



Article Potential Use of Municipal Waste Incineration Ash as a Hardening Slurry Ingredient

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Abstract: In recent years, there has been a marked increase in the amount of municipal waste generated in Poland. In the context of circular economy assumptions, the key is the availability of technologies that would make it possible to safely process and reuse waste, especially when it is difficult to manage. One such direction is thermal waste treatment. In 2020, 21.6% of all municipal waste was subjected to this process. Consequently, the amount of ash generated is significant (approximately 2,823,000 tons annually). One of the uses of waste materials is the sealing of earth hydrotechnical facilities, such as flood embankments, water dams, and embankments of waste landfills. For this purpose, cut-off screens made of hardening slurries are used. In order to improve the tightness and corrosion resistance of hardening suspensions, combustion by-products are added to their composition. The article presents an assessment of the possibility of using ashes from municipal waste incineration as an additive to hardening slurries. It also discusses the technological and operational parameters of hardening slurries with the addition of the ashes in question. Binding requirements for hardening slurries used for the construction of cut-off walls is also defined. The experiment showed that the tested hardening slurries meet most of the suitability criteria. Further research directions are proposed to fully identify other properties of hardening slurries in terms of their environmental impact.

Keywords: municipal solid waste; fly ash; hardening slurry; cement-bentonite slurry; cementitious materials; circular economy

1. Introduction

Municipal waste (MW) management is a challenge, even for highly developed countries, since there is a positive correlation between the economic growth of a country and the amount of generated waste [1]. According to SP (Statistics Poland) data [2], a more than 14% growth in the amount of generated MW was recorded in Poland in the years 2015 to 2018. This translated to an average of 325 kg waste collected per capita (MW is waste critical to the waste management system in Poland [3]). This value is significantly lower than the EU average (489 kg per capita in 2018 [4]). A similar situation can be observed in other countries of the region: Romania, Latvia, Slovakia, Estonia and the Czech Republic. It seems that this issue is directly associated with two phenomena—illegal landfills and waste burning in household furnaces [5]. Gradual tightening of the MW collection system and the growing environmental awareness of citizens suggest that the amount of MW collected in Poland will increase.

The Polish MW management system is governed by, among others, the Waste Act [3], which implements a number of EU directives in the field of waste management and environmental protection within Polish legislation [6–21]. The Act introduced a waste handling hierarchy, with "preventing waste generation" at its peak, followed by "preparation for re-use", "recycling", "other recovery processes" and "neutralization".



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Thermal treatment of municipal waste (TTMW) aimed at energy recovery is classified within the recovery group [22]. Indeed, 23% of all MW was managed in Poland in 2018 in this way [2], and a tendency to build new incineration plants has been observed. Cement plants could also play an important role in the incineration of municipal waste; however, using waste for this purpose is restricted by the limited amount of waste suitable for alternative fuel production and by the poorly developed waste processing industry in Poland [23].

The TTMW process should supplement re-use and recycling processes due to economic, technical and organizational reasons [4], which would enable closing the circulation at the level of recovery of energy contained in waste. Process by-products include slags, as well as bottom and fly ash, which in accordance with the circular economy (CE) concept and the waste handling hierarchy [22] should be managed in a way that they constitute a valuable product and are no longer treated as waste (currently, such waste is dumped, at a great cost for TT plants). It is expected that this will contribute to reduced greenhouse gas emissions and natural raw material consumption, as well as strengthening the process aspects of CE. For this purpose, it is necessary to identify the properties of generated waste and its applicability. In the literature on the subject, attempts are made to use ash from municipal solid waste in, among other things, building materials, especially in cement and concrete technology and in geotechnical applications [24–29].

This article aimed to research hardening slurries with two types of TTMW waste, which are designated 19 01 07* and 19 01 13* (* sign indicates hazardous waste) in accordance with [30]. The studies focus on the utilization of TTMW by-products in slurries dedicated for cut-off walls and the fundamental material properties in this respect, as shown in Table 1.

