five fold greater, in rapport with solid stage, in temperature 20°C, also under vacuum, for the removal of dissoluble remain salts.

-The samples taken from filtration process are dried up in oven with temperature 105 °C, then they are burnt in oven with temperature 950 °C, until the full removal of volatile contents (until constant mass), to determine the quantity of remain (undried) quantity of calcium oxide, with complex-metric analyse.

-The necessary stechiometry calculations of magnesite nitrate for the complete dissolution of calcium oxide is calculated according to the determinate reaction of dissolution:

-For 200 gram caustic gained of the burning of magnesite with chemical content of 6.92% CaO, with stechiometry calculation for the complete dissolubility of calcium oxide is necessary 36.60 gram magnesite nitrate ( $Mg(NO_3)_2$ ). For the best fluidity of reaction at right, +5% more of magnesite nitrate quantity is added more than the stechiometry one, respectively the additional quantity is: 36.60g 1.05= 38.43g  $Mg(NO_3)_2$ .

-The realisation of experiments is done in a wide diameter dish in order to secure the possibility of sampling and the fast filtration of samples after programmed time intervals has passed. Dish was closed with lid and it has access on turning on the thermometer for measurement of temperature and on placement of mixer's axle. The dish was selected by its shape to enable that the water mass to not be lost with evaporation during water heating process.

### Results of experimental researches

Massive magnesite is taken for research that with its characteristics of high content of calcium impurities, and with relative content of other impurities is the most adequate for the treatment according to this method. Sample of "Strezoci" magnesite is crushed until the granule size 0.3 mm, and the representative sample is gained where the granulometric analyses, chemical, mineralogical (thermo differential (DTA)and X- ray diffraction(XRD) analyses are done).



**Figure 1**. Magnesite "Strezoc" 62, 5x, PPL White crystals are dolomite and darks magnesite



**Figure. 2**. Magnesite "Strezoc" 62, 5x, XPL White crystals are dolomite and darks magnesite

Results of magnesite analyses are given in the following tables:

**Table1.** Granulometric analyses of magnesite.

Sieves holes (mm)	0.3	0.3-0.2	0.2-0,1	0.1- 0.063	-0.063	
Fractions in %	7.23	11.22	16.78	21.32	43.45	

**Table2.** Chemical analyses, H.P.> Lost during burning

H.P%	SiO <sub>2</sub> %	Al <sub>2</sub> O <sub>3</sub> +Fe <sub>2</sub> O <sub>3</sub> %	CaO %	MgO %	
51.30	0.72	0.33	3.55	44.10	

**Table3.** Rational chemical analyses

SiO <sub>2</sub>	CaCO <sub>3</sub>	CaCO <sub>3</sub> , MgCO <sub>3</sub>	MgCO <sub>3</sub>	others	
0.72%	1.40%	9.10%	88.45%	0.33%	

<sup>\*</sup>Magnesite and dolomite minerals are identified taking in consideration the gained results with microscopic, thermo differential (DTA) and X- ray diffraction (XRD) analyses, while the calcite composition is supposed, because it did not exist the possibility for its exact determination.

Samples for special experiments are burnt with same conditions in temperature 950°C and duration of 5 hours for the process of hydratisation of calcium oxide and for the dissolution of calcium hydroxide. The caustic produced from burning of magnesite is done with chemical, diffraction of powders and thermo differential (DTA) analyses. We could not determine the exact form of the granulometric analyse of caustic gained from magnesite. Analyses results of burnt caustic of magnesite are presented in table 4, respectively in Table 5.

Table.4. Presentation of chemical analyse of caustic from burning of magnesite

H.P.	SiO <sub>2</sub>	$Al_2O_3 + Fe_2O_3$	CaO	MgO	_
0.24 %	1.40%	0.64%	6.92%	90.80%	

H.P.> Lost during burning

**Table.5.** Rational chemicals of caustic from burning of magnesite (\*)

SiO <sub>2</sub>	CaO	CaO-MgO	MgO	MgCO <sub>3</sub>	others	
1.40%	1.53%	11.96%	84.01%	0.46%	0.64%	

<sup>\*</sup> Lime and Periclas minerals are identified taking in consideration the gained results with microscopic, thermo differential (DTA) and X- ray diffraction (XRD) analyses.

