Influence of the processed sunflower oil on the cement properties

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Abstract. Used oils (vegetable oil, animal oil, engine oil, etc.), which are essentially industrial wastes, have found application as secondary raw materials in some branches of industry. In particular, the only well-known and commonly-used way of utilizing wastes of vegetable oils is to apply them as raw materials in the production of biodiesel. The goal of the present study is to develop a conceptually new way of vegetable oil wastes utilization in the building industry. The test admixture D-148 was obtained from the processing of wastes of sunflower oil and it mainly consists of fatty acid diethanolamide. The test admixture was added to the cement system for the purpose of studying its influence on water demand, flowability, setting times, compressive strength and moisture adsorption. The test admixture D-148 at the optimal content 0.2 weight % causes 10% decrease in water demand, 1.7 time increase in flowability (namely spread diameter), 23% increase in grade strength and 34% decrease in moisture adsorption. The results of the present investigation make it possible to consider the final product of the waste sunflower oil processing as multifunctional plasticizing-waterproofing admixture.

1. Introduction
Food waste is food products that partially or completely have lost the initial customer appeal during production, processing, consumption or storage. They are divided into two categories: production waste (from food industry) and consumption waste (from households and different food services, e.g. cafes, restaurants, schools and hospitals).

Today there exist different methods of utilization of food industry waste in the building industry. Such waste is used as chemical admixtures, mineral additives and raw materials for alternative fuels.

It has been proposed to use eggshell, sugar cane bagasse and rice husk ash as mineral additives. The method of eggshell utilization was proposed in [1]. It considers reusing eggshell waste as an alternative raw material in soil-cement bricks. The results show that eggshell waste can be used in soil-cement bricks as a partial replacement for Portland cement in the range of up to 30 wt%.

The author [2] has proposed the use of sugar-cane bagasse ash in concrete. Sugar-cane bagasse is a fibrous waste-product of the sugar refining industry. Bagasse ash mainly contains aluminum ion and silica, so it is possible to use sugar-cane bagasse ash as cement replacement material (a pozzolanic additive) to improve the quality and reduce the cost of construction materials, such as mortar, concrete pavers, concrete roof tiles and soil cement interlocking block. The results of the fore-mentioned investigation show that the cement could be advantageously replaced with sugar-cane bagasse ash up to maximum limit of 10%.

Rice husk is an agricultural residue which accounts for 20% of the 649.7 million tons of rice produced annually worldwide. There have already been made a number of attempts to produce active
mineral additives by burning and grinding of the rice husk [3]. The results of the investigations have proved the possibility of replacement of up to 20 weight % of Portland cement with rice husk ash without a decrease in the strength, and the possibility of replacement of up to 10 weight % with the strength significantly increased.

It was proposed to use milk whey, molasses, sugar industry wastes and protein-contained products (for example, hydrolyzed blood) as chemical admixtures.

The most well-known chemical admixture which is widely used in the building industry (at least in the post-Soviet areas) is sulfite-yeast brew, being the yeast industry waste obtained during the processing of sulfite-cellulose liquor into nutritional yeasts. Such an admixture was firstly used as a plasticizer in the early 1930-ies [4, 5].

The members of the Chemistry department of Penza Institute of Engineering and Building have conducted the research and development work aimed at finding the possible ways of utilizing milk whey as chemical admixtures in concretes and mortars. In the building industry the milk whey has found application as a typical hydrophilic surfactant. The chemical composition of the milk whey allows it to be used as a chemical admixture for mortars and concretes, intended for modifying the rheological properties, retarding the setting and hardening times, wetting the hydrophobic aluminium powder used in cellular concrete manufacture, accelerating the lime hydration, etc. [6].

Molasses is a by-product material which is obtained from paper and sugar industries. The composition of molasses differs depending on the source it has been obtained, such as from reed or beet. Beet molasses consists of sucrose and other sugars (ash and nitrous materials) and water. About 4-8% of beet remains in molasses after the process. Molasses can be used as a water reducer or a retarding admixture, which satisfy the ASTM standards [7]. Also, molasses is used as a plasticizing admixture [8]. For example, for a long time concentrated molasses yeast brew has been used as a plasticizing admixture [9]. Such an admixture is the waste product of the nutritional yeast manufacturing and consists of the mix of humic substances and mineral salts.

