

Article Blast Furnace Slag, Post-Industrial Waste or Valuable Building Materials with Remediation Potential?

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Abstract: In recent years, the construction industry has struggled with a variety of issues such as material availability, supply channel management, and the increasing cost of construction materials. These issues have encouraged the search for replacements and substitutes for existing construction materials. Blast Furnace Slag is used in the construction industry as a mineral amendment or aggregate. Their use in Earth Construction, due to their post-industrial origin, may be associated with increased levels of potentially toxic elements (PTE) in the soil. This study aimed to evaluate the effectiveness of the immobilization potential of Blast Furnace Slag and to compare it with the addition of Blast Furnace Slag with Activated Carbon using different concentrations of these amendments. We were able to determine the concentrations of selected PTE (zinc, copper, nickel, cadmium and lead) in the soil, roots and aerial parts of Lolium perenne L., using different concentrations of Blast Furnace Slag (3%, 5% and 10%), and Blast Furnace Slag with Activated Carbon (3% and 5%) as soil amendments. Measurements were carried out with Flame Atomic Absorption Spectrometry (FAAS). Both the addition of Blast Furnace Slag and Activated Carbon with Slag increased plant biomass. The addition of slag effectively reduced the zinc, copper, cadmium and lead content of the soil, while the addition of Activated Carbon slag significantly increased the content of selected PETs in the roots and aerial parts of plants. It was considered reasonable to use Blast Furnace Slag with the addition of Activated Carbon in supporting the processes of the assisted phytostabilization of PTE polluted soils.

Keywords: Blast Furnace Slags; Activated Carbon; mineral amendments; immobilization; aggregates

1. Introduction

The sustainability economy currently presents a major challenge. In the construction sector, it concerns many aspects, particularly those that are related to the production of materials needed for the building investment projects. The diminishing resources of natural aggregates forces the industry to look for alternatives to these particularly important building materials. In recent years, these reasons have influenced an increase in the use of post-industrial materials and recycled concrete aggregate as materials for construction [1]. An innovative approach to the development of the building materials sector takes into account elements connected with the production, as well as the best possible knowledge of the physical and mechanical properties of a given material, but also with the recognition of the behavior of this material after its installation. Particularly important here is the impact of the material on the environment, and in the case of materials embedded in earth structures, their interference with the soil and water environment. A multi-aspect approach to materials design allows for the creation of Smart Building Materials (SBM). In recent decades, solutions have been searched for both to solve functional requirements and to support waste management, reducing landfills and caring for the environment. This has contributed significantly to an increase in innovative solutions dedicated to the construction sector. An excellent example of these applications is palm oil clinker [2], sugar



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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/). cane straw waste as a pozzolanic material [3,4], or rice hull as a cementitious material [5]. The most commonly used alternatives to natural aggregates are anthropogenic materials as materials from demolition and reused materials such as Recycled Concrete Aggregates and post-industrial waste such as Blast Furnace Slags or Fly Ash [6]. Anthropogenic materials do not have a uniform fixed chemical composition, which entails risks in with their use as part of a material mix in construction production. In addition, attention should be paid to the use of these materials in earth building. This is related to the contact of these materials with the ground-water environment, which can affect the leaching of PTE and their release into the environment. The origin of anthropogenic materials, especially post-industrial ones, has a direct impact on their density, porosity and pore structure [7].

Meanwhile, there are multiple methods of preventing the migration of PTE in the environment, such as stabilization, thermal desorption, nitrification, phytoremediation, or nanotechnology that can support the process of safe slag management in the earth building industry. Particular attention should be directed to the selection of an additive to support immobilization as a technology that has the potential to reduce negative environmental impacts. If the additive is to be used in conjunction with post-industrial materials in the earth building sector, it should have suitable chemical, mechanical and physical properties so that its effect on the resulting mixture does not have adverse effects on the properties of the resulting building material. From an environmental point of view, mineral additives should be recognized for their immobilization properties and their nature. In the case of PTE, it is necessary to determine where each metal is immobilized, whether the additive used affects immobilization in the soil, the roots, or the aboveground parts of the plant, and what effect it has on yields [8,9]. Based on this, the phytostabilizing properties of the applied additive can be interpreted as a technique that is assisted by the role of plants used in the process of protecting the soil surface from water and wind erosion and in reducing the amount of leachate generated after rainfall [10]. This is possible in situations where plants are able to develop dense ground cover and a strong branching root system [11]. The grass types investigated by the authors, with Lolium perenne L. among them, are used in the phytostabilization technique; moreover, it is one of the species most commonly used for grass plantings near road infrastructure [12]. The modern approach to Smart Building Materials design should be based on the reuse of waste materials, taking into account their processing in such a way that they can be safely reused. This should correlate with the enhancement of the mechanical and physical characteristics and properties of recycled materials. This will ensure that the full potential of these materials is reached [13].