A hardening slurry is a thixotropic mix (suspension) of water, binder and clay material, as well as, depending on the intended use, other ingredients (e.g., blast furnace slag and fly ash), used for the construction of building structures in the ground substrate or when filling gaps and openings in the ground [31–34].

Elements with a hardening slurry can be executed using single- or two-phase methods [31,33]. In the case of a single-phase method, a liquid hardening slurry in a narrow trench exerts hydrostatic pressure, ensuring excavation stability when deepening, and its components seal excavation walls, hence preventing slurry penetration into the ground. After reaching an assumed depth, the slurry remains in the excavation. Owing to binder content, the hardening slurry settles and turns into a porous body.

In contrast, the two-phase method uses expansion slurries, most usually bentonitebased, without added binder. The nature and conditions of excavation of narrow trenches are similar to the single-phase method, except for the fact that after reaching the design excavation depth, the expansion slurry is replaced with a hardening slurry, which leads to achieving greater structure homogeneity.

In particular, hardening slurries are used to build cut-off walls. Cut-off walls are employed to protect excavations against the inflow of groundwater, in embankments, dam substrates and levees, and to seal landfills (prevention of contaminants penetrating into the soil and groundwater) [31,35–37]. Table 1 shows specific requirements in terms of the properties of the hardening slurries used for cut-off walls in levees, as based on domestic experiments, together with their determination methods.

Properties	Unit	Value	Marking Method	
	Properties i	n liquid state		
Bulk density				
– diaphragm method (narrow-space excavation)		1.15–1.40		
– Deep Soil Mixing—DSM	g/cm ³	1.30-1.50	[40]	
– vibration method (Jet Grouted Diaphragm Wall—JGDW)		1.50–1.60		
Conventional viscosity (marsh funnel runoff time)	S	≤50 [40]		
Daily water loss	%	≤ 4.0	[41]	
Structural strength after 10 min	Ра	1.4–10.0	[40]	
	Properties after hardeni	ng after 28 days of curing		
Compressive strength	MPa	0.5–2.0	[42]	
Filtration coefficient k	m/s	$\le 10^{-8}$	Laboratory methods as for cohesive soils	

Table 1. Selected properties of hardening slurries used in cut-off walls in levees [38,39].

2. Materials and Methods

2.1. Hardening Slurries

The following materials were employed in developing hardening slurry recipes:

- tap water,
- sodium bentonite,
- portland cement CEM I 42.5 R cement,
- ash from the incineration of municipal waste deemed 19 01 07*-P1,
- ash from the incineration of municipal waste titled: 19 01 13*—P2.

The recipes of the designed hardening slurries are shown in Table 2.

Table 2. Recipes of designed hardening slurries per 1000 dm³ of water.

			Component			Indicator	
Recipe	Tap Water (dm ³)	Bentonite (kg)	Cement (kg)	Ash P1 (19 01 07*) (kg)	Ash P2 (19 01 13*) (kg)	Water/Dry Matter w/dm	Cement/Ash c/a
R1P1	1000	25	400	175	_	1.667	2.286
R2P1	1000	20	400	200	-	1.613	2.000
R3P1	1000	25	375	225	_	1.600	1.667
R4P1	1000	20	350	225	_	1.681	1.556
R5P1	1000	20	325	250	-	1.681	1.300
R1P2	1000	25	400	_	200	1.600	2.000
R2P2	1000	25	400	_	225	1.538	1.778
R3P2	1000	25	375	_	250	1.538	1.500
R4P2	1000	25	350	_	275	1.538	1.273
R5P2	1000	20	325	-	300	1.550	1.083

2.2. Municipal Solid Waste Ash

Additives to the slurry were MSW ashes listed as 19 01 07* (solid flue gas treatment waste—P1) and 19 01 13* (fly ash containing hazardous substances—P2) in accordance with [30], generated due to MW incineration in a grate furnace. Flue gas treatment processes involved flue gas denitrification by primary methods and a secondary selective

non-catalytic nitrogen oxide reduction (SNCR), as well as flue gas treatment using the semi-dry method with limewash slurry combined with the flux and ash method using activated carbon (aimed at reducing acidic contaminants, ash, heavy metals, dioxins and furans). Flue gas dedusting employing a fabric filter was also applied.

