THE MECHANICAL TREATMENT AS A METHOD OF INORGANIC SUBSTANCES PASSIVATION

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Abstract

The mechanopassivation effect of metal (II) oxides crystallizing by the structural type of halite under attrition treatment has been found out.

For the assessment of the activity decrease the following has been investigated: solution and aquation kinetics of CaO and MgO in water and solutions; spinel and calcium carbide formation kinetics using oxides pretreated mechanically by different modes; kinetics of CO_2 fixation and thermal desorption from the pretreated oxides surface; magnesia and phosphate cements set rate. It has been determined that the rate of studied processes with the participation of oxides subjected to attrition treatment reduces by a factor of tens and hundreds.

We suppose the cause to be the removal of the rough loosened layers containing the most of defects from the polycrystalline aggregates surface. As that neighboring zones accommodate, their surfaces flatten and the bonding area rises. Separated smallest particles form compact aggregates. The powder density increase and sharper diffraction reflection form confirm the microstructure regulating. Flat surfaces with lower quantity of defects provoke the hypoactivity in regard to water vapors and carbon dioxide.
The substances mechanopassivation study can be used to control the reaction rate with the participation of highly active reagents.

Introduction

The substances reactivity to a considerable degree depends upon their prehistory, particularly upon the modes of their thermal and mechanical pretreatment. In practice methods of the reactivity increase (activation) and its reduction (passivation) are used.

Under high-speed firing of inorganic substances their reactivity usually increases; such result is also achieved by mechanical activation. The joint action of these techniques frequently reduces their effectiveness as the material thermal treatment necessitates an evident decrease of structural defects concentration due to their accelerated relaxation through crystallization, recrystallization and other factors.

To reduce the inorganic substances reactivity, a hard firing is frequently used as it results in their recrystallization. But this technology is very energy intensive, and for such substances as calcium and magnesium oxides it does not always give essential beneficial effect.

The calcium and magnesium oxides find a wide application entering into the composition of different materials such as lime, magnesia cements, magnesium phosphate cement, etc. However it is practically impossible to manufacture any extensional products or constructions on their base because of their high rate of the interaction with tempering liquids and a considerable heat generation.

The magnesium and calcium oxides crystalline structures belong to the halite type but there are some differences between these structures. Magnesium ions with small dimensions occupy voids not deforming the crystal lattice and providing the maximum structure density. The ion radius ratio for calcium and oxygen (0.71) is close to the value 0.732 that is boundary for stability limits of coordination numbers 6 and 8. It reduces the CaO crystal lattice steadiness. As a result calcium oxide has a high hydration rate with a large heat generation (1160 kilojoules/mole) that results in some loosening and destruction of the calcium hydroxide initial framework, in other words, the destruction overpowers the structure formation resulting in a lower strength of the obtained lime hardened material.

It is well known that the mechanochemical treatment results in an activation of various materials including hydration activity increase of binding materials (works of G. Khodakov, L. Sulimenko and others). Under long-continued grinding some aggregation of obtaining fine particles which reduces the general material activity is to be observed. We have established that after a mechanical pretreatment by attrition (in a mortar or in a ball-ring mill) in contrast to impact action (in a jar or in a planetary mill) some reduction of calcium and magnesium oxides reactivity is observed. The degree of their chemical activity decrease is considerably higher than it can be explained by powders interfacial area reduction. So after an attrition of short duration the specific surface of MgO decreases by 20-30 per cent, while the activity of an oxide entering into the composition of magnesia cement decreases by 250-1000 per cent.

For the characteristic of oxides powders reactivity we have investigated:

- Solution rate and solubility of MgO;
- CaO hydration kinetics in water, in diluted solutions of orthophosphoric acid and in salt solutions;
- Carbonization rate of MgO and CaO and the following CO_2 thermal desorption from their surface;

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- Solid-phase reactions kinetics of the calcium carbide CaC_2 formation and magnesia spinel formation with mechanically treated oxides participation;
- Setting rate of binding compositions of phosphate and magnesia type.

The MgO Mechanical Treatment Influence upon its Solution Rate

It is well-known that magnesium oxide is not a readily soluble substance. The increased inertness of MgO as compared with CaO in respect of water is connected with a low solubility of the hydration product $Mg(OH)_2$ forming impermeable films on the initial material particles.

The rate of Mg^{2+} maximum concentrations and pH obtaining depends on the mechanical treatment duration, moreover, concentrations grow rapidly and reach their maximum (Fig. 1). Principal differences in the trend of curves for an impact action (Fig. 1 (a)) and an attrition treatment of oxide powder (Fig. 1 (b)-(c)) are observed.
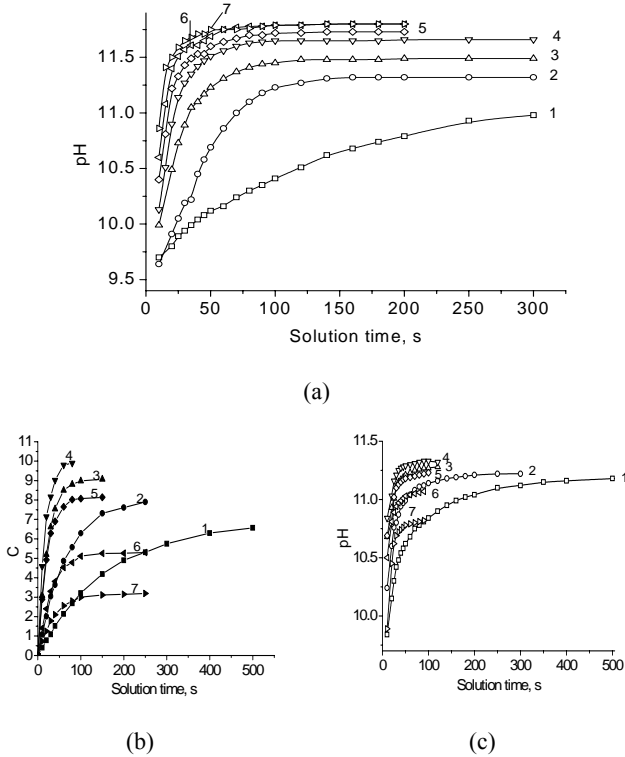

