Repair Mortars Containing Fly Ash and Crystalline Admixture

Nikol ŽIŽKOVÁ[a], Jakub HODUL[a], Ruben Paul BORG[b], Vít ČERNÝ[a]

[a] Brno University of Technology, Faculty of Civil Engineering, Veveří 95, 602 00 Brno, Czech Republic,
e-mail: zizkova.n@fce.vutbr.cz, hodul.j@fce.vutbr.cz, cerny.v@fce.vutbr.cz

[b] University of Malta, Faculty for the Built Environment, Msida MSD 2080, Malta,
e-mail: ruben.p.borg@um.edu.mt

Abstract

The paper discusses the utilisation of a by-product specifically a fly ash sourced from a landfill where it had been dumped over a period of several years. The fly ash had been produced from a coal burning power plant in Malta and landfilled in disused quarries in Bengħisa. The landfilled fly ash deposit dumped in the quarries is considered as an environmental hazard. The research addresses the potential use of the fly ash for recycling in the production of cement based materials particularly repair mortars. The paper presents the design and testing of repair mortars in which the fly ash is used as a partial replacement of cement. In order to improve the environmental resistance, the performance of the material with the addition of a crystalline admixture was assessed. The stabilisation of the fly ash in the mixture was verified through the assessment of physical-mechanical properties and through a microscopic examination of the microstructure of the mortar.

Keywords: *Fly ash, repair mortars, secondary crystallisation, stabilisation.*

Introduction

Fly ash is currently the most common pozzolan used worldwide and it is widely accepted that using it as an ingredient in cement mortars and concrete provides benefits the properties of the final product. Improvement in the properties of the interfacial transition zone (ITZ) between particles of aggregate and the binder matrix can also be attributed to the addition of fly ash [1]. Research shows that fly ash with a low calcium content (class F according to ASTM) improves ITZ properties even though it is less reactive than e.g. silica fume [2].

For several years waste in Malta was landfilled in different waste disposal sites without separation. The landfill sites did not include measures for the collection of leachate and gases emitted from the waste, as in the case of engineered landfills. Fly ash produced at the coal-burning power plant in Marsa Malta had been landfilled in quarries at a cliff-edge in Bengħisa in Malta. The two quarries at the Bengħisa site, which were managed by Enemalta Corporation, did not have any environmental protective measures or leachate collection system [3,4]. Coal was last used in the Marsa power station in 1995, when it was modified to run on heavy fuel oil. Fly ash produced by the Marsa power station when it was still coal-fired and which was dumped on the cliff-edge in Bengħisa, had high levels of radioactivity [4,5,6]. The Bengħisa landfill, containing large quantities of fly ash deposit, presents an environmental hazard. The Marsa Power Plant has since been decommissioned and the Maltese Islands now rely on the Dellimara natural gas-fired power plant and an interconnector with Sicily, together with renewable energy sources, for its energy supply.

The environmentally-conscious course of action is to seek a solution that does not limit itself to mere stabilisation and landfilling, but utilizes the fly ash as a raw material. Civil engineering is one of the areas where the ash could be used, particularly in concrete as supplementary cementitious material for partial replacement of the cement [4]. The benefits of using fine fly ash in cement composites are for e.g.

improved strength, fewer shrinkage cracks, or better sulphate and other chemical resistance [7], as well as resistance to high temperatures. A marked improvement due to the addition of fly ash to cementitious mortars was observed in materials exposed to a high temperature of 900 °C [8].

The goal of the research described in this paper was to design repair mortars using the landfilled fly ash, which was produced at the coal-fired power plant in Malta. In order to deliver the required properties, the research referred also to the use of one of the emerging technologies for protecting cement-based composites against aggressive environments known as “secondary crystallization” or “crystalline technology” [9]. The mixtures also included components which are available in the Republic of Malta. The research was conducted through collaborative activity between the Brno University of Technology, Faculty of Civil Engineering and the University of Malta, Faculty for the Built Environment, addressing the use of secondary raw materials in polymer cement mortar and concrete.

Experiments

The experiment examined the properties of polymer-modified repair mortars containing a crystalline admixture and varying amounts of fly ash (FA) at an age of 28, 60 and 90 days after casting. The mixtures contained the following raw materials: Portland cement, fly ash, dolomite sand, polymer admixture, cellulose ether, and crystalline admixture. The reference mixture is identified as F0X0 and contained no fly ash nor crystalline admixture.

The other mixtures differed in the amount of FA, which replaced up to 30% of cement. The composition of the mixtures is presented in the Table 1. The FA used had a high water-absorption and the mixes were developed with equal workability as the control reference mix, controlled using a flow table test. All tested mix formulations had a flow table result (diameter) of 130 mm.

Table 1: Composition of the mortars per m^3

Raw materials [kg·m^{-3}]	**Mixture ID**				
	F0X0	**F0X**	**F10X**	**F20X**	**F30X**
Cement CEM I 52.5 R	601.5	601.5	533.3	473.2	413.0
Fly ash (PFA)	0.0	0.0	60.2	120.3	180.5
Dolomite sand (0 – 2 mm)	1310.3	1310.3	1310.3	1300.3	1292.3
Water	261.9	261.9	261.9	271.4	278.9
Ethylene-vinyl acetate copolymer (EVA)	6.0	6.0	6.0	6.0	6.0
Cellulose ether	5.0	5.0	5.0	5.0	5.0
Crystalline admixture	0.0	8.0	8.0	8.0	8.0
Superplasticiser	15.3	15.3	15.3	15.8	16.3
W/C ratio	0.4	0.5	0.5	0.6	0.7

A. Materials and Properties

A.1 Cement

Portland cement CEM I 52.5 N manufactured in Albania was used as the binder; its basic properties according to EN 196-1, EN 196-3 and EN 169-6 are presented in the Table 2. Cement is not produced in Malta and is imported from other countries.