Ash labelled 19 01 07* is an odourless, homogeneous light-grey material, with a very fine homogeneous grain fraction. It exhibits dusting properties and a tendency toward lumping. Ash termed 19 01 13* is characterized with a heterogeneous structure (Figure 1), with a coarser grain size than the 19 01 07* ash. In this, unburned combustion process residues are present. Table 3 shows the chemical composition and selected physical properties of the tested ash.



(a)

(b)

Figure 1. Ash designated as 19 01 07* (**a**) and 19 01 13* (**b**).

Table 3. Selected chemical and physical properties of ash.

	Ash			
Properties	P1—19 01 07*	P2-19 01 13*		
	Mass Share (%)			
SiO ₂	5.43 ± 1.09	23.56 ± 4.71		
Al_2O_3	2.09 ± 0.42	0.64 ± 0.13		
Fe_2O_3	0.64 ± 0.13	3.06 ± 0.61		
$SiO_2 + Al_2O_3 + Fe_2O_3$	8.16 ± 1.64	27.26 ± 5.45		
TiO ₂	0.54 ± 0.108	2.119 ± 0.424		
MnO	0.040 ± 0.008	0.139 ± 0.028		
MgO	1.31 ± 0.26	3.08 ± 0.62		
CaO	39.16 ± 7.83	34.91 ± 6.98		
Na ₂ O	1.78 ± 0.36	1.16 ± 0.23		
K ₂ O	1.39 ± 0.28	0.44 ± 0.09		
P_2O_5	0.430 ± 0.086	1.423 ± 0.285		
SO ₃	4.11 ± 0.82	1.9 ± 0.38		
Cl	5.213 ± 1.043	0.376 ± 0.075		
F	0.18 ± 0.04	0.10 ± 0.02		
Loss on ignition [43]	21.4 ± 2.14	11.1 ± 1.11		
Fineness [44]	17.81 ± 1.66	78.82 ± 1.72		
Water demand [43] (%)	108 107			
Activity ratio [43] (%)	51 33			
Water extract reaction [45] (-)	12.2	12.5		

The oxide composition of ash was determined using samples made molten using wavelength dispersive x-ray fluorescent spectrometry (WD-XRF). References to the research methods applied when testing selected physical properties of ash can be found in Table 3.

The tested ash cannot be classified as fly ash when used in concrete, not only due to its origin, but also because of its physical properties and composition [43,46,47]. It is characterized by low total silicon, aluminium and iron oxide content (19 01 07*, in particular), which are the main ingredients of cement in addition to calcium oxide.

Loss on ignition that can impact the effectiveness of air-entraining admixtures is slightly above class C according to [43] in the case of the 19 01 13* ash, while exceeding this class almost twofold in the case of the second ash. Despite the significant variation of fineness test results, we observed no large differences in the workability of mortars with the added ash and no significant differences in the water demand (elevated in both cases). On the other hand, both ash types are characterized by a low hydraulic (despite the relatively high calcium oxide content—resulting from the flue gas desulfurization process) and pozzolanic (especially low silicon dioxide content in the 19 01 07* ash) potential, which is depicted by the very low activity indicators that were revealed after 27 days of slurry curing, based on the tested ash.

Unfortunately, the oxide and phase composition of the MW incineration ash is very variable [48–51] and depends on the incineration methods, as well as the quality and composition of the incinerated MW, which is impacted by, among others, quality and advancement of selective waste collection, recycling advancement degree, and environmental awareness and habits of the residents. This is why it is important to determine ash parameters experimentally, rather than basing this on literature sources.

Figure 2 shows selected morphology images of the tested ash acquired using the SEM technique with EDS analysis. Both tested ash types are characterized by varying morphology. In the case of the ash designated 19 01 13* (b), the visible spherical grains are not the zones constructed of aluminosilicate glass known from fly ash for concrete, but zones primarily consisting of iron. In the case of the ash listed as 19 01 07* (a), the zone is characterized by an element composition typical for ash.

