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Physico-Chemical Properties of Sewage Sludge Ash and Its Influence on the Chemical Shrinkage of Cement Pastes †

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† Presented at the 10th MATBUD'2023 Scientific-Technical Conference "Building Materials Engineering and Innovative Sustainable Materials", Cracow, Poland, 19–21 April 2023.

Abstract: According to European Union regulations regarding the storage and disposal of industrial waste, waste generated during the treatment of municipal sewage should be managed in an environmentally friendly manner. In order to reduce environmental risks and minimise volume, sewage undergoes thermal treatment. The resulting ash contains toxic components, so it is essential to properly dispose of it. For this reason, the possibility of utilising this type of waste in cement composites has been subject to preliminary verification. To this end, so far, basic tests regarding the parameters such as water demand and setting time have been performed for cement pastes containing ash from the incineration of sludge produced from municipal sewage (Sewage Sludge Ash—SSA). The main purpose of this article is to describe the chemical shrinkage of cement pastes containing this additive. CEM I Portland cement and fly ash obtained at the Thermal Sludge Disposal Station at the Płaszów Sewage Treatment Plant were used in this study. Cement was replaced with ash in the rates of 10%, 20%, and 30%. The results confirm that with an increase in the SSA additive, a reduction of chemical shrinkage of 9.5%, 21.4%, and 31% is observed at 10%, 20%, and 30% content of the additive, respectively. The presented results confirm the possibility of using this material as a cement replacement in cement composites.

Keywords: sewage sludge ash (SSA); cement pastes; chemical shrinkage

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Citation: Adamczyk, M.; Zdeb, T.; Tracz, T. Physico-Chemical Properties of Sewage Sludge Ash and Its Influence on the Chemical Shrinkage of Cement Pastes. *Mater. Proc.* **2023**, *13*, 26. https://doi.org/10.3390/materproc2023013026

Academic Editors: Katarzyna Mróz and Izabela Hager

Published: 15 February 2023

1. Introduction

Progressive urbanisation is indispensable in any developing society. With it, sewage treatment is becoming an increasing problem. The result of treatment is a large quantity of sewage sludge (SS), the amount of which corresponds only 1–3% of the volume of flowing sewage. However, with increasing urbanisation and economic progress, the amount of generated waste is starting to become a serious problem. EU regulations require us to dispose of this waste properly, due to its specific properties. This type of waste contains heavy metals and pathogenic organisms, which can have a highly negative impact on the environment and human health. In order to protect the environment and individuals, and to minimise the volume of sludge generated, it is subjected to thermal treatment. However, the ash produced by the thermal disposal of sludge (SSA) still contains heavy metals. The use of this ash and other wastes in cement materials seems to make the most sense due to its high immobilisation properties [1–6]. The idea of this type of utilisation of sludge seems to be highly appropriate, since, as the research of the authors of the study [7] demonstrates, these composites have the ability to almost completely immobilise heavy metals. Heavy metals content in ash depends primarily on the urbanisation and industrialisation of the area. The amount of fly ash resulting from the thermal disposal of sewage sludge and contaminated with heavy metals is a major problem in many developing countries.

Literature reports on the physical and mechanical properties of hardened cement composites containing SSA are quite widely described [8–12], as well as in our previous studies [13], while the number of publications on their durability is limited [13,14]. So far, it is difficult to find publications devoted to the problems of chemical and autogenous shrinkage of cement binders containing ash formed after thermal disposal of sewage sludge.

The reaction of cement with water reduces the volume of the mixture. This reduction can be calculated from the density of substrates and products of cement hydration. Volume changes of this nature are called chemical shrinkage or contraction, and they involve a smaller volume of water in the hydrated phases than its volume in the liquid phase. Contraction depends on the mineral composition of the cement. The C_3A phase shows the greatest contraction, while the C_2S phase shows the least [15]. Yodsudjai et al. [16] demonstrated that varying levels of C_3A contained in different types of cement play a major role in the behaviour of cement paste during chemical shrinkage. For this reason, replacing cement with SSA, and thus reducing C_3A, may result in a reduction of chemical shrinkage. In addition, due to the high content of hematite in the ash in question, its hydration can also affect the volume of the reaction products of the blended cement paste.

