

Synthesis of Copper Silicate ($\text{CuSiO}_3 \cdot \text{H}_2\text{O}$) using Copper Oxide, Quartz and Microbes

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Abstract- Microbes like bacteria, algae, fungi and virus play an important role to catalyst chemical reactions. In Nature, ores or minerals of different compounds are formed due to microbial environment and other factors like weathering. Microbial environment is also instrumental in forming copper containing silicate minerals. Chemical reactions occur under microbial environment because microbes have the ability to control or modify different factors like pH, chemical potential and temperature during reactions. In this paper, synthesis of copper silicate ($\text{CuSiO}_3 \cdot \text{H}_2\text{O}$) using copper oxide (CuO) and quartz (SiO_2) under microbial environment in the laboratory is being adopted to produce the material. XRD technique is used to confirm the formation of $\text{CuSiO}_3 \cdot \text{H}_2\text{O}$.

Keywords - Copper oxide, Quartz, CuSiO_3 , microbes, XRD.

I. INTRODUCTION

Minerals are inorganic compounds, crystalline, sometimes amorphous with specific chemical composition and structure. The composition of minerals are very simple such as sulphur (S) or quartz (SiO_2) or very complex such as the igneous mineral biotite [$\text{K}(\text{Mg}, \text{Fe}, \text{Mn})_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$]. Primary or igneous minerals crystallize during cooling of magma forms feldspars, pyroxenes and amphiboles, olivines, micas and silica. Minerals formed from chemical alteration (weathering or diagenesis) of primary minerals are called secondary minerals such as kaolinites, montmorillonites, illites; hydrated iron and aluminium oxides and carbonates. Microbes play a role in this transformation of primary to secondary minerals. Minerals formed by the precipitation from solution are called authigenic minerals. Microbes such as *Arthro bacter pascens*, *A. globiformis*, *A. simplex*, *Nocardia globerula*, *Pseudomonas fluorescens*, *P. putida*, *P. testosteroneii*, *Thiobacillus thiooxidans*; and fungi-*Trichoderma lignorum*, *Cephalosporium atrum* and *Penicillium decumbens* generate mineral acids in their vicinity that may soluble Li and Al or Si. The arsenic ores orpiment (As_2S_3), arsenopyrite (FeAsS) and enargite (Cu_5AsS_4) are also solubilized in this manner. *Thiobacillus ferrooxidans* leaches out 6% arsenic from carbonaceous gold ores and also accelerates leaching from arsenopyrite. Similarly antimony (Sb) minerals tetrahedrite ($4\text{Cu}_2\text{S} \cdot \text{Sb}_2\text{S}_3$) and stibnite (Sb_2S_3) are oxidized by *T. ferrooxidans* to pentavalent antimony. Mechanism for metasilicate polymer depolymerization is not known. However, microbes *Proteus mirabilis* and *Bacillus caldolyticus* are capable of doing this [1-12].

Therefore, microbial environment induce certain chemical reactions in the copper ores.

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The synthesis of copper compound is induced using microbial environment under laboratory conditions in our research. The microbes such as *Stenotrophomonas maltophilia*, *Pseudomonas putida*, *Pseudomonas aeruginosa*, *Enterobacter cloacae*, *Staphylococcus sciuri*, *Acinetobacter cacloaceticus*, *Pantoeau agglomerans*, and *Flavobacterium* spp. have been used in the chemical process to synthesize CuSiO_3 . All these microbes were concentrated together in the experimental container at the same time during the synthesis of the material.

The biotechnology utilizes microbial environment to produce required chemical reactions. Chemical reactions take place as a result of interaction physical, chemical and biological components with each other. These interactions play an important role for molecule or an element to modify its physicochemical form. This process is called transformation. However, the change is not one way, environment also plays a vital role in the modification of temperature, chemical reaction (pH), conductivity etc.

Three major forms of transformations have been observed in the cycling of elements in nature:

1. Physical transformations which include fixation, dissolution, precipitation and Volatilization.
2. Chemical transformations which include precipitation and solubilization of minerals and other Molecules.
3. Biochemical transformations in which the physical and chemical changes are brought about by living microbial processes. For example, the microbial process is involved in fixation and transformations during biosynthesis or biodegradation.

Besides these, certain other processes such as 'Spatial translocations' of materials (from water column to sediments or from soil to atmosphere) and changes in the physical environment such as pressure due to piling may also be involved [1-12].