Table 2: Basic parameters of the cement CEM I 52.5 N manufactured in Albania

Compressive strength [MPa]		**Flexural strength [MPa]**		**Blaine fineness [cm^2·g^{-1}]**	**Initial setting time [min]**	**Final setting time [min]**	**Specific gravity [kg·m^{-3}]**
7 days	**28 days**	**7 days**	**28 days**				
46.9	53.5	7.9	9.1	5 109	150	190	3 140

A.2 Fly ash

The Bengħisa fly ash (FA) used in the research was produced in the Marsa Power Station and subsequently landfilled in the Bengħisa quarries, on the island of Malta. The fly ash was extracted for the purpose of this research, directly from the quarry at a depth of 1m below the existing soil cover where the material was observed to be free from soil and any other contaminants. The sample was sealed in plastic bags and transported to the laboratory where it was oven dried for 24 hours at 105°C and sieved on a 250µm sieve prior to testing. The fly ash thus treated had a specific surface area of 4120 cm^2·g^{-1} and specific gravity of 2380 kg·m^{-3}. Figure 1 shows the particle size distribution and Figures 2 – 4 Scanning Electron Microscopy SEM images of the fly ash after drying and sieving. Particle size measurement was performed using the laser diffraction method with the MALVERN Mastersizer 2000 instrument. The pre-treated fly ash was measured through the dry method. The particle size analysis through laser diffraction is based on the principle that larger particles reflect laser beams at a smaller angle and with greater laser intensity, and smaller particles have a greater reflection angle and lower reflected beam intensity. The chemical composition determination conducted according to EN ISO 11885, EN 15410: 2011, ČSN 72 0105-1 standards [10-12] carried out on the Bengħisa fy ash indicates that the fly ash contains mainly SiO_2, Al_2O_3, CaO and Fe_2O_3 (see Table 3). With regard of the mineralogical composition, the fly ash (FA) is made up primarily of β-quartz, mullite (3 Al_2O_3·$2SiO_2$) and hematite (Fe_2O_3).

Table 3: Chemical composition of the Bengħisa fly ash [% wt. dry]

SiO_2	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**K_2O**	**Na_2O**
42.0	29.3	3.01	6.77	1.31	0.62	0.25

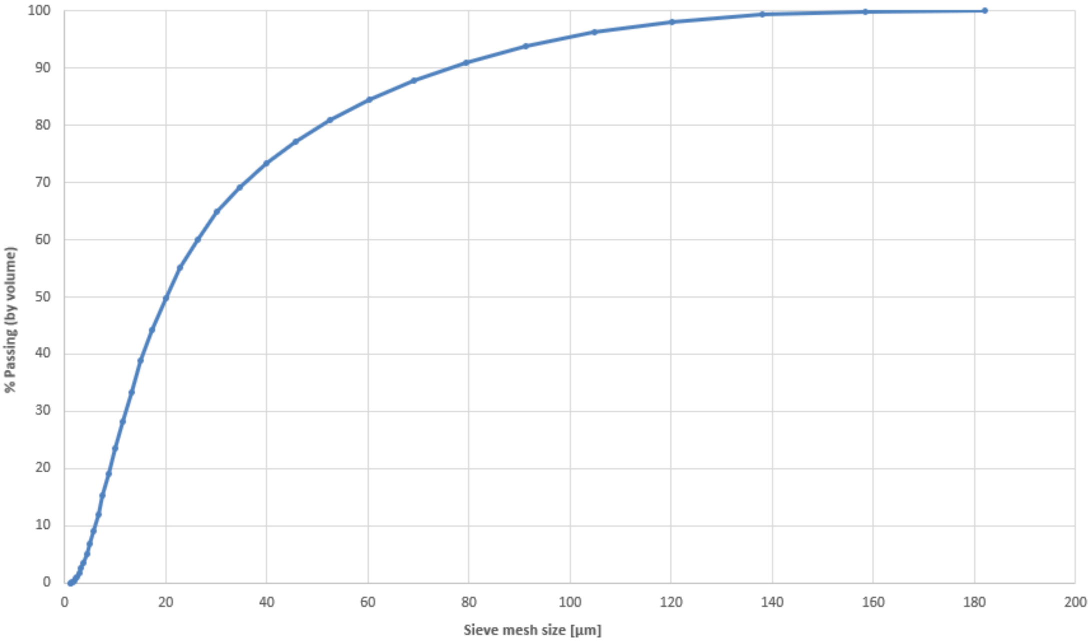

Figure 1: Fly ash particle size distribution (Laser Diffraction)

