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РЕГУЛИРОВАНИЕ АКТИВНОСТИ ВЯЖУЩИХ ВЕЩЕСТВ МЕХАНОХИМИЧЕСКИМИ МЕТОДАМИ

Н.Ф. Косенко, Н.В. Филатова

Надежда Федоровна Косенко, Наталья Владимировна Филатова *

Ивановский государственный химико-технологический университет, кафедра технологии керамики и наноматериалов, пр. Шереметевский, 7, Иваново, Российская Федерация, 153000
E-mail: nfkosenko@gmail.com, zyanata@mail.ru *

Установлено, что истирающая обработка оксидов металлов, кристаллизующихся по типу галита (CaO, MgO), понижает их реакционную способность. Скорость снижения активности заметно выше, чем это может быть объяснено уменьшением удельной поверхности оксида. Так, для MgO последняя снижается на 30-40 %, тогда как активность оксида в магнезиальном цементе – на 250-1000 % (в отличие от обработки ударного типа в вибромельнице). Аналогичные результаты были получены для взаимодействия между оксидом кальция и водой, растворами ортофосфорной кислоты и солей. Удельная поверхность порошка CaO до и после истирающей обработки по методу БЭТ снижается на 50-60 %, а изменения константы скорости находятся в пределах 1,5-34 раза. Подобная механическая обработка не вызывает сходных процессов в системах с оксидами бериллия и цинка (структурный тип вюртцита). Снижение реакционной способности оксидов магния, кальция и кадмия может быть связано с некоторыми изменениями формы поликристаллитов в ходе истирающей обработки. Продолжительное истирание приводит к скольжению плоскостей, выравниванию, что характерно для кристаллов кубической сингонии. Таким образом, несовершенный поверхностный слой, насыщенный дефектами, удаляется с зерен. Мельчайшие частицы, отделенные в процессе механической обработки от округлых зерен, на первой стадии (до 5 мин) проявляют повышенную активность, но впоследствии образуются мало активные плотные агрегаты. Более упорядоченные области, обнаженные при истирании, взаимодействуют медленнее, чем исходные зерна и отщепившиеся частицы. Благодаря этому, реакционная способность снижается. Кристаллиты оксидов цинка и бериллия, напротив, практически не изменяют своих очертаний в процессе истирания; их реакционная способность остается постоянной. Таким образом, механическое истирание оксидов, которые кристаллизуются по типу галита, действительно позволяет понизить их реакционную способность в довольно широких пределах. Это открывает новые возможности в химии вяжущих материалов, давая возможность достичь требуемого соответствия между скоростями химической реакции структурообразования в вяжущих системах, что является необходимым условием для образования прочных монолитных композиций.

Ключевые слова: реакционная способность, механоактивация, механопассивация, истирающая обработка, ударная обработка, вяжущие свойства, оксиды металлов, структурный тип галита, структурный тип вюртцита, фосфатные вяжущие системы

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BINDING MATERIALS ACTIVITY REGULATING BY MECHANICAL CHEMICAL METHODS

N.F. Kosenko, N.V. Filatova

Nadezhda F. Kosenko, Natalya V. Filatova *

Department of Technology of Ceramic and Nanomaterials, Ivanovo State University of Chemistry and Technology, Sheremetev ave., 7, Ivanovo, 153000, Russia
E-mail: nfkosenko@gmail.com, zyanata@mail.ru *

It has been established that some abrading treatment of metals oxides crystallizing by halite crystal type (CaO, MgO) reduces their reactive capability. The activity reduction rate was substantially higher than that which could be explained by reducing of oxide specific surface. So, it is reduced for MgO by 30-40 %, while the oxide activity in the magnesium cement – by 250-1000 % (contrary to an impact treatment in a vibration mill). Similar results have been obtained for the interaction between calcium oxide and water, solutions of orthophosphoric acid and salts. CaO powder specific surface before and after abrading treatment by BET method reduces by 50-60 %, while variations of rate constant ranged from 1.5 to 34 times. The same mechanical treatment has a little effect on similar processes in systems where beryllium and zinc oxides are present (structure type of wurtzite). The reactive capability reduction for calcium, magnesium and cadmium oxides can be connected with some changes in the form of polycrystallites' particles in the abrading treatment process. The more prolonged abrading leads to plane sliding and some exposing flat surfaces those are characteristic for crystals of cubic syngony. Thus, an irregular defect layer is removed from grains. Small particles separated in the course of a mechanical treatment from rounded grains at the first stage (up to 5 min) show an increased activity, and then quite dense low active aggregates are formed. The more ordered zones, exposed in the course of an abrading, react slower in comparison to the initial grains, as well as to thin particles being split out. Due to this process the chemical activity reduces. On the contrary, zinc and beryllium oxides crystallites in the abrading treatment practically do not change their outline character; their chemical activity remains constant. Thus, the mechanical abrading treatment of oxides, which crystallize by halite type, really allows reducing their reactive capability in quite wide limits. This opens new opportunities in chemistry of binding materials, allowing achieving needed proportion between rates of chemical interaction and structure-forming in binding systems, which is a necessary condition for a solid monolith compositions' formation.