(a)

(b)   (c)

Figure 1. Variation of pH (a) (c) and Mg^{2+} concentration (b) during MgO solution after vibromechanical (a) and attrition (b), (c) treatment. Treatment duration, min: $1 - 0$; $2 - 1$; $3 - 3$; $4 - 5$; $5 - 7.5$; $6 - 10$; $7 - 12.5$

Under the time increment of a powder mechanical activation in a jar mill maximum values of pH and slope ratio steadily increase, it is connected with augmentation of a material layer thickness in which under the impact action influence a structural disordering takes place (Fig. 1 (a)). Dependences obtained under attrition pretreatment of MgO (Fig. 1 (b)-(c)) have a different character: maximum concentrations values of ions Mg^{2+} and OH^- at first grow (curves 1-4) and then recede (curves 4-7).

Results processing has been carried out in conformity with the Khodakov equation [1]:

$$C = C_\infty (1 - e^{k\tau}) \qquad (1)$$

where C and C_∞ - instant and maximum ion concentrations, mole/l, respectively; k – effective rate constant, s^{-1}; τ – solution time, s.

For pH tester values this equation has been interpreted in corresponding terms, in this connection OH^- content in the solution has been taken up as an instant concentration. See Fig. 2 for results.
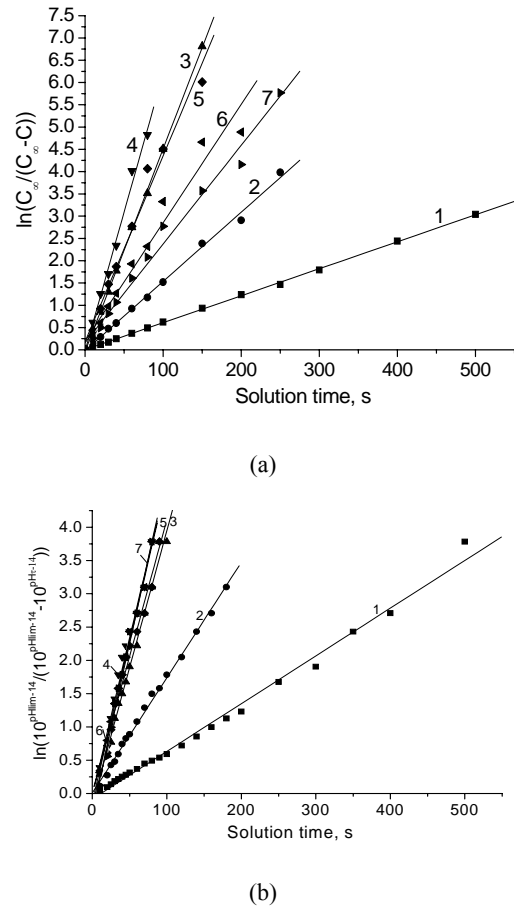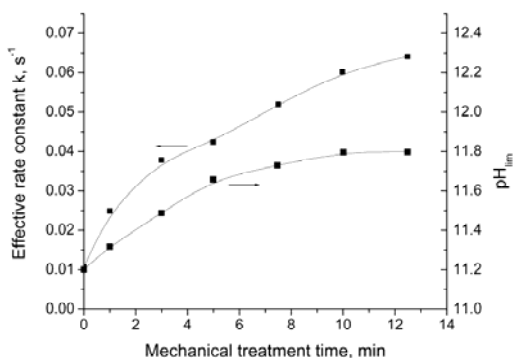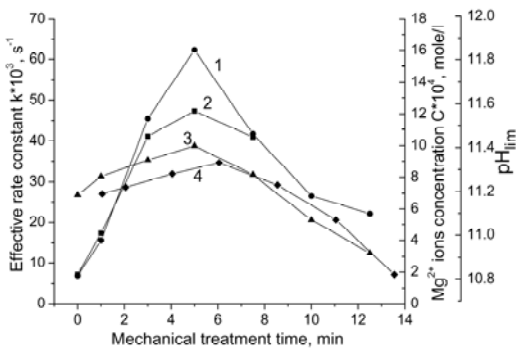

(a)

(b)

Figure 2. $\ln C_\infty/(C_\infty\text{-}C) - \tau$ (a) and $\ln(10^{pH\lim-14})/(10^{pH\lim-14} - 10p^{H\tau-14})\text{-}\tau$ (b) curves for MgO solution after mechanical treatment. Attrition duration, min: $1 - 0$; $2 - 1$; $3 - 3$; $4 - 5$; $5 - 7.5$; $6 - 10$; $7 - 12.5$

When increasing of impact treatment duration of MgO powder effective solution rate constants and pH values steadily grow converging to maximum (Fig. 3(a)), whereas under attrition k values (Fig. 3(b), curves 1,2) and maximum ion concentrations values pass through maximum corresponding to five-minute oxide treatment (Fig. 3(b), curves 3,4). The process rate constant rapidly reaches its maximum value; it indicates some destruction of only surface layer of oxide material. The hydroxylation of Mg^{2+} ions in defect positions with the following their transition into solution becomes easier.

