Ash-slag binders derived from thermal power plant wastes

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Abstract. This research deals with the Portland cement hydration processes in the presence of chemical additives. The slag-alkyne binders based on bottom ash are under investigation. It has been solved the problem of utilization the wastes from the thermal power plants. The components of slag-alkyne binders have been tested, normal gravity of cement mixture with the additives has been determined, and cement mixture curing period was measured. The possibility of deriving the ash-slag binders of the thermal power plant wastes was discovered. The methods of mathematical experiment planning were applied to assess the influence levels of chemical additives on the properties of alkyne slag binders. The presented results provide the thermal power plants with a solution to how the industrial wastes can be disposed of in an environmentally friendly fashion. The spreadsheets with research data are provided along with the equations for the binders’ properties correlation with the number of chemical additives used and its fraction in the total composition.

1. Introduction
The current trend of construction development presupposes the preservation of concrete as the main structural material in particular for infrastructure development with improving its environmental, economic, and other aspects.

For that reason, for the future development of cement production, today it is an important matter to address the energy-saving and environmental challenges, including the application of new energy-saving technologies and cutting the emissions of harmful substances (carbon, sulfur, and nitrogen) into the environment.

One of the main ways to reduce energy consumption is to produce composite types of cement. It saves the clinker component of cement through the use of active mineral additives, such as blast furnace slag and TPP ash. Utilization of the thermal power plant wastes holds a significant economic advantage since it reduces harmful emissions into the environment as well as preserves construction resources.

This paper investigates the efficiency of thermal power plant wastes utilization through the production of structural materials. Fly ash is a result of burning solid fuel. After being caught by electrostatic precipitators in the dry state, it proceeds into the ash trap for further production. It is a fine-grained material that can be used without additional grinding. The fly ash introduction into the
concrete composition increases the aggregate resistance of the mixture during the period between the beginning and end of the setting of the cement mixture. The bottom ash may be used in concrete intended for the manufacture of any reinforced concrete structures: from ordinary building structures to dams, piers. This material has already won recognition among a large number of civil engineers [1].

Nowadays, the technology of using ash for the production of structural materials is patented in the UK and the US. The inventors are trying to find partners for the development and application of this technology in China, Japan, Southeast Asia, Europe, and India [2].

2. Investigation results

2.1. Materials for concrete using ash slag

When burning solid fuel in furnaces at a temperature of about 1200 – 1700 °C, thermal power plants generate a large tonnage of solid mineral waste, composed of slag and fly ash. Small and light grains with a specific surface area of 1500 - 3000 cm² / g comprise around 90 % of the total volume. They are being removed from the furnace by gases. The coarse grains settle at the bottom of the furnace, forming the slag [3-7]. At modern thermal power plants, coal burned in a pulverized state. The slag formed by the adhesion of the softened ash particles in the volume of the furnace and accumulates in the slag bin under the firebox.

The maximum size of slag grains in the composition of the slag ash mixture is not more than 20 mm. The ash removed from the furnace with flue gases (ash removal) and trapped during its purification in cyclones and electrostatic precipitators. Most ash fragments have a spherical, smooth, glass surface texture. The size of the spherical particles varies from a few microns to 50-60 microns, presented in Figure 1.

![Figure 1. Spherical particles of fly ash](image)

Ashes of thermal power plants have different chemical composition depending on the type of coal burned. The ash obtained from coal shale is less acidic than the ash from burning the brown coal [8-11].

During the combustion of coal at thermal power plants in Ukraine, amounts of ash and slag produced annually are 7 - 9 million tons (50 - 200 grams of ash per 1 kWh of electricity produced).

It should be noted that the share of ash processing in Ukraine is in the range of 10 %, while in the USA this figure reached 20%, in the UK – 60 %, in France - 72 %, in Finland - 84 %.

2.2. Research methodology

Initial materials for the solution are Portland cement, quartz sand, additives (fly ash, anhydride, caustic soda). All the testing equipment and tools used to conduct the experiment was certified and cleared for
operation. All the testing equipment and tools used for the experiment were checked and certified. The testing method provided determining the bending and compression strength of the specimens with sizes of 40×40×160 mm.

For the specimens manufacturing, we used the cement mixture of the following composition: three parts of a regular sand, one part of cement and 0.39 parts of water (water-cement ratio of 0.39). The mixture was of plastic consistency.

It was mechanically agitated, compacted, and charged into the rectangular-shaped molds using a vibrating pad. The specimens were kept in the molds inside of a tank with a hydraulic shutter for 24 hours. The rest of the curing period they were stored underwater until the term of strength testing [4-5].

The normal density of the cement mixture and the curing time were determined according to the standard procedure described in [6].

The essence of planning experiments and choosing the composition of aerated concrete using statistical and mathematical methods is to establish the relationship between the given properties of the mixture and the properties of the starting materials. The mathematical correlation obtained is used to find optimal solutions.