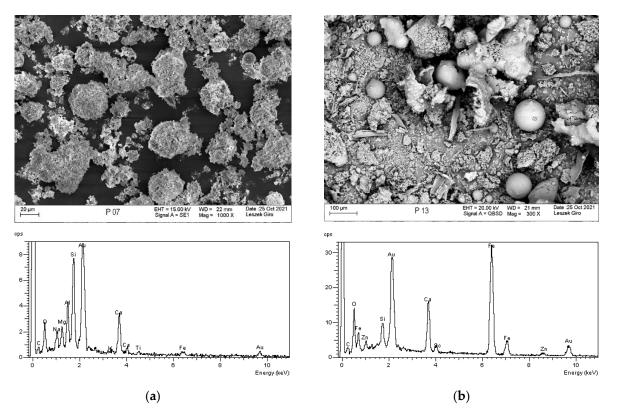


Figure 2. SEM photo with EDS analysis involving ashes 19 01 07* (a) and 19 01 13* (b).

The conducted studies indicate that the application of ash in concrete technology will cause problems. As a result, the authors suggest using them in the hardening slurry technology.

2.3. Hardening Slurry Testing Methods

Liquid slurries were tested in terms of process properties related to

- Bulk density, important due to preserving narrow-space excavation stability and the displacement of the slurry by the target material (in the event of a two-phase incorportation method). Bulk density was determined using a Baroid arm scale [40].
- Conventional viscosity, important due to hardening slurry production and transport technology (e.g., pumping), excavation hollowing ease under its cover and its displacement from the excavation. Conventional viscosity was determined using a flow viscometer (Marsh funnel [52]). The time (in seconds) for the outflow of a 1000 mL of liquid slurry was measured (in a 1500 mL slurry poured into a funnel) [40]. The Type B uncertainty [53] for this type of measurement was estimated at 1.2 s.
- Daily water loss, which is a percentage measure of slurry sedimentation (segregation tendencies), homogeneity and stability. Daily water loss was determined as a percentage share of water volume spontaneously escaping from a 1.0 dm³ slurry after a motionless day in a calibrated measuring cylinder [41]. The Type B uncertainty [53] for this type of measurement was estimated at 0.6%.
- Structural strength (highest value of shearing stress, at which the dispersion system structure is destroyed), primarily responsible for excavation wall stability. This property counteracts separation of soil grains and ensures the required stability of slurries contaminated with worked soil [31]. Structural strength was determined using a shearometer after a 10 min motionless standstill of the slurry [40].

After 28 days of curing in tap water, hardening slurry samples were tested for performance properties related to

- Compressive strength, which is one of the basic hardening slurry parameters on which a material is based. Compressive strength was determined using cubic samples in accordance with [42]. If required, sample bases in contact with the universal testing machine head were levelled with plaster.
- Hydraulic conductivity k_{10} (filtration coefficient), which is a property that is particularly important when using the slurry to seal the substrate. The hardening slurry filtration coefficient (at a water temperature of +10 °C) was determined with a variable hydraulic gradient. The method was selected due to the relatively low slurry conductivity (similarly to cohesive soils), which ensured the long time required to obtain equilibrium between water inflow and outflow to/from the samples, necessary when testing conductivity using a method with a constant hydraulic gradient. The test with a variable gradient involved determining, at specified times t_1 , t_2 , etc., the values of hydraulic pressures h_1 , h_2 , etc., exerted by the water column in the supply tube, with a sectional area a, during liquid flow through a sample with a height (length) Li and a cross-sectional area A_p . Under these conditions, hydraulic conductivity k_T (at a temperature of T) was calculated using Formula (1), which after taking into account the impact of the filtration liquid temperature, could be converted into hydraulic conductivity k_{10} (at a temperature of +10 °C) and according to Formula (2).