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In the caustic gained from the burning of magnesite, the representative sample is prepared for hydratisation with distilled water in duration of 30 minutes and in temperature 25°C, where chemical, thermo differential (DTA) and X- ray diffraction (XRD) analyses are done. Results of caustic hydratisation gained from the burning of magnesite are presented in table 6, respectively in table 7.

**Table.6**. Presentation of chemical analyse for hydratised caustic

H.P	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub> +Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	
13.34%	1.21%	0.55%	6.00%	78.90%	

H.P.> Lost during burning

**Table.7.** Presentation of rational chemical analyse for hydratised caustic

SiO <sub>2</sub>	CaO	Ca(OH) <sub>2</sub> Mg(OH) <sub>2</sub>	Mg(OH) <sub>2</sub>	MgCO <sub>3</sub>	MgO	others	
1.21%	2.02%	16.44%	26.21%	0.42%	53.15%	0.55%	

<sup>\*</sup>Portland, Periclas, Brucite and Calcium carbonate are identified taking in consideration the gained results with microscopic, thermo differential (DTA) and X- ray diffraction (XRD) analyses. Magnesite is not presented in X-ray, however it is presented in rational chemical analyse because it is notified in caustic burnt from magnesite but in small quantity and certainly it could not be registered with X-ray analyse.

### Results of parameters influence in calcium oxide dissolubility

Calcium oxide dissolubility of hydratised caustic gained from burning of magnesite is analysed according to temperature, magnesite nitrate concentration (respectively stechiometry calculations of magnesite nitrate, for the complete dissolubility of calcium oxide), phase's rapport and granulation of granules size.

#### Influence of temperature in the scale of calcium oxide dissolubility

Influence of temperature in the quantity of calcium oxide dissolubility in caustic gained from burning of magnesite is analysed with +5% more of magnesite nitrate solution more than the stechiometric (equivalent) quantity calculated (for the complete dissolubility of calcium oxide) in rapport of solid/liquid phases = 1:5, and with velocity of suspension mixture of 750 rot/min. Researches are done in temperature; 298 K, 313 K, 328 K and 343 K. From the gained results (table 8); we can conclude that the dissolubility process of calcium oxide in caustic is a fastest and efficient process with the help of magnesite nitrate in the presented conditions. During the dissolution process of caustic in temperature 298 K and duration of 5 minutes, calcium oxide in caustic gained from burning of magnesite of 6.92% (table 4), is decreased to 2.20% of quantity, respectively calcium oxide dissolubility 68% is gained. After duration of dissolution process of 1h, the quantity of indissoluble calcium oxide has value 0.57% while the dissolubility scale reaches the value efficiency over 91%. It is ascertained by experimental analyse that the scale of calcium oxide dissolubility is evidently increased with the increase of temperature.

Results on the influence of temperature in 342 K, show that after 5 minutes of dissolution, the quantity of calcium oxide in caustic burnt by magnesite of 6.92% (table 4), is decreased in the value 1.17%, during which the dissolubility scale has reached over 83%.

After the duration of 1h, of dissolution, indissoluble calcium oxide is decreased to the value 0. 33%, respectively calcium oxide dissolubility is over 95%.

**Table.8.** Results of temperature influence in quantity of calcium oxide dissolubility

Dissolution concentration g. Mg(NO <sub>3</sub> ) <sub>2</sub> /kg	Temperature (K)	Dissolubility indicators M, W		Dissolution	time (h)		
dissolution			0.083	0.166	0.333	0.5	1.0
		M (%)	2.20	1.69	1.15	0.91	0.57
38.43	298	W (%)	68.21	75.58	83.38	86.85	91.76
		M (%)	1.72	1.37	1.03	0.81	0.48
38.43	313	W (%)	75.14	80.20	85.12	88.29	93.06
		M (%)	1.51	1.12	0.79	0.68	0.38
38.43	328	W (%)	78.18	83.82	88.58	90.17	94.51
		M (%)	1.17	0.78	0.59	0.51	0.33
38.43	343	W (%)	83.09	88.73	91.47	92.63	95.23