(a)

(b)

Figure 3. Influence of vibromechanical (a) and attrition (b) treatment duration upon MgO solution rate determined according to pH instrument data ((a); (b), curve 2) and the change of Mg^{2+} concentration (b), curve 1) and upon maximum pH values ((b), curve 4) and Mg^{2+} concentration ((b), curve 3)

Figure 4. Photomicrographies of MgO crystals with no treatment (a), after attrition (b), (c), after vibromechanical treatment (d)-(f). Treatment duration, min: (a) – 0; (b), (c), (e), (f) – 10; (d) – 30. (Mark values correspond to 20 μm.)

The more long-continued attrition results in flat areas sliding and uncovering of flat surfaces that are character for crystals of the cubic system including magnesium oxide (Fig. 4(a)-(d)). At the same time irregular imperfect layer removes from grains. Broken bonds concentration decreases; the violated coordination in the lattice is partly reestablished; the electrostatic interaction becomes stronger; deformed areas volume reduces. In other words, the system optimizes the powder surface reducing the concentration of defects which are in excess in respect of their equilibrium concentration. As a result of these processes the chemical activity reduces; it is confirmed by the solution rate constant reduction. Thus the peculiar effect of a mechanochemical microstructure surface regulating is observed. Small particles separated from rounded grains during the mechanical treatment initially (up to 5 min) show increased solubility, and then they form very compact aggregates (Fig. 4(e)) having low activity.

The analogous powder treatment in a jar mill does not result in some surface regulating (Fig. 4(f)).

The sedimentation analysis (Fig. 5) shows that the powder granulometric composition changes a little, i.e. regrinding of coarse-grained particles is compensated by the interface diminution during aggregation.
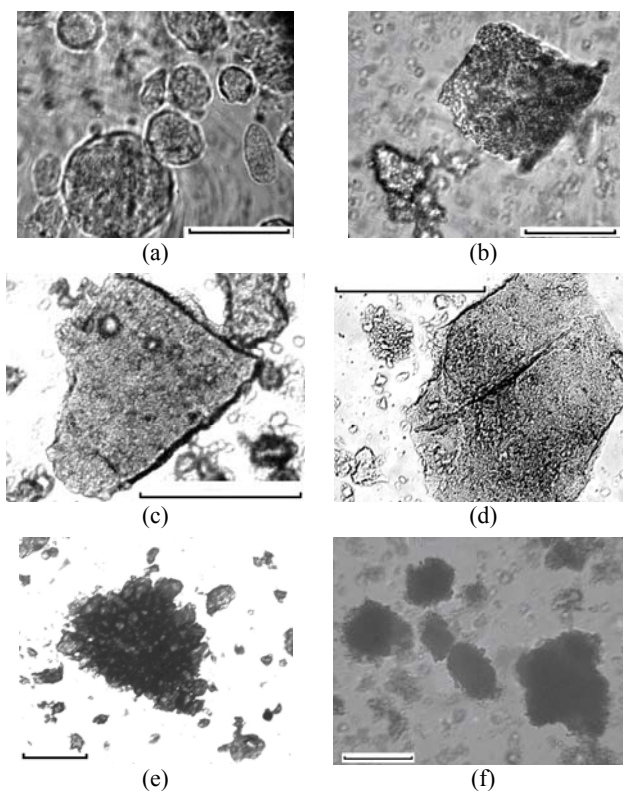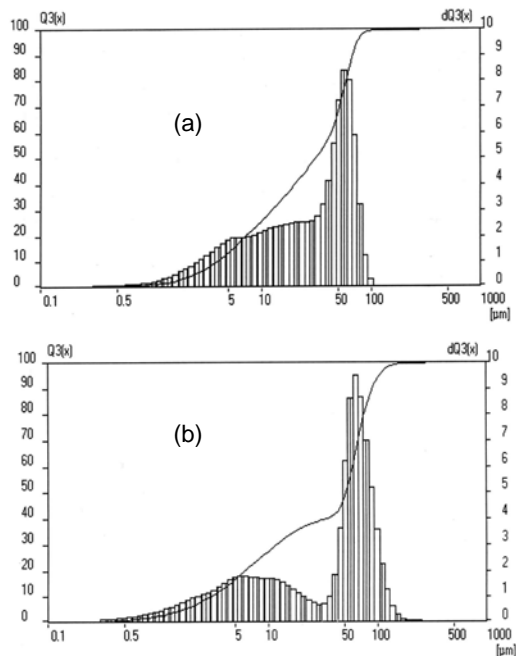

Figure 5. MgO particles distribution curves with no treatment (a), after attrition during 10 min (b)
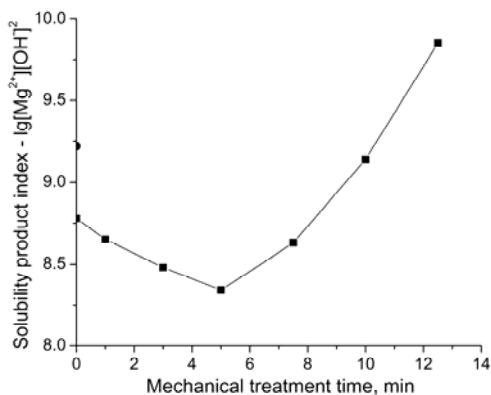
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Figure 6. Influence of attrition treatment duration upon MgO solubility (Horizontal line corresponds to the reference solubility product index value 9.22.