$$k_T = \frac{a \cdot L_i}{A_p \cdot \Delta t} \ln \frac{h_1}{h_2},\tag{1}$$

$$k_{10} = \frac{k_T}{0.7 + 0.03T} \tag{2}$$

where k_T —hydraulic conductivity at a temperature of T (m/s); k_{10} —hydraulic conductivity at a temperature of +10 °C (m/s); *a*—supply tube sectional area (m²); L_i —tested sample

height (m); A_p —sample cross-sectional area (m²) $\Delta t = t_2 - t_1$ —time between hydraulic pressure measurements h_1 , h_2 (s); h_1 , h_2 —hydraulic pressure values at t_2 , t_1 (m); *T*—filtration liquid temperature (°C).

Figure 3 shows a diagram of a test bench for studying the filtration coefficient of hardening slurries.

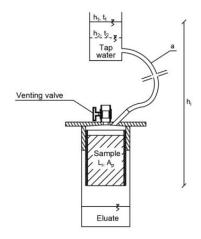


Figure 3. Hardening slurry filtration coefficient test bench diagram.

3. Results and Discussion

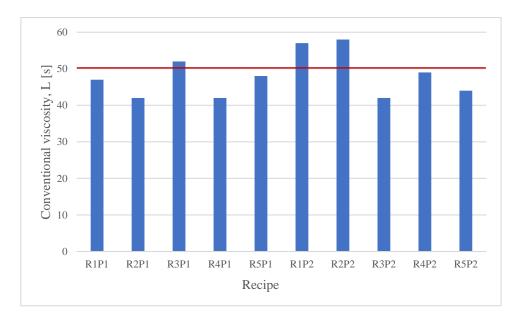
Processing properties of the tested hardening slurries are listed in Table 4.

		Parameter				
ρ	Density ρ (g/cm ³)	Conventional Viscosity L (s)	Water Loss 24 h O _d (%)	Structural Strength after 10 min τ (Pa)	Value pH (-)	
R1P1	1.330	47	7.0	2.8	12.16	
R2P1	1.320	42	7.0	2.1	12.12	
R3P1	1.320	52	3.0	5.3	12.03	
R4P1	1.315	42	5.0	6.7	11.96	
R5P1	1.310	48	2.0	6.0	11.96	
R1P2	1.340	57	6.0	8.5	12.58	
R2P2	1.350	58	5.0	12.0	12.57	
R3P2	1.315	42	7.0	5.0	12.59	
R4P2	1.360	49	2.0	8.0	12.56	
R5P2	1.345	44	2.0	6.5	12.56	

Table 4. Processing properties of the tested hardening slurries.

Liquid slurry density is at a level sufficient to ensure stability of the hollowed excavation (Tables 1–4). The increase in the hardening slurry density occurs together with increasing cement/ash (c/a) ratio, only for recipes with the P1 ash (19 01 07*). The densities for these slurries range from 1.31 to 1.33 g/cm³. No relationship between waste dosage and slurry density was observed for the P2 ash (19 01 13*). The highest density value of 1.36 g/cm³ was recorded for the R4P2 recipe, while the R3P2 recipe demonstrated the lowest value of 1.315 g/cm³.

In reference to the assumptions adopted at the slurry recipe stage [31], conventional viscosity shall fall within a range that enables hydraulically transporting the slurry to the incorporation location; see Table 1 and Figure 4. The highest viscosity is achieved by slurries obtained with added P2 ash (R1P2 and R2P2). There is no clear correlation between this parameter with composition indicators (w/dm or c/a). It should be noted that three



recipes are evaluated negatively from the perspective of the presented criteria (Table 1): R3P1, R1P2 and R2P2.

Figure 4. Conventional viscosity of the tested hardening slurry samples.

Daily water loss (Table 4, Figure 5) in the tested hardening slurries ranges from 2.0% to 7.0%. It is evident that this parameter is significantly impacted by the amount of added ash. In the case of high ash content (P1 or P2), the slurry composition (in general) recorded lower loss values. Only the R3P1, R5P1, R4P2 and R5P2 recipes were evaluated positively according to the criteria (Table 1).

