# Evaluation of Phosphate and Carbonate Based Biominerals For In-situ recovery (ISR) operations

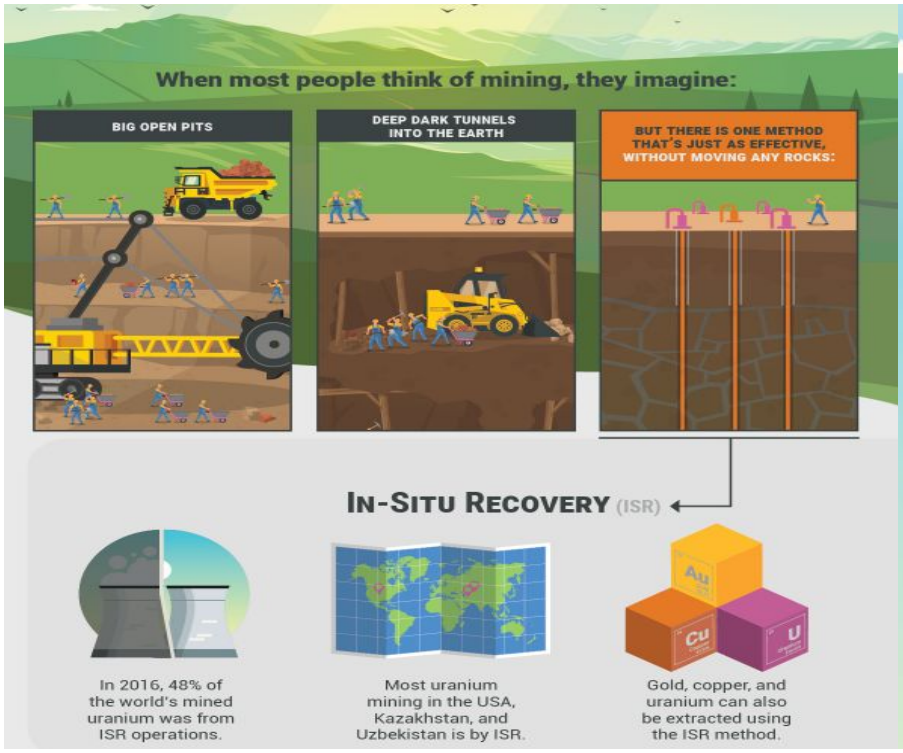
Presenter: Pelin Polat
PhD student
School of Civil and Mechanical Engineering
Curtin University
WA, Australia

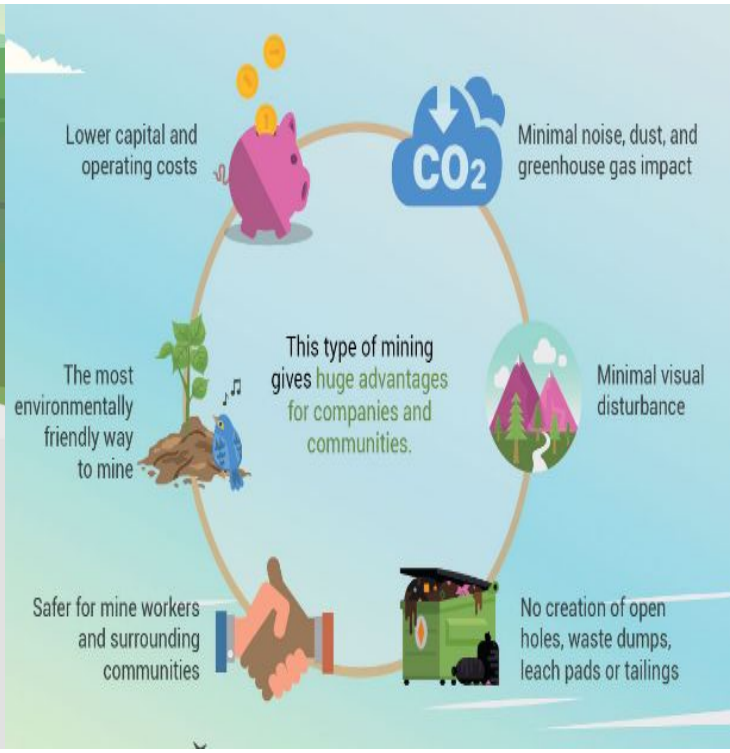
ALTA 2024

## Content

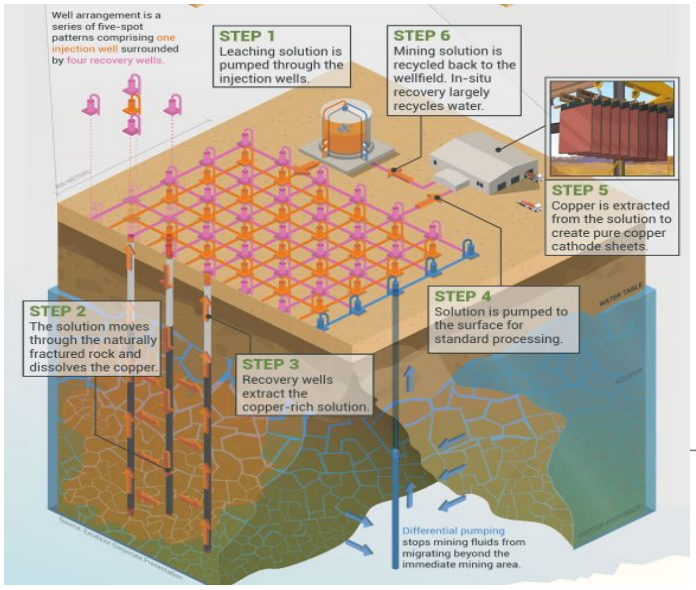
- Introduction to ISR
- Barriers and containments in practice
- Biocementation
- Our research
- Outcomes

