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PELLETIZATION OF FLY ASH FOR UTILIZATION IN DYNAMIC SORPTION PROCESSES

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Abstract: Fly ash, a byproduct of coal combustion in thermal power plants, has transitioned from industrial waste to a valuable technogenic raw material. Its alumino-silicate composition, porous structure, large specific surface area, and sorption activity make fly ash an efficient and low-cost sorbent for removing metal ions from acidic mine waters but only in discontinuous (static) systems. Its small particle size and poor hydraulic properties limit its application in continuous (dynamic) water treatment systems. This study aims to produce fly ash pellets with suitable properties for use as a sorbent in dynamic- column purification systems. By agglomerating fly ash with cement and plasticizer, pellets with enhanced mechanical properties such as compressive strength, impact strength, abrasion resistance, and disintegration time in water were developed. These pellets promise to improve the applicability and effectiveness of fly ash in dynamic water treatment processes, offering an economical and efficient solution for removing metal contaminants from wastewater.

Keywords: fly ash, sorbent, agglomeration, cement, plasticizer

1 INTRODUCTION

As economies continuously develop, people's living standards improve. However, this progress also heightens the demand for energy and other resources, resulting in environmental pollution issues like water and air contaminants. In today's world, there

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are numerous advanced technologies for wastewater treatment that effectively reduce pollutant levels to concentrations safe enough for discharge into watercourses or for recycling as technical water in the production process. Recently, significant attention has been focused on selecting and producing cost-effective sorbents with high metal-binding capacities.

Fly ash (FA), an industrial byproduct of coal combustion, consists of fine particles. The rapid pace of industrialization and the high demand for electricity have led to the annual discharge of hundreds of millions of tons of FA worldwide. While coal-fired power generation supplies energy for both daily life and industrial activities, it also contributes to air and water pollution, disrupting ecological cycles. If FA is released directly into the atmosphere from power plant chimneys without proper treatment, it pollutes the air and poses significant health risks to humans (Bartoňová, 2015).

As science and technology have advanced, FA from thermal power plants has transformed from an industrial waste product into a valuable raw material, known as technogenic raw material (Iyer and Scott, 2001; Zhuang et al., 2016; Park et al., 2014). The properties of FA largely depend on the type of coal used and the combustion conditions. Due to its alumino-silicate composition, porous structure, large specific surface area, and sorption activity, FA has emerged as an efficient and low-cost sorbent for the removal of metal ions from acidic mine waters (Alterary and Marei, 2021; Lanzerstorfer, 2018; YAO et al., 2015; Mohan and Gandhimathi, 2009; Bayat, 2002). However, the small particle size and poor hydraulic properties of FA pose challenges for its use in dynamic water treatment systems. Therefore, the aim of this study is to produce FA pellets with properties that are suitable for use as a sorbent in column purification systems. By transforming FA into pellets, the idea is to enhance its applicability and effectiveness in dynamic water treatment processes, thereby providing an economical and efficient solution for removing metal contaminants from wastewater.

2 FLY ASH PELLETS PREPARATION

The initial components for the preparation of pellets were FA, Portland cement, plasticizer, and water.

2.1 Fly ash characterization

Fly ash, the residue of the lignite combustion from the cyclones and electrostatic filters in the Nikola Tesla B Thermal Power Plant (TENT B), Obrenovac, Serbia was used.

Chemical composition of FA, shown in Table 1, indicates that the dominant components are silicon dioxide and aluminum oxide, with significant amounts of calcium and iron oxides.

Table 1 Chemical analysis of FA

Content (mass %)							
SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	K_2O	Na_2O	TiO_2
47.80	30.53	8.69	5.47	2.29	1.49	0.25	1.02
Cd	Pb	Zn	Cu	Cr	Ni	Mn	LOI
0.005	0.04	0.021	0.005	0.022	0.03	0.045	1.45

It can be concluded that the FA belongs to the Class F (according to the ASTM C618 standard), which indicates its pozzolanic properties and that some agents for improving binding characteristics (cement, plasticizer, lime) should be used in the pelletization process.