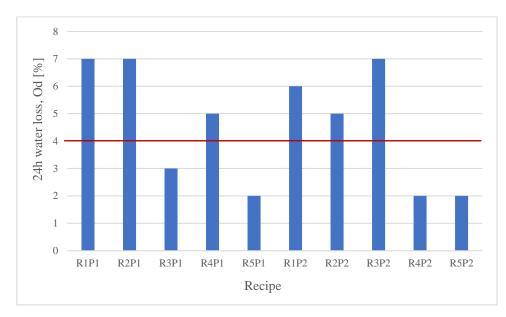


Figure 5. Daily water loss in tested hardening slurry recipes.

When analysing the results showing structural strength after 10 min (Table 4), it can be seen that only one recipe (R2P2) recorded a value higher than 10.0 Pa (the limit value according to the criterion from Table 1). The other recipes satisfy the requirement set out in Table 1. It can be noted that this parameter is significantly impacted by the amount of added cement.

The pH values shown in Table 4 range from 11.96 (R5P1 recipe) to 12.59 (R3P2 recipe). These values prove the high alkalinity of the tested slurries. Higher pH values were

recorded for the recipes with the P2 ash (12.56 to 12.59), which contains more alkali (Table 2). In addition, slightly higher ash and cement doses (600–625 kg) were used in the case of the recipes with the P2 ash, compared to the slurries that incorporated P1 ash (575–600 kg).

When analysing the values obtained during the study of the hardening slurry process parameters (density, conventional viscosity, daily water loss and structural strength), it can be concluded that only three recipes, R5P1, R4P2 and R5P2, satisfied the set-out criteria and are suitable for use as a cut-off wall material constructed using the most common methods, i.e., in narrow-space excavation (diaphragm method), deep soil mixing (DSM) or using the vibration method (narrow-space method) [31].

Basic performance parameters of the tested hardening slurries (after hardening) are listed in Table 5. The values in parentheses are standard deviation (for f_c) and variation coefficient (for k_{10}).

	Parameter			
Recipe	Compressive Strength f _c (MPa)	Hydraulic Conductivity k ₁₀ (m/s)		
R1P1	0.53 ± 0.03	$1.40 imes 10^{-8}~(\pm 6\%)$		
R2P1	0.52 ± 0.07	$5.02 \times 10^{-8} \ (\pm 12\%)$		
R3P1	0.42 ± 0.07	$1.34 imes 10^{-7} \ (\pm9\%)$		
R4P1	0.32 ± 0.02	$1.70 imes 10^{-7} (\pm 15\%)$		
R5P1	0.28 ± 0.03	$2.10 imes 10^{-7} (\pm 8\%)$		
R1P2	0.33 ± 0.04	$1.47 imes 10^{-7}$ ($\pm 8\%$)		
R2P2	0.28 ± 0.02	$1.39 imes 10^{-7} (\pm 6\%)$		
R3P2	0.21 ± 0.03	$2.86 imes 10^{-7} (\pm 4\%)$		
R4P2	0.22 ± 0.01	$2.88 imes 10^{-7} (\pm 7\%)$		
R5P2	0.21 ± 0.01	$1.01 imes 10^{-6} \ (\pm 18\%)$		

Table 5. Performance parameters of the tested hardening slurries.

Compressive strengths of the tested hardening slurries range from 0.21 to 0.53 MPa. Higher f_c values were recorded for slurries with the P1 ash: 0.28–0.53 MPa. Figure 6 shows compressive strength f_c of hardening slurries, depending on the c/a (cement/ash) ratio for the developed recipes. The figure reveals an increase in the f_c value, together with increasing c/a ratio, for all analysed hardening slurry recipes (regardless of the ash type). A strong correlation between the c/a ratio and the compressive strength f_c can be noted. A positive correlation is confirmed by the Pearson correlation coefficient calculated at an assumed confidence interval of 95%. Owing to the value of the *r* coefficient, the $f_c = f(c/p)_{P1}$ and $f_c = f(c/p)_{P2}$ correlations for hardening slurries, with the coefficient value of $r_{(P1)} = 0.95$ and $r_{(P2)} = 0.91$, respectively, can be deemed statistically significant. A slightly higher value of the activity ratio (Table 2) in the P1 ash resulted in greater f_c values in the case of both ash types, the main component impacting the f_c values obtained for the tested hardening slurries is the cement used. Only the two following recipes were evaluated positively, according to the criteria for slurries set out in Table 1: R1P1 and R2P1.

