## **ZEOLITES - SUSTAINABLE BUILDING MATERIAL**

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#### Abstract:

Zeolites are one of the few minerals that have been studied for remediation in the environment. Due to their ability to change ions, as well as the fact that they bring certain improvements such as increasing cations to exchange soil capacity and soil moisture, improving hydraulic conductivity, increasing yields in acidic soils and reducing the ingress of heavy metals into plants (Allen and Ming 1995).

Soil remediation can be done by planting zeophytes (volcanic tuff) in the most endangered parts of the soil contaminated soils. Based on the data on some physico-chemical characteristics of volcanic tuff, the analysis in this paper can conclude the high effectiveness that would be obtained when applying for passive decontamination and revitalization of heavy metal contaminated soils from the areas around the Lead Smelter and zinc from Veles.

#### Introduction

Zeolite is a rare natural mineral of volcanic origin, created by the natural reaction between condensate of volcanic steam and ocean waters in specific geological conditions. There are about 276 species of natural zeolites, and based on their morphological structure they appear in three basic forms: fibrous, leafy and crystalline. Contains trace elements such as sodium, calcium, potassium and magnesium, which are of great importance for our health. Zeolites are considered to be completely useful and widely used minerals, the use of which will increase even more in the future. The discovery of zeolites in 1756 in the form of large widespread, easily exploitable near-monomineral deposits in tuffoid sedimentary rocks in the EU and other countries opened a new chapter in these useful industrial minerals whose properties are used in industry, agriculture and the environment. The general formula of zeolites is: (Ca, Sr, Ba, Na2, K2) Al2Si2-10O8-24 2-8 H2O The content of water molecules depends on the ratio Al: Si and the characteristics of the crystal structure. The Al: Si ratio is variable within certain limits. The change in the silicon content also leads to structural changes, ie. changes in the bonding of silicon-oxygen and aluminum-oxygen tetrahedra. For zeolites that are low in silicon are characteristic rings made of 4 tetrahedra, for those with medium silicon content are characteristic rings of 6 tetrahedra, and for zeolites rich in silicon are rings of 5 tetrahedra. Zeolites with a higher silicon content contain more water molecules which are released at a temperature of about 150  $\Box$ C, while zeolites with a lower silicon content have a smaller number of water molecules and are released at a higher temperature of about 500C. The release and reception of water is done gradually, so that changes in physical and optical properties caused by changes in water content can be monitored. This structural feature allows the change of cations. As a result, Ca and Na are replaced by K, Mg, Fe.



Figure 1. Structured on zeolite

Some authors use the ring character of zeolite structures for structural systematization of zeolite minerals. Zeolites are divided into three groups: fibrous, leafy and cubic. In fibrous zeolites, the four-membered rings are connected to the fifth ring in the form of chains that are parallel to the "c" axis. The chains are linked together by common oxygen atoms. Na + ions and water molecules are found in the channels between the chains. In leaf zeolites, the rings are connected in layers. As a result of this structure, these zeolites have a perfect fracture that is parallel to the layers. In isometric or square zeolites, the four-membered, six-membered, and eight-membered rings are connected in cages that are connected to each other by common oxygen atoms. Large cations and water molecules are found in the cavities.

## Methodology and data analysis

Urban heavy metal pollution has been the subject of many studies. Regional soil pollution occurs mainly in industrial areas and in centers with large settlements, where factories, traffic and municipal waste are the main sources of metals. Due to the diverse and continuous changes in urban areas, it is necessary to first

determine the natural distribution and methods for determining the changes in nature caused by human activity.

The city of Veles is located in the valley of the river Vardar, about 55 km south of the capital Skopje. Veles, with its many characteristics and features, is a specific urban and industrial area. Its peculiarities originate from its geographical position, because it is located in the very center of Macedonia, as well as from the economic and social character of its development.

Numerous researches carried out by various institutions that have determined the contamination of the soil with heavy metals from the wider environment of the Lead and Zinc Smelter in Veles, as a necessity is imposed their decontamination and revitalization.



Карта 3b. Геолошка карта на Велес и неговата околина (дигитален теренски модел) Map 3b. Geologic map of the Veles area (digital elevation model)

Figure 2 Geological map of Veles

The zinc and lead smelter "Zletovo" is located in the city of Veles. The starting point in the programming (1960) was the construction of a capacity that would enable the processing of lead-zinc concentrates from the lead and zinc mines "Zletovo - Sasa". It was built from 1971 to 1973, this period of construction for the conditions that prevailed in our country was a kind of record, especially when taking into account the number, size and complexity of the facilities. The smelter first started the lead and zinc furnaces on October 10, 1973, and has been operating

for almost 30 years. In 2003, the production line of the then metallurgical complex finally closed. There is a lot of soil pollution around the smelter in Veles.

Soil remediation can be done by planting zeophytes (volcanic tuff) in the most endangered parts of the soil around Veles (according to the geochemical atlas of Veles and its surroundings made in 2008) near the Lead and Zinc Smelter, as well as in public areas in the city of Veles. Based on the data on some physico-chemical characteristics of the volcanic tuff, it can be concluded that the high effectiveness would be obtained when applying for passive decontamination and revitalization of heavy metal contaminated soils from the areas around the Lead and Zinc Smelter from Veles.

Based on the geochemical atlas of Veles and its surroundings and according to the preliminary calculations of the municipality of Veles, the total public area for decontamination is about 65 943 m<sup>2</sup> and the total agricultural area in the vicinity of the smelter Veles is about 641 000 m<sup>2</sup>.



Карта 54а. Критична загаденост на површинскиот слој од почвата во Велес и неговата околина Map 54a. Critically polluted topsoil in the Veles area

Figure 3 Critical pollution of soil layer in the vicinity of Veles

Orientation calculation for the required amount of zeophyte for remediation at 20-60 cm soil depth in Veles:

Preliminary calculation for lead, cadmium, arsenic, zinc:

For remediation of the total public area in Veles ~  $65943 \text{ m}^2$ 

For remediation of agricultural area in the vicinity of Veles: ~  $641000 \text{ m}^2$ 

A total of 20,000 - 30,000 tons of zeophyte is needed for remediation of Public area and agricultural area for 20 and 60 cm depth of soil in Veles or about 3,000,000 - 4,000,000 euros

In order to use the zeofit for remediation of the polluted agricultural areas in Veles, it is necessary to first dislocate the Slag Landfill from MHK "Zletovo" - Veles, because it is still a serious burden on the environment in Veles.

In order to review the possibilities for remediation of the site with slag near Veles, in 2007 within the CARDS 2006 program, for the needs of the Ministry of Environment and Physical Planning, a Feasibility Study for remediation of pollution from MHK Zletovo was prepared - Veles within the project "Development of remediation plans with financial aspects for the elimination of industrial hotspots." The project was funded by the European Union and was implemented by the consortium Eptisa - DHI.

Within this project, it is estimated that about 1.8 million tons of slag containing lead and zinc have been deposited at the site. The location is not covered with other inert material and therefore emissions are possible in the air, surface, groundwater and soils that are not so large and mobile but have a negative impact on the environment. The river Vardar passes near the location of the slag landfill.

## Conclusion

Human impact on the biosphere is very wide and complex and can often lead to reversal processes. All the changes that result from human activity disturb the natural balance of any ecosystem that has formed for a long time. Based on the above, it can be concluded that zeolites are minerals that are widely used. Zeolite minerals enable adsorption, cation exchange, dehydration-rehydration, etc. which contributes to their use in remediation of contaminated soils.

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