Mineralogical analysis showed that quartz is the main phase, while mullite and plagioclase are present in smaller quantities. Also, the amount of the amorphous phase is significant.

Particle size distribution, performed by laser light diffraction method using Helos (H1597) & Sucell R4, Sympatec GmbH, Figure 1, indicates that FA contains 40-80% of particles below 150 µm while their average size is 100 µm.

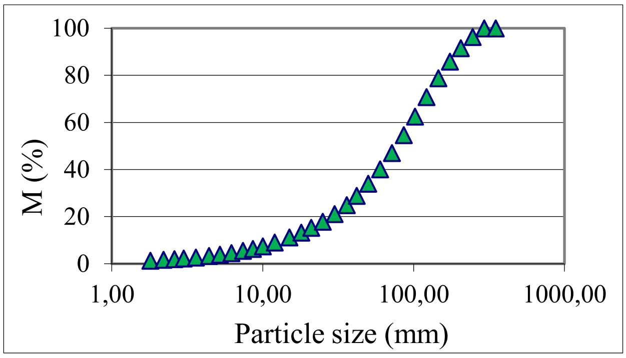

Figure 1 Particle size distribution of FA

The basic **physical properties** of FA were determined by the laser light scattering method, Table 2.

Table 2 Physical properties of FA

D_{10} (µm)	D_{50} (µm)	D_{90} (µm)	Specific surface area (cm^2/g)	ρ (g/cm^3)
13.33	77.43	197.23	4487.52	0.56

2.2 Cement characterization

The chemical composition, physical and mechanical properties of cement, used as a binder, according to the manufacturer's specification, are shown in Tables 3 and 4.

Table 3 Chemical analysis of Portland cement

Component/ content (%)							
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	P_2O_5
21.10	5.42	2.38	63.18	2.35	0.74	0.23	0.12
SO_3< 4 %	Cl	Na_2O_{eq}	ZnO	Mn_2O_3	SrO	TiO_2	
3.56	0.0386	0.72	0.038	0.11	0.099	0.245	

Table 4 Physical and mechanical properties of cement

Property	Value
Specific surface area of particles according to Blaine	4010 cm^2/g
Density	3.11 g/cm^3
R32	8.39 %
Initial setting time	130 min
Final setting time	160 min
Consistency	28.4 %
Expansion	0.5 mm
Compressive strength, after 2 days	35.5 MPa
Compressive strength, after 28 days	60.9 MPa
Flexural strength, after 2 days	6.7 MPa
Flexural strength, after 28 days	9.3 MPa

2.3 Plasticizer characterization

A highly efficient superplasticizer of the new generation (hyperplasticizer)- Cementol Hiperplast 463 (manufactured by TKK, Slovenia) was used as a chemical additive. The following advantages are listed in the technical data sheet of the product: high early and final strengths, improved water impermeability, slower carbonation, concreting at higher temperatures, durability, etc.

The characteristics of this superplasticizer are in accordance with the SIST EN 934-1 and SIST EN 934-2 standards and are given in Table 5.

Table 5 Physico-chemical properties of the used superplasticizer

Property	Declared values with permissible deviations
Appearance	brown yellow liquid
Density, 20°C	1.08 ± 0.02 kg/dm^3
Dry matter content	32.0 ± 1.6%
pH value	6.5 ± 1
Water soluble chlorides content	-
Alkali content (Na_2O equivalent)	< 3.0 %

The effect of this chemical additive depends on the type and amount of cement, the water-cement factor, the composition of the aggregate and the dosage of the superplasticizer itself.

The approximate dosage is between 0.2 and 1.5 kg per 100 kg of cement. It is used concentrated to the prepared fresh mixture or diluted with water, whereby it is optimal to use it after 70-80% of water has been added. The manufacturer recommends a mixing time of 3 min after adding the superplasticizer, with a minimum of 1 minute.

