Chemical activity score of siliceous rocks in development of self-cleaning cement material

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Abstract. The development of photocatalytically active cement materials characterized by a complex of positive properties, such as self-cleaning ability, decompose atmospheric air pollutants, eliminate unwanted odors, etc., is actual scientific direction in the field of building materials science. It is known that ‘core-shell’ compositions obtained by precipitation of photocatalyst particles on dispersed carriers (substrates) are one of the effective types of photocatalytic additives for cement systems. It should be noted that mineral raw materials of various genesis can act as a substrate. Foreign and domestic experience in obtaining ‘core-shell’ photocatalytic systems for cement materials shows that the type of photocatalytic agent carrier has a primary influence on the final parameters of the synthesized composite modifier. The purpose of this study was to establish patterns of influence of the composition of 3 types of opal-cristobalite rocks (diatomite, trepel, opoka) on their chemical activity. It was identified that the reactivity of siliceous rocks grows in the order of trepel → opoka → diatomite. Meanwhile, it was recorded that increase in the content of opal silica in the composition contributed to growth in the sedimentary rock reactivity. The obtained research results indicate the prospects of using diatomite and opoka as dispersed carriers of photocatalytic agents in the composition of self-cleaning cement concretes.

1 Introduction

The development of high performance cement concretes, the modification of the structure of which is provided by the use of chemical and mineral additives of various mechanisms of action, is an actual scientific direction in the field of building materials science [1–11]. Photocatalytic additives are a special type of modifiers that contribute to the creation of photocatalytically active cement systems characterized by a complex of positive properties, such as self-cleaning ability, decompose atmospheric air pollutants, eliminate unwanted odors, etc. [12–14]. The widespread use of photocatalytically active self-cleaning cement materials in the construction industry will allow to implement the basic provisions of ‘green building’ concept.

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It is known that ‘core-shell’ compositions obtained by precipitation of photocatalyst particles on dispersed carriers (substrates) are one of the effective types of photocatalytic additives for cement concretes. It is worth noting that mineral raw materials of various genesis can act as a substrate [15–17].

Siliceous rocks are promising raw materials to synthesize hetero-oxide photocatalytic modifiers for cement concretes. They are characterized by high chemical affinity with hydrate phases of cement stone, as well as increased pozzolanic activity because of the presence of reactive partly crystallized opal-cristobalite-tridymite (OCT) phase in the material structure. OCT phase is a complex of crystalline, cryptocrystalline and amorphous silica types, such as cristobalite, tridymite and opal [18, 19]. It is known that diatomites, trepels and opokas are the main siliceous rocks [19–21].

Foreign and domestic experience in obtaining ‘core-shell’ photocatalytic systems for cement materials shows that the type of photocatalytic agent carrier has a primary influence on the final parameters of the synthesized composite modifier [15–17]. In this regard, it is necessary to have data on the composition, structure parameters and physico-chemical properties of the mineral raw materials used, including its chemical activity, in order to qualitatively assess the effectiveness of the substrate.

The purpose of this study was to establish patterns of influence of the composition of 3 types of siliceous rocks (diatomite, trepel, opoka) on their chemical activity with revealing of the most promising raw materials for mineral substrates of photocatalysts in the composition of self-cleaning cement concretes.

### 2 Materials and methods

The studied opal-cristobalite rocks were diatomite (DMT), trepel (TPL) and opoka (OPK) respectively from the Atemarsky, Dubensky and Alekseevsky deposits (the Russian Federation, the Republic of Mordovia). Specific surface area values of DMT, TPL and OPK powders are presented in Table 1.

**Table 1.** Specific surface area values of studied samples of siliceous rocks.

<table>
<thead>
<tr>
<th>Type of studied siliceous rock</th>
<th>Specific surface area of siliceous rock, m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diatomite</td>
<td>2.0</td>
</tr>
<tr>
<td>Trepel</td>
<td>1.2</td>
</tr>
<tr>
<td>Opoka</td>
<td>1.3</td>
</tr>
</tbody>
</table>

The chemical composition of opal-cristobalite rocks was researched by X-ray spectral fluorescence spectrometry using ARL Perform'X 4200 spectrometer (Rh Kα radiation). Based on the studied results of the elemental composition of samples the recorded concentrations of separate chemical elements were converted to the content of their oxides.

The direct chemical method, which consists in determining the amount of absorbed CaO by one gram of additive from a saturated solution of calcium hydroxide when heated for 8 hours (paragraph 14 of the Russian State Standard GOST R 56593-2015), was used at the first stage in order to confirm the pozzolanic reaction occurrence and to clarify the pozzolanic activity degree \( (C_{pA}) \) of siliceous rocks.