Casein is the principle protein in bovine milk, which is mainly responsible for the functionality of milk proteins. As a chemical admixture, the application of casein can be tracked back to ancient Rome [10]. At that time, builders added various organic additives to mortars to adjust certain mortar properties. For example, the addition of sugar, fruit syrup and blood extended the workability time of mortars. The addition of malt, beer and urine could improve the durability and frost resistance, etc. Casein as well as some casein contained products were generally used as plasticizer or stiffening agent, which could improve the workability or adjust the consistency of cementitious mortars. Today in the construction industry casein is by far the most widely used dispersant in self-levelling underlayments.

Foam forming substances obtained from the protein-contained products can be used as an effective admixture during foam concrete production [11]. Such protein-contained products include blood, skin, bones, horns and hoofs, feathers, fish scale, oil cake of oil crops and milk products and after processing (hydrolysis, evaporation, chemical modification) they give extremely stable foam as a foam admixture. The example of such admixtures is the protein foam admixture CreenFroth-P.

The purpose of the present article is to extend the range of raw materials resources for the building industry, especially enlarging the number of waste products in general and food waste products in particular that could be used in cement and concrete industries. One of the possible approaches is the utilization of waste vegetable oil as a chemical admixture for hydraulic binding materials. Waste vegetables oils are already widely used in biodiesel production [12-14]. The largest producers of such types of food wastes are food service areas – cafes and restaurants. So, the one of the objectives of the present study is the development of a conceptually new way of waste vegetable oil utilization, namely in the building industry.
2. Experimental program

2.1. Materials

Ordinary Portland cement type I/500 and fractioned river sand (0,315-0,900) were used in the investigation.

Test admixture (D-148) is a product of the chemical reaction between the waste sunflower oil components and diethanolamine in the presence of the alkali promoter (0.5 weight %) and glycerine. The reaction was conducted in the presence of the excess amount of diethanolamine. The final product (D-148) consists of the following components: sun oil fatty acid diethanolamide, small amount of sun oil fatty acid salts, small amount of diethanolamide and glycerol.

2.2. Test methods

The influence of the admixture on the cement system was estimated according to the following characteristics: compressive strength on 1, 3 and 28 days of hardening, water demand, setting times, spread diameter according to mini-slump test, and moisture adsorption.

For compressive strength, water demand, setting times and moisture adsorption tests cement samples have been prepared in the following way. The test admixture dissolved in water was added to the cement and mixed for 15 min in the lab ball mill. For mini-slump test the already prepared cement samples were mixed with sand for 5 min in the lab ball mill.

Compressive strength of cement after 1, 3 and 28 days of hardening was tested on cube samples with dimensions of 20*20*20 mm. Water demand and setting times were measured with mini-Vicat apparatus.

Mini-slump test is carried out by using a mini cone to evaluate flowability of cement-sand suspension. The truncated cone is placed on a smooth and non-absorbing metallic plate filled with cement-sand suspension and lifted. The resulting final diameter of the fresh cement-sand mix sample is the mean value of two measurements made in two perpendicular directions. The measured spread diameter is related to plasticizing effect of the admixture. The higher the spread diameter, the higher the plasticizing effect of the admixture.

For moisture adsorption test the method of determining hydrophobic property was used. According to this method powder cement samples were put in the exsiccatator with 100 % relative humidity for 15 weeks. The mass gain of the cement was measured. The lower the mass gain, the higher the waterproofing properties of the cement samples.