In the construction industry, alternative aggregates are mainly used in earth and road construction. Admixtures of cement, lime or active fly ash are also used to increase the carrying capacity of aggregates. Stabilized aggregates are widely used in the construction industry, especially for sub-base layers for roads, airports and urban roads and as a reinforced base for railroad structures with heavy and fast train traffic due to their properties that increase the bearing capacity of the material and its compressive strength. They are also used for the construction of self-contained temporary pavements on roads and streets with less traffic and in storage and parking yards [14–16]. Blast Furnace Slag is a post-industrial material and is exported in tanks to heaps as a waste material after smelting in the blast furnace. This material is characterized as containing many minerals, mainly silicates and calcium and magnesium aluminosilicates [17,18]. Worldwide, Blast Furnace Slag production exceeds several dozen million tons (about 25 million) annually. The composition of Blast Furnace Slag, depending on the area or place of acquisition, can vary, especially in terms of the content of major oxides such as SiO₂, Al₂O₃ and CaO. Blast Furnace Slag has a pH of an alkaline nature [19,20]. The stabilizing activators used can adversely affect the immobilization of PTE in adjacent soils, so the use of mineral additives with detoxifying properties such as Activated Carbon is considered. Activated Carbons are effective adsorbents for the removal of a wide range of organic and inorganic pollutants dissolved in aqueous or gaseous media. A high sorption capacity is associated with a well-developed internal pore and surface structure. It is also influenced by the presence of

a wide range of functional groups on the surface. Research on Activated Carbon in recent years has focused on its modification and characterization. This is in order to address environmental challenges and the growing demand for cleaner air and water. [21–25].

The article presents research aimed at understanding the immobilization properties of PTE in plants and soil after the addition of blast furnace slag and the effect of amendment Activated Carbon on this process. The second objective of the study was to assess the environmental safety of using post-industrial materials, in this case, Blast Furnace Slag, in earth structures (e.g., embankments) and road structures (road substructure). Since the chemical composition of Blast Furnace Slag is not homogeneous, in the first stage of the research we carried out tests with different contents of slag to better recognize the nature and course of immobilization in soil, roots and aerial parts. A comparison of the test results after the addition of Activated Carbon led to a better understanding of the nature and direction of the immobilization process and the determination of the concentration of Slag and Activated Carbon for boosting the process.

A novelty presented in this article is a combination of Blast Furnace Slag additives with Activated Carbon, which has not been investigated before. Research to date has been conducted on the introduction of a single modifying amendment to the soil. In this article, previous research concerning the environmental safety of Blast Furnace Slag [13] was verified but also challenged with the research considering a second modification in the amount of Activated Carbon. This procedure allowed us to evaluate the interaction and immobilization potential of these amendments. This is a new approach that aims to assess the influence of the successful introduction of modifications in the previously identified material. The use of different concentrations of the introduced amendment should be considered important, and deepened the impact assessment.

2. Materials and Methods

2.1. Blast Furming Slag Characteristics

The general characteristics of the chemical composition were identified, thereby demonstrating the structure of the material studied. The chemical composition of the Blast Furnace Slag material is shown in Table 1. The major components of the Blast Furnace Slag are silicon, aluminum, and calcium. The pH of the material was analyzed and determined to be 9.63. An alkaline pH is an important factor in helping to stabilize and prevent the leaching of PTE.

Parameter	Unit	Blast Furnace Slag
pH	-	9.63
Carbon	%	1.22
Oxygen	%	32.15
Sodium	%	8.11
Magnesium	%	1.52
Aluminum	%	21.41
Silicon	%	26.53
Potassium	%	1.12
Calcium	%	7.21
Ferrous	%	0.73

Table 1. Chemical composition of Blast Furnace Slag.