At the second stage the indirect method of the paragraph 9.4.1.9 of the Russian State Standard GOST R 56178-2014 was applied to determine the chemical activity of sedimentary rocks directly in the cement system. This method consisted in studying the effect of silica additives (SA) on the strength of fine-grained concrete hardening under
thermal and humidity treatment conditions. The research objects were cement concretes obtained at binder–sand ratio equal to 1/3. The content of opal-cristobalite rocks was 10 % by weight of the binder (Portland cement + SA) in the modified cement systems. The activity coefficient of silica additives ($C_{SA}$) was calculated as the ratio of the compressive strength parameters ($R_1$ and $R_0$, MPa) respectively for concrete samples of the modified and non-modified compositions

$$C_{SA} = R_1/R_0$$

3 Results and discussion

Table 2 shows the data on the chemical composition of the studied siliceous rocks.

Table 2. Chemical composition of the researched opal-cristobalite rocks (wt. %).

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>Diatomite</th>
<th>Trepel</th>
<th>Opoka</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>81.47</td>
<td>75.98</td>
<td>82.13</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.34</td>
<td>9.62</td>
<td>6.05</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.11</td>
<td>4.11</td>
<td>3.48</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.97</td>
<td>1.49</td>
<td>1.16</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.43</td>
<td>0.50</td>
<td>0.48</td>
</tr>
<tr>
<td>CaO</td>
<td>0.91</td>
<td>1.59</td>
<td>1.05</td>
</tr>
<tr>
<td>MgO</td>
<td>0.67</td>
<td>1.01</td>
<td>0.84</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.37</td>
<td>0.29</td>
<td>0.32</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.12</td>
<td>0.31</td>
<td>0.30</td>
</tr>
<tr>
<td>other (loss on ignition)</td>
<td>6.61</td>
<td>5.10</td>
<td>4.19</td>
</tr>
</tbody>
</table>

The study results revealed the dominance of silicon, aluminum and iron oxides in the chemical composition of opal-cristobalite rocks (wt. %): 75.98–82.13 (SiO₂); 5.34–9.62 (Al₂O₃); 3.11–4.11 (Fe₂O₃) (Table 2). At the same time the high value of Al₂O₃ concentration (9.62 wt. %) recorded for the trepel sample indicate an increased content of clay minerals (primarily micas and hydromicas) in it compared to diatomite and opoka.

The concentration ofopal silica (amorphous and cryptocrystalline SiO₂ of opal and opal-cristobalite-tridymite phase) in siliceous rock samples was determined using a complex of complementary physico-chemical research methods. The content of opal SiO₂ for diatomite, trepel and opoka, respectively, amounted to 68 wt. %, 40 wt. % and 59 wt. % (83 %, 53 % and 72 % of the total amount of silica) (Fig. 1). The decrease in the amount of opal silica in trepel and opoka compared to diatomite with similar total content of SiO₂ (75.98–82.13 wt.%) (Table 1)) is due to shift in the balance towards increase in the concentration of other forms of silica such as quartz and SiO₂ of clay minerals.
The pozzolanic activity degree of siliceous rocks ($C_{PA}$), which amounted to 110.1 mg/g, 99.8 mg/g and 109.6 mg/g for diatomite (DMT), trepel (TPL) and opoka (OPK), respectively (Fig. 2, (a)), was established using the direct chemical method the Russian State Standard GOST R 56593-2015.

Figure 2 (b) shows also the research results of the effectiveness of silica additives in the formulation of fine-grained concrete. It was identified that the activity coefficient of opal-cristobalite rocks ($C_{SA}$) increases in the row of trepel → opoka → diatomite (0.96 → 1.07 → 1.13 rel. units). Thus, modifiers based on diatomite and opoka have chemical activity in the cement system (with $C_{SA} > 1$).

It was revealed that the values of the pozzolanic activity degree ($C_{PA}$) and the activity coefficient in fine-grained concrete ($C_{SA}$) for opal-cristobalite rocks are quite closely related to the parameters of their chemical composition. In particular, growth in the content of opal SiO$_2$ ($\omega_{opal\ silica}$) contributes to increase in the reactivity of siliceous rocks, which is confirmed by the established correlation dependences ($R^2=0.952$ and $R^2=0.999$ (Fig. 2, (a) and (b), respectively)).
Fig. 2. Correlation dependences of the pozzolanic activity degree (a) and the activity coefficient in fine-grained concrete (b) for the studied siliceous rocks on the opal silica content in their composition.
4 Conclusions

According to the research results, it was found that 2 types of siliceous rocks, such as diatomite and opoka, have increased pozzolanic activity and reactivity in fine-grained concrete. The increased efficiency of diatomite and opoka is caused by the peculiarities of their chemical-mineralogical composition, in particular, the high content of opal silica in the amorphous and cryptocrystalline forms, which predetermines the prospects of using these siliceous rocks as dispersed carriers of photocatalytic agents in the formulation of self-cleaning cement materials.

Acknowledgments

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References