Key words: reactive ability, mechanical activation, mechanical passivation, abrading treatment, impact treatment, binding properties, metals oxides, halite structural type, wurtzite structural type, phosphate binding systems

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INTRODUCTION

It is known that a strong structure of a conglomerate on the base of a binding material is formed in the case if the rate of any chemical reaction between components of the binding system is closely corresponding to the structure forming rate.

Along with that, some compositions are setting too quickly and with substantial heat release, that leads to loosening and disintegration of the initial frame of news growths and makes it impossible to form a stable structure. In particular, the following combinations can be referred to as such compositions: lime and water, calcium and magnesium oxides with orthophosphoric acid, and a range of binding systems of magnesium setting.

To reduce reactive ability of binding component in relation to a tempering liquid the preliminary high-temperature processing is widely used, as well as a dilution with any inert component, partial neutralization of an acid tempering liquid (particularly phosphoric acid), etc. To reduce the lime activity it was suggested to use an artificial cooling (the removal of a released hydration heat), which promotes to increase the lime stone strength by an order (works by B.V. Osin and L.G. Shpynova). Complex polyfunctional additives allow reducing the heat release rate, and maintaining sufficiently the high strength of a lime stone (30-50 MPa) at the minimal porosity (10-20%) due to the hydration setting. The penetration into CaO crystalline lattice of small sized cations, like Si^{4+}, Al^{3+}, Fe^{3+}, which exert high polarization capability in the burning process, also limits rate of O^{2-} ions' protonization when the hydration occurs [1].

It is known that in the course of a mechanical chemical processing the activation of various materials takes place, including some increase in the hydration activity of binding materials (works by L.M. Sulimenko, G.S. Khodakov, and others). In case of a prolonged grinding, the aggregation of obtaining thin-dispersed is observed, which reduces activity of material as a whole.

Experimental technique was described in [2-4].

RESULTS AND THEIR DISCUSSION

While having been investigating of an abrading treatment on the reactive capability of calcium and magnesium oxides, we have established [2-4] that the reduction rate of their activity was substantially higher than that which could be explained by reducing of MgO specific surface; it is reduced by 30-40 %, while the oxide activity in the magnesium cement – by 250-1000%.

It is found that with increasing time of MgO powder abrading (contrary to an impact treatment in a vibration mill, Fig. 1a) values of effective constants of dilution rate (Fig. 1*b*, curves 1, 2) and top values of ions concentrations (Fig. 1*b*, curves 3, 4) reach the maximum peak.

The more prolonged abrading leads to plane sliding and some exposing flat surfaces that are characteristic for crystals of cubic syngony, to which magnesium oxide relates (Fig. 2b). Thus an irregular defect layer is removed from grains. Due to this process the chemical activity reduces which is confirmed by reduce in oxide dilution rate. Small particles separated in the course of a mechanical treatment from rounded grains at the first stage (up to 5 min) show an increased solubility, and then quite dense aggregates are formed (Fig. 2c) that have low activity [5].

Similar results have been obtained in the course of the research of the interaction between calcium oxide and water (Fig. 3*a*), solutions of orthophosphoric acid (Fig. 3*b*, *c*, *d*) and salts (Table 1). Some inflexions appear on the relations, which are especially distinct for water and acid low concentrations (Fig. 3*a*, *b*). With growth of H_3PO_4 concentration this effect is mitigated (Fig. 3*c*, *d*).

