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Possibilities of 'siliceous' bacteria as biological agents for silicate removal

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Rock composed of silicate and aluminosilicate minerals makes up the main mass (some 95%) of the Earth's crust. Under the influence of physical, chemical, and biological factors, rock weathering occurs. Microorganisms-producers of mineral and organic acids affect minerals. Some microorganisms which precipitated silica within their cells, can create and break down organocilicates. 'Siliceous' bacteria from the leached silicate use not only NH^+, K^+, PO_4^{3-}, and other elements of mineral nutrition, but primarily SiO_4^{4-} (and probably Al^{3+}), which embed in its capsule. The interest in the study of 'siliceous' bacteria has caused their possible application in agriculture and biogeotechnology. Within this paper we analyze whether 'Siliceous' bacteria can be applied in biotechnological processes, such as: 'Soilification' of ash landfills, 'desilicification' of oil shale as alternative energy source, and leaching of rare elements such as gallium from bauxite. This provides an opportunity for biobeneficiation and optimization of these processes in order to facilitate obtaining desired scattered and rare metals as well as environment protection.

Possibilities of "siliceous" bacteria as biological agents for silicate removal

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Introduction. Rock composed of silicate and aluminosilicate minerals makes up the main mass (some 95%) of the Earth's crust. Soil microorganisms did not find only habitat in the soil, but they play an essential role in the dissolution, migration, and redeposition of various elements making up the rock minerals, as well as in the formation of crusts of weathering, ore deposits and soils resultant from these processes [1].

Weathering of silicate minerals leads to the destruction of their crystalline structure through the reaction of hydrolysis (acidolysis, alcalolysis and complexolysis), which involves the ions H^+, OH^- and H_3O^+. The process of the destruction of heterogenous silicate and aluminosilicate minerals is given below.

$$M^+mineral^- + H^+OH^- \rightarrow H^+mineral^- + M^+OH^-$$

where: M^+ mineral$^-$ is the original mineral, H^+mineral$^-$ is the weathered mineral, and M^+ are cations of metals that are present in the mineral.

"Siliceous" bacteria from the leached silicate use not only NH^+, K^+, PO_4^{3-}, and other elements of mineral nutrition, but primarily SiO_4^{4-} (and probably Al^{3+}), which embed in its capsule. The interest in the study of "siliceous" bacteria has caused their possible application in agriculture and biogeotechnology [2,3].

The effect of these bacteria on silicates and aluminosilicates is associated with the formation of gelatinous capsules of exopolysaccharides (EPS). Capsules contain sucrose, galactose, mannose, and amino sugars. Silicon is commonly found attached to the capsule [4]. It can be assumed that the formation of capsules result of decomposition of silicates. Experiments confirmed the positive correlation between the amount of dissolved silica and quantities generated capsule [5].

Use of "siliceous" bacteria in agriculture is possible because of an ability of mobilization of potassium from aluminosilicate and its use instead of potassium fertilizers. It was described the possibility of application of the "siliceous" bacteria in biogeotechnology to obtain aluminum from bauxite with high content of silica and iron [6].

In this paper we will also describe possible use of "siliceous" bacteria as potential "biological agents" for:

- **Desilicification of oil shale during preparation of kerogen concentrate,**
- **Leaching of rare elements such as gallium from bauxite,**
- **Soilification of landfills of fly ash.**

Desilicification. Reserves of **oil shale** in Serbia amount to about 3 billion tons, while the largest deposit for open-pit and underground exploitation is situated in the locality of Aleksinac, Serbia. The average content of the organic substance in Aleksinac shale is about 20%, with a dominant share of kerogen (more than 95%). The mineral part comprises about 20% carbonates, approximately 10% pyrite and the rest are aluminosilicates.

Investigation of the chemical composition and structure of kerogen requires its isolation from sedimentary mineral matter. Depyritization was previously conduct using strains of chemolithoautotrophic bacteria *At. ferrooxidans* [7].

To determine whether the composition and structure of the sedimentary organic matter had changed during bacterial desilicification with *B. circulans*, the properties of the organic material in the reference sample were compared with the properties of the same material in the bacterially treated sample.

Desilicification experiments, which consisted of leaching for 30-days with *B. circulans*-Jordan in a modified Ashby's medium, were repeated four times. In all of these experiments, a progressive decrease in the pH was observed, indicating that organic acids, responsible for the desilicification, 7 were constantly being produced. In spite of this, the leaching effect, expressed *via* the sum of SiO_2, Al_2O_3 and Fe_2O_3 relative to the contents of the same oxides in the reference sample, was not 100 % efficient. The composition of the organic matter during bacterial desilicification remained stable, thus demonstrating the advantages of bacterial *vs* chemical demineralization processes [8, 9]. The experiments of bacterial demineralization showed high efficiency in removal of pyrite (*ca* 91%) and silicates (*ca* 40%).

Table 1. Composition of the reference and bacterially treated samples

	Reference sample	Bacterially treated sample
Atomic Ratios		
H/C	1.79	1.75
$O+S_{org}/C$	0.18	0.26
Ash, %	53.80	43.40
Content of ash components, relative to the reference sample, %		
Al_2O_3	7.80	6.20
SiO_2	38.60	29.00
Fe_2O_3	4.80	3.60

Leaching of rare elements. Gallium became interesting because of the application in computer semiconductor industry. Gallium is found and extracted as a trace component from bauxites mine in Jajce (Bosnia and Herzegovina). The highest level of leached gallium that we achieved by "siliceous bacteria" was near 70%. Bauxite is the most important sources of gallium in which the amount can be few dozen ppm. Biogeotechnological extraction of gallium from bauxite would have all the advantages of biohydrometallurgical processes. It has been confirmed leaching of 66.7% gallium compared to the initial amount of 18 ppm.

Soilification. The role of **"siliceous bacteria"** in soilification from parent rock has long been proven. The reports on the bacterial diversity of ash layer from landfills are scarce. Bacillus species are predominated in an municipal solid waste incineration ash layer at a landfill [10]. These microorganisms can be also found in the ash from thermoelectric power plants. In the old ash landfills the proportion of "siliceous bacteria" within the total amount of microorganisms is higher than in fresh landfills. Our hypothesis is that landfills of fly ash from lignite combustion in power plant and also from incinerated municipal solid waste can be effectively soilificated by the action and application of these microorganisms.

Conclusions. Bacterial desilicification of the oil shale may be estimated as promising. The raw shale was found to be an advantageous substrate and the efficiency in leaching the aluminosilicates by the used *B. circulans* strains with this substrate was *ca* 20% in 4 weeks. The results indicated the "siliceous bacteria" as potential "biochemical agent" for the removal of carbonates and silicates.

Leaching of almost 70% of Gallium present in Bauxite provides an opportunity for optimization of this process in order to facilitate obtaining the desired scattered and rare metals. Soilification of the landfills of fly ash from lignite combustion in power plant or from incinerated municipal waste by "siliceous bacteria" will reduce the problem of pollution and enhance the natural processes. Since "siliceous bacteria" are the pioneers in the landfills they will enable and prepare the environment for life of other microorganisms and plants.

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