Active mineral additives of sapropel ashes

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Abstract. The goal of the presented research is to establish a scientific rational for the possibility of sapropel ashes usage as an active mineral additive. The research included the study of producing active mineral additives from sapropels by their thermal treatment at 850-900 °C and afterpowdering, the investigation of the properties of paste matrix with an ash additive, and the study of the ash influence on the cement bonding agent. Thermogravimetric analysis and X-ray investigations allowed us to establish that while burning, organic substances are removed, clay minerals are dehydrated and their structure is broken. Sapropel ashes chemical composition was determined. An amorphous ash constituent is mainly formed from silica of the mineral sapropel part and aluminosilicagels resulted from clay minerals decomposition. Properties of PC 400 and PC 500A0 sparopel ash additives were studied. Adding ashes containing Glenium plasticizer to the cement increases paste matrix strength and considerably reduces its water absorption. X-ray phase analysis data shows changes in the phase composition of the paste matrix with an ash additive. Ash additives produce a pozzolanic effect on the cement bonding agent. Besides, an ash additive due to the aluminosilicagels content causes transformation from unstable calcium aluminate forms to the stable ones.

1. Introduction

More than a half of all the Russian lacustrine sapropel reserves are available on the territory of West Siberia. As of 2013, 174 deposits were found in Omsk region. The volume of the sapropel reserves is 156…186 million tons. Lake Puchai of the Tyukalinsk district is the main sapropel deposit, with the annual production up to 20 thousand tons. As sapropel belongs to the renewable natural resources its extraction, processing and application may be predicted [1].

Active mineral additives of sapropel ashes are obtained when sapropelic raw materials are burnt at a certain temperature. Sapropelic raw materials consist of water, mineral (silica, clay, carbonates, iron compounds, etc.) and organic parts. While burning the organic part is removed. The mineral part of sapropels is formed from skeletal sediments of aquatic vegetation (diatoms) and microorganisms. The genesis of this mineral constituent predetermines the amorphous silica content. Amorphous silica SiO₂ is an ingredient of active mineral (pozzolanic) cement additives [2]. Besides silica, there are some other reactants of a pozzolan reaction, these are aluminosilicagels (nAl₂O₃·mSiO₂). They are obtained by burning of sapropelic raw materials, resulted from clay minerals decomposition.
2. The study of obtaining active mineral additives from sapropel
Thermogravimetric analysis and X-ray investigations with the Shimadzu DTG-60 analyzer were used for studies of sapropel thermal transformation. Effects of the exothermic reactions leading to organic substance decomposition, oxidation and carbonization are registered on the DTA curves of the Puchai sapropels at 305-315 and 490-500 °C as well as at the temperature range of 655 – 815 °C. A weak endothermic effect at 540-560 °C occurs when aluminosilicates lose their hydroxyl groups. At 875-885 °C an endothermic effect without an obvious loss of weight is registered. It is connected with mica (muscovite) structure breaking and with melt formation due to aluminosilicates.

X-ray investigations were carried out in the D8 Advance (Bruken) X-ray powder diffractometer with the CuKα-radiation. Puchai sapropels contain phases of silica SiO₂, albite Na(AlSi₃O₈), muscovite KAl₃(AlSi₃O₁₀)(OH)₂ and hydrosilicate H₁₀Si₁₀O₁₅. Phases of muscovite and hydrosilicate disappear after sapropel burning and additional phases Fe₂O₃ and Na(AlSi₂O₆) are formed in the ash.

On the basis of the experimental results it is determined that organic substances are removed while burning; clay minerals are dehydrated, their structure is broken and aluminosilicates are formed. It leads to increase of the reacting capacity of the material amorphous constituent. However, if the material is burnt longer, the ashes reaction activity starts decreasing since the amorphous components are turned into new crystalline phases.

Ashes obtain pozzolanic properties at the temperature of raw material burning which is higher than those of organic substances removal and of clay minerals dehydration and decomposition. Heat treatment has a significant influence on ash activity. Burning time depends on the type of sapropel, the origin and composition of sapropelic raw materials.