In this paper, the synthesis of CuSiO_3 has been carried out by using copper oxide (CuO) and quartz (SiO_2) under microbial environment. Atmospheric moisture (H_2O) also played an important role in this experiment. As stated above, we can surmise that microbes such as bacteria, virus, algae and fungi etc. are capable of transformations or perform chemical reactions.

II. OBJECTIVES

1. To synthesize CuSiO_3 using copper oxide (CuO) and quartz (SiO_2) in a laboratory utilizing microbial environment.
2. The XRD data of the synthesized material is compared with the standard reference XRD data for the confirmation of successful synthesis of CuSiO_3 .

III. GEOLOGICAL RELATIONSHIP

Microbial metabolism effects are present wide range of natural environments. Microbial fixation of copper plays an important role in its mineral formation. Supergene oxidation, leaching and sulfide have had an important role in mineralization of copper ores [13,14]. Supergene activity occurs due to the abrupt descent of the water table in the subplanar pediments in response to episodes of cordilleran uplift under semiarid climatic conditions [15-17]. Precipitation of copper minerals and mineraloids occurs from supergene activity through neutralization of strongly acidic water transfer.

Copper silicate precipitation is similarly due to fluid pH increase in an environment dominated by neutral-to-alkaline waters with low contents of SiO₄⁻⁴ derived through feldspar kaolinization in more proximal zones [18]. Microbes reproduce in such environments under acid rock drainage and supergene processes involving ores are influenced by the metabolic processes of methanogenic and methanotrophic microbes [19, 20]. Moreover, unless the microbial activity is ongoing, the microbes are unlikely to be preserved, so that the only record of their activity would be unambiguous geochemical products of the organisms, such as the carbon isotopes. The pH value have been the dominant control on the precipitation of copper mineral like chrysocolla in exotic deposits, attributing precipitation to the neutralization of a solution containing complexed Cu⁺² ions and dissolved silica as follows [19]



Gibbs Energy of reaction for above equation is 35.948 kJ/mol. Because the reaction has a positive ΔG, it is thermodynamically unlikely that amorphous chrysocolla would precipitate from a solution containing Cu⁺² and H₄SiO₄ unless the pH of the solution increases. So, microbes controls the chemical environment required for mineral formation in nature. This results in the geochemical process in the ores. This control of chemical environment by microbes to modify the material is called as Catabolic plasmids [21].

IV. EXPERIMENT

The existence of pure CuSiO₃ was considered non-existent. In physics, CuSiO₃ represents a further example of a quasi-one-dimensional spin (½), ant ferromagnetic Heisenberg chain system. These properties CuSiO₃ are important in semiconductor technology and other industrial technologies.

In our research, CuSiO₃ is synthesized in laboratory. To synthesize the required material, 100 mg copper oxide (CuO) and 100mg quartz (SiO₂) were mixed in a cylindrical container made up of non magnetic material. The microbes such as Stenotrophomonas maltophilia, Pseudomonas putida, Pseudomonas aeruginosa, Enterobacter cloacae, Staphylococcus sciuri, Acinetobacter cacloaceticus, Pantoeau agglomerans, and Flavobacterium spp. were concentrated together around the mixture of CuO and SiO₂ with some moist air already present inside the container. The experimental container which contained the mixture of compounds and microbes was kept under low magnetic field

of around 10⁻² Tesla. Under magnetic field, it was observed in some research papers that microbes move along a specific direction and they show some unique characteristics [22, 23]. The experiment was carried out for 12 hours at room temperature 27°C. After 12 hours the sample was taken out from the experimental container. Then XRD was carried out on the prepared sample which confirmed the formation of CuSiO₃. The microbial system concentrated around the mixture of CuO and SiO₂ played an important role to combine the molecules to form CuSiO₃.2H₂O. These microbes controlled the temperature, pH value, chemical potential of the reaction and various other parameters like physical environment to carry out chemical reaction [24,25]. The systematic arrangement of the experiment is shown in the figure 1.

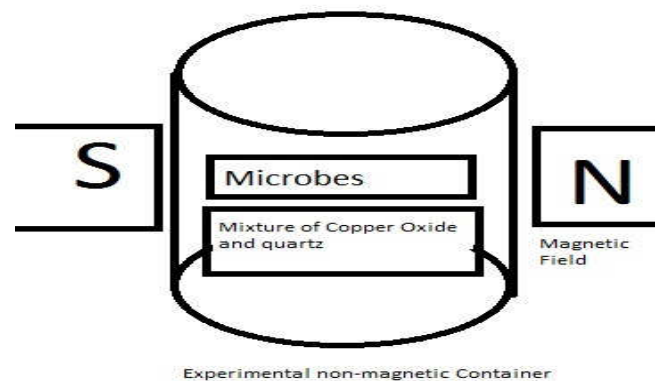


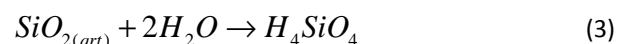
Figure 1 Experimental arrangement for the synthesis of CuSiO₃

The reaction between CuO and quartz involved the following steps in microbial environment in presence of atmospheric moisture [26].

