

USE OF SILICEOUS EARTHS FROM REFINING PROCESSES FOR PRODUCTION OF ADDITIVES CONTROLLING THE PROPERTIES OF CEMENT MORTARS AND CONCRETES

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Abstract: It was found that the used siliceous earths containing adsorbed and occluded organic substances are partially decomposed in the hydrothermal process like fresh earths to form alkaline silicates. The introduction of oxidizing agent to the hydrothermal treatment of used oiled siliceous earths resulted in partial oxidation of hydrocarbons to high molecular weight acids. As a result, a mixture composed of sodium silicates, sodium salts of organic acids (soaps) and non-reactive hydrocarbons was formed. It was shown that this product obtained from oxidative hydrothermal decomposition of used siliceous earths can be used as an additive to cement mortars to reduce their setting time and water absorbability.

Key words: bleaching earths, water-repelling additives, ash-cement mortars.

Introduction

Siliceous earths have been used in some older Polish refineries in the "Filtrol" process as the so-called bleaching earths for the finishing refining of oil bases. Used siliceous earths obtained during this process constitute a waste that contains from 30 % mass to 60 % mass of organic substances. Waste earths are sometimes gathered on temporary dumps hazardous to the environment. It is estimated that about 10 - 20 thousand tonnes of used siliceous refining earths are deposited on the dumps of refineries located near Carpathians. Despite numerous attempts, no effective way of utilizing used refining siliceous earths has been found yet.

This work reports the possibility of utilizing used siliceous earths in the production of building materials. It was assumed that soluble silicates and soaps can be obtained from oiled siliceous earths by strong base treatment. These products are well-known modifiers of cement mortar which reduce first of all the setting time of mortar and the water absorbability of concrete produced. Agents for concrete modification especially cheap ones are in wide demand by building industry (Grunau 1970; ACI Material Journal 1987; RILEM Conference 1990).

Experimental

Post-refining earth obtained during the "Filtrol" process in Jedlicze Refinery was a subject of the investigation. The used siliceous earth studied in this work con-

tained 36 % mass of organic matter. The process of hydrothermal decomposition was carried out at temperatures of 100 - 105 °C during 1 hour using 10 - 20 % by mass solutions of sodium hydroxide and oxidants introduced into a reaction mixture (Steininger 1991; Steininger et al. 1993). The obtained product was added to ash-cement and cement mortars. The properties of mortars were determined according to Polish Standards, i.e. setting time, water absorbability and mechanical compressive strength (PN-72/B-06250; PN-72/B-04300).

Results

The chemical composition of solutions after hydrothermal decomposition of the used earth and the degree of dissolution of this earth are presented in Tab. 1. The obtained post-reaction mixture can be used as a water-repelling additive for cement and ash-cement mortars. The means and conditions of production of the above mentioned additive are the subject of patent application (Steininger et al 1993). The additive was introduced to a cement in the amount of 1 - 5 wt. %. The P-35 cement (from Górażdze cement plant) and pit sand were used in the experiments (1 mass part of cement, 3 mass parts of sand). The ash from Siechnica thermal-electric power station was used for the preparation of ash-cement mortars. It was mixed with the cement in the same ratio (1:3).

Figs. 1 and 2 show how the additive (prepared from used oiled siliceous earths) affects the properties of cement and ash-cement mortars.

Table 1: Chemical composition of solutions obtained from hydrothermal decomposition of the used oiled siliceous earth.

| Concentration of NaOH [%mass.] | Degree of dissolution [%mass.] | Concentration [kg/m ³] | | | | | | SiO ₂ /Na ₂ O module | Content of soaps [%mass.] |
|--------------------------------|--------------------------------|------------------------------------|-------------------|--------------------------------|--------------------------------|------|------|--------------------------------------------|---------------------------|
| | | SiO ₂ | Na ₂ O | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | MgO | | |
| 10 | 9.6 | 229.7 | 65.8 | 1.28 | 0.16 | 1.97 | 0.17 | 3.59 | 11.3 |
| 15 | 25.6 | 321.4 | 106.3 | 2.85 | 0.29 | 1.72 | 0.08 | 3.12 | 12.6 |
| 20 | 36.6 | 269.2 | 155.0 | 3.72 | 1.26 | 2.99 | 1.81 | 1.81 | 11.8 |