The dependence of solubility product index values upon the mechanical treatment duration (Fig. 6) has the minimum corresponding to the maximum solubility of magnesium oxide. The initial powder solubility increase (left branch of the curve) by a factor of 2.6 is changed by the solubility reduction by a factor of 33 (right branch).

The CaO Hydration Kinetics in Water, in Diluted Solutions of Orthophosphoric Acid and in Salt Solutions

Figure 7, illustrates dependences characterizing CaO hydration rate. Owing to the considerable heat generation an intense heating-up of the mixture of calcium oxide and water is observed. The realization of attrition pretreatment of the initial powder results not only in some retardation of the interaction with water but also in the conversion level decline (less slaking temperature values); when the mechanical treatment duration increase the CaO passivation effect intensifies.

The oxide activity reduction in principle may be connected with the surface formation of hydroxide and carbonate on the surface. But their quantity in the product is very small, moreover, infrared-spectral bands corresponding to valency and deformation vibrations of OH-groups coordinated around calcium atoms (3650 and 1030-1150 cm^{-1}) and to carbonate groups vibrations (880 and 1410-1450 cm^{-1}) are essentially weakened.

Analogous results have been obtained during the investigation of the interaction of calcium oxide with orthophosphoric acid solutions of different concentrations (Fig. 7 (b)-(e)). In this case the considerable reaction retardation is also observed. The dependences gain bends which are especially clear expressed for water and low acid concentrations (Fig. 7(a)-(b)). H_3PO_4 concentration increase reduces this effect (Fig. 7(d)-(e)).

For the quantitative assessment of the hydration rate line sections slopes were taken up as effective rate constants: k' – for middle parts, k'' – for intervals of rapid temperature growth (Table 1).
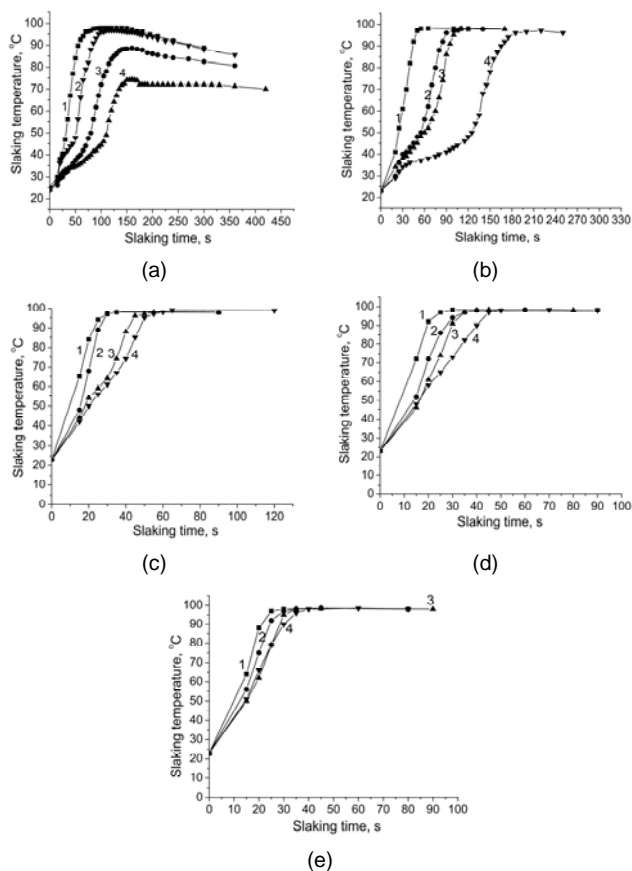

Figure 7. Influence of CaO attrition treatment upon its hydration process in water (a) and H_3PO_4 solutions (b)-(e). H_3PO_4 concentration, %: (b) – 1.2; (c) – 7.6; (d) – 12.1; (e) – 15.4. Attrition duration, min: 1 – 0; 2 – 5; 3 – 10; 4 – 15.

Table 1. Effective CaO hydration rate constants

Attrition treatment duration, min	Effective rate constants k'_{eff}/ k''_{eff}, s^{-1}, under H_3PO_4 concentration, %				
	0	1,2	7,6	12,1	15,4
0	0.50±0.01 / 1.8±0.1	- / 2.0±0.1	- / 2.9±0.1	- / 3.4±0.1	- / 3.1±0.0
5	0.35±0.03 / 1.6±0.1	0.42±0.03 / 1.6±0.1	- / 3.4±0.4	- / 2.4±0.1	- / 3.6±0.1
10	0.31±0.01 / 1.1±0.1	0.38±0.02 / 1.7±0.2	1.3±0.2 / 2.2±0.2	- / 3.0±0.1	- / 3.0±0.1
15	0.11±0.01 / 0.89±0.08	0.12±0.01 / 1.2±0.0	1.3±0.1 / 2.1±0.1	- / 1.7±0.1	- / 2.6±0.1

Lime grains subjected to attrition treatment become more compact (volume weight increases by ~ 15 per cent), because their hydration runs mainly on the surface. Paste-like hydrated films saturated with calcium hydroxide are formed on particles surface; they slow down subsequent water penetration to unslaking internal lime layers; the slaking process is gradually decelerates. At the same time k' values diminution after attrition treatment by a factor of 3.5-4.5 can not be explained only by the specific surface reduction (50-60 per cent by the BET-method) and by particles compaction. Evidently grains surface state change and larger regulating of their outer layers structure, i.e. microstructure regulating of surface layers plays an important part.