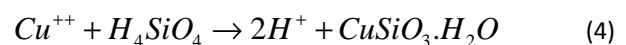
Copper oxide dissociated into ion Cu⁺⁺ in presence of moisture, XRD results showed the presence of Cu in the synthesized sample of CuSiO₃.H₂O



The quartz reacts with water molecules in atmosphere to form silicic acid.



The Cu⁺⁺ ions react with silicic acid to form CuSiO₃.H₂O



V. XRD ANALYSIS

The x-ray diffraction analysis was carried out on x-ray diffractometer. The synthesized CuSiO₃ sample, which was analyzed on XRD, consisted of x-ray tube with Cu K-Alpha. The chart depicted had peaks which ran from 5° to 90° for CuO, SiO₂ compounds and from 5° to 120° for synthesized CuSiO₃ material consuming current of 30mA and voltage of 40 kV at temperature 25°C. The XRD chart was given numbers coinciding the numbering of the sample peaks.

VI. RESULTS

The synthesis of copper silicate (CuSiO₃) using copper oxide, quartz and microbes was carried out successfully

under laboratory conditions at room temperature 27°C. The formation of CuSiO_3 is confirmed by XRD data by comparing it with standard reference data given in table 1. The XRD pattern of CuO and SiO_2 are shown in figure 2 and figure 3 respectively. The XRD pattern of synthesized CuSiO_3 is shown in figure 4. XRD results showed the presence of Cu which is important formation of Copper silicate ($\text{CuSiO}_3 \cdot \text{H}_2\text{O}$).

Table 1 XRD analysis data for synthesized CuSiO_3 sample and reference data

S. No.	Interpretation of XRD data for the synthesized sample			d-spacing from the reference XRD data file	
	2θ values	d-spacing	Relative intensity	d-spacing	Relative intensity
1	35.66	2.58	100	2.59	100
2	36.59	2.45	14.03	2.44	40
3	42.51	2.12	3.22	2.11	50
4	61.64	1.50	23.34	1.50	40
5	66.37	1.41	17.19	1.42	50

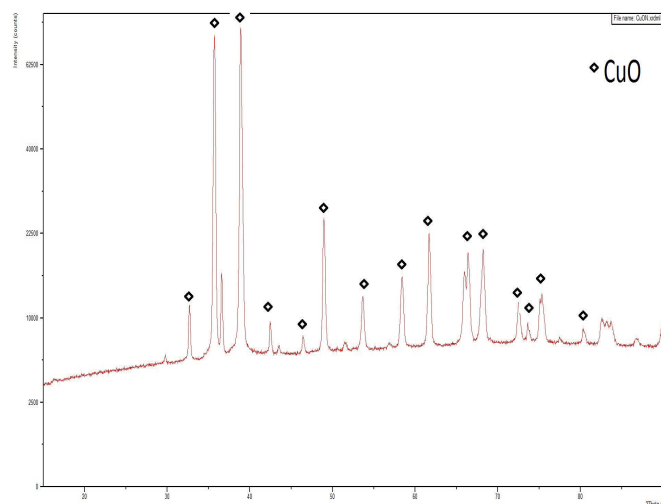


Fig. 2 XRD Pattern for copper oxide (CuO) used in the experiment.

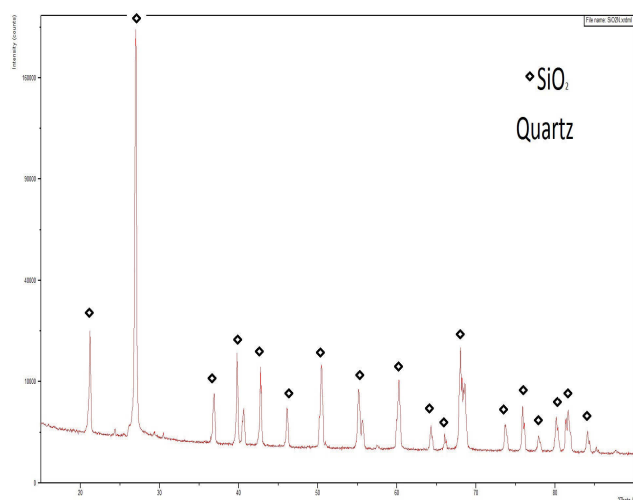


Fig. 3 XRD Pattern for Quartz (SiO_2) used in the experiment.