The construction of mathematical correlations is carried out based on special experiments with its subsequent refinement in the production environment.

During the process of the experiment, all factors varied at three levels - average (basic), lower and upper levels based on the research objectives. The levels differed from the basic one by the constant value called the interval of variation. Based on the number of factors and research objectives, the experiments were carried out according to the matrix shown in table 1.

**Table 1.** The results of calculations of the span structure.

| № of exp. | X₁ | X₂ | X₃ | Variables values |
|-----------|----|----|----|------------------|
|           | X₁ Ash, % | X₂ Anhydride, % | X₃ Soda, % |
| 1         | 1   | 1   | 1   | 20  | 5   | 10  |
| 2         | -1  | 1   | 1   | 10  | 5   | 10  |
| 3         | 1   | -1  | 1   | 20  | 2   | 10  |
| 4         | -1  | -1  | 1   | 10  | 2   | 10  |
| 5         | 1   | 1   | -1  | 20  | 5   | 2.5 |
| 6         | -1  | 1   | -1  | 10  | 5   | 2.5 |
| 7         | 1   | -1  | -1  | 20  | 2   | 2.5 |
| 8         | -1  | -1  | -1  | 10  | 2   | 2.5 |
| 9         | 1   | 0   | 0   | 20  | 3.5 | 6.5 |
| 10        | -1  | 0   | 0   | 10  | 3.5 | 6.5 |
| 11        | 0   | 1   | 0   | 15  | 5   | 6.5 |
| 12        | 0   | -1  | 0   | 15  | 2   | 6.5 |
| 13        | 0   | 0   | 1   | 15  | 3.5 | 10  |
| 14        | 0   | 0   | -1  | 15  | 3.5 | 2.5 |
| 15        | 0   | 0   | 0   | 15  | 3.5 | 6.5 |

To simplify the recording and subsequent calculations, the upper level of factors will be denoted by (+1), the middle level – by (0) and the lower level – by (-1), that is equivalent to the translation of factors into the new code (normalized) scale:

\[ X_i = \left( X_i - X_{i0} \right) / \Delta X_i, \]  

where \( X_i \) is the value of the \( i \)th factor in the new code scale; \( X_i \) is the value of the \( i \)th factor in natural scale; \( X_{i0} \) is the basic level of the \( i \)th factor; \( X_i \) is the variation intervals of the \( i \)th factor.

Variable factors: \( X_1 \) - ash, %; \( X_2 \) - anhydride, %; \( X_3 \) - caustic soda, %.
2.3. Research results

Table 2 shows the indicators of the beginning and end of the curing period of specimens.

Table 2. The effect of additives on the curing time of cement.

| № of exp. | Ash | Additive % | Curing period, h/min |
|-----------|-----|------------|---------------------|
|           |     | Anhydride  |                     |
|           |     | Soda       |                     |
|           |     | beginning  | end                 |
| 1         | 20  | 10         | 4.5                 | 2^{4}h 5^{10min} |
| 2         | 10  | 10         | 4.5                 | 2^{50h} 5^{10min} |
| 3         | 20  | 2.5        | 4.5                 | 2^{40h} 5^{10min} |
| 4         | 10  | 2.5        | 4.5                 | 2^{30h} 5^{10min} |
| 5         | 20  | 10         | 2.5                 | 3^{10h} 5^{10min} |
| 6         | 10  | 10         | 2.5                 | 3^{10h} 5^{10min} |
| 7         | 20  | 2.5        | 2.5                 | 3^{50h} 6^{10min} |
| 8         | 10  | 2.5        | 2.5                 | 3^{40h} 5^{10min} |
| 9         | 20  | 6.5        | 3.5                 | 6^{10min} 5^{10min} |
| 10        | 10  | 6.5        | 3.5                 | 3^{10h} 5^{10min} |
| 11        | 15  | 10         | 3.5                 | 2^{40h} 5^{10min} |
| 12        | 15  | 2.5        | 3.5                 | 2^{40h} 5^{10min} |
| 13        | 15  | 6.5        | 4.5                 | 6^{10min} 5^{10min} |
| 14        | 15  | 6.5        | 2.5                 | 3^{50h} 5^{10min} |
| 15        | 15  | 6.5        | 3.5                 | 3^{50h} 5^{10min} |
| 16        | 15  | 6.5        | 3.5                 | 3^{10h} 5^{10min} |
| 17        | 15  | 6.5        | 3.5                 | 2^{50h} 5^{10min} |

According to the mathematical design of the experiment, the equation has the form: $Y = 2.806$, which means that the variation of additives does not have a significant effect on the time of onset of curing, and for this series of samples it began after 2 hours 42 minutes.

The dependence of the curing time on the consumption of ash, anhydride and caustic soda at maximum consumption of additives has the form: $Y = 5.2$, which means that the variation of additives does not have a significant effect on the curing time, namely the curing end for this series of samples began after 5 hours 12 minutes after injection into the water mixture.