In spite of relative stability of particles sizes the attrition treatment is accompanied by violated layers removal from polycrystalline blocks surface and by the partial microroughness elimination. The more smoothed surface formation (Fig. 8(a)-(c)) results in the reactivity reduction. During mutual grinding-in of neighboring grains a part of imperfect surface layer is rubbed away making high-active fine particles which form compact aggregates (Fig. 8(d)).
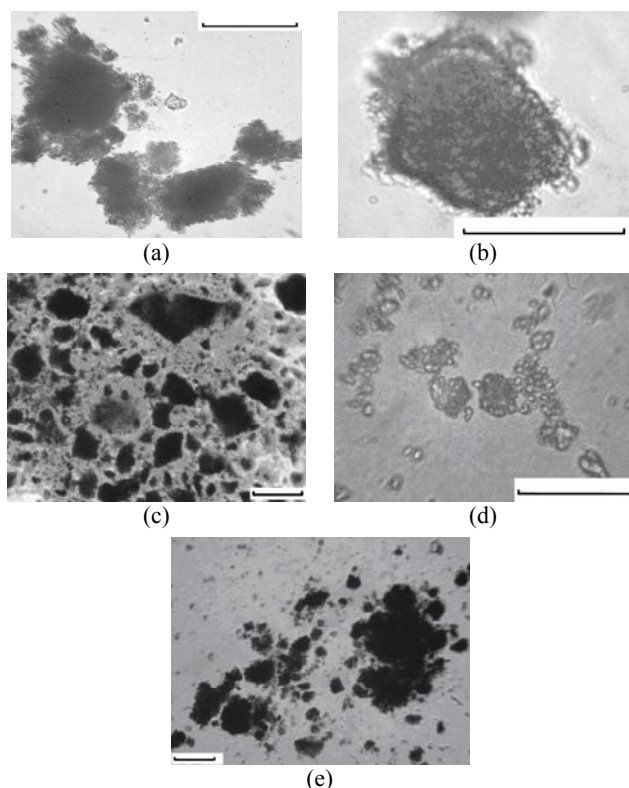

Figure 8. Photomicrographs of CaO after the treatment in a ball-ring mill (a)-(d) and a jar-mill (e). Treatment time, min: (a) – 5; (b), (d), (e) – 10; (c) – 15. (Mark values correspond to 20 μm.)

The interaction between CaO and phosphoric acid runs very rapidly and results in the formation of hardly permeable surface phosphates covers on the initial particles surface in addition retarding water diffusion to uncombined calcium oxide.

With the replacement of orthophosphoric acid by salts solutions (chlorides, nitrates) dependences character does not change. The same principal curves kind is evidence of the analogous hydration mechanism. In solutions with increased concentrations electrolytes discharge forming colloid micelles of $Ca(OH)_2$, it results in diffusive layers separation and more active subsequent hydration process. The surface passivation effect at that reduces.

Khodakov [1] noticed that molecular-compact aggregation coupled with the lattice destruction does the establishment of the unique correlation between dispersity and powders activity impossible. Seemingly the change of solid phase surface state takes on special significance because of different activity of separated parts (Butyagin [2] warned against the identification of the whole particles surface and their reactive surface). So more regulating zones uncovered during attrition enter into a reaction with a smaller rate in comparison with initial (untreated) grains and separated fine particles.

The Kinetics of MgO and CaO Carbonization and the following Decarbonization of Products

It was of interest to investigate the carbonization process of treated calcium and magnesium oxides surfaces. It is known that initial chemisorptive bonds are localized on active adsorption centers, therefore the surface non-uniformity and different structure defects must influence essentially upon the quantity of added substance.

The forming carbonate quantity was determined over mass growth. The conversion degree was calculated by the equation: $\alpha = \Delta m/m_o$.

Dependences α upon the duration of oxides contact with carbonic gas for different modes of powder pretreatment are shown on Fig. 9.

Figure 9. Influence of CaO pretreatment mode upon the quantity of the forming calcium carbonate: 1 – initial (untreated) CaO powder; 2 – oxide treated in a jar mill; 3-5 – oxide treated in a ball-ring mill 5, 10 and 15 min respectively

High values of the conversion degree indicate that components interact chemically since chemisorptive bonds form only in limits of monomolecular layer. This fact is also confirmed by dependences linearity in coordinates of the Ginstling-Brounshtein equation (Fig. 9(b)):

$$1 - \frac{2}{3}\alpha - (1-\alpha)^{\frac{2}{3}} = k'\tau. \qquad (2)$$

The limiting stage is CO_2 diffusion through the forming carbonate layer.

As expected, the maximum values of the conversion degree and effective carbonization reaction rate constant correspond to an impact pretreatment of oxides (Fig. 9(a)-(b), curves 2; Table 2). At impact action moments (10^{-5}-10^{-6} s) local power transmitted to the crystalline structure is able to achieve 10^7-10^8 Joule/(cm^3·s) [2], that results in defects accumulation, surface layers loosening and essential complication of the surface relief (Fig. 4(f); Fig. 8(e)).

