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Exploration of Chemical Composition and Properties of Ancient Silver Mine Slag

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Abstract: This study explores the pozzolanic properties of ancient silver mine slag, the by-products of historic silver extraction processes, to assess its potential as a modern secondary resource for cement. Traditionally regarded as waste, these residues contain minerals that, when processed, exhibit binding qualities beneficial in construction. Through a series of tests, including grinding the slag to fine particles and blending it with cement, the study confirms that ancient slag demonstrates significant pozzolanic activity, which can strengthen and enhance cement properties. The findings reveal that this material aligns with ASTM standards for fly ash, indicating its suitability for use in sustainable construction applications. Utilizing such metallurgical remnants could contribute to both waste reduction and economic recycling efforts. This research highlights the bridge between ancient metallurgy and modern sustainable practices, suggesting that historical waste products can be repurposed to meet contemporary industrial needs and support environmental sustainability.
Keywords: Pozzolanic properties; Ancient silver distillation; Secondary raw material sources; Waste management; Economic recycling.

1. Introduction

Silver has long held a position of economic and cultural importance across civilizations, forming a cornerstone of trade, wealth, and technological advancement. Its extraction and processing, which date back to antiquity, have been achieved through various metallurgical techniques. Among these, the process of silver distillation, an ancient method of refining silver from ores, involves heating the ores to high temperatures [1-4]. This thermal process yields metallic silver but also generates by-products commonly termed “slag” or “residues.” Historically, these by-products were considered waste and discarded. However, recent research suggests that these residues may have untapped potential as secondary raw materials, particularly in the construction industry. The presence of certain minerals within ancient silver slag may impart useful characteristics, such as pozzolanic activity, which could support its use in cementitious applications [5-7].

In modern construction, sustainability and resource efficiency have become key drivers of material innovation. Traditional pozzolanic materials, which contain reactive silicate and aluminosilicate compounds, play an important role in reducing the environmental footprint of construction practices. When mixed with calcium hydroxide, these materials undergo a chemical reaction that contributes to concrete durability, strength, and resistance to chemical degradation. By partially replacing conventional cement materials with pozzolans, the industry can reduce clinker consumption, leading to decreased carbon emissions and improved energy efficiency. This shift aligns with global environmental priorities, making the identification of alternative pozzolanic sources a critical area of research [7-9].

Various studies have investigated the pozzolanic properties of industrial by-products and mine wastes, such as flue gas desulfurization gypsum, copper and gold flotation tailings, and coal ash. These studies have established that many types of mine residues can be successfully incorporated into construction materials, resulting in enhanced concrete durability, reduced permeability, and overall improvements in material performance. Such approaches provide dual benefits: they allow for efficient waste management while offering a sustainable alternative to fully mined or manufactured construction materials. Within this context, ancient silver mine slag emerges as a promising, yet underexplored, candidate for pozzolanic applications [10-16].

The utilization of mine wastes as supplementary cementitious materials has gained significant attention in recent years due to its potential environmental and economic benefits (Table 1). Among these mine wastes, ancient silver mine slag stands out as a promising candidate for pozzolanic applications [15]. Pozzolan, when mixed with cement, reacts with water to exhibit binding properties, enhancing the durability and workability of concrete and mortar.

Table 1. Studies done before this study

Year	Waste type	Application area	Results	References
2023	Flue Gas Desulfurization (FGD) gypsum	Concrete additive	Increased durability and workability	[17]
2023	Copper flotation waste	Cement additive	Increased water resistance and durability	[18]
2022	Coal ash	Mortar and concrete additive	Increased strength and flowability	[19]
2022	Gold flotation waste	Ceramic and brick production	Increased material strength and durability	[20]
2021	Nickel flotation waste	Asphalt additive	Increased density and stability	[21]

Despite the potential of ancient silver slag as a pozzolan, its properties remain largely uncharted in current literature. Few studies have systematically evaluated ancient mine residues for their pozzolanic characteristics, particularly those from the silver distillation processes used in historic metallurgical practices [17-21]. Given the unique composition of these slags, which may include silicates and other compounds conducive to pozzolanic activity, it is essential to understand their suitability as sustainable construction materials. Pozzolanic reactivity, chemical composition, and physical properties such as fineness all contribute to the feasibility of utilizing these ancient residues as cement additives [22-25].