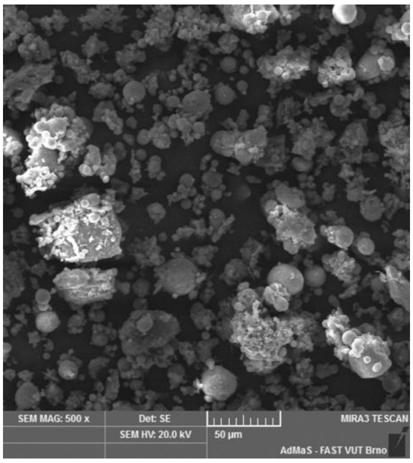

Figure 2: SEM image of the fly ash

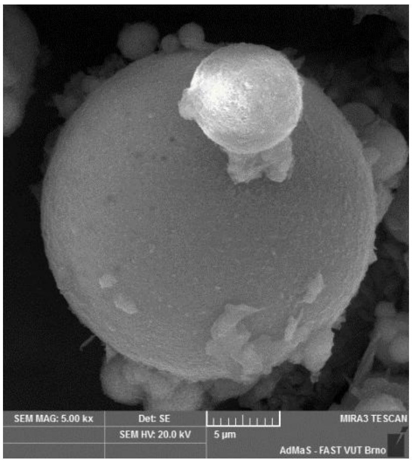

Figure 3: SEM image: detail of a fly-ash cenosphere

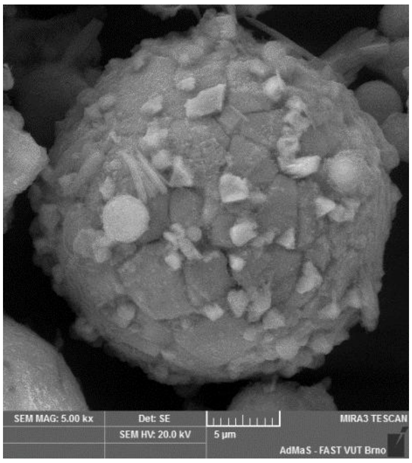

Figure 4: SEM image: detail of a fly-ash cenosphere

A.3 Dolomite sand

Dolomite sand sourced in Italy was a major component of the polymer-cement mortar developed in this research. The dolomite sand was first oven dried and then sieved through a 2.0 mm sieve to achieve the required aggregate portion similar to a standard sand with a granulometry of 0 – 2 mm. Figure 5 shows the particle size distribution of the dolomite sand. The content of fine particles smaller than 300 µm was approximately 25% and the residue consisted of 0.3 – 2.3 mm grains. The dolomite sand sieve analysis was performed according to the standard EN 933-1:1997 [14].

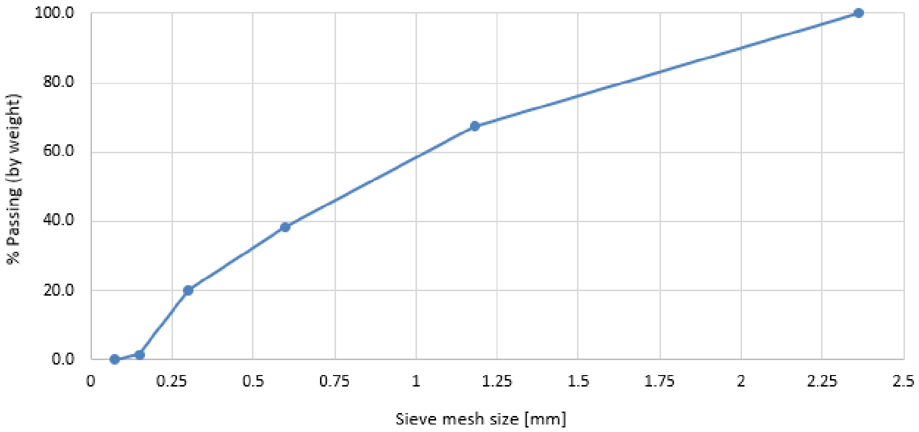

Figure 5: Dolomite sand sieve analysis

A.4 Crystalline admixture

The chemical composition (according to EN ISO 11885, EN 15410: 2011, ČSN 72 0105-1 and ČSN 72 0117 [10-13]) of the Xypex crystalline admixture produced by Xypex Chemical Corporation is in the Table 4.

Table 4: Chemical composition of the Xypex crystalline admixture

Chemical composition of CA [% wt.]									
SiO_2	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**SO_3**	**K_2O**	**Na_2O**	**Cl^-**	**Organic Substances**
11.50	2.34	1.74	45.70	0.73	2.05	0.39	6.61	0.03	7.03

A.5 Ethylene and vinylacetate copolymer (EVA)

The EVA copolymer is used to improve the properties of fresh and hardened mortars. Fresh mortars benefit through a lower water demand while retaining an extended workability. This is due to the surface-active compounds in the polymer emulsion, which allow cement particles in the mixture to disperse more easily. In hardened mortars EVA copolymer creates a polymer film that improves adhesion, flexural and compressive strength, and water absorption by sealing pores and preventing the ingress of moisture. The research described herein is based on a copolymer named VINNAPAS 4020N, produced by Wacker Chemie AG.

A.6 Cellulose ether

Cellulose ether extends the workability of fresh cementitious mortars and, by increasing retention capacity, prevents the fresh mixture from releasing water into the substrate, which helps improve the final properties of the hardened mortar. The product used here was Culminal manufactured by Ashland.

A.7 Superplasticiser

Superplasticisers have the ability to markedly reduce the amount of water in the mixture without reducing workability. The superplasticiser used here was MasterGlenium 51 produced by BASF.

B. Methods

Six sets of mortar prism specimens with dimensions of 40×40×160 mm were prepared. The first set was stored for 28 days at a temperature of 23 °C and relative humidity of 95% (23 °C+95% RH), the second set was stored for 60 days at 23 °C+95% RH and the third set was stored for 60 days at 23 °C+95% RH and then placed for 62 days in a solution representing seawater. The concentration of the solution was 15%, and a fresh solution was prepared every 21 days. At the age of 28, 60 and 90 days the samples were tested for physical-mechanical properties and their microstructure was examined. The experiments were carried out through the collaboration between Brno University of Technology and University of Malta. The three-point flexural strength and the compressive strength were determined in accordance to EN 196-1 [15] and the dry bulk density of hardened mortar was determined in accordance to EN 1015-6 standard [16]. The study of the microstructure of selected specimens was conducted in order to gain a better understanding of the strength test results: DTA analysis was performed using a Mettler Toledo TGA/DSC 1 (heating rate 20 °C per minute; air atmosphere) and Scanning Electron Microscopy SEM imaging with a TESCAN MIRA3 XMU. Leaching behaviour of the fly ash and the mortar mixture, where 30% of cement was replaced with the fly ash was tested in compliance with Decree No. 294/2005 Coll., Annex No. 2, which defines leachability classes according to the maximum permissible values of indicators; i.e. concentration of pollutants in the eluate ($mg \cdot l^{-1}$), according to ČSN EN 12457-4 standard [17].

