Effect of phase and size characteristics of fly ash from power station on properties of bitumen composites

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Abstract. Fly ash from power stations is one of the effective fillers in bitumen binders due to its high specific surface area in origin state. This paper is focused on study of effect of phase and size characteristics of fly ashes on properties of bitumen binder. In this work a high-calcium (FA1) and low-calcium (FA2) fly ashes are used. According to chemical and mineral composition of FA1 is reactive in water medium because it contains hydraulic minerals. FA2 is hydraulically inert mainly consisting of aluminosilicate vitreous phase. FA1 is characterized by higher specific surface vs. FA2 according to Blain method data but lower specific surface measured with BET method. It can be associated with high porosity of FA2 that significantly influence on bitumen content in binding system. Lower packing density of FA2 particles leads to reducing of strength characteristics in bitumen composite. Low adsorption of bitumen to surface of FA1 particles initiates hydration process of reactive minerals as well as formation of ettringite phase that leads to extension of the binder system and structure decompaction. Bitumen composites based on FA2 with higher adsorptive capacity is characterized by more stable structure.

1. Introduction

At present time the interest to energy- and resource-saving technologies in construction industry including road area grows all over the word. To reduce the consumption of expensive bitumen binder as well as enhancement of thermal, mechanical characteristics and fatigue effect the introduction of high-disperse mineral powders and fillers into bitumen cement is applied.

The most popular mineral powders are from limestone and dolomite rocks. By-products from energy, metallurgical and chemical industry also are used, but their application is limited due to insufficient knowledge about effect in binder system taking into account variation in phase, size and structure properties. So, additional study in this area is required.

In this paper the high-disperse wastes from power stations – fly ashes – as the most suitable mineral fillers that intensively applied in bitumen binder [1]–[3] systems are studied. But, taking into account the insufficient understanding of fly ash features its effect in bitumen binders should be studied complexly to development the general concept of structure formation process and design the recommendation of its application.

Thus, in this work the influence of phase and size characteristics of fly ash on properties of bitumen composite is studied.
2. Experimental Part

2.1. Materials

Two types of fly ashes from Russian power station are used: high-calcium fly ash Nazarovsk power station (Krasnoyarsk Territory) —obtained by dry removing (FA1); low-calcium fly ash (particle size is 60 mm) from Omsk power station (Omsk) obtained by wet removing (FA2).

The construction viscous bitumen BND 60/90, (Russia) is used as organic binder (penetration is 60 mm).

2.2. Methods

Chemical and mineral compositions of fly ashes are realized with XRF and XRF analysis, respectively measured by 9900 WorkStation with embedded diffraction system Thermo Fisher Scientific. Qualitative XRD-analysis is accomplished with database PDF–2 (ICCD) and by Full profile method with DDM v.1.95e program [4].

Dispersity of fly ashes is determined by following parameters:
- Size distribution measured with laser particle analyzer FRITSCH Analysette 22 NanoTec plus;
- Specific surface area measured by Blain method;
- Specific surface area measured by BET method with SORBI-M equipment.

Microstructure of fly ashes is studied by SEM analysis with electron microscope TESCAN MIRA 3 LMU.

3. Results and Discussions

3.1. Chemical and Mineral Compositions of Fly Ashes

The studied fly ashes are characterized by different chemical (Table 1) and mineral (Table 2) compositions due to different type of coal recourse and location of coal mining.

**Table 1. Chemical composition of fly ashes.**

| Type of fly ash | SiO₂ | Al₂O₃ | CaO   | Fe₂O₃ | MgO | SO₃ | Na₂O | K₂O | TiO₂ | LOI |
|-----------------|------|-------|-------|-------|-----|-----|------|-----|------|-----|
| FA1             | 31.55| 8.84  | **37.80** | 8.99  | 6.31| 4.40| 0.76 | 0.20| 0.26 | 3.15|
| FA2             | 55.33| 29.92 | **2.57**  | 7.48  | 1.90| –   | 0.45 | 0.42| 1.10 | 8.29|

According to data from Table 1 the lime factor \( M_0 \) is calculated by following:

\[
M_0 = \frac{(CaO+MgO)}{(SiO₂+Al₂O₃)}
\]  

For FA1 parameter \( M_0=1.45 \) and for FA2 \( M_0=0.05 \). On the base of these data and in compliance with [5], [6] FA1 is high-calcium fly ash characterized by good reactivity in water medium and can be used as binding component. FA2 is low-calcium fly ash that inert in water and reactive in alkaline medium only (for example, geopolymer) and can be used as reactive mineral additive in cement. Mineral compositions of the studied fly ashes are differed also (Table 2).

