Mechanical Activation, Mineral Powders, Chemical Modification, Solid-Phase Reactivity, Polyorganosiloxanes

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Abstract. Mechanochemical reactivity of nonfunctional organosilicon polymers with the most typical structure (linear, cyclolinear, three-dimensional) was studied: polyphenylsiloxane (PPS), polyvinylsiloxane (PVS), polydimethylsiloxane liquid (PMS-6) and dimethylsiloxane rubber (SKTN).

1. Introduction

The study of polyorganysilsesquioxanes and polydiorganysiloxanes reactivity with respect to inorganic materials of aluminosilicate composition was carried out on cement-mineral compositions (CMC).

Polyorganosiloxanes were introduced when grinding cement-sand mixture in the amount of 0.5% of cement weight, both separately and in combination with C-3 superplasticizer.

The study of modifiers reactivity was carried out with IR spectroscopy and extraction methods. Modified CMCs were subjected to extraction in chloroform. The difference in the mass of the introduced and extracted modifier was used to judge the amount chemically fixed on the surface of the cement-mineral powder. IR spectra were registered for confirmation.

The complex of physical and chemical studies performed showed that in the process of mechanical activation non-functional polyorganosiloxanes enter into solid-phase chemical interaction with cement-mineral systems with formation of organosilicon derivatives containing associated functional -OH groups. At the same time, the three-dimensional polyorganosiloxanes possess the highest reaction capacity.

The following regularities were established: mechanochemical reaction capacity of non-functional polyorganosiloxanes increases in proportion to the time of mechanical activation and the amount of modifier introduced; C-3 superplasticizer initiates the processes of chemical interaction of polyorganosiloxanes with inorganic materials of aluminosilicate composition.

Comparison of the reaction capacity of non-functional polymers with the reaction capacity of monomers using the example of a dimethyldichlorosilane hydrolyzate showed that under identical conditions of mechanical activation, the reaction capacity of monomers is much lower (2 times or more) than that of polymers.

One of the areas of mechanochemical technology is chemical modification of dispersed inorganic materials with the purpose of giving them certain properties.

Chemical modification is widely used in the production of inorganic pigments, mineral powders,
special types of binders and other materials.

Organic compounds are mainly used as chemical modifiers, a separate group of which includes organosilicon compounds (OSC), containing functional reactive groups.

Non-functional organosilicon compounds, due to their chemical inertness, are not used.

The thesis "a siloxane bond under the influence of mechanical forces can break and form new chemical bonds" was taken for the basis of research.

The authors conducted research towards studying the possibility of chemical modification of inorganic aluminosilicate materials with non-functional organosilicon compounds on the example of cement-mineral systems.

Nonfunctional organosilicon polymers polyorganosiloxanes: polyorganylsilsesquioxanes and polydiorganylsiloxanes with the most typical structure: linear, cyclolinear and three-dimensional were selected for the research.

Polyorganylsilsesquioxanes are solids obtained from the synthesis of trifunctional monomers with the general chemical formula (RSiO1.5). Polydiorganylsiloxanes - linear organosilicon liquids based on bifunctional derivatives of silicon with the general chemical formula (R₂SiO)ₙ.

Polyphenylsiloxane (PPS) and polyvinylsiloxane (PVS) with molecular weight of 5,000 cu were selected from polyorganylsilsesquioxanes, differing in the type of radical and the degree of completion of the structure. PPS has predominantly linear structure; PVS has incomplete three-dimensional structure.

Among the polydiorganylsiloxanes, we selected polydimethylsiloxane liquid (PMS-6) with molecular weight of 1 thousand cu and dimethylsiloxane rubber (SKTN) with molecular weight of 200 - 250 thousand cu.

With the purpose of studying reactivity of polyorganylsilsesquioxanes and polydiorganylsiloxanes, Portland cement and sand (70:30 by mass) were subjected to mechanical activation in a ball mill for two hours in the presence of organosilicon modifiers (PPS, PVS, SKTN, PMS-6).

Modifiers were introduced in the amount of 0.5% of cement weight, both separately and in combination with S-3 superplasticizer.

The study of modifiers reactivity in relation to cement-mineral compositions (CMC) was carried out using IR spectroscopy and extraction methods.