2.4 Pelletization procedure

During the pellets production, two series of mixtures were used, both composed of 90 % FA with 10 % cement, whereby the first one (FA+C+P) was moisturized by water with plasticizer and the second (FA+C) only by water.

Table 6 Components for pellets production

Series	Fly ash	Cement	Plasticizer	Water
FA+C+P	90 %	10 %	0.15 ml	275 ml
FA+C	90 %	10 %	-	300 ml

C-cement, P-plasticizer

Pelletization was performed in a pelletizer with disc dimensions of 40 cm diameter and 10 cm depth, an inclination of 50º and a speed of 15 rpm. Fly ash was mixed with cement as a binder. Tap water was added to the amount necessary for an optimal process and smooth operation of the pelletizer. The estimation of the required quantity of water is based on experience. In the case of plasticizer application, less water was added due to the steric effect of plasticizers based on polycarboxylate chains. The plasticizer acts by being gradually absorbed into the cement particles; polymer molecules cross-link the cement particles and prevent them from joining. Absorption takes place gradually and over a longer period.

Figure 2 shows the process of FA agglomeration in the pelletizing disc.

Figure 2 Pelletization of FA

After preparation in the pelletizer, the prepared "green" pellets were cured for three days in an atmosphere with 90% humidity; then they were dried in a laboratory drying oven and dry sieved using a vibro sieve into four size classes.

After each pelletization and sieving, the grain composition of the pellets was determined, which was within similar limits regardless of their composition. The adopted mean value of the granulometric composition is shown in Figure 3.

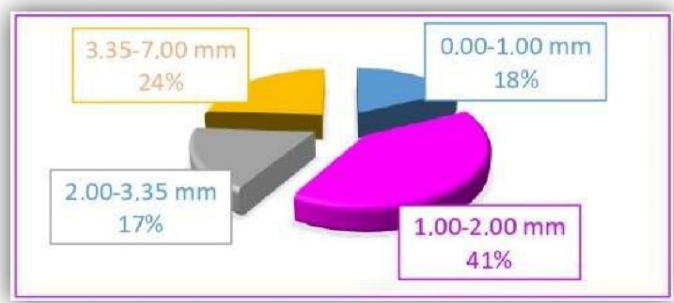

Figure 3 Average granulometric composition of pellets

Figure 4 shows a dominant presence (41 %) of the grain size class ranging from 1.0 to 2.0 mm, which is desirable considering that optimal batching of dynamic water purification systems requires particle sizes in the range of 1.0-5.0 mm. Also, it is obvious that the share of less desirable pellets for dynamic purification systems is below 20%.

3 MECHANICAL PROPERTIES OF THE PELLETS

The quality of the produced FA pellets was estimated by mechanical properties testing compressive strength, impact strength, abrasion resistance, and time of disintegration in water.

The resistance of pellets to compression, impact, and abrasion are properties crucial for transport and handling before their actual use. In the case of using pellets in dynamic purification systems (columns), it is necessary to know the time of pellets' disintegration in water to ensure that they do not break down during the column's operating cycle.

3.1 Compression or crush test

The compressive strength of pellets was tested on a set of 10 pellets using a standard hydraulic laboratory press (Tonindustrie, Germany) to determine the maximum pressure a pellet can withstand without breaking. The testing was conducted according to the procedure and recommendation that pellets should withstand a minimum of 0.5 kg/pellet, which enables secure further handling, suggested by the company Mars Mineral (Albert and Langford, 1998).

Table 7 presents the average values of the obtained compressive strength results for FA pellets by grain-size classes.

Table 7 Compressive strength of pellets by grain-size classes

	1.0-2.0 mm	2.0-3.35 mm	3.35-7.0 mm
		kg/pellet	
FA+C+P	0.45	0.60	1.12
FA+C	0.32	0.51	0.73

Based on the values shown in Table 7, it is noted that pellets exhibited satisfactory compression resistance, especially the coarser pellets. The maximum achieved compressive strength of the pellets for the 1.0-2.0 mm size class is just below the lower limit value of 0.5 kg/pellet, which can be considered satisfactory. For coarser size classes, the achieved compressive strength is significantly above the lower limit value. The ability of these pellets to withstand significant pressure without breaking suggests that they are robust enough for handling and use in water purification systems. This property is essential to ensure that the pellets do not disintegrate under the mechanical stress of operational conditions. The presence of plasticizer improves mechanical stability of the pellets.