In determining the strength of the samples, tests were performed after 2, 7 and 28 days (table 3). According to the mathematical design of the experiment, the equation of dependence of quantity and variation of additives on flexural strength at the age of 2 days has the form:

$$Y = 2.85 - 0.2x_2 - 0.15x_3 - 0.814x_1^2 - 0.564x_2^2 - 0.614x_3^2 + 0.0625x_1x_3 (2)$$

The maximum value of bending strength is achieved at the average level of variable factors, the minimum strength is at the maximum and minimum additives content (see figure 2).

The correlation curves at the average concentration are shown in figure 4. The maximum value of bending strength is reached at the average level of the variable factors. The minimum strength is at the maximum and minimum content of additives. The correlations at the minimum concentration of additives are shown in figure 3.

The maximum value of strength is at the average level of variable factors, the minimum - at the maximum content of additives. Analysing the data from figures 2 - 4, we conclude that the highest bending strength at the age of 2 days is obtained at the average level with an average component consumption of 2.7 MPa and the minimum at the maximum level with the highest material consumption.
Table 3. The average values of the cement stone strength based on the variables.

| № of exp. | Additives, % | Bending strength |
|-----------|--------------|-----------------|
|           | Ash | Anhydride | Soda | 2 days | 7 days | 28 days |
| 1         | 20  | 10        | 4.5  | 0.6    | 4.1    | 7.1     |
| 2         | 10  | 10        | 4.5  | 0.4    | 3.1    | 6       |
| 3         | 20  | 2.5       | 4.5  | 0.8    | 8.5    | 9       |
| 4         | 10  | 2.5       | 4.5  | 0.9    | 7.3    | 12.8    |
| 5         | 20  | 10        | 2.5  | 0.6    | 1.5    | 6.7     |
| 6         | 10  | 10        | 2.5  | 0.9    | 3.5    | 5.3     |
| 7         | 20  | 2.5       | 2.5  | 1.1    | 6.1    | 11.6    |
| 8         | 10  | 2.5       | 2.5  | 1.2    | 7.1    | 10.8    |
| 9         | 20  | 6.5       | 3.5  | 2.5    | 1.9    | 9.7     |
| 10        | 10  | 6.5       | 3.5  | 2.1    | 3.1    | 8.3     |
| 11        | 15  | 10        | 3.5  | 2.3    | 1.3    | 7.5     |
| 12        | 15  | 2.5       | 3.5  | 2.8    | 4.1    | 9.7     |
| 13        | 15  | 6.5       | 4.5  | 2.3    | 3.3    | 6.3     |
| 14        | 15  | 6.5       | 2.5  | 2.7    | 3.8    | 7.3     |
| 15        | 15  | 6.5       | 3.5  | 2.5    | 4.1    | 9.3     |
| 16        | 15  | 6.5       | 3.5  | 2.5    | 4.0    | 9.3     |
| 17        | 15  | 6.5       | 3.5  | 2.6    | 4.1    | 9.4     |

Figure 2. The dependence of the flexural strength at the age of 2 days on the consumption of ash, anhydride and caustic soda (maximum +1)
3. Conclusion

All components of the mixture complied with state standards. The density of cement mixture was not affected by the variation of the content of additives and corresponded to the value stated in the regulatory documents, NGT = 0.28%.

Test results show that the change in the content of the additives is not affected by the curing time. The beginning of the curing period in all samples occurred after 2 hours and 42 minutes, the end was registered after 5 hours and 12 minutes. Requirements of the normative document are as follows: beginning - not earlier than 00:45 h/min, the end - not later than 10:00 h/min. The results of the experiment comply with the standard.

The maximum compressive strength at the age of 2 days was obtained at an average level with an average consumption of additives (15% ash, 6.5% anhydride and 3.5% soda) and was 6.66 MPa. The obtained strength did not correspond to any brand of cement in DSTU B В.2.7-181:2009 “Alkali cements. Specifications”.

The maximum compressive strength at the age of 7 days was obtained at the minimum level with a minimum concentration of additives (10% ash, 2.5% anhydride and 2.5% soda) and is 10.78 MPa. The
obtained strength did not correspond to any brand of cement in DSTU B В.2.7-181:2009 “Alkali cements. Specifications”.

The maximum compressive strength at the age of 28 days was obtained at the minimum level of variable factors with the lowest consumption of additives (10% ash, 2.5% anhydride and 2.5% soda) and was 24.3 MPa. The obtained strength did not correspond to any brand of cement in DSTU B В.2.7-181:2009 “Alkali cements. Specifications”.

Under these conditions and components, unfortunately, we failed to obtain a mixture based on fly ash and Portland cement brand 500 with the addition of anhydride and caustic soda, which would meet the requirements of the regulatory document, namely DSTU B C.2.7-181:2009 “Alkali cement. Specifications”.

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