2. Materials and Methodology

Ash produced during the incineration of sewage sludge generated at the Płaszów sewage treatment plant belonging to the Municipal Water and Sewage Company in Kraków was used as the material for this study. The treatment plant has its own sludge thermal disposal station with a capacity of about 64 tonnes of dry matter per day. The ash is produced by incineration of the pre-dried and centrifuged sludge in a fluidised bed furnace at a temperature of approx. 850 °C. In addition, pure CEM I 42.5R Portland cement was used in this study. The basic chemical composition of the materials used in this study is presented in Table 1. During testing of binders containing SSA, a series of cement pastes containing 0%, 10%, 20%, and 30% ash were made, replacing cement by weight.

Table 1. Chemical composition of SSA with the used CEM I 42.5R cement.

Component [%]	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O_e	SO_3	P_2O_5	MgO	Cl^-	LOI
SSA	29.9	9.6	22.5	13.5	1.0	0.1	18.0	-	0.15	0.3
Cement	19.8	4.9	2.7	64.6	0.48	2.9	-	1.0	0.024	2.9

The scope of the conducted measurements mainly focused on determining the value of chemical shrinkage during the early curing period of cement pastes containing SSA as an additive (7 days). Chemical shrinkage was determined based on an improved dilatometry method developed by the team of Zhang et al. [17]. The method was based on ASTM C 1608 Standard Test Method for Chemical Shrinkage of Hydraulic Cement Paste [18]. The measurement set-up consisted of a 500-mL conical flask that was set on a magnetic stirrer. The measurement set-up is presented in Figure 1.

The magnetic stirrer was introduced into a conical flask and 100 g of binder was introduced. Then, distilled water was poured in, after removing air bubbles. A vacuum chamber was used for this purpose, with internal pressure of 40 mb, and the time in which the water was subjected to the vacuum was 15 min. The entire set-up was placed on a magnetic stirrer constantly stirring the suspension. The flask was then plugged tightly with a rubber stopper with a 10-mL pipette with a measurement accuracy of 0.1 mL. The pipette was filled with oil to avoid water loss from the measuring system due to evaporation. The mixing process at 750 rpm continued for the entire period of conducting measurements, i.e., 7 days. The cement content of the binder was gradually replaced by the addition of SSA at 10%, 20%, and 30% by weight. Changes in the volume of liquid in the pipette were recorded every 30 min throughout the measurement period. In addition, the test stand was placed in an enclosed fume hood to maintain constant test conditions (Figure 1). A series of measurements were also performed for the properties of SSA. Chemical composition was determined by XRF X-ray fluorescence method. Phase composition was determined by XRD using a Philips PW1830 device. Grain size distribution was measured with the Malvern

Instruments Mastersizer 2000 laser diffraction particle size analyser. The specific surface area value was determined using the BET method with the Quantachrome NovaWin 2200 device. Other measurements of cement pastes, such as standard consistency and setting times were made in accordance with PN EN 196-3 [19]. Setting times were measured using a CONTROLS VICAMATIC 3 automatic Vicat apparatus.