# Background






**Commonly used lixiviants in ISR operations**

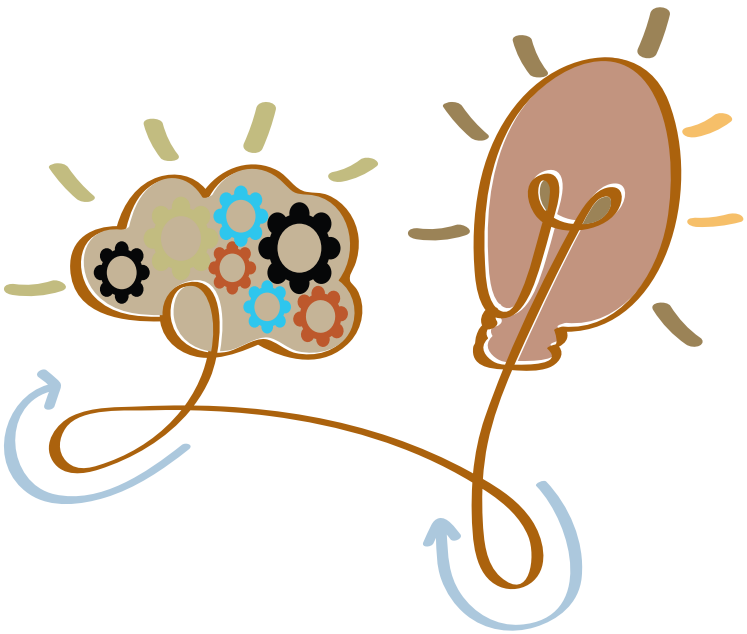
| Lixiviant | Co-reagents | Conditions | Dissolved metal species |
|---|---|---|---|
| Glycine | NaOH, oxygen | High pH | Au, Cu, Co, Fe, Si, Al, Ni, Zn, Ca, |
| Sulfuric Acid | | Low pH | Cu, Ni, Sc, Re, REES, Y, Se, Mo, V, U |
| Ammonium sulfate | Ammonia, oxygen | High pH | Cu |
| Water | | Brine | K, Na, Li |

## Challenges of ISR

- **Containment of leaching agents**
- Monitoring and managing subsurface fluid flow
- Ensuring minimal disturbance to surrounding ecosystems
- Addressing potential groundwater contamination concerns

**Different types of barriers and containments in practice**



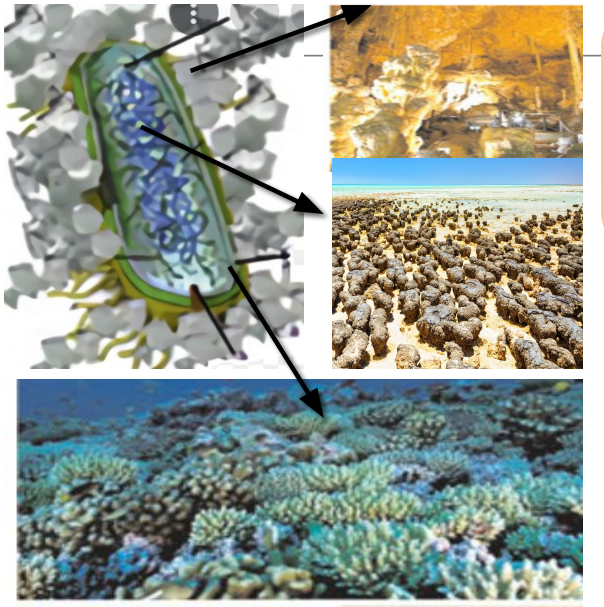



**The Problems With Current Barrier And Containment In Practice**

- **Inefficacy**
- **Viscosity**
- **Environmental toxicity**
- **Cost**

***Get inspiration from…. Nature***

# Microbially induced mineral precipitation (biocementation)



**Natural process by which microbes form inorganic minerals and polymers as part of their basic metabolic activities**

**Recorded in a range of geological structures varying from travertines, corals, stromatolites to beach rocks in terrestrial and marine environments**