A chemical analysis for PTE content is shown in Table 2, where the determinations for blast furnace rumen are compared with the those for the Standard [26].

Parameter	Unit	Standard [26]	Blast Furnace Slag
Zinc	mg/kg	2000	156.44
Copper	mg/kg	600	45.92
Nickel	mg/kg	300	41.22
Cadmium	mg/kg	15	1.21
Lead	mg/kg	600	38.27

Table 2. The chemical analysis for PTE in Blast Furnace Slag.

Blast Furnace Slag is characterized by high porosity, which can be observed in the electron microscope (SEM) images (Figure 1). In addition to the significant porosity of the Blast Furnace Slag, the presence of fine material fractions on its surface can be observed. The specific density of Blast Furnace Slag is 2.4 g/cm³, which is a typical value for this type of aggregate.



Figure 1. Overview photo of the Blast Furnace Slag used in study (**a**). Scanning electron microscopy (SEM) image at $5000 \times$ magnification of the Blast Furnace Slag (**b**).

2.2. Activated Carbon Characteristics

Activated Carbon was used in this experiment (Figure 2) and was obtained from different species of deciduous trees with a specific density of 2.04 g/cm^3 , a bulk weight of 411 kg/m^3 and pH value of 6.1.



Figure 2. Overview photo of the Activated Carbon used in the study.

2.3. Experimental Soil

The experiments were carried out in polyethylene pots weighing 5.0 kg using soil sampled at a depth covering approximately the top layer (0–30 cm) and from areas located near a national two-lane road located in the region of Central Poland. The soil had a pH of 8.52. The perennial ryegrass (*Lolium perenne* L.) was selected as a test plant. The seeds of perennial ryegrass, weighing 5 g, were sown into pots. The seeds germinated between 5 and 8 days later. The plants were watered every other day with deionized water to 60% of the maximum water holding capacity of the soil. At the end of the experiment (approximately 42 days after sowing the seeds), the plants were harvested, weighed, and separated into aboveground and root parts. The PTE content of the experimental soil is presented in Table 3.

Parameter	Unit	Standard [26]	Experimental Soil
pН	-	-	8.52
Zinc	mg/kg	2000	1328.56
Copper	mg/kg	600	485.28
Nickel	mg/kg	300	320.11
Cadmium	mg/kg	15	21.92
Lead	mg/kg	600	256.62

Table 3. The chemical analysis for PTE in experimental soil.

Blast Furnace Slag was mixed with experimental soil at concentrations of 3.0%, 5.0% and 10.0% in triplicate. For comparison, planting on soil without slag addition was used as a control trial in triplicate. Then, the PTE contents of the soil, roots, and aerial parts of the plants were determined. Activated Carbon (3.0% and 5.0%) was then added to these concentrations of Blast Furnace Slag. The PTE content of the soil, roots and aerial parts of the plants was again determined. Each test was performed in triplicate ($\Sigma = 33$ pots).

2.4. Plant Material Analyses

Plants were pulled from the pot in such a way as to avoid root damage. The collected samples of *Lolium perenne* L., were then cleaned with ultrapure water and air-dried at room temperature for two weeks. The samples were then ground to a fine powder using an analytical mill (Retsch type ZM300, Hann, Germany) and stored at ambient temperature, protected from light and in clean containers for subsequent chemical analysis. Roots and shoots were oven dried at 55 °C to a stable weight, and the dry biomass was recorded. A representative sample was mineralized in nitric acid (65% w/w, POCH, Gliwice, Poland) and using a microwave oven (Milestone Start D, Milan, Italy). After filtration, the digestion products were brought to a 100 mL volume using deionized water. The extracts were analyzed for their total PTE concentration—zinc, copper, nickel, cadmium and lead were determined by flame atomic absorption spectrometry (FAAS) using an iCE-3000 spectrophotometer (Thermo Scientific, Waltham, MA, USA). A five-point calibration was performed with standard solutions. Each sample was processed in triplicate.