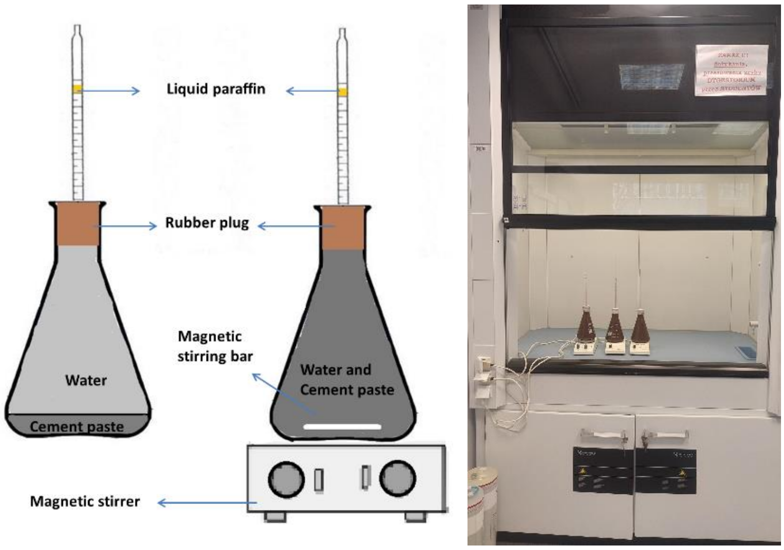

Figure 1. Chemical shrinkage measurement set-up.

3. Research Results and Discussion

The chemical composition of the ash mainly contains oxides of silicon (SiO_2), aluminium (Al_2O_3), and iron (Fe_2O_3), suggesting that the material has the potential to react with calcium hydroxide, and thus to exhibit pozzolanic properties. The sum of the masses of these oxides regardless of the sludge production season exceeded 60%.

A high content of P_2O_5 results in an increase in the setting time of the binders, as demonstrated later in this study. The presence of ions carrying corrosion hazards such as sulphates, chlorides, and alkalis appear to be at low and safe levels given the criteria included in the PN EN 450-1 [20] standard for fly ash. As a result of incineration, health-hazardous bacteria and organic matter are removed from SSA. Therefore, according to the 2012 Act on waste [21], it becomes stabilised.

According to the roentgenogram presented in Figure 2, three main crystalline phases can be distinguished due to the specific oxide composition. The dominant phase is inert silica, occurring mainly in the form of β-quartz. It is not an amorphized structure mainly resulting from the relatively low temperature during fluidised bed sludge treatment, i.e., at approx. 850 °C. Iron occurring mainly in the third oxidation number forms a hematite phase. In addition, due to the high content of phosphate oxides resulting from the high content of detergents in the sewage, the formation of a crystalline calcium-aluminium phosphate salt with the general formula of $Ca_9Al(PO_4)_7$ occurs.

The grain size distribution is unimodal with a distinct peak at diameters between 40 μm and 50 μm. The full range of grain sizes is from 0.3 μm to 100 μm. The grain sizes of d_{10}, d_{50}, and d_{90} are 1.8, 25.8, and 63.0 μm, respectively. The BET specific surface area, in turn, was 3900 m^2/kg. The specific density of SSA was at the level of 2.90 g/cm^3. Full granulometry is presented in Figure 3.

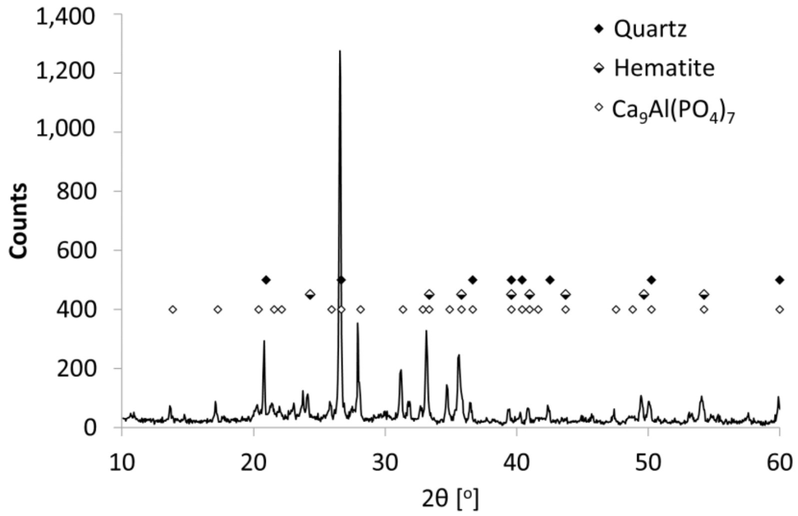

Figure 2. SSA phase composition.