This study pioneers a comprehensive assessment of the pozzolanic potential of ancient silver mine slag, positioning these residues as viable alternatives to traditional pozzolanic materials. By systematically grinding, analyzing, and testing the slag's pozzolanic activity, this research offers new insights into how ancient metallurgical by-products can be harnessed in contemporary construction applications. The approach taken in this study serves as a bridge between ancient and modern practices, contributing both to sustainable material science and to the broader effort of environmental conservation. This novel exploration highlights the value of ancient metallurgical waste as a resource for modern-day waste management and sustainable building solutions, marking a significant advancement in the field of eco-friendly construction materials.

2. Materials and methods

2.1 Materials

The ancient silver distillation process is known as a metallurgical process used for the extraction of silver from ores during ancient times. This process typically involves the smelting of ores followed by the separation of the resulting metallic silver. During the silver distillation process, unwanted substances are also generated along with the metallic silver. These unwanted substances are known as residues, which are the by-products left behind after metallurgical processes (Figure 1).

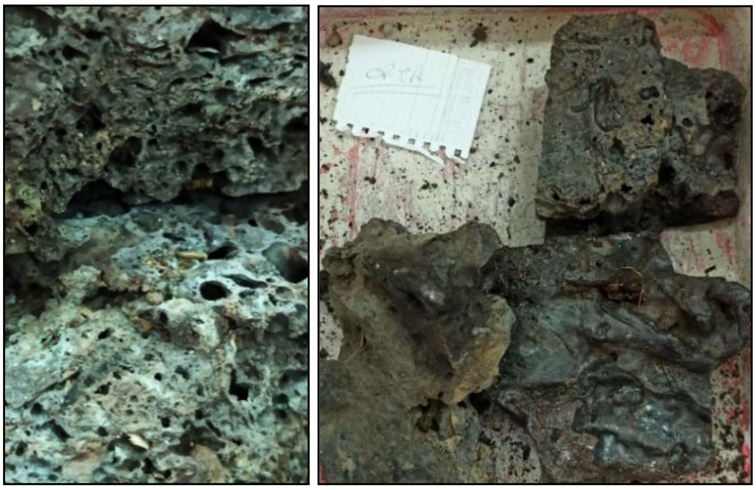

Figure 1. Ancient Silver Mine Slag

The residues produced as a result of the ancient silver distillation process are commonly described as slag or residues. These residues are formed as a result of the smelting of other minerals contained in the ore or the combination of the ore with by-products during the metallurgical process. Although these residues are generally separated from metallic silver, they may still contain traces of silver and other metals.

2.2 Method

2.2.1 Sample Collection

The ancient silver mine slag to be examined was obtained from the Eastern Black Sea region of Turkey. The slag samples collected from different areas of the site have varying chemical compositions and tenors (Figure 2).

Figure 2. Study area where samples were collected.

2.2.2 Size Reduction Process

In this study, the samples collected from the site were crushed to sizes ranging from -2.0 mm to +2.0 mm using a jaw crusher and then ground in a ball mill. The ground samples were also subjected to size fraction analysis using the Mastersizer 2000 instrument (Figure 3).