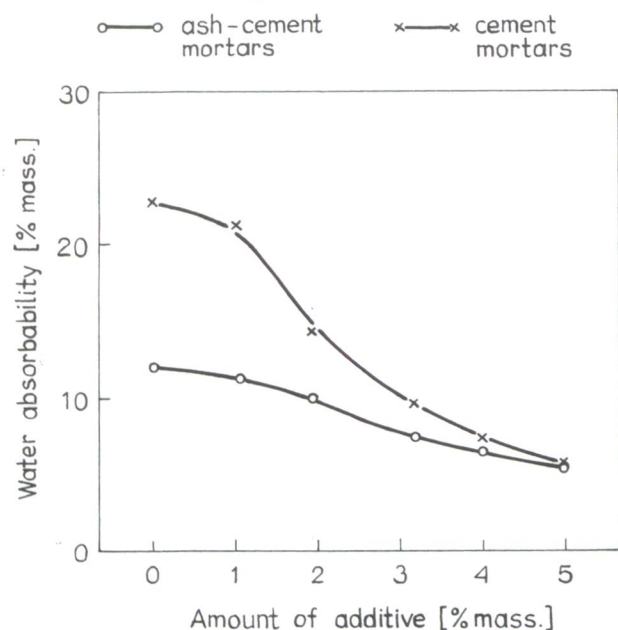
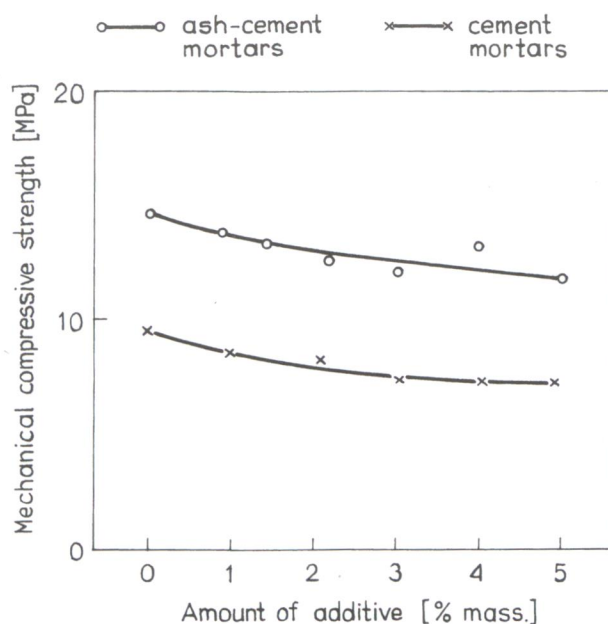
Table 2: Effect of the modifying agent on the setting time of ash-cement and cements mortars.

| Additive amount, % mass → | 0 | 1 | 2 | 3 | 4 | 5 |
|---------------------------|--------------------|-----|----|----|----|----|
| | setting time, min. | | | | | |
| ash-cement | 220 | 130 | 85 | 20 | 12 | 10 |
| cement | 200 | 130 | 90 | 18 | 12 | 12 |

It can be seen from Fig. 1 that with an increasing amount of the additive, the water absorbability decreases. However, the cement mortars are less susceptible to the water-repelling action of the additive than are ash-cement mortars. This is probably caused by two times higher initial absorbability of the latter in comparison with the cement mortars. Fig. 2 shows the relationship between mechanical compressive strength of mortars and the amount of the additive introduced. Comparing both figures it follows that the additive can be introduced to the mortar in the amount not higher than 2 % mass. Further increase in the amount of the additive causes a slight decrease in water absorbability, and simultaneously, a decrease in mechanical strength of the prepared mortars.

Additionally the mortar samples were subjected to 20 cycles of freezing - defrosting (PN-72/B-04300; Powers 1956). After this treatment no changes have been observed in the mechanical compressive strength of these mortars.

The influence of the additive studied on the setting time of ash-cement and cement mortars was examined using Viscata apparatus (penetrometer) (PN-72/B-04300). The results of the measurements are shown in Tab. 2. The data in Tab. 2 show that the introduction of the additive has an advantageous effect on the setting time of ash-cement and cement mortars. The presence of the additive in mortars in the amount so much as 1 % mass decreases nearly two times the setting time.

**Fig. 1.** Effect of the water-repelling additive on the water absorbability of cement and ash-cement mortars.**Fig. 2.** Effect of the water-repelling additive on the mechanical compressive strength of cement and ash-cement mortars.

Conclusion

It was found that post-reaction mixtures from oxidative hydrothermal decomposition of post-refining, used oiled siliceous earths can be used as water-repelling additives to cement and ash-cement mortars to reduce their water absorbability and setting time.

This strategy could be useful for the utilization of used siliceous earths lying useless on dumping sites, many of which are temporary and not sufficiently protected from environmental problems.

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