2.5. Research Methodology

Figure 3 presents a scheme of the tests performed. Section 2.3 describes the sample preparation process and research parameters. The research was divided into two stages. In the first stage, the effect of the addition of Blast Furnace Slag alone to the control soil was performed at concentrations of 3%, 5% and 10%. In the second stage, the mixtures were expanded by adding Activated Carbon at concentrations of 3% and 5%. This procedure allowed us to compare the results of the chemical analysis (description of tests carried out in Section 2.4) on the content of the selected PTE of samples containing only the addition of Blast Furnace Slag and Blast Furnace Slag enriched with Activated Carbon. This allowed us to better recognize not only the possible concentrations of these additives but also the effect of concentrations and additives on PTE allocations in plant parts.



Figure 3. Diagram of the research performed.

2.6. Statistical Analysis

A statistical analysis of the results was performed using R Studio software. Data were analyzed using a one-way analysis of variance (ANOVA). When the assumptions of ANOVA were not met, the Kruskal–Wallis test by ranks was used as the statistical method. Tukey's test (HSD) was used to identify significant differences between variables.

3. Results

3.1. Effect of Blast Furnace Slag Concentration and Activated Carbon Application on the Biomass of Lolium perenne L.

Figure 4 presents the biomass results in grams from each of the pots. This figure compares the biomass results for the control samples without and with Blast Furnace Slag added at concentrations of 3%, 5%, and 10%, and the slag enriched with the addition of 3% and 5% of Activated Carbon. The highest yield was obtained at a Blast Furnace Slag concentration of 3%, averaging 18.0g (SD \pm 0.36) of dry biomass per sample, representing a 45% increase in the experimental plant yield compared to the control series. These results were then compared with mineral Activated Carbon additions of 3% and 5%. In both cases, the yield was lower with the Activated Carbon additive than the yield obtained with the Blast Furnace Slag additive alone. Higher yields were obtained for the 3% concentration of Activated Carbon in the samples, combined with the 3% concentration of Blast Furnace Slag in the sample. For these samples, an average of 16.25g (SD \pm 0.25) of dry biomass was obtained. Both the addition of Blast Furnace Slag (37% on average) and Blast Furnace Slag with Activated Carbon (19% on average) had higher yields compared to the control series.



Figure 4. Amount of resulting biomass of *Lolium perenne* L. using different concentrations of Blast Furnace Slag (BFS) and Activated Carbon (AC).

3.2. PTE Immobilization Efficiency in Lolium perenne L.-Soil Amended Blast Furnace Slag

Figure 5 shows the content of the tested PETs in the soil with the specified level of Blast Furnace Slag at 3%, 5% and 10%, respectively, compared to the control series. The application of Blast Furnace Slag significantly reduced the content of all of the tested PETs. The contents of zinc, copper, cadmium and lead in the soil significantly decreased by an average of 14% for zinc, 16% for copper, 21% for cadmium and 13% for lead for the control series. For nickel, a significant increase in the concentration of this metal was observed in the samples containing the Blast Furnace Slag addition for the control series by an average of 10%.



Figure 5. Cont.



Figure 5. PTE content in soil with the addition of Blast Furnace Slag (BFS).

The content of the tested PTE in individual plant parts in the root and aerial parts at specific contents of Blast Furnace Slag of 3%, 5% and 10%, respectively, in relation to the control series is presented in Figure 6. This allowed us to determine the level of metal immobilization in individual plant parts. The application of Blast Furnace Slag significantly reduced the cadmium content by an average of 40%, nickel content by an average of 14% and slag copper content of 10% by an average of 23% in the aerial parts of the plants. In the case of zinc, an increase in the concentration of this metal in the aerial parts of the plant by an average of 33% was observed. There were no significant differences in the concentration of lead in the aerial parts. The content of zinc in the roots increased by 35%, copper and lead by 38%, cadmium by 37%, whereas for nickel, it decreased on average by 20% in comparison with the control series. Moreover, it was observed that zinc increased the immobilizing properties of this PTE in both the roots and aerial parts of plants after the application of Blast Furnace Slag additives.



Figure 6. Cont.



Figure 6. PTE content in roots and aerial parts in plants with Blast Furnace Slag (BFS).