Results and discussion

The results of bulk density, compressive and flexural strength tests of the mortars performed after 28, 60 and 90 days are presented in Figures 6 – 8 below.

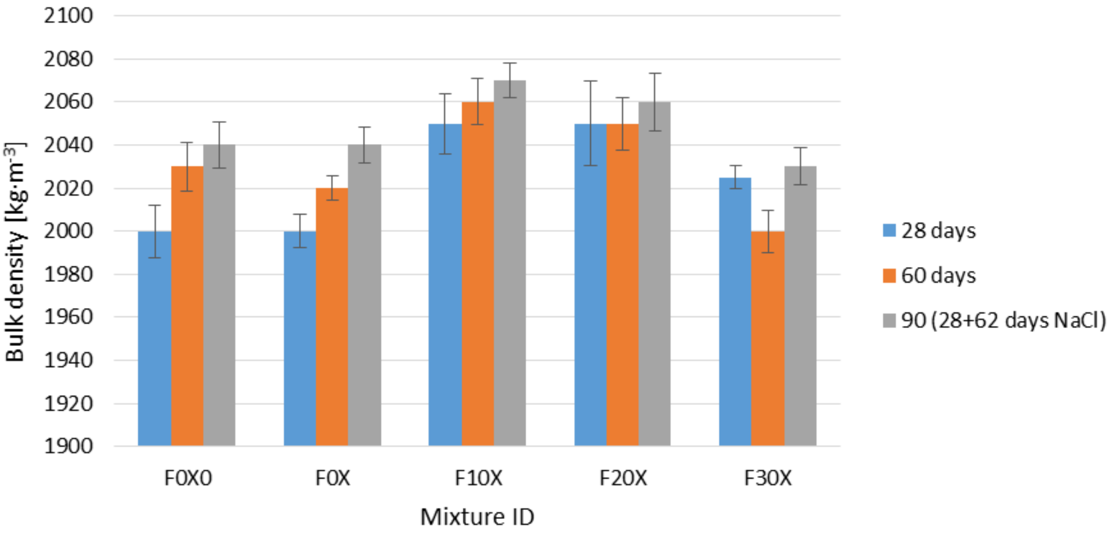

Figure 6: Determination of the bulk density

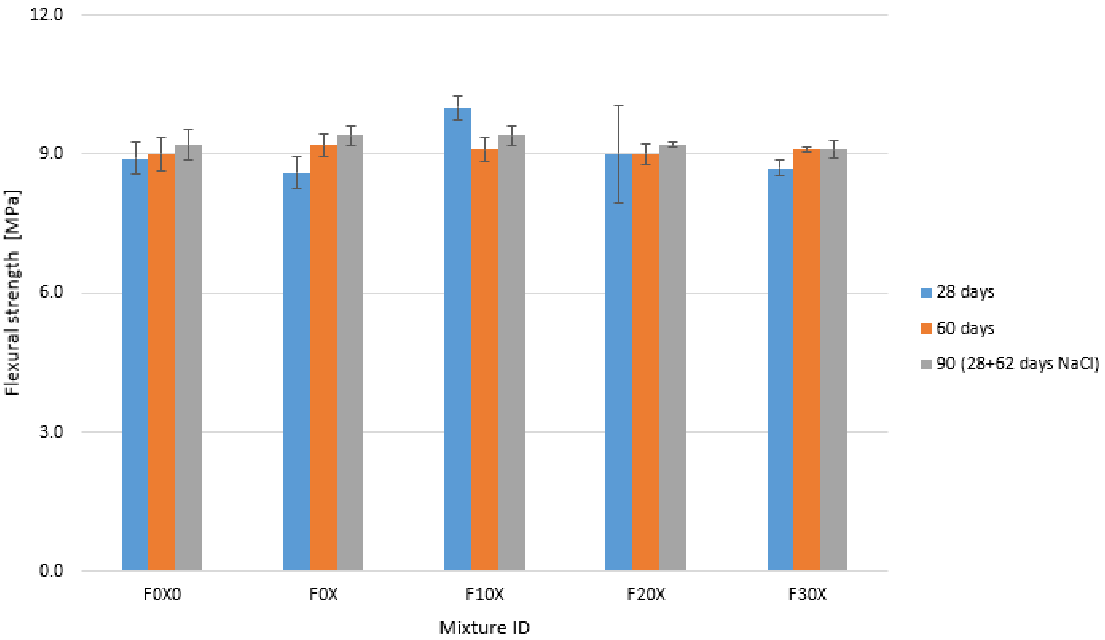

Figure 7: Determination of the flexural strength

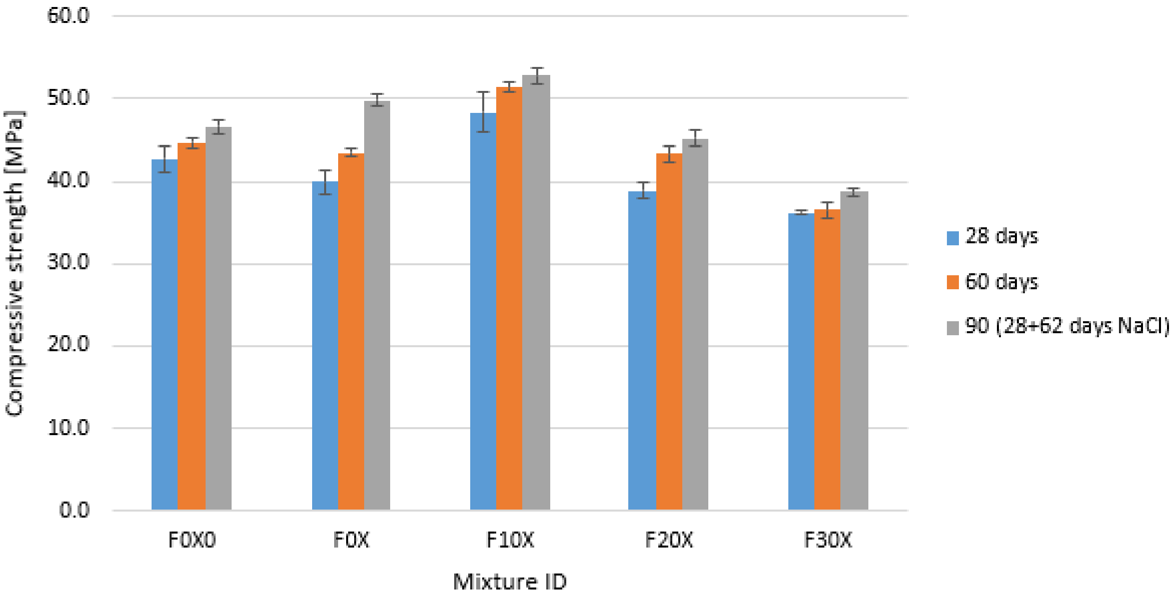

Figure 8: Determination of the compressive strength

As the figures above show, the highest values of bulk density, flexural strength, and compressive strength were reached in the mortar that contained the crystalline admixture and fly ash as a 10% cement replacement. Mixtures that contained more fly ash required additional water, which influenced both bulk density and strength.