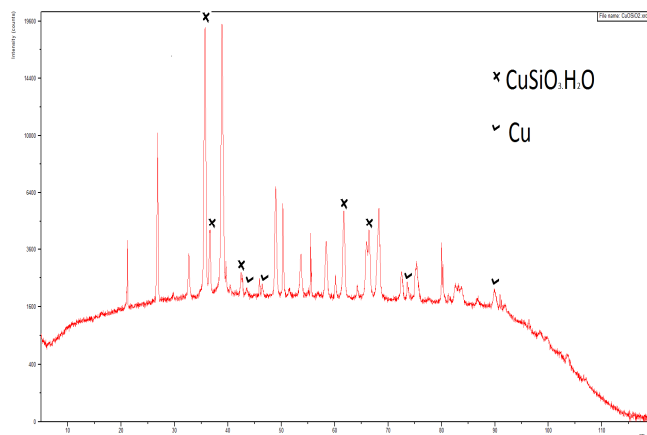


Fig. 4 XRD Pattern for synthesized Copper Silicate ($\text{CuSiO}_3 \cdot \text{H}_2\text{O}$).

VII. CONCLUSIONS

Microbes carry out oxidation-reduction reactions in order to obtain energy for growth and cell maintenance. The amount of energy released per electron equivalent of an electron donor oxidized varies considerably from reaction to reaction. Reduction reaction requires electron acceptor type reaction. Full energy reaction ΔG is obtained; the free energy for the donor half reaction is added to the acceptor half reaction [27-29]. The microbes play an important role in many chemical reactions like photosynthesis, fermentation, leaching and oxidation-reduction reactions in Nature. The microbes have an accessory DNA element present in the cytoplasm called as catabolic plasmids. The plasmids are circular and confer on their host the ability to transform or recycle not only complex molecule, but naturally occurring and synthetic molecules as well [21].

In nature, geochemical reactions occurred in the copper ores where microbes played an important role for their transformation into a key or important mineral. For example precipitation of copper mineral like chrysocolla (copper silicate) was carried out by specific microbes [19]. So, copper silicate can be prepared in laboratory by using microbes. In this paper, an experiment was carried out to synthesize the CuSiO_3 compound under microbial environment in low magnetic field. The microbes modified the molecules copper oxide (CuO) and quartz (SiO_2) mixture in presence of moisture (H_2O) to a chemical formula Copper silicate (CuSiO_3). The confirmation of formation of copper silicate was done by XRD data. The difference between the above discussed experiment and geochemical process in natural copper silicate ores is the change in microbial environment and respective compounds used for synthesis.

In the above discussed experiment, all the microbes *Stenotrophomonas maltophilia*, *Pseudomonas putida*, *Pseudomonas aeruginosa*, *Enterobacter cloacae*, *Staphylococcus sciuri*, *Acinetobacter cacloaceticus*, *Pantoeau agglomerans*, and *Flavobacterium spp.* have the ability to change or modify the substance. All these microbes have the ability to control or change chemical potential, free energy, pH value, temperature, oxidation-reduction process and physical environment like pressure required for proper chemical reaction between two or more molecules [24,25]. This experimental result concludes that microbes

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have the ability to carry out chemical reaction between copper oxide and quartz to transform them into copper silicate.