3.3. PTE Immobilization Efficiency in Lolium perenne L.—In Soil Amended Blast Furnace Slag and Activated Carbon

Subsequently, tests with the mineral amendment of Activated Carbon at concentrations of 3% and 5% were analyzed (Figure 7). There was a significant reduction in the soil zinc content for the 3% Activated Carbon amendment soil, by an average of 25% and for the 5% amendment soil by 18% compared to the control series. For copper it was 30% and 18%, respectively, for cadmium 18% and 15%, and for lead 23% and 17%, for which the results are presented in Figure 7. For nickel, there was no significant difference from the control series with the 3% addition of Activated Carbon, while for the 5% addition a significant difference was observed with a reduction of, on average, 8% in the content of this metal in soil with an addition of 5% and 10% Blast Furnace Slag compared to the control series. For the other concentrations of 3% slag, no increase in the immobilization of this element in soil was observed.



Figure 7. Cont.



Figure 7. PTE content in soil with the amendment of Blast Furnace Slag (BFS) and Activated Carbon (AC).

Figure 8 shows the effect of using 3% and 5% Activated Carbon as a mineral amendment to enhance PTE immobilization in roots and aerial parts of plants. There was a significant effect of the applied Activated Carbon concentration on the increase in immobilizing properties of zinc (on average by 53% in roots and by 65% in aerial parts with 3% Activated Carbon and by 38% in roots and by 63% in aerial parts of the plant with 5% Activated Carbon), copper (correspondingly, 63% and 50% for 3% Activated Carbon and 49% and 30% for 5% Activated Carbon) and cadmium (correspondingly 60% and 38% for 3% Activated Carbon and 40% and 17% for 5% Activated Carbon), concerning the control series. For these elements, there was a decrease in the immobilization of metals in the roots and aerial parts of plants when 5% Activated Carbon was added. For nickel, no significant differences from the control series were observed for both 3% and 5% Activated Carbon. In the case of lead, a significant increase in the concentration of this metal in the roots was observed, which was higher in the case of the 3% addition of Activated Carbon, by 55% on average, and no significant differences in the immobilization properties of the aerial parts were observed.



Figure 8. Cont.



Figure 8. PTE content in roots and aerial parts of plants with the amendment of Blast Furnace Slag (BFS) and Activated Carbon (AC).

4. Discussion

The production of building materials including concrete, aggregates and stabilizing mixtures has a significant impact on the environment and ecology. The annual production of concrete involves the consumption of a large amount of materials and has a significant impact on CO_2 emissions, which contributes to the perception that the construction industry has a negative impact on the environment [27,28].

However, the challenges the construction industry faces impose the responsibility to better adapt to the principles of sustainable development policies.

This prompts both researchers and entrepreneurs to search for solutions that meet multiple applications (SMB). This also applies to construction materials, and in particular the use of aggregates as materials with a very wide range of applications in construction. This is especially true for aggregates used in earth construction due to their direct contact with the soil and water environment. The aggregate is not only expected to perform its function, but also to be environmentally safe. This approach is relatively new and is based on increasing awareness related to environmental protection, climate protection and the depletion of natural resources [29–34].

The recycling of aggregates from post-industrial waste such as Blast Furnace Slag, due to its non-homogeneous nature depending on the products generated in the furnace, presents a challenge. In recent years, there have been many publications addressing the issue of slag management [35–37]. Previous publications mainly focus on the physical and mechanical properties of this material and often overlook the environment in which it is incorporated. Additionally, one of the ways of managing Blast Furnace Slag is to use it as an aggregate in the base course of road construction. Although the content of selected PTE (Table 1) in the investigated slag is in accordance with the current standard [38], due to the application of the material in the soil–water environment, this should be correlated with the amount of PTE contained in the soil directly adjacent to the road infrastructure. This is because exhaust fumes, road surface abrasion or tires are factors that additionally affect the PTE content in areas directly associated with the road infrastructure. This may lead to the accumulation of these elements in the environment. Moreover, these pollutants that have not been subjected to phytostabilization can also disperse into the environment in the form of dust [39–41].

Although they can be observed by summing the amounts of the selected PTE for the experimental soil (originating from the areas adjacent to the road infrastructure) with the determination of the metals contained in the Blast Furnace Slag, the standard permits the content of nickel (361.33 mg/kg) and cadmium (23.13 mg/kg), while the content of copper (531.2 mg/kg) and zinc (1485.0 mg/kg) can be considered as high.