**Table 2. Mineral compositions of the fly ashes.**

| Mineral phase | Content, wt. % | Mineral phase | Content, wt. % | Mineral phase | Content, wt. % |
|---------------|----------------|---------------|----------------|---------------|----------------|
|               | FA1  | FA2  | FA1  | FA2  | FA1  | FA2  | FA1  | FA2  | FA1  | FA2  |
| Vitreous phase| 49.26| 49.97| 7.61 | 19.34| –    | –    | 26.36|      |      |      |
| Magnetite     | 1.56 | 3.49 | 7.02 | –    | Calcite| 0.69 | –    |      |      |      |
| Portlandite   | 3.47 | –    | CaO₆₆| 4.09 | –    | C₃A  | 21.34| –    |      |      |
| C₃AF          | 4.11 | –    | –    | 0.85 | –    | –    | –    |      |      |      |

The FA2 consists of following crystal phases: quartz, mullite and magnetite i.e. mineral composition is typical for low-calcium fly ash [7]. The FA1 consists of following crystal phases including Ca-minerals: anhydrite (CaSO₄), CaO₆₆, portlandite (Ca(OH)₂), calcite (CaCO₃), tricalcium aluminate (3CaO·Al₂O₃), tetracalcium alumoferrite (4CaO·Al₂O₃·Fe₂O₃) and some of periclase (MgO).
All phases but calcite react with water resulting in a new phase formation that explains a high value of $M_o$ parameter ($M_o = 1.45$).

According to quantitative XRD-analysis the vitreous phase content in both fly ashes is equivalent (Table 2). SEM-analysis (Figure 1) demonstrates the microsphere prevalence (especially in FA1) (Figure 1a) and presence of unburned carbon (Figure 1b). Also FA2 consists of anisotropic particles including porous inclusions and carbon residue. The values of LOI in the both fly ashes are significantly differed. That is associated with application of different coal recourses. Brown coal combustion initiates formation of carbon residue up to 4% (FA1), and bituminous coal combustion forms 3–12% of carbon residue (in FA2) [6].

![Figure 1. Microstructure of fly ash particles: a – FA1; b – FA2.](image)

So, vitreous phase of FA1 generally consists of microspheres. In case of FA2 the vitreous phase components are microspheres, carbon residue and anisotropic glass components.

### 3.2. Fly Ash Dispersity

Laser grain-size analysis demonstrates different dispersity of the fly ashes (Figure 2). For FA2 the size distribution is bimodal in range of 0.1–100 μm with dominant particle size of 20 and 45 μm. For FA1 the size distribution is unimodal in range of 0.1–50 μm with dominant particle size of 15 μm. For FA1 the more narrow range of particle distribution vs. FA2 is typical.

The higher dispersity of FA1 is confirmed by specific surface area data obtained with laser diffraction analysis and Blain method (Table 3). However specific surface area data determined with BET method is significantly higher for FA2 vs. FA1. It can be associated with microporosity of unburned carbon aggregates in FA2 (Figure 1) and leads to filler porosity in general as well as enhancement of adsorption capacity [6].
3.3. Properties of Fly Ashes as Fillers in Bitumen Binder

Applied FA1 and FA2 are studied as mineral fillers MP-2 (non-carbonate rocks and industrial wastes) according to Russian Standard 52129–2003 [8] (Table 4).

Table 4. Basic characteristics of fly ash as mineral component in bitumen binders.

| Parameter                                      | According to Russian Standard 52129-2003 for mineral fillers MP-2 | FA1   | FA2   |
|------------------------------------------------|------------------------------------------------------------------|-------|-------|
| Real density, g/cm³                             | –                                                                | 2.78  | 2.10  |
| Bulk density, g/cm³ (under load of 40 MPa)     | –                                                                | 1.92  | 1.27  |
| Porosity, % (under load of 40 MPa)             | ≤ 40                                                            | 30.9  | 39.5  |
| Humidity, wt. %                                | ≤ 2.5                                                           | 0.31  | 0.35  |
| Bitumen content, g per 100 cm³ of filler        | ≤ 80                                                            | 47    | 74    |
| Expansion of bitumen samples, vol. %           | ≤ 3.0                                                           | 3.4   | 1.75  |
| Water resistance of bitumen samples            | <0.7                                                            | 0.81  | 0.72  |

Porosity of fly ash depends on range of particle distribution, particle shape and microporosity. Also porosity of mineral filler influences on volume of free space in loaded material that hereafter will be filled by binding component when bitumen binder formation.