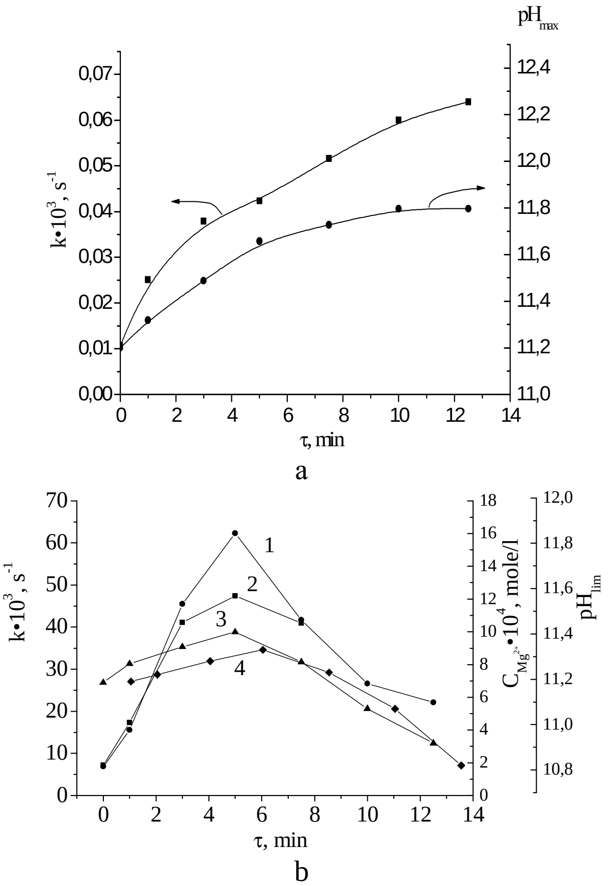

Fig. 1. Influence of vibration (a) and abrading (b) treatment period on MgO dilution rate, determined by pH-metry data (a, b) and by variations of Mg^{2+} ions concentration (b, curve 1), and maximum values of the solution pH (b, curve 4) and Mg^{2+} concentration (b, curve 3)

Рис. 1. Влияние длительности вибрационной (а) и истирающей (b) обработки на скорость растворения MgO, определенную по данным pH-метрии (a, b) и по изменению концентрации ионов Mg^{2+} (b, кривая 1) и максимальные значения pH раствора (b, кривая 4) и концентрации Mg^{2+} (b, кривая 3)

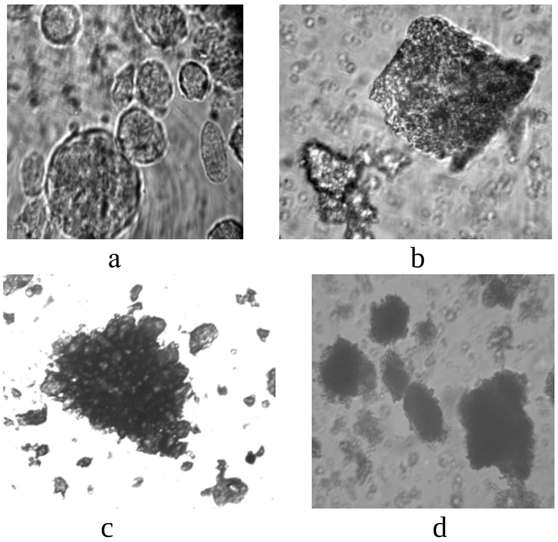

Fig. 2. Microphotographies of MgO crystals: no treatment (a), after abrading (b, c), after vibration treatment (d)

Рис. 2. Микрофотографии кристаллов MgO без обработки (a), после истирания (b, c), после виброобработки (d)