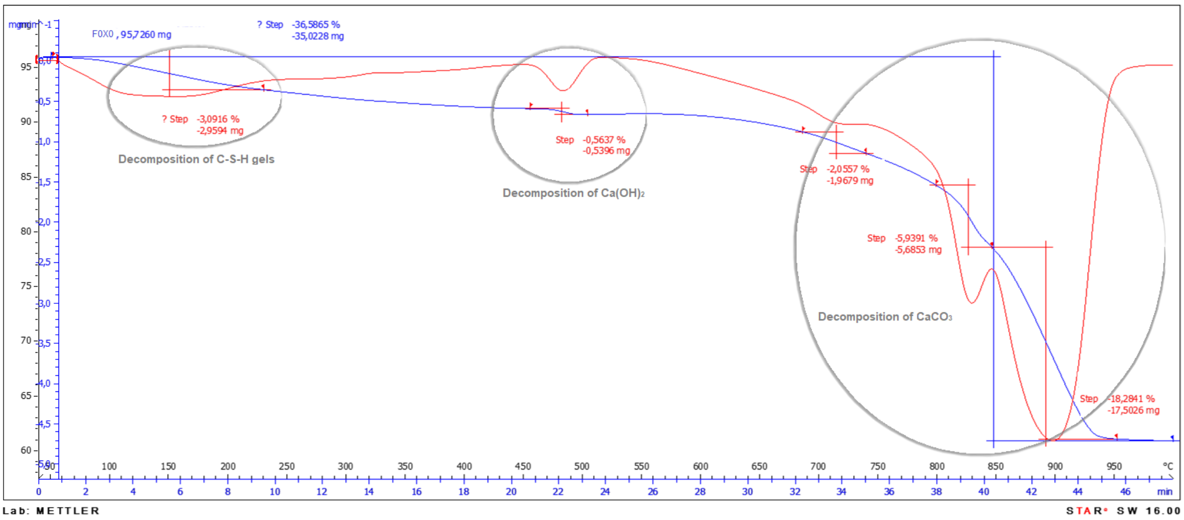

Figure 9: DTA record of mixture F0X0 after 60 days

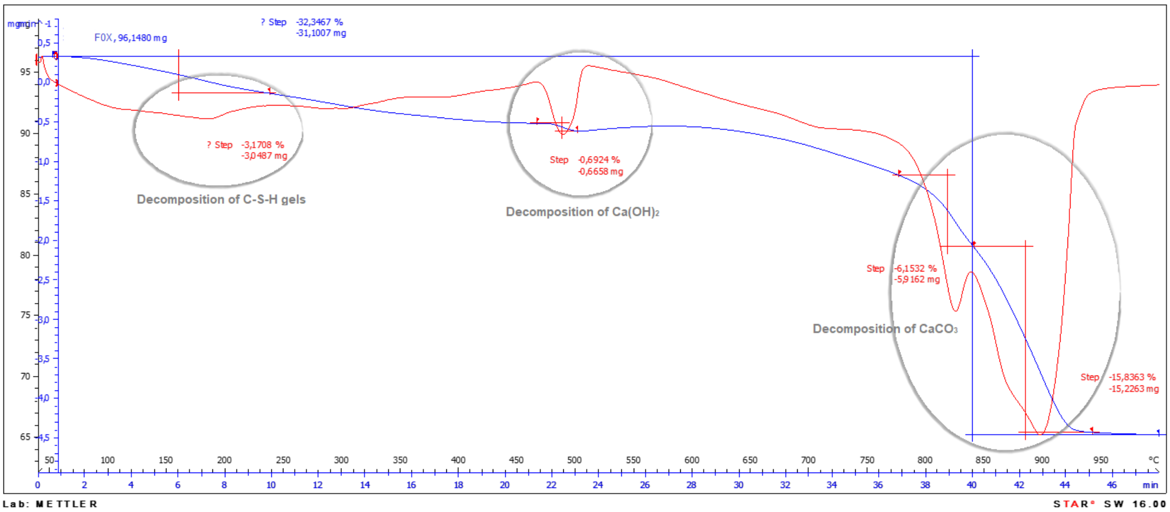

Figure 10: DTA record of mixture F0X after 60 days

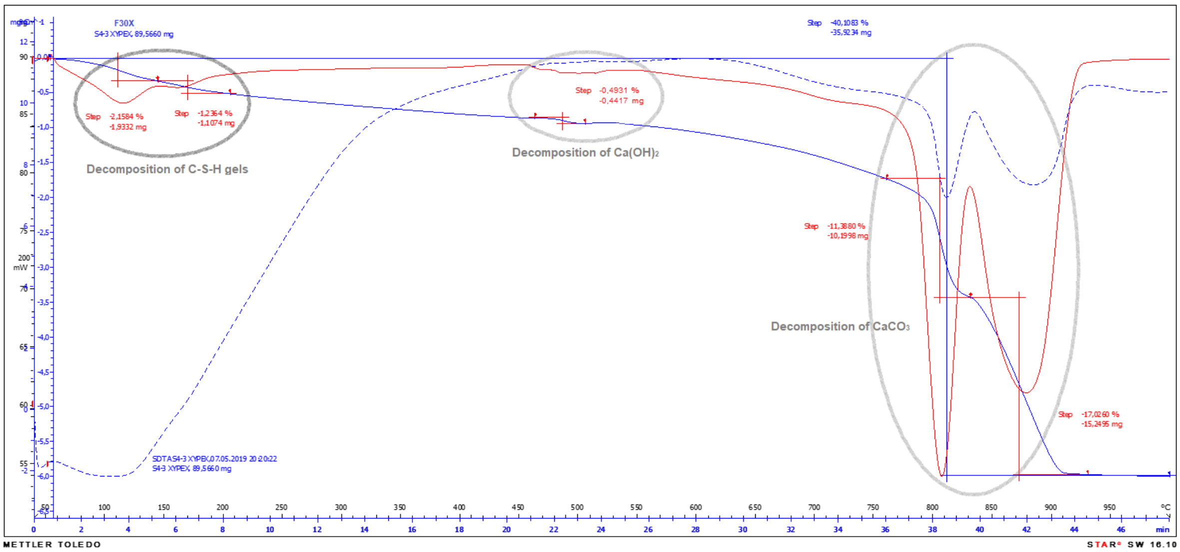

Figure 11: DTA record of mixture F30X after 60 days

Figures 9 – 11 show DTA records of mortars: F0X0 (reference), F0X (no FA but containing CA) and F30X (containing both FA and CA). All the mortars underwent three basic reactions: decomposition of C-S-H phase, $Ca(OH)_2$ and $CaCO_3$. Mass loss content and mass content are shown in the Table 5. The presence of portlandite ($Ca(OH)_2$) in the sample F30X was confirmed also by X-ray powder diffraction (XRD) analysis.

Table 5. Results of DTA – mass loss and mass content

Mixture ID	**Mass loss corresponding to decomposition [%]**			**Mass content [%]**	
	C-S-H	**$Ca(OH)_2$**	**$CaCO_3$**	**$Ca(OH)_2$**	**$CaCO_3$**
F0X0	3.09	0.53	26.28	2.31	59.72
F0X	3.17	0.69	21.99	2.85	49.97
F30X	3.39	0.49	28.41	2.01	64.57