After attrition treatment the rate of oxides interaction with carbon dioxide decreases; the duration prolongation of this mechanical action moreover retards the reaction (Table 2).

Table 2. Effective rate constants of CaO and MgO carbonization and formed $CaCO_3$ and $MgCO_3$ decarbonization[*]

Oxide pretreatment mode	Effective rate constants, s^{-1}, for the reaction of	
	carbonization k'·10^6	decarbonization k''·10^3
With no treatment	9.9 ± 0.7	1.2 ± 0.1
	1.0 ± 0.1	2.9 ± 0.1
Treatment in a jar mill	19 ± 1	1.0 ± 0.1
	2.5 ± 0.1	2.4 ± 0.1
Treatment in a ball-ring mill, min:		
5	7.7 ± 0.6	1.4 ± 0.1
	0.8 ± 0.1	3.0 ± 0.2
10	4.5 ± 0.4	1.5 ± 0.2
	0.32 ± 0.02	3.2 ± 0.3
15	1.9 ± 0.1	1.9 ± 0.1
	0.07 ± 0.01	3.4 ± 0.2

[*] The numerator stands for CaO ($CaCO_3$), and the denominator – for MgO ($MgCO_3$).

The study of subsequent thermolysis of obtained $CaCO_3$ and $MgCO_3$ shows that carbonates formed on the surface of oxides pretreated by different methods decompose with differing rate (Fig. 10; Table 2). For decarbonization process CO_2 residual was taken up as the conversion degree.

Results processing has been carried out in conformity with the equation of contracting sphere:

$$1 - (1-\alpha)^{\frac{1}{3}} = k''\tau. \qquad (3)$$

Carbonates formed in a considerable quantity on the surface of oxides pretreated in a jar mill decompose a little slower than those obtained on oxides crystallites after attrition treatment. In the first case carbonate layers form both on the outer side and on the insides of loosened aggregates, they fill up the pores making difficulties for CO_2 thermal desorption from the reaction zone and giving an opportunity for recarbonization.
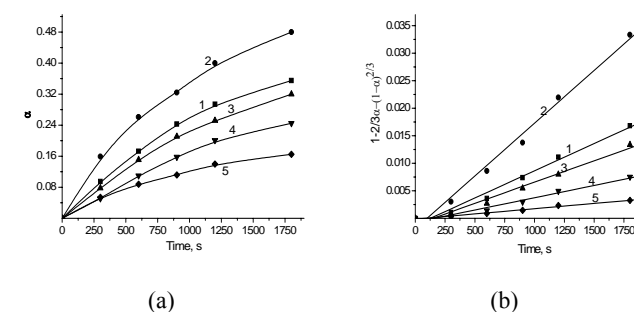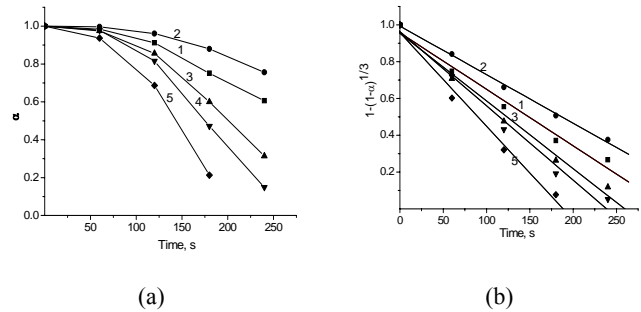

(a) (b)

Figure 10. Influence of CaO pretreatment mode upon the decomposition rate of the formed calcium carbonate: 1 – initial (untreated) CaO powder; 2 – oxide treated in a jar mill; 3-5 – oxide treated in a ball-ring mill 5, 10 and 15 min respectively

The Kinetics of Calcium Carbide Formation

The calcium carbide synthesis from CaO and amorphous carbon has been studied. Since, as it has been established above attrition and impact action results in different degree of material regulating, a starting batch was prepared by differing modes:

- Simple mixing of components;
- Mixing of CaO pretreated in a ball-ring mill with C;
- Combined pretreatment of a mixture CaO + C in a ball-ring mill;
- Combined pretreatment of a mixture CaO + C in a planetary mill.

The synthesis was carried out in a microwave oven (2.45 GHz frequency; 6 kW power). The choice of a magnetron oven sets conditions for high-speed and intense self-heating of an initial mixture in an electromagnetic field; it results in CaC_2 formation with a minimal unproductive carbon loss.

Amorphous carbon was introduced into the batch with 5 per cent excess with respect to the reaction stoichiometry: CaO + 3 C = CaC_2 + CO ↑.
Calcium carbide content was determined by a quantity of liberated acetylene. CaC_2 content in a product was taken up as the conversion degree.

In the course of the reaction oxide grains are covered by product layer (Fig. 11(a)) through which amorphous carbon diffuses for the further reaction processing. For experimental results the Ginstling-Brounshtein diffusion model of treatment (2) has been chosen.