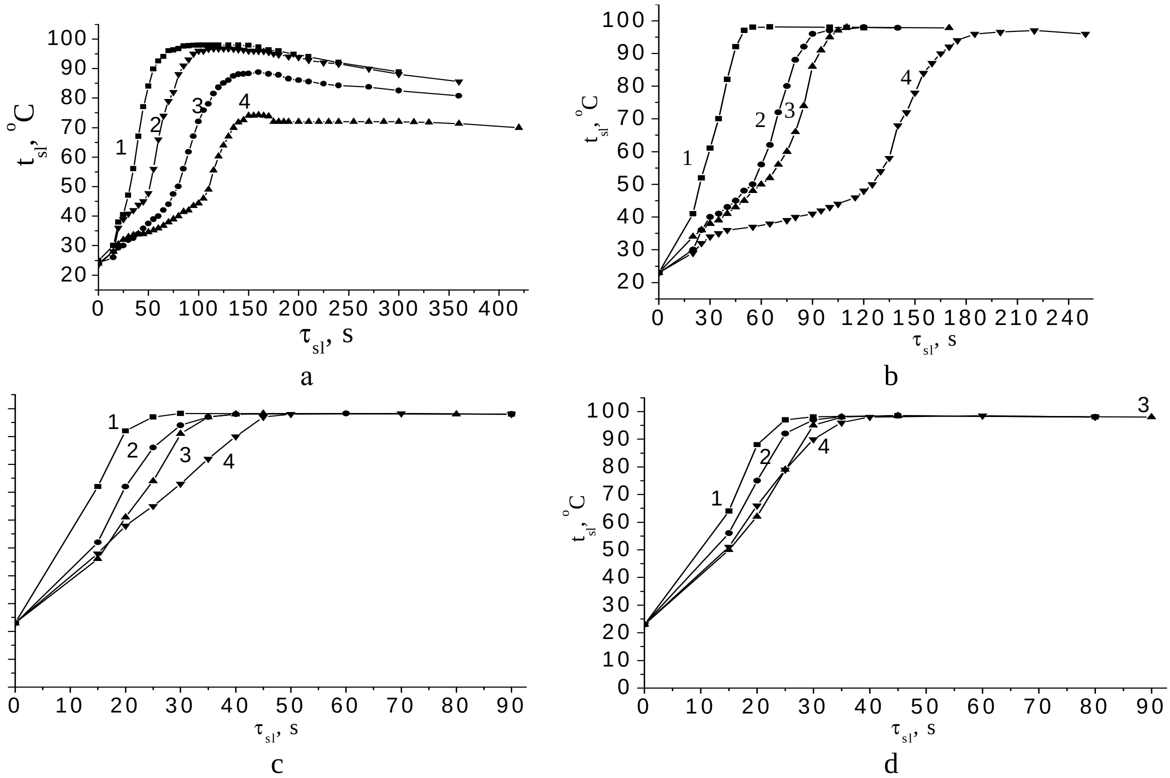

Fig. 3. Influence of CaO abrading treatment on its hydration in water (a) and H_3PO_4 solutions (b-d). H_3PO_4 concentrations, %: b – 1.2; c – 12.1; d – 15.4. Abrading time, min: 1 – 0; 2 – 5; 3 – 10; 4 – 15

Рис. 3. Влияние истирающей обработки CaO на процесс его гидратации в воде (a) и растворах H_3PO_4 (b-d). Концентрация H_3PO_4, %: b – 1,2; c – 12,1; d – 15,4. Время истирания, мин:
1 – 0; 2 – 5; 3 – 10; 4 – 15

Table 1

Effective hydration rate constants of calcium oxide in salts solutions

***Таблица 1.* Эффективные константы скорости гидратации оксида кальция в растворах солей**

Abrading treatment duration, min	Effective hydration rate constants k'				
	Water/Вода	$CaCl_2$ (5%)	$Ca(NO_3)_2$ (5%)	$Ca(NO_3)_2$ (10%)	$Ca(NO_3)_2$ (15%)
0	0.50 ± 0.01 1.8 ± 0.1	0.68 ± 0.02 1.4 ± 0.1	0.44 ± 0.02 1.2 ± 0.1	0.31 ± 0.07 1.6 ± 0.4	0.40 ± 0.01 5.6 ± 0.1
5	0.35 ± 0.03 1.6 ± 0.1	0.32 ± 0.01 1.1 ± 0.1	0.44 ± 0.02 1.2 ± 0.1	0.40 ± 0.03 1.6 ± 0.1	0.37 ± 0.03 2.3 ± 0.1
10	0.31 ± 0.01 1.1 ± 0.1	0.08 ± 0.02 1.5 ± 0.1	0.10 ± 0.01 1.5 ± 0.1	0.16 ± 0.01 1.0 ± 0.1	0.40 ± 0.01 3.9 ± 0.1
15	0.11 ± 0.01 0.89 ± 0.08	0.02 ± 0.00 1.2 ± 0.1	0.03 ± 0.01 1.6 ± 0.1	0.14 ± 0.01 1.1 ± 0.1	0.28 ± 0.01 2.0 ± 0.01

Measurements of CaO powder specific surface before and after abrading treatment by BET method have shown a reduction in this characteristic by 50-60%, while variations of rate constant k'_{ef} ranged from 1.5 to 34 times. Presumably, changes in the condition of the solid surface are of a substantial significance. So, the more ordered zones, exposed in the course of an abrading, react slower in comparison to the initial grains, as well as to thin particles being split out.

To confirm the fact of the slowdown of CaO hydration in solutions, terms of compositions' setting have been determined. For the initial calcium oxide, when calcium chloride (5-10%) as a tempering liquid was used, it was not possible to determine the start of setting due to the rapid reaction; the end of setting was observed in ~20 sec, end of setting – 30-32 sec.

Compared were the results obtained for a large number of metals oxides belonging to the II group of the Periodical table, crystallizing in various systems. So, alkali-earth metals oxides and cadmium oxide have the structure of halite NaCl. Beryllium and zinc oxides, in which covalent bond plays a substantial part, form the lattice of wurtzite ZnS type.