The crystalline admixture in combination with fly ash influences the increase in C-S-H phase content. The mixture containing FA registered an increase in the C-S-H phase and a decrease in $Ca(OH)_2$, which indicates that a pozzolanic reaction took place; i.e. a reaction between amorphous silicon dioxide and aluminosilicates with calcium hydroxide, producing compounds similar to those formed during Portland cement hydration. The chemical reaction between a pozzolan and calcium hydroxide results primarily in the formation of calcium silicate hydrates (C-S-H) which could vary in composition and structure [18]. The pozzolanic reaction can be presented as follows [19]:

$$x\,Ca(OH)_2 + y\,SiO_2 + z\,H_2O \rightarrow xCaO{\cdot}ySiO_2{\cdot}zH_2O \qquad (1)$$

The mixtures were also examined using the Scanning Electron Microscope SEM. Figures 12 – 17 show images of 60-day old mortars. Mortar F30X containing CA and FA showed crystals formed by the CA. Clearly visible are the fly ash particles undergoing pozzolanic reaction and being integrated into the cement matrix.

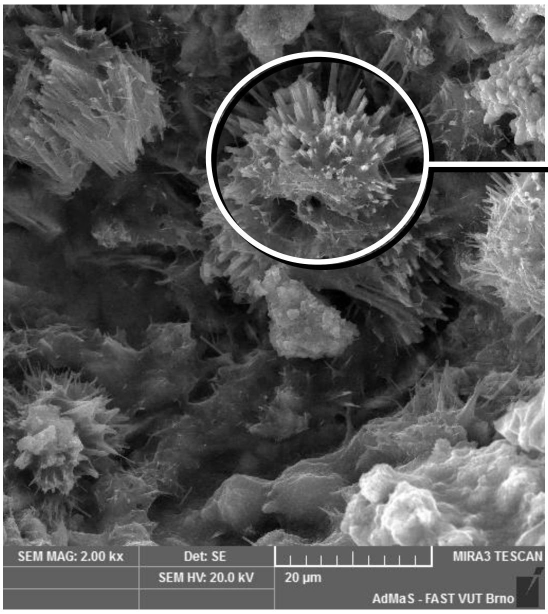

Figure 12: SEM image of mixture F30X – pore

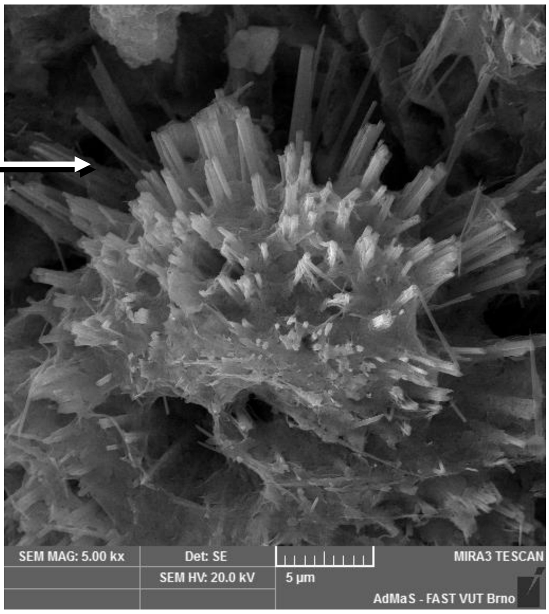

Figure 13: SEM image of mixture F30X – detail of the crystalline formed inside of pores