M -CaO % remained (insoluble) in caustic burnt from magnesite

W- CaO dissolved

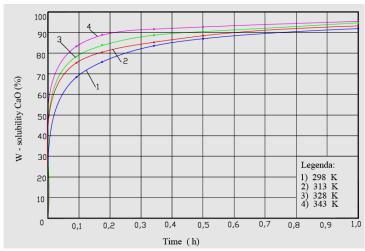


Figure 3. Temperature influence in quantity of calcium oxide dissolubility, according to table (8)

Based on the gained results we can conclude that temperature is a very important factor in the dissolubility process of calcium oxide and that the increase of temperature has the greatest influence in the increase of the scale of calcium oxide dissolubility, respectively in all working parameters the temperature has shown greatest influence. The best results from the done experiments are reached in the temperature 343 K.

From experiments we can conclude that the process is successfully developed and it is enough fast and it is not indispensable to realize in the temperature higher than se 298-343 K, which ensures the exothermal character to process.

# Influence of concentration in the scale of calcium oxide dissolubility

The influence of concentration of magnesite nitrate in the indicator of calcium oxide dissolution is researched for the values: 1) stechiometry +0%, 2) stechiometry +5%, 3) stechiometry +10%, 4) stechiometry +15%, calculated in rapport with stechiometric quantity necessary for the complete dissolubility of calcium oxide. Other parameters values are kept constantly: temperature 298 K, rapport of solid/liquid stages = 1:5, and with velocity of suspension mixture of 750 rot/min.

Based on the gained results (Table 9), we can conclude that the increase of the magnesite nitrate quantity in dissolution respectively the increase of magnesite nitrate concentration

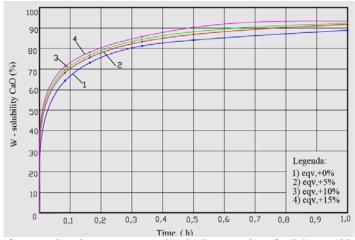
influences positively in the transport of reaction to the right, from the highest scale of calcium oxide dissolubility.

**Table.9.** Results of influence of magnesite nitrate concentration in the quantity of calcium oxide dissolution

Dissolution concentration	Stechiometry Dissolubili calculations + indicators		Dissolution time (h)					
g. Mg(NO <sub>3</sub> ) <sub>2</sub> /kg dissolution	%	M, W	0.083	0.166	0.333	0.5	1.0	
		M (%)	2.40	1.86	1.30	1.10	0.77	
36.60	+ 0%	W (%)	65.32	73.12	81.21	84.10	88.87	
		M (%)	2.20	1.69	1.15	0.91	0.57	
38.43	+ 5%	W (%)	68.21	75.58	83.38	86.85	91.76	
		M (%)	2.11	1.60	1.08	0.82	0.54	
40.28	+ 10%	W (%)	69.51	76.88	84.39	88.15	92.20	
		M (%)	1.99	1.51	0.98	0.67	0.46	
42.09	.+ 15%	W (%)	71.24	78.18	85.84	90.32	93.35	

M -CaO % remained (insoluble) in caustic burnt from magnesite

W- CaO dissolved



**Figure 4.**Influence of magnesite nitrate concentration in the quantity of calcium oxide dissolution, according to table 9. (eqv- stechiometry calculations)

If for e.g. the results of the first and the last experiments are compared in (table 9) results that with increase of the magnesite nitrate quantity +15% over the stechiometric value, for the complete dissolubility of calcium oxide, in process after 5 minutes of dissolution, the efficiency of the scale of calcium oxide dissolubility reaches the values from 65.32% to 71.24%, while after duration of 1h, of dissolution the scale of calcium oxide reaches the values from 88.87% to 93.35%. In this process the indissoluble calcium oxide in remain caustic from burning of magnesite, after dissolution by 1h, has decreased in the remain quantity from 0.77% to 0.46%. Based on the presented results it can be seen that with the increase of the magnesite nitrate quantity over the stechiometric calculated value, for the complete dissolution of calcium oxide in caustic gained from burning of magnesite, positive results are achieved in development of dissolution processes, but efficiency of results are the lowest than the one achieved from influence of temperature in the scale of calcium oxide dissolubility.