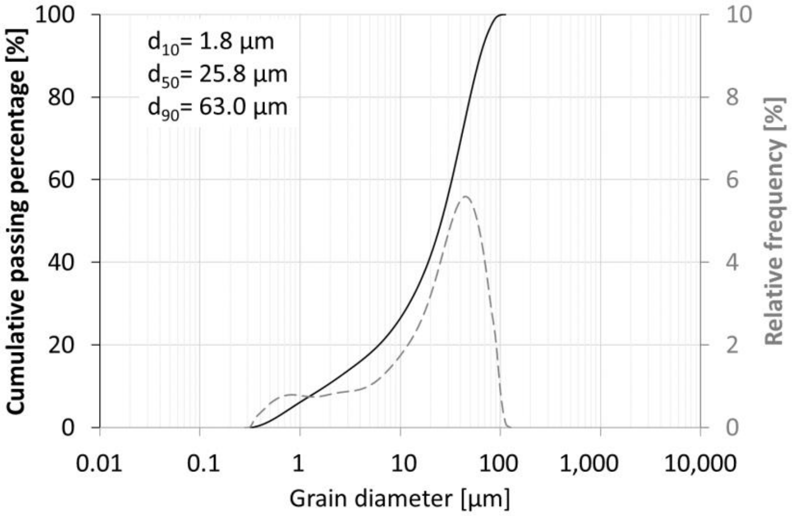

Figure 3. SSA grain size distribution.

Due to the high phosphate content in SSA, setting times were measured for binders containing SSA. Measurements of setting times were performed in accordance with PN EN 196-3 [19], which means that it had a different w/b ratio connected with standard requirements. The results are presented in Figure 4. The pastes prepared in this way were subjected to setting time tests. The addition of SSA at a level of 30% of the weight of the binder causes a sharp increase in the initial and the final setting time for the binder. The initial setting is doubled in length, while the final setting time is extended by approx. 60%. This phenomenon has been observed by a number of researchers [22–24], who attribute the setting delay properties of phosphate ions to the hindered hydration of cement grains. This is due to the fact that PO_4^{3-} ions react with Ca^{2+} ions in the liquid phase of the paste. The consequence of this process is the precipitation on the surface of the cement grains of calcium phosphate $Ca_3(PO_4)_2$ with low solubility. It takes the form of a finely crystalline and poorly permeable layer, the presence of which greatly impedes the hydration process. The crystallisation process can also occur in the pores of the paste, so that phosphate ions can not only affect the setting time but also the strength of the paste [22]. In addition, the grain size distribution and grain morphology of SSA, presented in Figure 3, results in a significant increase in the water demand of the analysed binders, as shown in Figure 5.

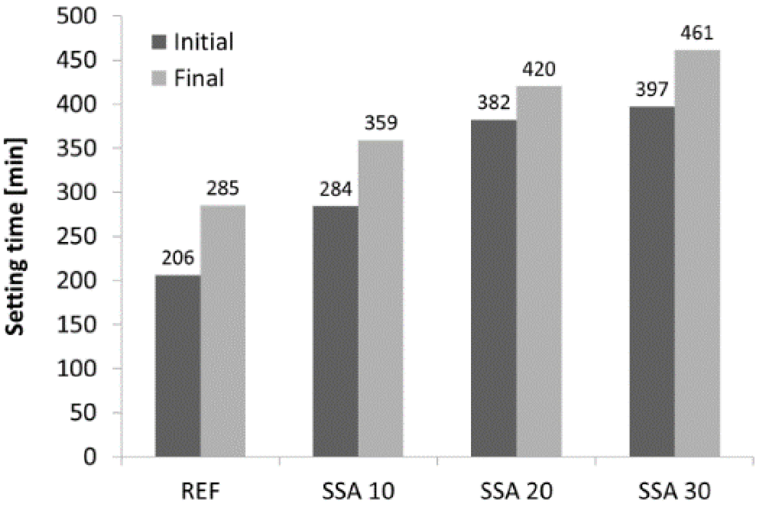

Figure 4. Setting time of cement binders with SSA content.