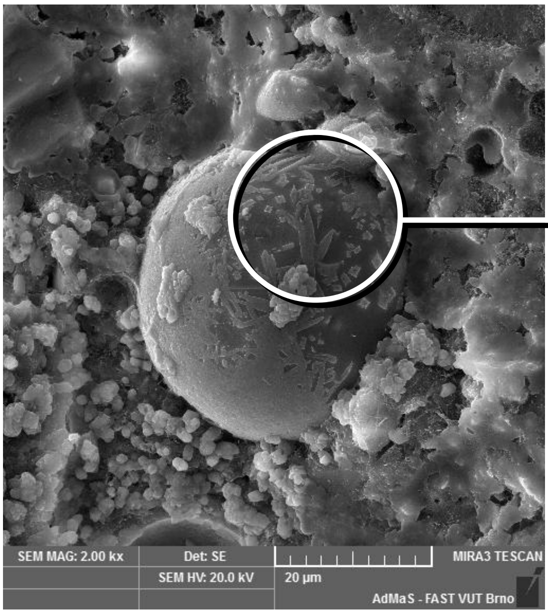

Figure 14: SEM image of mixture F30X – detail of a fly ash particle undergoing pozzolanic reaction

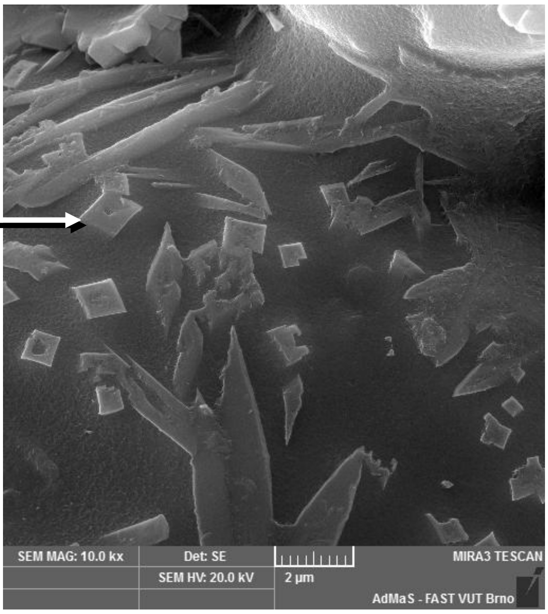

Figure 15: SEM image of mixture F30X – detail of a C-S-H phase being formed

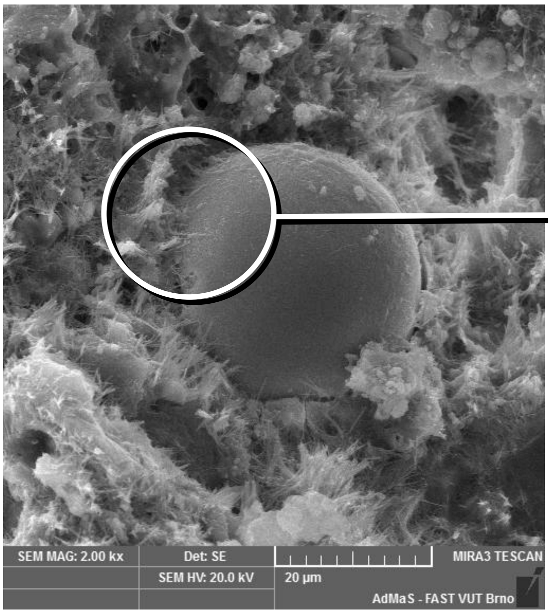

Figure 16: SEM image of mixture F30X – detail of a fly ash particle integrated in the cement matrix

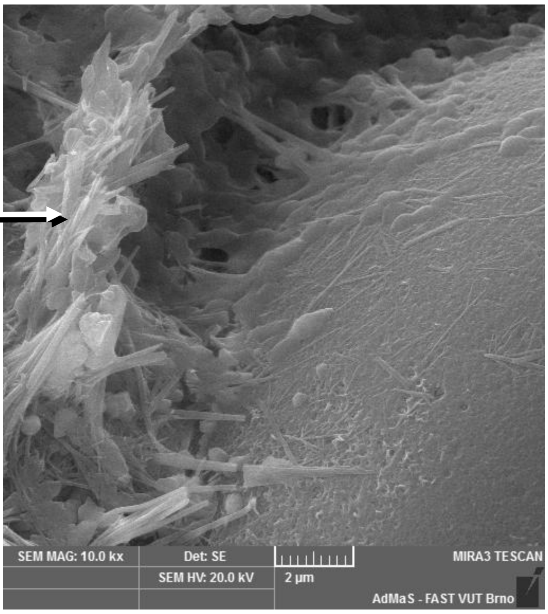

Figure 17: SEM image of mixture F30X – detail of the fly-ash/cement matrix interface

The effect of the chemical composition of the amorphous and crystalline phases of fly ash on the compressive strength of fly ash cement mortar has been assessed and reported in literature [20]. The fly ash cement mortars were made by replacing 25% of cement with 16 types of fly ash. It was found that the chemical parameters have a higher correlation with the 91-day strength than with the 28-day strength of fly ash cement mortars, as the pozzolanic reaction progressed further after 91 days. The results obtained in the present research confirmed that the incorporation of Bengħisa fly ash in the mortar positively influenced the compressive strength in the long term. However, the ongoing pozzolanic reaction was observed after 60 days. It is reported that it is possible to use 20% of optimized fly ash instead of 10% non-optimized by changing the particle size distributions of fly ash used [21]. The experiments in the present research confirmed that the mixture with 10% cement replaced with the Bengħisa fly ash (non-optimized) performed best in terms of strength, corresponding with literature [17]. One of the most effective ways to reduce the environmental burden associated with the production of cementitious materials is to intensify the wider use of supplementary cementitious materials in cement composition [22].