3.2 Impact or drop test

The impact strength of pellets is tested by dropping a set of 10 pellets weighting 100 g in total, 25 times from a height of 457 mm onto a steel plate 9 mm thick. The sample is then sieved on a sieve of appropriate mesh size (depending on the grain size class being tested), and the mass of the undersize is weighted. The results are presented as a mass percentage with respect to the initial sample mass and should not exceed 5% (rarely 10%) of the total initial sample mass.

Table 8 presents the average values of the obtained impact strength results for FA pellets by grain-size classes.

Table 8 Impact strength of pellets by grain-size classes.

	1.0-2.0 mm	2.0-3.35 mm %	3.35-7.0 mm
FA+C+P	10.5	9.3	9.2
FA+C	19.3	16.1	14.6

Based on the values shown in Table 8, it is noted that pellets with cement and plasticizer fully meet the standard criteria regarding impact resistance. Pellets with cement without plasticizer are below the standard criteria, thus indicating that the plasticizer plays a crucial role in improving this property.

3.3 Abrasion resistance

The resistance of pellets to abrasion is tested by sieving a group of pellets weighing 100 g on a mechanical laboratory sieving device with a sieve of appropriate mesh size (depending on the granule size class being tested) for 5 minutes. The mass percentage of the class being tested is then determined, which should not exceed 5% of the total sample mass.

Table 9 presents the average values of the obtained abrasion resistance results for FA pellets by grain-size classes.

Table 9 Abrasion resistance of pellets by grain-size classes

	1.0-2.0 mm	2.0-3.35 mm	3.35-7.0 mm
FA+C+P	0.52	3.13	3.17
FA+C	1.59	4.86	4.98

The abrasion resistance results demonstrate that these pellets have a high resistance to wear and tear. This is crucial for maintaining the integrity of the pellets over time, which is important in dynamic water treatment systems. Both series exhibited satisfactory abrasion resistance values; however, pellets without a plasticizer showed lower abrasion resistance, reinforcing the importance of the plasticizer in enhancing this property.

3.4 Time of disintegration in water

The time of disintegration of pellets in water is tested by immersing three pellets from each group in water at room temperature and measuring the time needed for complete disintegration. Disintegration is visually determined.

Table 10 presents the average values of the obtained results for time of disintegration in water of FA pellets by grain-size classes.

Table 10 Time of disintegration of pellets by grain-size classes

	1.0-2.0 mm	2.0-3.35 mm	3.35-7.0 mm
		h	
FA+C+P	> 48	> 48	> 48
FA+C	> 48	> 48	> 48

The time of disintegration in water results show consistent values across different pellet series. This suggests that the pellets, regardless of the presence of a plasticizer, maintain their structural integrity for a similar duration when submerged in water. This consistency indicates that all tested formulations are suitable for use in water purification systems where maintaining pellet integrity during the operational cycle is crucial.

4 CONCLUSION

The research demonstrated that FA can be effectively pelletized using cement as a binding agent, with the addition of a plasticizer to enhance mechanical properties. The resulting pellets exhibited satisfactory compressive strength, impact strength, abrasion resistance, and resistance to disintegration in water, making them suitable for use in dynamic water purification systems. By converting FA into pellets, this study offers a practical and cost-effective approach to utilizing this industrial byproduct in wastewater treatment, thereby contributing to both environmental protection and resource recovery. Future research should focus on optimizing the formulation of FA pellets to further enhance their mechanical properties. Exploring different proportions of binding agents and plasticizers can provide deeper insights into developing even more durable and efficient pellets. Additionally, long-term studies on the performance of these pellets in real-world water treatment systems will be beneficial in validating their practical applicability and durability.

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