So, lower porosity value for FA1 vs. FA2 is associated with difference of bitumen content value (Table 4). The bitumen content parameter is "bitumen – filler" ratio provided the required viscosity of binding system. Difference in bitumen content values is higher (74 and 47 in FA1 and FA2, respectively) vs. difference in porosity values (41.4% and 36.3% under load of 10MPa in FA1 and FA2, respectively) that is connected with difference in specific gravity values for the fly ashes (Table 3).
5). Relation between these parameters (bitumen content, porosity) is confirmed by earlier studies [9], [10].

According to Russian Standard 52129–2003 [8] the optimal bitumen content, providing the water saturation of bitumen binder samples of 4–5 % (cylinders with diameter and height of 25 mm pressed under load of 10 MPa) (Table 5).

**Table 5.** Properties of bitumen binders depending on component composition.

| Parameter | FA1 | FA2 |
|-----------|-----|-----|
| Bitumen content (of fly ash, wt. %) | 18  | 19  |
| | 18,5 | 18  |
| | 24  | 36  |
| | 37  |     |
| Volume content of component, (unit fraction) | Fly ash | 0.622 | 0.623 |
| | Bitumen | 0.308 | 0.317 |
| | Pores | 0.070 | 0.060 |
| Water saturation, vol. % | 6.15 | 4.9  |
| | 3.5  | 28.1 |
| | 21.0 | 5.9  |
| Mass specific gravity of bitumen binder, g/cm³ (under a load of 10 MPa) | 2.040 | 2.057 |
| | 2.065 | 1.929 |
| | 1.368 | 1.514 |
| | 1.528 |     |
| Fly ash porosity in bitumen binder structure, % (under a load of 10 MPa) | 37.8 | 37.7 |
| | 37.7 | 47.9 |
| | 47.4 | 47.0 |
| | 46.9 |     |

According to data from Table 5 the optimal bitumen content (by wt. %) in FA2-biased bitumen binder is two times higher vs. FA1-biased bitumen binder (37% vs. 18.5 %, respectively) providing the porosity values of 6% in both cases. At the same time "fly ash – bitumen" ratio in the both binders is significantly different (1.96 and 1.3 for binders with FA1 and FA2, respectively) due to higher porosity of FA2 (46.9%) vs. FA1 (37.7%). Growing of bitumen concentration in the binder leads to the binder structure compaction until direct particle contact [11] and porosity reduction (Table 5).

Higher bitumen requirement in FA2-based binder is connected with higher surface area FA2 (according to BET method) and higher adsorption capacity vs. FA1 (Table 3).

Lower adsorption capacity of FA1 leads to layering of bitumen binder and hydration of Ca-mineral in the fly ash to ettringite formation that initiates expansion of bitumen binder samples of 3.4% at least.

3.4. Strength Properties of Bitumen Binders with FA1 and FA2.

For optimal composition of bitumen binders the parameters of expansion, shirt-term water resistance and strength at different temperatures (0°C, 20°C, 50°C) are determined according to Russian Standard 52129–2003 [8]. Before the strength test the bitumen samples are thermostated for a hour. According to experimental data in Table 6 strength value of FA1-based bitumen binder is higher vs. FA1-based bitumen binder in all temperature range due to higher packing density of solids in the FA1-based bitumen binder according to characteristics of fly ash as well as bitumen binder porosity presented in Table 4 and 5, respectively. Data variations are in range of 16–20%.

**Table 6.** Strength characteristics of bitumen binders.

| Parameter | FA1 | FA2 |
|-----------|-----|-----|
| Compressive strength, MPa | at 20°C | 4.02 | 3.20 |
| | at 0°C | 6.77 | 5.68 |
| | at 50°C | 0.89 | 0.74 |
| Heat-stability coefficient R20/R50 | 4.50 | 4.30 |
| Thermal stability coefficient R0/R50 | 7.57 | 7.61 |

According to experimental data the heat-stability coefficient and thermal stability coefficient are calculated (Table 6). The resulting data are equivalent and demonstrate the possibility of application of optimal composition of fly ash based bitumen binder in equal temperature range.

4. Summary
The study results for FA1 and FA2 as mineral fillers in road bitumen composites demonstrate significant differences in structure formation, physical and mechanical properties of based construction materials. FA2 is characterized by high porosity and low particle packing density leading to growth of bitumen requirement and reducing of strength parameters vs. FA1.

At the same time FA1 has a better bitumen adsorption capacity providing more stable composite structure. Low adsorption capacity of FA1 initiates layering process and structure decompaction under water effect.

So, effect of phase and size characteristics of mineral fillers including fly ash on bitumen composites is basic. Study of mineral fillers in this binding system should be complex to forecasting the final properties of road materials as well as development of application guideline.

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