REFERENCES

1. R. M. Atlas, and R. Bartha, Microbial ecology. Fundamentals and Applications. Benjamin/Cumming Pub. Co., Inc., 1998.
2. L. Bhatnagar, and B. Z. Fathepure, Mixed cultures in Detoxification of hazardous waste. In: Mixed Cultures in Biotechnology, Zeikus, G. and Johnson, E. A., eds., McGraw-Hill, Inc., p. 293-340, 1991.
3. T.D. Brock, Biology of Microorganisms. 2/e. Prentice-Hall, Englewood Cliffs, NJ., 1974.
4. E.S. Deevey Jr., Mineral cycles. Sci. Amer., 223(3), p.149-158, 1991.
5. R.L. Dimmick, H. Wolochow, and M.A. Chatigny, Evidence that bacteria can form new cells in airborne particles. Appl. Environ. Microbiol., 37, p.924-927, 1979.
6. P.N. Hobson, and N.J. Poole, In: Microorganisms in action: Concepts and applications in Microbial Ecology. Blackwell Sci. Pub., Oxford., p.302, 1988.
7. W.E. Krumbein, On the precipitation of aragonite on the surface of marine bacteria. Naturwissenschaften., 61, p.167, 1970.
8. S.I. Kuznetsov, M.V. Ivanov, and N.N. Lyalikova, Introduction to Geological Microbiology. McGraw Hill, New York., p. 26, 1963.
9. R. Lynd Lee, J. Weimer Paul, H. van Zyl Willem, and S. Pretorius Isak, Microbial Cellulose Utilization: Fundamentals and Biotechnology. Microbiol. Mol. Biol. Rev., 66 (3), p.506-577, 2000.
10. R.Y. Morita, Calcite precipitation by marine bacteria. Geomicrobiol. J., 2, p. 63-82, 1980.
11. D.M. Webley, R. B. Duff, and W.A. Mitchell, A plate method for studying the breakdown of synthetic and natural silicates by soil bacteria. Nature, 188, p.766-767, 1960.
12. T. Yanagita, Natural Microbial Communities: Ecological and physiological features. Japan Sci. Soc. Press, Tokyo and Springer-Verlag, Berlin, p. 417-425, 1990.
13. R. H. Sillitoe, Epochs of intrusion-related copper mineralization in the Andes: Journal of South American Earth Sciences, 1, p. 89-108, 1988.
14. R.H. Sillitoe, Supergene oxidized and enriched porphyry copper and related deposits: Economic geology, 100, p. 723-768, 2005.
15. R.H. Sillitoe, Studies on the controls and mineralogy of the supergene alteration of copper deposits, northern Chile: [Dissertation], London, England, University College London., p.498, 1969.
16. C. Mortimer, The Cenozoic history of the southern Atacama desert, Chile: London, Journal of the Geological Society, 129, p. 505-526, 1973.
17. A.H. Clark, R.M. Tosdal, E. Farrar, and V.A. Plazolles, Geomorphologic environment and age of supergene enrichment of the Cuacone, Quellaveco, and Toquepala porphyry copper deposits, southeastern Peru: Economic geology, 85, p.1604-1628, 1990.
18. D.W. Newberg, Geochemical implications of chrysocolla-bearing alluvial gravels: Economic geology, 62, p. 932-956, 1967.
19. D.B. Johnson, and K.B. Hallberg, The microbiology of acidic mine waters: Research in Microbiology, 154, p. 466-473, 2003.
20. D.L. Kelley, K.D. Kelley, W.B. Coker, B. Caughlin, and M.E. Doherty, Beyond the obvious limits of ore deposits: The use of mineralogical geochemical, and biological features for the remote detection of mineralization, Economic geology, 101, p. 729-752, 2006.
21. M.J. Pemberton, and R. Schmidt, Catabolic Plasmids, Encyclopedia of Life Sciences, John Wiley & Sons, Ltd., 2001.
22. Svetlozar Velizarov, Electrical and Magnetic fields in microbial biotechnology: possibilities, limitations and perspectives, Electro and Magnetobiology, 18(2), p.185-212, 1999.
23. Lukas Fojt, Ludek Strasak, Vladimir Vetterl, and Jan Samarda, Comparison of the low-frequency magnetic field effects on bacteria Escherichia coli, Leclercia adecarboxylata and Staphylococcus aureus, Bioelectrochemistry, 63, p.337-341, 2004.
24. S.R. Gopishetty, M.T. Louie, and M.V. Subramanian, Microbial Transformations of Natural Products, Phytochemistry and pharmacognosy, Encyclopedia of life support systems.
25. Mohamed, S. Mervat, Degradation of methomyl by the novel bacterial strain Stenotrophomonas maltophilia M1, Electronic Journal of Biotechnology, 12 ()2009.
26. Naama Shlomovitch, Miryam Bar Matthews, Amit Segev, and Alan Matthews, Sedimentary and epigenetic copper mineral assemblages in the Cambrian Timna Formation, southern Israel, Isr. J. Earth Sci., 48, p.195-208, 1999.
27. J.E. Bailey, and D.F. Ollis, Biochemical Engineering Fundamentals, McGraw-Hill, New York, 1986.
28. E.H. Battley, Energetics of Microbial Growth, Wiley, New York, 1987.
29. P.L. McCarty, Stoichiometry of biological reactions, Prog. Water Technol., 7, pp.157-172.