Modified CMCs were extracted with hot chloroform in Soxhlet apparatus during 24 hours. Then, the solvent was evaporated, and the obtained extract was dried to constant weight at 800 °C / 10 mm. Hg. Art. The difference in the mass of introduced and extracted modifier was used to judge the amount chemically fixed on the surface of the dry cement-mineral mixture.

To confirm that organosilicon compounds were extracted from the modified cement-mineral compositions, their IR spectra were recorded.

The research results showed that in the process of mechanical activation, polyorganylsilsesquioxanes and polydiorganylsiloxanes enter into chemical interaction with cement-mineral systems (Table 1). Moreover, the highest percentage of chemical grafting - 88% - was observed for polyvinylsiloxane (PVS), which is probably due to the peculiarity of its composition, which has incomplete three-dimensional structure.

The percentage of chemical grafting of SKTN and PMS-6 polyorganylsiloxanes, despite their difference in molecular weight, was practically at the same level, within 60%.

It is established that C-3 superplasticizer initiates the process of chemical grafting of polyorganylsilsesquioxanes and polydiorganylsiloxanes onto the surface of cement-mineral systems. So, for example, the amount of chemically grafted PPS was 23% higher, PVS - more than 9%, and SKTN - more than 27%, compared with the amount of chemically grafted organosilicon modifiers introduced without S-3 superplasticizer.

The analysis of the spectral data of extracts from cement-mineral compositions showed that in the IR spectra of extracts with addition of SKTN and PMS-6 there are absorption bands in the area of 1020, 1093 cm⁻¹, which are typical for vibrations of the siloxane bond in linear polydimethylsiloxanes; absorption bands in the area of 1260, 798 cm⁻¹, typical for vibration of the silicon-carbon bond in the
Si–CH₃ fragment, and in the area of 2962 cm⁻¹, corresponding to vibrations of the carbon–hydrogen C–H bond in the methyl radical. In addition, absorption bands are observed in the area of 3100–3600 cm⁻¹, which are typical for the associated hydroxyl, which was absent in the initial OSC and appeared during mechanical activation.

In the IR spectrum of the extract from cement-mineral compositions with the addition of SKTN + C-3, there are no vibrations of carbon-carbon C–C bond in the area of 3000 - 3100 cm⁻¹ and 1600 cm⁻¹, characteristic of aromatic systems, in the area of 1000 - 1100 cm⁻¹, related to the sulfur–oxygen bond S–O, which indicates the absence of the superplasticizer C-3 leaching from CMC.

In the IR spectra of extracts from cement-mineral compositions with the addition of PVS, we noted absorption bands in the area of 1000 - 1100 cm⁻¹, typical for vibrations of siloxane bonds, as well as absorption bands in the area of 1593, 2855, 2926 cm⁻¹ related to vinyl radicals CH₂ = CH. Moreover, the absorption bands have complex vibrational structure, which indicates the heterogeneity of polyvinylsiloxane. However, in the IR spectrum with the addition of PVS + C-3, we can see that C-3 somewhat reduces the heterogeneity of polyvinylsiloxane.

In the IR spectra of extracts from cement-mineral compositions with the addition of polyphenylsiloxane in the area of the siloxane bond manifestation, there are absorption bands in the area of 1030, 1134 cm⁻¹, characteristic of PPS. In addition, there are absorption bands in the area of 1430 cm⁻¹, typical for vibrations of the Si–C₆H₅ bond and an absorption band in the area of 1600 cm⁻¹, related to skeletal vibrations of C–C bonds of the benzene ring, as well as a triplet in the area of 3000–3100 cm⁻¹, characteristic of valence vibrations of the CH bond of the benzene ring.

In the IR spectra of extracts from cement-mineral compositions with complex additives PVS + C-3 and PPS + C-3, there were no absorption bands characteristic of superplasticizer C-3.