3. Results and discussions

Dependences between water demand, setting times, compressive strength, spread diameter of the cement-sand mortar and the test admixture content are presented in Table 1.

| D-148 content, weight % | Spread diameter, mm | Water demand, % | Setting times, h-min | Compressive strength, MPa / day |
|-------------------------|---------------------|-----------------|---------------------|-------------------------------|
|                         |                     |                 | initial             | final                        | 1    | 3    | 28   |
| 0.00                    | 120                 | 25.0            | 0-45                | 3-00                         | 17.8 | 30.5 | 39.5 |
| 0.04                    | 179                 | 24.0            | 0-45                | 3-20                         | 20.8 | 32.4 | 35.4 |
| 0.08                    | 198                 | 24.0            | 0-55                | 3-30                         | 16.4 | 23.6 | 33.3 |
| 0.20                    | 201                 | 22.5            | 1-00                | 3-40                         | 16.5 | 26.3 | 48.5 |
| 0.60                    | 195                 | 18.0            | 1-30                | 4-00                         | 12.1 | 21.4 | 24.0 |
Dependence between the cement moisture adsorption and admixture content is presented in Figure 1.

![Figure 1. Dependence between moisture adsorption and the test admixture content.](image)

According to the table data, namely the changes of water demand of cement pastes and spread diameter of the cement-sand mortars, the test admixture can be considered as a plasticizing/water-reducing admixture. A plasticizing admixture is a chemical compound added to concrete/mortar before or after it is mixed in order to produce concrete/mortar using less water while maintaining the material’s workability, or to produce concrete/mortar with higher workability while maintaining the constant water demand.

As already known, plasticizing admixtures are broadly classified into two categories: normal and high range [15]. The normal plasticizing admixtures are also called “plasticizers” or water reducers, while the high range plasticizing admixtures are called “superplasticizers”. While the normal plasticizing admixtures can reduce the water demand by 5 – 10%, the high range plasticizing admixtures can cause a reduction of 15 – 40%.

The test admixture causes the maximum water demand to decrease up to 28 % (at admixture content 0.6 weight %). This result makes it possible to consider the test admixture as superplasticizer (at admixture content 0.6 weight %). The samples with 0.2 weight % admixture content show optimal plasticizing results (the largest spread diameter and the water demand decreased up to 10 %) that allows considering the test admixture as plasticizer or water reducer.

The main feature of plasticizing admixtures is the plasticizing effect, namely the ratio of changes in concrete/mortar workability after adding the plasticizing admixture to its composition. But plasticizing admixtures cause the decrease in the early strength along with increasing workability. That is why in the studies of admixtures one must take into account the term “rational plasticizing effect”, meaning the plasticizing effect that is not accompanied with strength decrease [16].

The main physical-mechanical characteristics (water demand, spread diameter and compressive strength) being considered, one can observe that optimal content of the test admixture (D-148) falls within the limit of 0.2 weight %. At such admixture content the samples have the largest spread diameter and lower (by 10 %) water demand. Early compressive strength is decreased negligibly (by 14 % after 3 days of hardening) but grade strength is higher by 23 % or almost by one grade.
The test admixture not only decreases early strength but also retards setting times, which is more obvious at higher admixture contents. But at optimal admixture content (0.2 weight %) early strength decrease and setting times retardation are negligible.

The test admixture gives the cement hydrophobic properties, this being especially apparent at 0.2-0.6 weight %. The samples with 0.6 weight % of the test admixture have the best hydrophobic properties, in other words, the lowest mass gain (49 % lower in comparison with the control sample).

The optimal admixture content is 0.2 weight %. At this content cement samples have the largest spread diameter, lower water demand (by 10 %), higher grade strength and additionally hydrophobic properties. After 15 weeks moisture adsorption of the cement samples with 0.2 weight % of the test admixture was 34 % lower in comparison with the control ones.

4. Conclusions
The results of the investigation enable to arrive at the following conclusions:
1. The final product of the waste sunflower oil processing can be used as a chemical admixture in cement, mortar and concrete.
2. The test admixture D-148 is normal range plasticizing admixture, which at the optimal content causes 10% decrease in water demand, 1.7 times increase in spread diameter and 23 % or almost one grade increase in grade strength.
3. The test admixture gives the cement hydrophobic properties and causes moisture adsorption to decrease by 34 % (at optimal content).
4. The test admixture obtained during the processing of food industry wastes can be utilized in the building industry as a multifunctional plasticizing - waterproofing admixture.

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