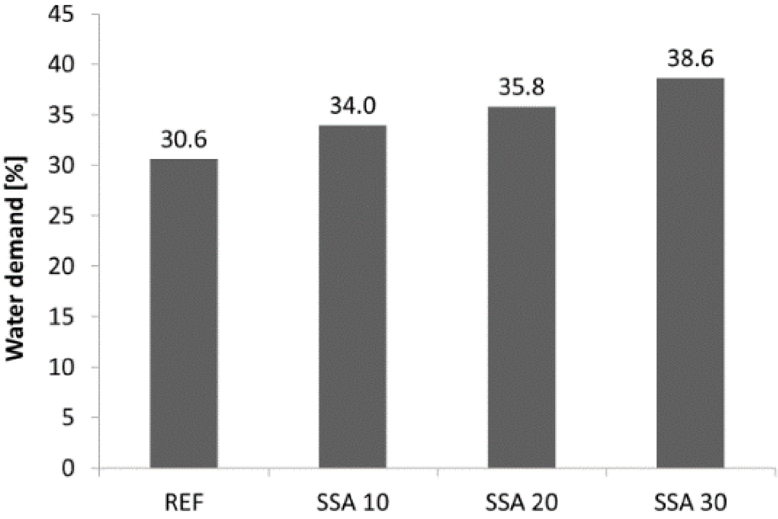

Figure 5. Water demand of the analysed binders.

The chemical shrinkage of cement binders containing various pozzolanic additives in their composition is well described in the literature [25–28]. However, it is difficult to find any reports on the effect of SSA addition on the chemical shrinkage of such binders. Cement pastes with the addition of highly reactive pozzolanic materials (silica fume), are characterised by high degree of chemical shrinkage. The main reason is the reaction, as a result of which calcium hydroxide reacting with pozzolana molecules forms an additional C-S-H phase. In the presence of reactive silica, calcium ions are steadily consumed, which maintains their concentration at a low level. The result is further dissolution of clinker grains and thus an increase in chemical shrinkage. In the absence of pozzolana, the concentration of Ca^{2+} ions stabilises at the level of saturated solution, thus inhibiting the dissolution of clinker grains and their hydration, and consequently reducing chemical shrinkage [26]. Materials with a lower specific surface area and thus lower pozzolanic reactivity, such as fly ash, used as cement additives, result in lowering the chemical shrinkage of such binders. These additives do not undergo a pozzolanic reaction in the initial hydration phase, but only act as fillers. The fine particles of the additives fill the free spaces between the cement grains and reduce the amount of water involved in the reaction. Therefore, the level of chemical shrinkage, due to the reduced amount of clinker grains replaced by pozzolanic material with lower reactivity, is reduced especially in the initial stages of hydration. The level of this shrinkage clearly increases as hydration progresses over the long term. This effect is associated with the formation of a C-S-H phase on the surface of the mineral additive grains. However, the content of hydrated calcium silicates is lower than in the reference binder (without mineral additive); hence, the final chemical shrinkage value remains lower [28].

The chemical shrinkage of binders with the addition of ash from sewage sludge incineration has been determined for pastes containing SSA in amounts ranging from 0 to 30%, in 10% increments. In addition, in order to obtain information regarding the behaviour of the SSA additive in the presence of water, the change in its volume without cement (SSA100) was measured. The results are presented in Figure 6.