In the reaction carbon oxide CO segregates from grains surface and does not block the forming of a continuous product layer. Effective reaction rate constants are brought in the Table 3.
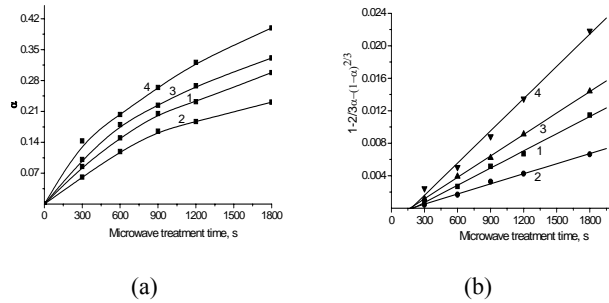
Figure 11. Microwave synthesis kinetics of calcium carbide when using: untreated mixture of CaO and carbon (1); mixture of pretreated CaO in a ball-ring mill with carbon (2); mixture of CaO and carbon jointly treated in a ball-ring mill (3); mixture of CaO and carbon jointly treated in a planetary mill (4)

Table 3. Effective rate constants of the microwave calcium carbide synthesis

Mixture preparation mode	Effective rate constants $k \cdot 10^6$, s^{-1}
Simple mixing	6.5 ± 0.4
Mixing of pretreated CaO in a ball-ring mill with carbon	3.9 ± 0.2
Joint treatment of CaO and carbon in a ball-ring mill	8.2 ± 0.4
Joint treatment of CaO and carbon in planetary mill	12.3 ± 0.7

Rate constants values may be disposed in descending line for batches:

$$[CaO + C]_{impact} > [CaO + C]_{attrition} > CaO + C > [CaO]_{attrition} + C.$$

It is known that impact and sliding are accompanied by a local material heating-up which in conditions of a direct contact of reagents promotes the more intensive reaction run. At the same time in such conditions certainly some carbon loss due to its oxidation will be observed.

Combined pretreatment of a mixture CaO + C in a mill of impact action results in its maximum activation and thus in a considerable acceleration of the synthesis. The attrition of an initial mixture also increases the solid-phase reaction rate although to a less degree. It is interesting that effective rate constants differ only by a factor of 1.5 whereas power intensity of mills increases by a factor of 60. The main reason of the process accelerating after a treatment in a ball-ring mill seems to be providing of maximum reagents contact under attrition by means of some increase of touching zones area. Naturally the real particles contact area is considerably smaller than macroscopic flat surface because the latter has complicated microscopic relief, but during sliding under load some lapping of non-homogeneous surfaces takes place.

The attrition treatment of CaO results in the microstructure regulating due to some reduction of substance polycrystallites imperfection and thanks to the formation of compact aggregates having reduced reactivity.

The Set Rate of Binding Compositions including Passivated Metal (II) Oxides of Phosphate and Magnesia Type

For the corroboration of oxides passivation evidence set terms of some binding compositions have been determined by the standard method (the Vicat device).

At this stage the results for larger oxides number of metals belonging to II group of the Periodic system have been juxtaposed. Alkaline-earth metals oxides and cadmium oxide form crystal structure of halite type. Beryllium and zinc oxides in which covalent interaction plays an important part have a lattice of wurtzite type.

The comparative study of the conduct of binding systems including indicated oxides and solutions of orthophosphoric acid or some salts (chlorides, nitrates, sulphates) as tempering liquids. During set the number of local sections in which a distance between neighboring particles becomes comparable with particles sizes increases. It results in intergrowth contacts formation due to coordination and hydrogen bonds. Cohesive contacts assemblage in cementing phase provides the binding dispersion hardening. Thus, in our opinion, the formation rate of these contacts is able to characterize the reactivity of oxides developing binding properties.

Figure 12 presents dependences characterizing initial and final sets of binding paste containing mechanically treated calcium oxide and diluted H_3PO_4 solutions of different concentrations. Under such conditions the set process considerably decelerates, initial set moves away from practically momentary to 4.5-5.5 min.

Set terms of compositions including oxides of beryllium, magnesium, cadmium, zinc and orthophosphoric acid solutions are presented in Table 4. It is clear disclosed the essential retardation of the chemical interaction of magnesium and cadmium oxides crystallizing by halite type whereas the same mechanical treatment has a little influence upon analogous processes in systems with the participation of beryllium and zinc oxides (wurtzite type). The results obtained for the same oxides using water-salt tempering liquids evidence these regularities (Table 5).
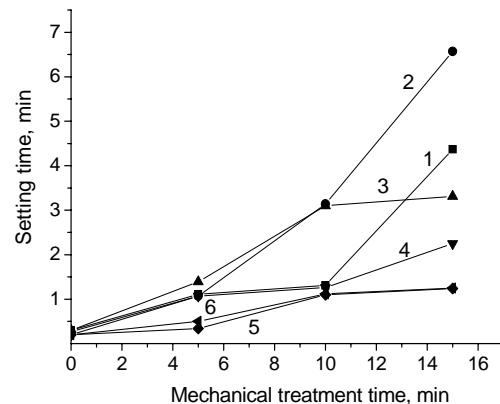

Figure 12. Influence of attrition treatment CaO and H_3PO_4 concentration upon initial setting time of phosphate composition. H_3PO_4 concentration, %:1 – 1.2; 2 –3.1; 3 –4.9; 4 –7.6; 5 –10.3; 6 – 15.4

Table 4. Influence of oxides attrition treatment upon the setting time of phosphate compositions