**Table 1. Reactivity of polyorganosiloxanes of non-functional type in relation to cement-mineral systems.**

| #№  | Modifier, % of cement weight | Time of mechanical activation, (hrs.) | Amount of chemically grafted modifier, (%) of introduced modifier weight |
|------|-----------------------------|-----------------------------------|-------------------------------------------------|
| 1    | SKTN -                      | 0,5                               | 42,5                                            |
| 2    | SKTN -                      | 2                                 | 59                                              |
| 3    | PMS-6 -                     | 0,5                               | 45                                              |
| 4    | PMS-6 -                     | 2                                 | 60                                              |
| 5    | SKTN 1                      | 2                                 | 54                                              |
| 6    | PVS -                       | 2                                 | 81                                              |
| 7    | PVS 1                       | 2                                 | 88                                              |
| 8    | PPS -                       | 2                                 | 43                                              |
| 9    | PPS 1                       | 2                                 | 53                                              |

For comparison, we carried out studies of monomers reactivity on the example of dimethyldichlorosilane hydrolyzate, which is the feedstock for production of polydimethylsiloxane liquids (PMS) and silicone rubbers, and which is a mixture of cyclic oligomers with general formula (R₂SiO)n, with prevailing value of n = 3 and 4.

Hydrolyzate of dimethyldichlorosilane in the amount of 0.5 - 0.7% of cement weight was introduced in the process of mechanical activation of cement-mineral compositions, both separately and together with C-3.

Extraction of monomer-modified cement-mineral compositions in chloroform (Table 2) showed that the percentage of chemically grafted monomer was 20.3%, which is 2 to 4 times lower than the number of chemically grafted non-functional polyorganosiloxanes under the same conditions of mechanical activation. At the same time, the indicator of chemical grafting of dimethyldichlorosilane hydrolyzate increased as its amount increased in CMC, as well as with introduction of monomer...
together with the addition of C-3 superplasticizer.

The result was somewhat unexpected, because dimethyldichlorosilane hydrolyzate is a mixture of 3-4 dimethylsiloxane cycles, which are quite labile. However, at the same time, such compounds are quite volatile (boiling point of the order of 150 - 170°C), therefore, partial removal of these components from the sphere of interaction with cement-mineral compositions is possible during the mechanical activation process.

It was established that in the IR spectrum of the CMC extract with the addition of dimethyldichlorosilane hydrolyzate there are absorption bands of 1026 and 1089 cm⁻¹, which are typical for vibrations of the Si-O bond in polydimethylsiloxanes. The absorption band of 1260 cm⁻¹ confirms the presence of Si (CH₃)₂ fragments; the presence of the absorption band in the area of 2962 cm⁻¹ corresponds to vibrations of C–H bonds in methyl radicals.

Noteworthy is the presence of the absorption band in the area of 3100–3600 cm⁻¹, due to the presence of hydroxyl groups that were not present in the initial dimethyldichlorosilane hydrolyzate. Similar hydroxyl-containing organosilicon compounds formed in the process of mechanical activation and are already functional.

Based on the obtained experimental data, we can conclude that the nature of interaction of polymers and monomers with cement-mineral systems during mechanical activation is the same.

### Table 2. Reactivity of dimethyldichlorosilane hydrolysate in relation to cement-mineral systems.

| №  | OSC, % of cement weight | C-3, % of cement weight | Time of mechanical activation, hrs | Amount of chemically grafted modifier, % |
|----|-------------------------|------------------------|-----------------------------------|----------------------------------------|
| 1  | 0.5                     | -                      | 2                                 | 20.4                                   |
| 2  | 0.5                     | 1                      | 2                                 | 49.3                                   |
| 3  | 0.7                     | -                      | 2                                 | 48.4                                   |
| 4  | 1.0                     | -                      | 2                                 | 70.8                                   |

2. Conclusion
The performed set of physicochemical studies showed that in the process of mechanical activation non-functional organosilicon polymers (polyorganosilsesquioxanes and polydiorganylsiloxanes) enter into solid-phase chemical interaction with cement-mineral systems with formation of organosilicon derivatives containing associated functional - OH groups. At the same time, three-dimensional polyorganosiloxanes have the highest reactivity.

The reaction capacity of non-functional polyorganosiloxanes increases in proportion to the time of mechanical activation and the amount of modifier introduced.

Superplasticizer C-3 initiates the processes of chemical grafting of non-functional organosilicon compounds (polymers and monomers) onto the surface of cement-mineral systems.

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