In Table 2 there are presented terms of setting for compositions including beryllium, magnesium, cadmium, zinc oxides and H_3PO_4 solutions.

Table 2

Influence of abrading treatment of oxides on setting time for phosphate compositions

***Таблица 2.* Влияние истирающей обработки оксидов на сроки схватывания фосфатных композиций**

Treatment duration, min	Setting start, h-min-sec	Setting end, h-min-sec
	$BeO - H_3PO_4$	
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	Quick setting	0-02-00
5	0-02-00	0-04-30
10	0-51-30	1-47-40
15	More than 3.5 hrs	Not established
	$CdO - H_3PO_4$	
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

It can be clearly seen that there occurs a substantial slow-down of the chemical interaction of magnesium and cadmium oxides, which crystallize by halite type, while the same mechanical treatment has a little effect on similar processes in systems where beryllium and zinc oxides are present (structure type of wurtzite). These regularities can be confirmed by results obtained when water-salt tempering agents had been used for the same oxides.

The reactive capability reduction for calcium, magnesium and cadmium oxides can be connected with some changes in the form of polycrystallites' particles in the abrading treatment process.

On the contrary, zinc oxide crystallites in the abrading treatment practically do not change their outline character (Fig. 4), which fact corresponds to their constant chemical activity (Table 2).

Apart from microphotographs, as a confirmation of some micro-structural ordering the following can be considered: an increase in powders' density, the sharper peaks form in diffractograms, IR-spectra. Plane surfaces with little defects show the smaller activity in reacting with water vapors and CO_2 [3]. Besides, the calorimetric determination of the energy, accumulated in the mechanical treatment process, has shown its substantial increase when high-energy-intensive impacting equipment (planetary, vibration mills) had been used, while preliminary powders' abrading leads to some decline in this characteristic.

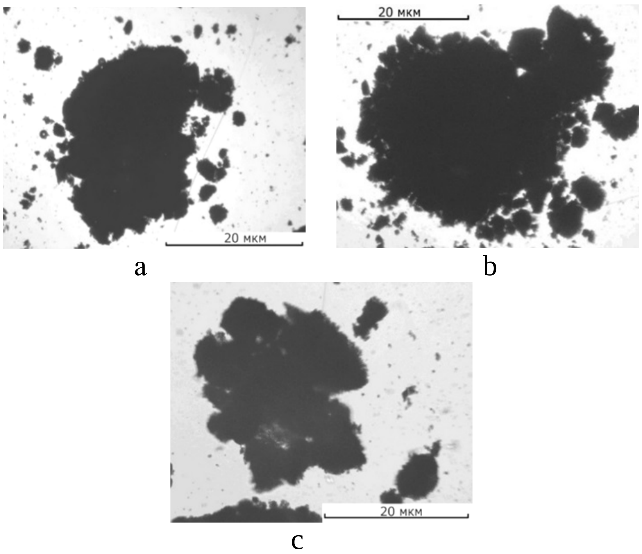

Fig. 4. Microphotographies of ZnO crystals. Abrading treatment time, min: a – 0; b – 5; c – 10

Рис. 4. Микрофотографии ZnO. Длительность истирающей обработки, мин: a – 0; b – 5; c – 10

It was also noted that the mechanical passivation has shown itself for several other oxides which crystallize by halite NaCl type (NiO in particular).

Thus, the mechanical abrading treatment of oxides, which crystallize by halite type, really allows reducing their reactive capability in quite wide limits. This opens new opportunities in chemistry of binding materials, allowing achieving needed proportion between rates of chemical interaction and structure-forming in binding systems, which is a necessary condition for a solid monolith compositions' formation.

The abrading treatment is certainly the more economic in comparison with a prolonged high-temperature burning (1200-1600 °C and higher), which is applied at present for reducing activity of some oxides. It is necessary to admit that the range of investigated substances that change their reactive capability under the influence of a mechanical treatment of abrading type is rather limited, but the fact that there are among them such important oxides, from the technological point of view, as CaO and MgO, makes this work to be efficient and promising.

CONCLUSIONS

The MgO dilution in water after vibration and abrading treatment was studied. The impact treatment leads to the continuous growth of the dilution rate while dilution characteristics dependences have maxima in the course of abrading.

Some slowdown of abraded CaO with water, solutions of orthophosphoric acid and salts; the slowdown degree is proportional to the abrading time. The similar result is obtained for phosphate binding compositions setting time.

Obtained observations are explained in the terms of some micro-structural ordering of metals oxides crystallizing by halite type.

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