Sapropel ashes were produced by burning at 850 - 900 °C and after powdering. The quantitative analysis of the ashes was conducted on the Varian 710-ES «Agilent Technologies» (Al, Fe, Ca, Mg) atomic emission spectrometer and the AA-6300 «Shimadzu» (Na, K) atomic absorption spectrometer, with the silica being determined by a gravimetrical method, GOST 2642.3-97, Table 1.

| Table 1. Chemical composition of sapropel ashes, %. |
|-----------------------------------------------|
| Sapropel deposit | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | Na₂O | K₂O | MgO |
| Puchai          | 67,72 | 14,54 | 5,74  | 3,37 | 1,17 | 2,23 | 2,33 |
| Zhiloy Ryam     | 67,30 | 12,03 | 5,91  | 2,67 | 1,37 | 2,45 | 1,92 |
| Gorkoe          | 63,40 | 7,08  | 3,79  | 8,82 | 2,41 | 1,76 | 5,55 |
| Gorchakovskoe   | 56,59 | 13,92 | 6,69  | 7,11 | 2,17 | 2,30 | 9,32 |

Ashes amorphous constituent reactivity was determined by the pozzolanic activity. Y.M. Butt and V.V. Timashev’s method was used for determining the pozzolanic activity, in %. Its value for the ash of lake Puchai was 47, and 46 and 34 for the ashes of lake Zhiloy Ryam and lake Molokovskoe respectively.

3. The study of the paste matrix properties with sapropel ashes additives
The ashes influence on the set cement strength properties was the determinative factor for evaluating the efficiency of the ashes pozzolanic activity (GOST 5802-86). Cement mixes were prepared with Portland cement PC 400 and PC 500A0 (additives = 0) produced at Topkinsky cement factory. The Glenium 115 superplasticizer of the “BASF Construction Systems” company was applied for water reducing.

According to the analysis of strength characteristics of the PC 400-based paste matrix (after 28 days of near-water hardening at 20 ± 5 °C) it was found that ashes (8…10 % of the cement weight) with the plasticizer increase the strength by 42…56 % [3]. Compounds with the sapropel ashes of lake
Puchai reveal the highest strength. The PC 500A0-based paste matrix characteristics are given in Figure 1 and Table 2.

![Figure 1](image.png)

**Figure 1.** Compressive strength of the PC 500A0-based paste matrix with Glenium (Gl) and sapropel ash: a – 5 %, b – 10 %, c – 15 %; 1 – composition without additives, compositions with additives Gl and ashes of the lakes: 2 – Puchai, 3 – Zhiloy Ryam, 4 – Gorkoe.

**Table 2.** Paste matrix characteristics.

| Additive availability | Compressive strength, MPa | Water-cement ratio, W/C | Water saturation, % | Deflection strength, MPa |
|-----------------------|---------------------------|------------------------|---------------------|-------------------------|
| Without additives     | 65,1                       | 0,27                   | 17,6                | 7,05                    |
| Glenium (Gl)          | 89,8                       | 0,20                   | -                   | 7,57                    |
| Ash                   | 39,4                       | 0,27                   | -                   | -                       |
| Gl and ash 6 %        | 98,7                       | 0,21                   | -                   | 11,3                    |
| Gl and ash 8 %        | 110,5                      | 0,23                   | 3,0                 | 13,47                   |
| Gl and ash 10 %       | 98,4                       | 0,23                   | -                   | 7,93                    |
| Superplasticizer-1 and ash 8 % | 81,8 | 0,28 | 9,2 | - |

A PC 500A0-based construction mix additive containing 8 % of the Puchai ash and 1 % of the Glenium 115 superplasticizer increases strength of paste matrix by 70 % and reduces water absorption from 18 to 3 %. Temperature changes during ash production and the degree of ash grinding made it possible to increase paste matrix strength by 94 %.

4. The study of the sapropel ash action mechanism in concrete

To study the influence of an ash additive it was decided to explore the paste matrix phase composition (Figure 2). On the X-ray diagrams of the paste matrix with an ash additive peaks corresponding to the Portlandite (d/n = 4,89; 1,97; 1,76) go down. New peaks corresponding to stable crystallized cubic hydrated calcium aluminates C3AH6-type (d/n = 5,14; 4,4; 3,35; 2,78; 1,95; 1,66) appear. Besides
pozzolan activity, an ash additive causes transformation from unstable aluminate forms to the stable ones which provide a steady durability during the period of paste matrix use.

**Figure 2.** X-ray diagram of the paste matrix with an additive sapropel ash.

5. Conclusion

Thus, adding sapropel ashes to the cements increases paste matrix strength and reduces its water absorption. It has been found that sapropel ashes function as active mineral additives due to the reactive amorphous component, containing SiO$_2$ and Al$_2$O$_3$ in a certain ratio.

Both negative (raw material) sapropels and solid wastes after removal of the organic part including biologically active substances during thermal and chemical processing can be used as raw materials for producing active mineral additives. Waste petroleum and carbon-mineral sorbents, sorbent carriers and catalysts derived from sapropels can be used as raw materials [4].

Producing cement active mineral additives from sapropel ashes is a separate trend in complex processing of Omsk region sapropelic raw materials.

References

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