The leaching behaviour of the fly ash and mortar F30X (containing the highest amount of fly ash; i.e. 30%) was tested in compliance with ČSN EN 12457-4, and it was found that no dangerous pollutants were leached out of either material. Given the measured concentrations and limits defined by the standard, the material met the requirements for leachability class IIa, making it suitable for surface applications. Table 6 shows the values of pollutant concentrations in the eluate. The amount of each dissolved compound in the F30X eluate is influenced by the high amount of hardened cement paste.

Table 6: Values of pollutant concentrations in the eluate

Parameter	Bengħisa fly ash	Mixture F30X	Limit (IIa)	Unit	Verdict
pH value	7.75	12.5	min. 6	-	pass
Dissolved organic carbon	23.8	52.0	max. 80	$mg \cdot l^{-1}$	pass
Chlorides	13.2	10.1	max. 1500	$mg \cdot l^{-1}$	pass
Fluorides	< 0.200	< 0.400	max. 30	$mg \cdot l^{-1}$	pass
Sulphates e.g. SO_4^{2-}	8.20	7.96	max. 3 000	$mg \cdot l^{-1}$	pass
Dissolved solids after drying (105°C)	122	1 800	max. 8 000	$mg \cdot l^{-1}$	pass
Hg	< 0.00100	< 0.00100	max. 0.2	$mg \cdot l^{-1}$	pass
As	< 0.0500	< 0.0500	max. 2.5	$mg \cdot l^{-1}$	pass
Ba	0.0704	1.83	max. 30	$mg \cdot l^{-1}$	pass
Cd	< 0.00500	< 0.00500	max. 0.5	$mg \cdot l^{-1}$	pass
Cr	0.0193	0.0714	max. 7	$mg \cdot l^{-1}$	pass
Cu	< 0.0100	< 0.0100	max. 10	$mg \cdot l^{-1}$	pass
Mo	< 0.0200	< 0.0200	max. 3	$mg \cdot l^{-1}$	pass
Ni	< 0.0200	< 0.0200	max. 4	$mg \cdot l^{-1}$	pass
Pb	< 0.0500	< 0.0500	max. 5	$mg \cdot l^{-1}$	pass
Sb	< 0.0500	< 0.0500	max. 0.5	$mg \cdot l^{-1}$	pass
Se	< 0.0250	< 0.0250	max. 0.7	$mg \cdot l^{-1}$	pass
Zn	0.0261	0.0402	max. 20	$mg \cdot l^{-1}$	pass

Conclusions

The Bengħisa fly ash produced at the Marsa power plant in Malta and sourced from the Bengħisa quarries disposal site was assessed for the potential partial replacement of cement in repair mortars. Previous studies had demonstrated the potential use of the fly ash as a supplementary cementitious material, for the production of cement based materials with improved performance [4]. All the mixtures tested in the present research possessed the required physical-mechanical properties, namely high compressive and flexural strength. The results show that the mixture with 10% of cement replaced by fly ash performed best in terms of strength. Incorporating the fly ash in the polymer-cement matrix with the crystalline admixture solidified the material, as evidenced by the results of tests of leaching behaviour. The crystalline admixture also improves the resistance of the mortar against the ingress of seawater. This research and analysis of the results were performed through cooperation between Brno University of Technology, Faculty of Civil Engineering and the University of Malta, Faculty for the Built Environment, addressing the recycling and the use of secondary raw materials in polymer cement mortars and concrete.

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Správková malta využívající vedlejší produkt a krystalizační přísadu

***Nikol ŽIŽKOVÁ**[a], **Jakub HODUL**[a], **Ruben Paul BORG**[b], **Vít ČERNÝ**[a]*

[a] *Vysoké učení technické v Brně, Fakulta stavební, Veveří 95, 602 00 Brno, Česká republika,*
e-mail: zizkova.n@fce.vutbr.cz, hodul.j@fce.vutbr.cz, cerny.v@fce.vutbr.cz

[b] *University of Malta, Faculty for thr Built Enironment, Msida MSD 2080, Malta,*
e-mail: ruben.p.borg@um.edu.mt

Souhrn

Článek se zabývá možností využití druhotné suroviny, konkrétně popílku pocházejícího ze skládky, kde byl ukládán po dobu několika let. Tento popílek je vedlejším produktem uhelné elektrárny na Maltě a k jeho skládkování byly vyhrazeny nepoužívané lomy v místě Benghisa. Popílek uložený v lomech je považován za nebezpečí pro životní prostředí. Výzkum se zaměřuje na potenciální využití popílku za účelem výroby materiálů na bázi cementu, a to zejména správkových malt.

V článku je představen návrh a testování správkových malt, ve kterých se popílek používá jako náhrada cementu. Pro zlepšení odolnosti vyvinuté správkové malty vůči povětrnostním podmínkám byl posuzován také vliv přídavku krystalizační přísady. Stabilizace popílku ve směsi byla ověřována posouzením fyzikálně-mechanických vlastností a sledováním mikrostruktury správkové malty pomocí elektronového mikroskopu.

Keywords: *Popílek, správkové malty, sekundární krystalizace, stabilizace.*