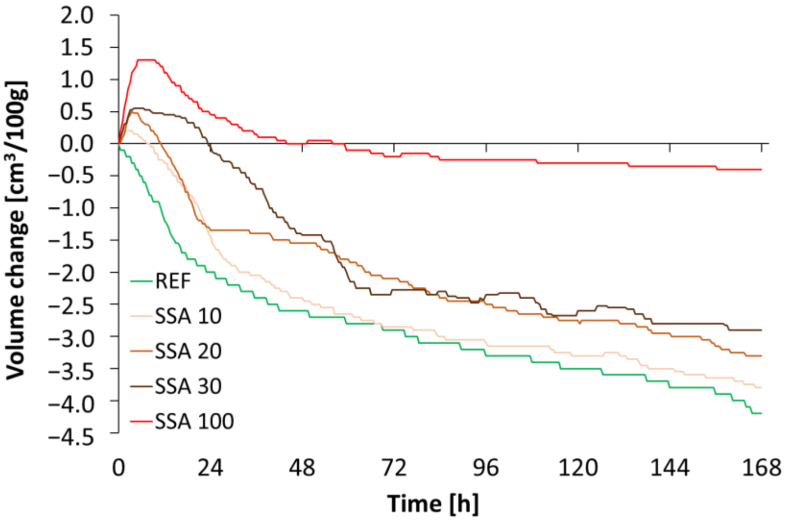

Figure 6. Chemical shrinkage of cement binders containing SSA additive.

The reference sample shows an increase in chemical shrinkage throughout the hydration period. The volume change was 4.2 $cm^3/100$ g of binder after 168 h of hydration. Samples containing SSA additive show a slight expansion during the initial hydration period. The level of this expansion increases with increasing amounts of additive used and reaches its highest value of 0.55 $cm^3/100$ g of binder at 30% SSA content. Pastes containing SSA additive undergo expansion in the initial stage of hydration, i.e., up to 6 h. It is likely that this phenomenon is influenced by two mechanisms occurring simultaneously. On the one hand, the presence of phosphate ions causes crystallisation of low solubility calcium phosphate salts on the surface of clinker grains, which entails a reduction of the rate of hydration and, at the same time, the phenomenon of contraction. The hydration of hematite (Fe_2O_3), a component of the SSA additive, occurs in parallel. Upon contact with water, hydration products appear on its surface [29], which, according to the authors of the publication [30], constitute the goethite (FeOOH) phase. The molar volume of goethite is almost 1.5 times that of its non-hydrated form as hematite. It is also worth mentioning that with the increasing degree of hydration of hematite, e.g., to $Fe(OH)_3$, the molar volume more than doubles [31,32]. In the next phase of the hydration of binders with SSA, the shrinkage of the tested binders becomes the dominant effect. Its course depends on the content of the SSA additive. Increasing the amount of the cement replacement additive reduces chemical shrinkage relative to the reference binder by 9.5%, 21.4%, and 31.0% at 10, 20, and 30% of SSA in the binder, respectively.

4. Conclusions

Despite the significant changes in the technological properties of SSA-containing binders, mainly concerning their setting time and water demand, this additive does not preclude its use in cement composites. SSA content is possible even at the level of 30% by the weight of cement causing an acceptable level of reduction of the performance of binders. Due to their high water demand, it becomes necessary to use superplasticizers during the preparation of mortars or concretes. The results of chemical shrinkage tests confirmed that the addition of SSA has a positive effect on this characteristic, reducing its value by up to approx. 30%. This is due to its rather low pozzolanic reactivity and relatively small specific surface area. Reducing the amount of cement in the paste further increases the reduction of chemical shrinkage. The effect of hydration of hematite grains in SSA, with simultaneous inhibition of the cement hydration process by the activity of phosphate ions in the initial phase of binder hydration, entails the occurrence of an expansion effect, facilitated by increasing amounts of added SSA.

Author Contributions: Conceptualization, M.A. and T.Z.; methodology, M.A.; validation, T.Z. and T.T.; investigation, M.A.; resources M.A and T.Z.; writing—original draft preparation, M.A.; writing—review and editing, T.Z. and T.T. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: Publication cost of this paper was covered with funds from the Polish National Agency for Academic Exchange (NAWA): “MATBUD’2023—Developing international scientific cooperation in the field of building materials engineering” BPI/WTP/2021/1/00002, MATBUD’2023.

Conflicts of Interest: The authors declare no conflict of interest.

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