Hydraulic conductivity k_{10} of the tested hardening slurries ranged from 1.01×10^{-6} to 1.40×10^{-8} m/s. Significantly lower k_{10} values were recorded for slurries with added P1 ash. Figure 7 shows the hydraulic conductivity k_{10} of the tested hardening slurries in relation to the c/a (cement/ash) ratio. A relationship between the c/a ratio and the hydraulic conductivity k_{10} can be observed. A negative correlation is confirmed by the Pearson correlation coefficient calculated at an assumed confidence interval of 95%. The resulting *r* coefficient value allows designation of the $k_{10} = f(c/p)_{\text{P1}}$ correlations for hardening slurries with added P1 ash as statistically significant. In this case, $r_{(\text{P1})} = -0.99$. In terms of the requirements set out in Table 1, only the R1P1 recipe is close to satisfying them.

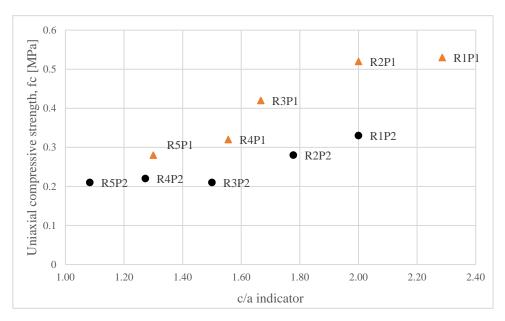


Figure 6. Compressive strength f_c of the tested hardening slurries depending on the cement/ash (c/a) ratio.

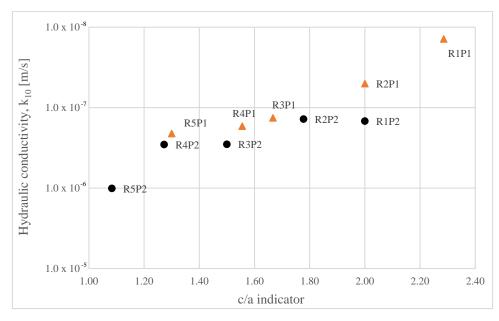


Figure 7. Hydraulic conductivity k_{10} of the tested hardening slurries, depending on the cement/ash (c/a) ratio.

4. Conclusions

The conducted analysis involving the properties of hardening slurries developed using municipal waste incineration ash combined with CEM I 42.5 Portland cement indicates that slurries incorporating P1 ash (19 01 07*) achieved more favourable parameters. The R1P1 slurry recipe was the closest to meeting all requirements associated with its use for the construction of flood embankments through following different execution technologies. The limit 24 h water loss value was not obtained in the case of process properties. However, this is not an insurmountable barrier, and, to some extent, it depends on a detailed specification of the dedicated slurry material. The simplest way to improve this parameter may be to increase the amount of bentonite or its activity. With regard to hydraulic conductivity, the obtained value slightly exceeded the required criterion. Hence, a slight

modification of ingredient proportions—higher binder content, in particular—should lead to a successful outcome.

The conducted study demonstrated that municipal waste incineration ash designated as 19 01 07* and 19 01 13* exhibits the potential to be an additive to hardening slurries, despite its specific properties and morphology.

Due to the difficulties with utilizing such waste in other types of building materials, the research on its applicability in relation to the hardening slurry technology should be continued as an expansion to environmental studies, i.e., leaching of hazardous compounds and their immobilization.

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