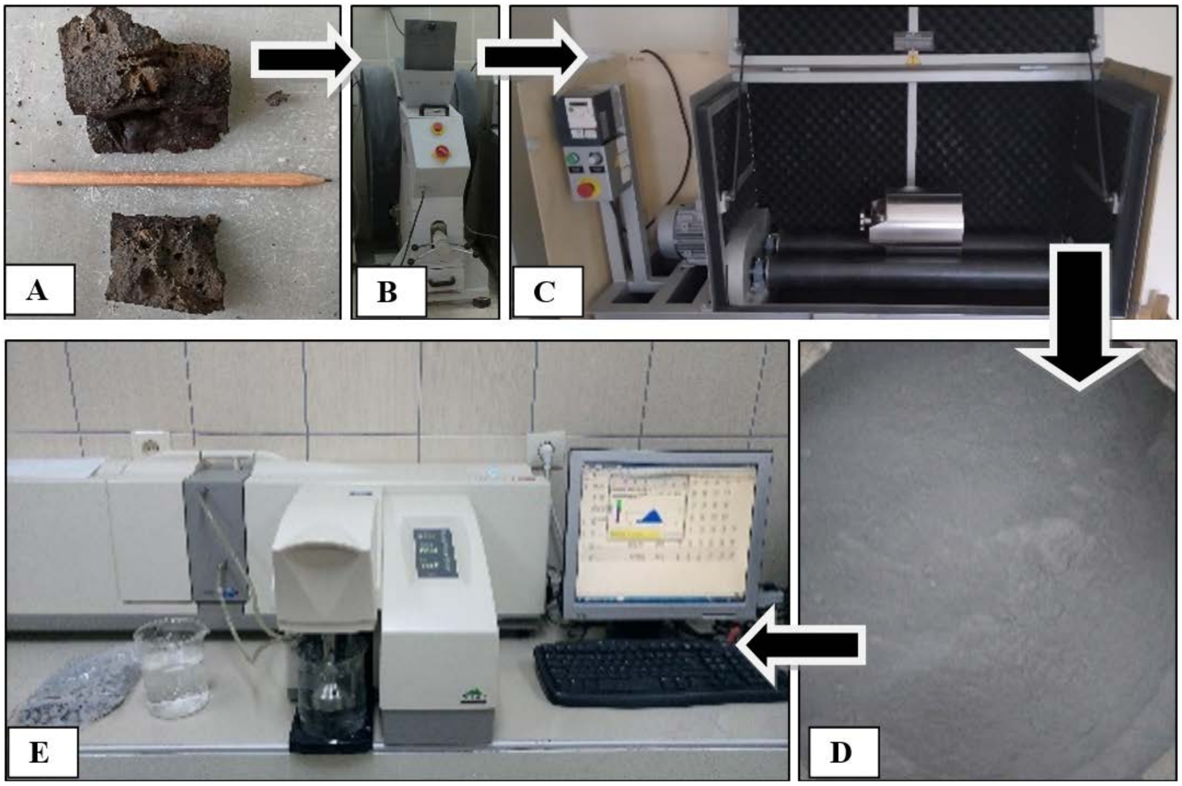

Figure 3. Process of size analysis of Ancient Silver Mine Slag.

2.2.3 Chemical Analysis

X-ray fluorescence (XRF) analyses were conducted to determine the chemical compositions of the slag samples used in the study. The findings are discussed in the results section.

2.2.4 Mineralogical Analysis

Petrographic descriptions were made on rock samples brought from the Ancient Silver Mine Slag field. Figure 4 presents a view of rock samples brought from the field and thin section samples prepared. Thin sections were prepared for petrographic examinations, and examinations were conducted under a petrographic microscope.

Figure 4. Thin section analyses of Ancient Silver Mine Slag.

3. Results and discussion

In the experimental studies, c was used. Their chemical compositions are given in Table 2 and physical properties in Table 3. Chemical analyses of samples taken from the ancient mine site revealed high levels of Silicon Oxide (SiO2) at 37.61%, followed by Iron (Fe) at 25.28% and Calcium Oxide (CaO) at 20.15%. The Ancient Silver Mine Slag contains a high ratio of active silica and calcium due to the melting of silver at high temperatures and the remaining material. Additionally, the quantity of "SiO2 + Al2O3 + Fe2O3" in Ancient Silver Mine Slag is 72.35%.