### Influence of phases rapport in the scale of calcium oxide dissolubility

Researches for the influence of stages rapport in the scale of calcium oxide dissolubility are realised in hydratised caustic gained from the burning of magnesite in temperature 289 K, with 5% greater of magnesite nitrate quantity, in rapport with the necessary stechiometry

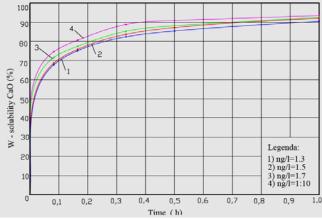
calculation, with mixture velocity 750 rot/min. for the rapport of solid / liquid phases = 1:3; 1:5; 1:7; and 1:10.

Table10. R	Result of rapport	of solid	liquid phases	in the a	uantity of calciur	n oxide dissolubility
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Dissolution	Report of solid	Dissolubility		Dissolu	ution time (h	)	
concentration g.Mg(NO <sub>3</sub> ) <sub>2</sub> /kg dissolution	/ liquid phases.	indicators M, W	0.083	0.166	0.333	0.5	1.0
		M (%)	2.25	1.74	1.24	1.03	0.68
64.05	1:3	W (%)	67.49	74.86	82.08	85.12	90.17
		M (%)	2.20	1.69	1.15	0.91	0.57
38.43	1:5	W (%)	68.21	75.58	83.38	86.85	91.76
		M (%)	1.98	1.58	1.04	0.84	0.55
27.45	1:7	W (%)	71.39	77.17	84.97	87.86	92.05
		M (%)	1.78	1.36	0.79	0.65	0.47
19.22	1:10	W (%)	74.28	80.35	88.58	90.61	93.21

M -CaO % remained (insoluble) in caustic burnt from magnesite

In different rapports of stages with the additional magnesite nitrate quantity +5% above the stechiometric value, the considerable changes of the concentration of magnesite nitrate in suspension occur in dissolubility process, hereupon the change of rapports of stages in special manner presents a kind of influence of magnesite nitrate concentration in calcium oxide dissolubility.



**Figure 5.**Influence of phases rapport in the scale of calcium oxide dissolubility, according to Table 10. (ng/l – solid/liquid phase)

From the gained results (table 10), it can be concluded that with the change of the rapport of stages, the good dissolubility of oxide calcium is achieved. The results gained at researches for the calcium oxide dissolubility, are approximate to a certain extent with the results gained by the influence of temperature, respectively by the quantity of magnesite nitrate concentration.

The greatest changes in the scale of calcium oxide dissolubility are noticed if the comparison of results from the first and the fourth experiment (table 10) is done.

During the dissolution process, in rapport of solid/liquid phases = 1:3; after 5 minutes of dissolution, efficiency of calcium oxide dissolubility reaches 67.49%, while after duration of 1 h, of dissolution, efficiency of calcium oxide dissolubility reaches 90.17%. If the comparison for same time periods is done, where rapport of solid/liquid phases = 1:10, efficiency of calcium oxide dissolubility after 5 minutes of dissolution reaches to 74.28%, whereas after dissolution efficiency of calcium oxide dissolubility reaches to 93.21%.

From the gained experimental results, it results that the highest scale of calcium oxide dissolubility can be achieved not just with the change of temperature and the increase of nitrate magnesite quantity, which economically it is unaccepted, but also with the adjustment of the rapport of stages in the concrete cases can result as the best solution.

W- CaO dissolved

## Influence of granulation in calcium oxide dissolubility

For the influence's research of granulation of the granules in the scale of calcium oxide dissolubility, the experimental analyses are realised at temperature 298 K, with dissolubility suspension, with concentration of magnesite nitrate +5% stechiometry calculations, with complete dissolubility of calcium oxide, and with velocity of suspension mixture of 750rot/min. Analyses are done for the granulations of granules with size 0-0.3 mm; 0.3-0.5 mm; 0.5-1 mm and 1-2 mm.