The authors indicated a significant effect of Blast Furnace Slag on the growth and yield of *Lolium perenne L*. The highest yield of this plant, compared to the control series, was found after the application of 3% Blast Furnace Slag. Similar results were obtained in an

earlier study on the effect of slag on yield by Negim et al. [42], Wang and Cai [43], and Radziemska et al. [13].

The application of Blast Furnace Slag has been proven to have a beneficial effect on reducing the immobilization of PTE in soil, which has the effect of reducing its further migration into the environment [44]. Previously, the positive effect of 3% Blast Furnace Slag amendment in soil on the yield of *Pinellia ternata* L. was verified by Ng et al. [45]. The effect of Blast Furnace Slag on the immobilization of zinc, copper, cadmium and lead in plant roots was also demonstrated compared to the control series. This means that a positive effect on reducing the exceedance of the cadmium standard in the studied soil.

Although Activated Carbon can be produced from carbonaceous materials (such as petroleum waste, wood, coal or lignite), it is also possible to use biomass waste as a raw material for its production. This significantly increases the availability of this product. This is a cheaper alternative that reduces the cost of producing Activated Carbon [46]. Activated Carbon consists of functional groups bonded by layers of aromatic rings. They have chemical properties similar to those of aromatic hydrocarbons. Therefore, it is believed that chemical reactions involving aromatic hydrocarbons also occur with Activated Carbons. The existence of surface functional groups on the carbon matrix means that by using thermal or chemical treatments, it is possible to produce adsorbents adapted to specific functions. These carbons have a high affinity for metals compared to the native carbon which we believe influenced the increased immobilization of PTE when added to control soil [46,47].

The addition of Activated Carbon will decrease the immobilization of zinc, copper, cadmium and lead in the soil. In addition, when using a concentration of 3% Blast Furnace Slag with 5% Activated Carbon, the level of nickel in the soil also decreased.

Based on the presented results, it can be concluded that the application of various soil amendments to improve the physical and chemical properties of the soil and reduce the uptake of PTE by plants can be a beneficial method of remediation [48]. It should be noted that the concentration of PTE in plants depends mainly on the specific characteristics of plant species, the ability of the root system to uptake the element and soil pH, granulometric composition and organic matter content [48,49]. The authors recognized the phytostabilizing potential of the tested mixtures with the use of 3% Activated Carbon resulting from the immobilization of PTE in plant roots as one of the most important features following the concentration of PTE in the soil [50]. Further research in this area should also include the use of other plant species to verify the conclusions of this article. According to the conducted research and performed analyses, it is necessary to draw attention to the high remediation potential of Blast Furnace Slag reinforced with the addition of Activated Carbon. The selection of appropriate concentrations of these materials should be based on previous studies of the soil to which the material would be applied and a recognition of remediation requirements in a particular area. Based on the above studies, it can be concluded that both Blast Furnace Slag and its mixtures with Activated Carbon are not a potential environmental hazard, and mixtures of these compounds can be further explored for use in earth structures.

5. Conclusions

The main conclusions and observations of the article are as follows:

- The amendment of Activated Carbon has the effect of reducing the immobilization of zinc, copper, cadmium and lead in the soil.
- Application of 3% Blast Furnace Slag concentration along with 5% Activated Carbon reduced the nickel level in the soil.
- The phytostabilizing potential of the tested mixtures with 3% Activated Carbon was found to be a result of the immobilization of PTE in plant roots and a decrease in the concentration of PTE in soil.
- Slower germination of plant seeds was observed, delayed on average by 2 days in the case of mixtures with mineral Activated Carbon amendment, which was reflected in

yields. The smallest effect on yield was observed for 3% Activated Carbon amendment, combined with 3% Blast Furnace Slag.

 A high remediation potential of Blast Furnace Slag reinforced with Activated Carbon was found. The selection of appropriate concentrations of these materials should be based on previous soil analyses and a recognition of remediation requirements in a particular area.

Answering the question posed in the title of this article, the conducted research and analysis allow us to conceive of Blast Furnace Slag as an environmentally safe material that also has remediation potential. Moreover, its other physical, chemical and mechanical properties suggest that it will be a valuable material or a component of mixtures for designing smart construction materials.

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