Table 2. Chemical properties of Ancient Silver Mine Slag [3]

Material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	%Na^2	Blaine cm^2/g
Ancient Silver Mine Slag	37,61	9,46	25,28	20,15	0,76	0,14	1,20	0,27	1959

Tablo 3. Physical properties of Ancient Silver Mine Slag [3]

Material	Reactive Silica (%)	Glow Loss (%)	Limestone (%)
Ancient Silver Mine Slag	27,69	3,41	64,15

The chemical analysis revealed a Blaine value of 1959 cm^2/g. For a substance to act as a pozzolan, a Blaine value of around 1500 cm^2/g is expected. In their study, Külekçi et al. 2022 investigated the pozzolanic properties of cement by adding different amounts of antique slag powder. As a result of their study, they found the 28-day average strength of the added samples to be 2.89 MPa [1]. Pozzolans, containing reactive silica, react in an aqueous environment with the free lime resulting from cement hydration to form calcium silicate hydrates through the following chemical reaction:

$$2Ca(OH)_2 + SiO_2 + H_2O \rightarrow 2CaO.SiO_3.nH_2O \quad (1)$$

This reaction is known as the basic pozzolanic reaction. As a result of this rather slow reaction, hydration products similar to the silicate components of Portland cement are formed. However, this reaction takes place over a long period due to the formation of free lime and the slow nature of the pozzolanic reaction, leading to the gradual development of strength through pozzolanic activity. Pozzolans are expected to exhibit good reactivity over time, resulting in improved microstructure and strength. Therefore, the content of reactive silica is crucial for the material to be used as a pozzolan. The analysis revealed that the active silica content in the Ancient Silver Mine Slag is determined to be 27.69%. After the grinding process at 700 rpm for 1200 minutes, it was observed that 50% of the total material (d50) of the ancient silver mine slag was below the size of 0.081 mm (Figure 5).

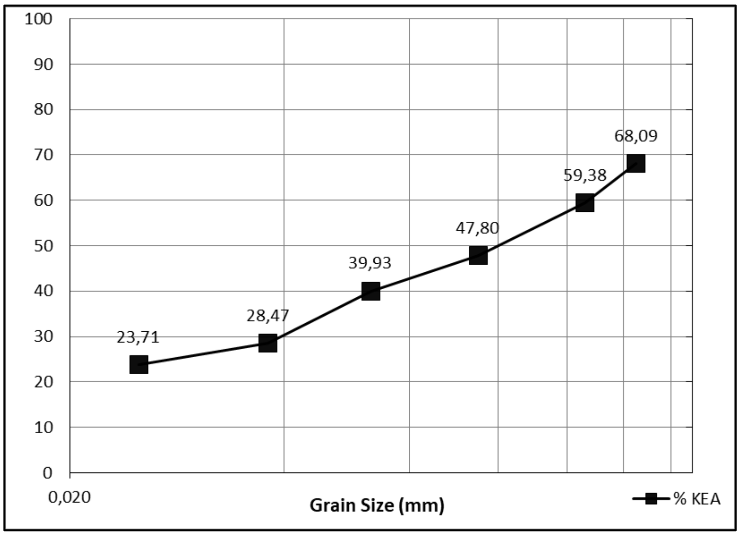

Figure 5. Particle size analysis result of ancient silver mine slag

As a result of the thin section examinations, it was determined that the ancient silver mine slag contained mostly Plagioclase mineral (Figure 6). It was also revealed that the structure has a spherulitic texture.