**Table11.** Results of the influence of granulation of the granules in solid phase, in the quantity of oxide dissolubility

Dissolution concentration	Granulation of	Dissolubility	3					
g.Mg(NO <sub>3</sub> ) <sub>2</sub> /kg dissolution	the granules (mm)	indicators M, W	0.083	0.166	0.333	0.5	1.0	
		M (%)	2.20	1.69	1.15	0.91	0.57	
38.43	0 - 0.3	W (%)	68.21	75.58	83.38	86.85	91.76	
		M (%)	2.40	2.02	1.58	1.31	1.08	
38.43	0.3 - 0.5	W (%)	65.32	70.81	77.17	81.07	84.39	
		M (%)	2.89	2.57	2.07	1.83	1.56	
38.43	0.5 - 1	W (%)	58.24	62.86	70.09	73.55	77.46	
		M (%)	3.37	3.10	2.69	2.41	2.06	
38.43	1 - 2	W (%)	51.30	55.20	61.13	65.17	70.23	

M –CaO % remained (insoluble) in caustic burnt from magnesite

W- CaO dissolved

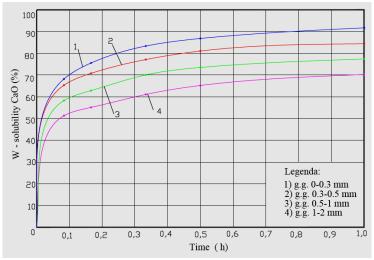


Figure 6.Influence of granulation in calcium oxide dissolubility, according to Table 11.

Experimental results are given in table 11, from which we can conclude that with the change of the granulation of granules in solid stage, the values of calcium oxide dissolubility are gained which are different from the gained ones with the change of temperature, with concentration of magnesite nitrate and the change of the rapport of stages.

The greatest difference in the scale of calcium oxide dissolubility is noticed if the comparison of results is done from the first with the fourth experiment (table 11) where we ascertained that in the dissolution of 5 minutes, for the granules 0-0.3 mm, in the solid stage it is reached the calcium oxide dissolubility in 68.21%, whereas after dissolution for 1h, the scale of dissolubility reaches to 91.76%.

For the same time period of granules from 1-2 mm in the solid stage, calcium oxide dissolubility after dissolution of 5 minutes has values of 51.30%, respectively after dissolution for 1h reaches the values to 70.23%.

From the analyses of experimental results, it can be concluded that the highest desirable scale of calcium oxide dissolubility can be achieved, not just with the increase of temperature and the increase of nitrate magnesite quantity, but also with crushing of granules in solid phase, where with this process it is contributed in the increase of the general surface of reaction, and in great mass it influences in the shortening of distances for difundation of reagents inside the solid phase and out of it.

Crushing of material in solid phase influences evidently in the increase of reaction velocity, and it brings also economical benefit during the real development of processes in production.

#### Conclusion

From the presentation of researches and results we conclude that:

- 1. With the dissolution of magnesite with the magnesite nitrate dissolution, it is possible to remove calcium from it (it is accounted as calcium oxide) as the harmful impurity and that with the satisfactory velocity of dissolution and with fairly high velocity of dissolution. The scale of calcium oxide dissolubility, after 5 minutes of dissolubility was 65-83%, whereas after dissolution of 1 hour was 88-95%, under the conditions determined for working parameters: temperature 298-343 K, concentration of magnesite nitrate with the calculated stechiometric quantity to stechiometric quantity +5%, report of phase from: 1 = 1:3; to 1:10, duration of dissolutions 30-60min, the smallest granulation of granules in solid phase and velocity of mixture of 750 rot./min.
- 2. The dissoluble quantity of calcium oxide depends not just from conditions of realisation of the dissolution process but also from the working conditions for the previous phases: burning of magnesite in caustic and hydratisation of burning magnesite. With detailed analyses for all phases of process is possible that with the great insurance to define the working conditions from which the scale of purification of calcium oxide would have been also higher from the gained one based on these researches.
- 3. With these researches it is verified that the purification of magnesite can be performed with high scale while valorising also its sub products, without remain and sensitive pollution in environment, which it was also the purpose of application of this method.
- 4. Selection of optimal conditions for all phases of methods requires calculation of technical-economical analyse.

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