Composition	Treatment duration, min	Initial setting time, h-min-s	Final setting time, h-min-s
$BeO – H_3PO_4$	0	0-28-15	0-38-20
	5	0-26-50	0-37-50
	10	0-21-45	0-40-15
	15	0-29-30	0-42-25
$MgO – H_3PO_4$	0	Fast setting	0-02-00
	5	0-02-00	0-04-30
	10	0-51-30	1-47-40
	15	> 3.5 h	Undefined
$CdO – H_3PO_4$	0	0-00-35	0-02-25
	5	0-04-45	0-09-00
	10	0-42-00	1-15-00
	15	1-15-30	2-30-00
$ZnO – H_3PO_4$	0	0-12-00	0-13-50
	5	0-06-50	0-07-40
	10	0-09-10	0-10-45
	15	0-10-00	0-11-15

Table 5. Influence of oxides attrition treatment upon the setting time of compositions with water-salt tempering liquids

Composition and salt concentration	Treatment duration, min	Initial setting time, h-min-s	Final setting time, h-min-s
$MgO – MgCl_2$ (20 %)	0	1-24-45	2-47-05
	5	2-03-10	2-41-10
	10	3-01-15	3-18-35
	15	3-25-15	3-46-30
$MgO – Mg(NO_3)_2$ (15 %)	0	0-21-05	0-34-44
	5	0-54-30	1-06-45
	10	0-40-30	2-57-14
	15	3-15-50	3-36-41
$CdO – CdCl_2$ (15 %)	0	0-01-20	0-01-45
	5	0-02-05	0-03-00
	10	0-02-10	0-03-20
	15	0-02-20	0-05-50
$CdO – CdSO_4$ (15 %)	0	0-10-10	0-11-25
	5	0-14-05	0-17-50
	10	0-19-15	0-20-25
	15	0-27-55	0-30-05
$ZnO – Zn(NO_3)_2$ (15 %)	0	0-09-40	0-13-30
	5	0-16-10	0-17-45
	10	0-16-20	0-18-05
	15	0-16-50	0-19-10
$ZnO – ZnSO_4$ (15 %)	0	0-01-30	0-01-45
	5	0-01-10	0-01-25
	10	0-01-20	0-01-35
	15	0-01-20	0-01-30

The specific surface area diminution of treated powders owing to aggregation is not so large (from 20-30 to 50-60 per cent by BET-method) in order to explain chemical interaction rate reduction by a factor of tens and hundreds. Seemingly the determining factor is the uncovering of relatively low imperfect flat surfaces whiles separated fine particles having a large reserve of surface free energy easily aggregate into very compact formations which interact with a tempering liquid with a rate characteristic for large particles of a correspondent size (Fig. 4, 8).

On the contrary, zinc oxide crystallites do not change the surface character during the mechanical treatment (Fig. 13), that corresponds to the approximately constant chemical activity of them (Tables 4, 5).
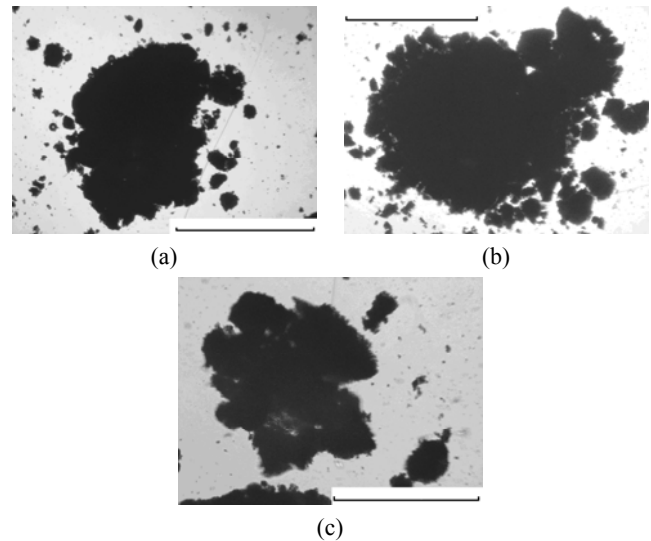

Figure 13. ZnO photomicrographies. Attrition treatment duration, min: (a) – 0; (b) – 5; (c) – 10 (Mark values correspond to 20 μm.)

Some powder compactness growth, more sharp form of X-ray diffraction reflections and IR-spectrums may serve as an independent corroboration of the microstructure regulating. Flat low imperfect surfaces show a small activity in respect of water vapors and carbon dioxide. Besides calorimetric estimation of stored energy value during a mechanical treatment indicates its essential increase under using of apparatus with high energy intensity of impact action (planetary, jar mills), while preliminary attrition treatment generates some reduction of this characteristic. The mechanopassivation effect has been also observed for some others oxides crystallizing by halite type, specifically NiO.

Thus, the mechanochemical attrition treatment of substances crystallizing by halite type really allows decreasing reactivity of these oxides in rather wide range.

It opens new abilities in the chemistry of binding materials; giving chance to obtain a proportion between rates of chemical interaction and structure formation that is a necessary condition for the forming of durable monolithic.

The attrition treatment is undoubtedly more economical in comparison with prolonged hard firing (1200-1600 °C and more) which is applied at present for some oxides activity reduction.

The mechanopassivation effect may be also promising for regulation of medical products rate solution, corrosion rate reduction, leaching decrease, etc.

It is necessary to recognize that nowadays the list of known substances reducing their reactivity under attrition treatment influence is not too long, but the presence of such important from technological point of view oxides as CaO and MgO does this work expedient and promising.

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