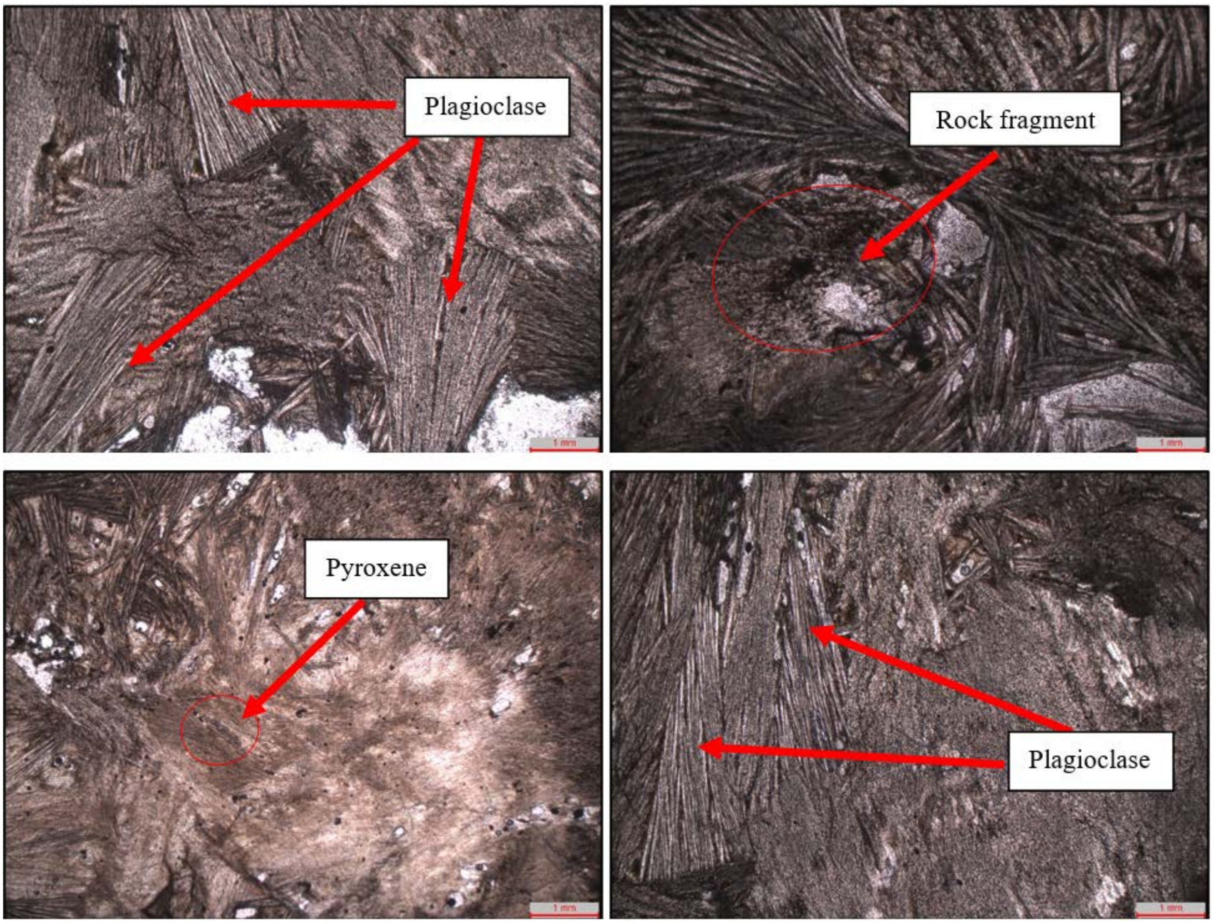

Figure 6. Thin section image analysis of ancient mine slag

4. Conclusions

This study aimed to investigate the pozzolanic properties of the residues left from silver distillation processes in ancient times. The research involved grinding the silver residues to cement sizes and examining their chemical properties, which revealed that these residues may possess pozzolanic activity. This finding suggests that materials considered as waste in ancient times could have properties suitable for contemporary needs. Additionally, significant implications were drawn in terms of waste management and economic recycling. The findings of this study will serve as a crucial reference point for future research and industrial applications regarding ancient metallurgical residues.

The results found are given below:

1) According to ASTM standards, a material must have a “SiO_2 + Al_2O_3 + Fe_2O_3” content higher than 70% to be classified as fly ash. The study revealed that the content of these components in the Ancient Silver Mine Slag is 72.35%. Therefore, the Ancient Silver Mine Slag can be used as fly ash material.

2) One of the most important values for a material to act as a pozzolan is the Blaine value, which is expected to be 1500 cm^2/gr. In this study, the Blaine value of the Ancient Silver Mine Slag was found to be 1959 cm^2/gr. Thus, it can also be used as a pozzolan.

3) Another value that affects the use of a material as a pozzolan is the active silica content. It is expected to be above 20%. The analysis revealed that the active silica content in the Ancient Silver Mine Slag is 27.69%.

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