Wide range of minerals can precipitate

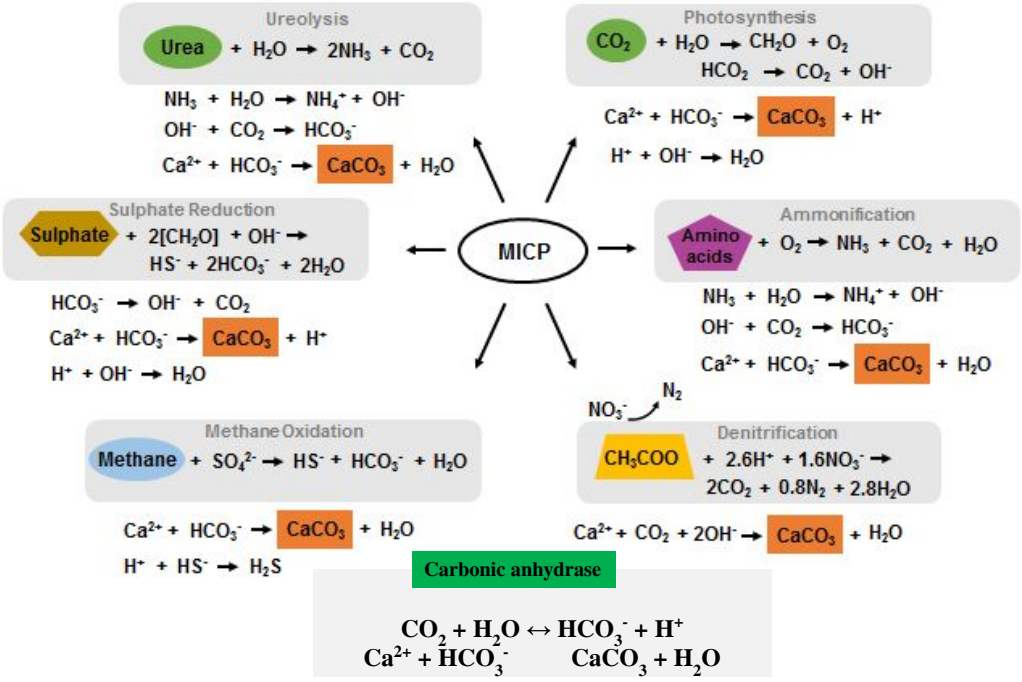
- Carbonates
- Phosphates
- Sulphides
- Oxides
- Silicates

Bio-mineralization of calcium carbonates in natural structures (A) Corals (B) Stromatolites (C) Limestone cave www.sciencedaily.com

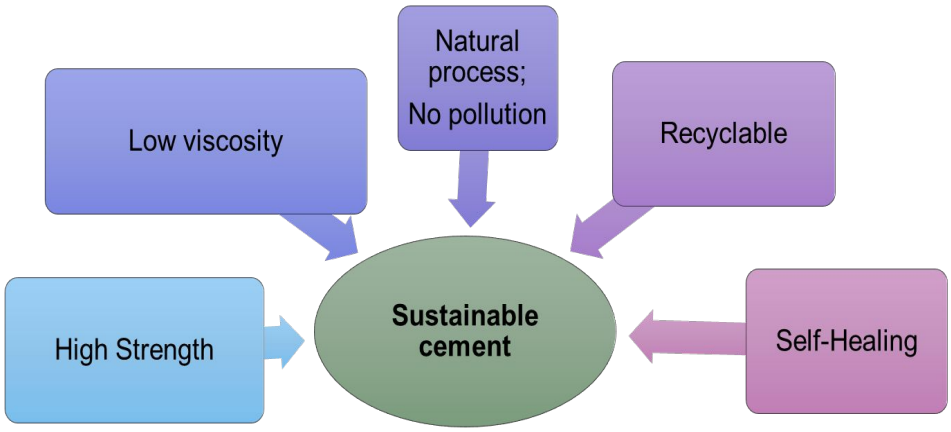
(Murugan, et al. 2021; Dhami, et al., 2013)



# *Bacterial metabolic routes in MIMP*

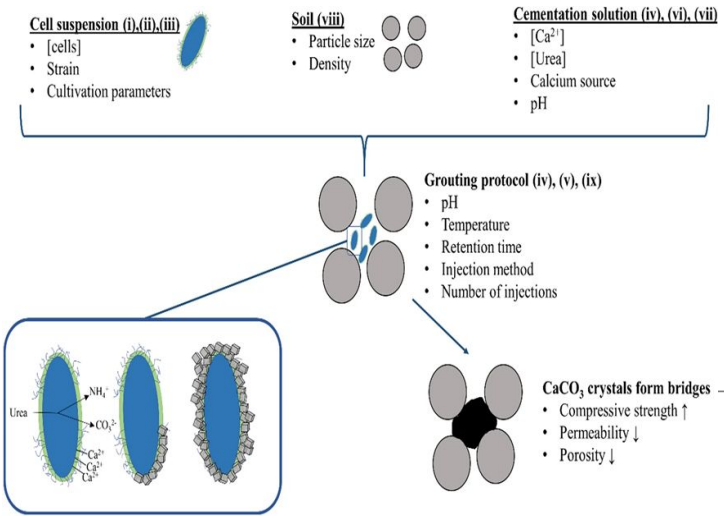


# Benefits of MIMP






# Microbially induced calcium carbonate precipitation (MICP)




Rev Environ Sci Biotechnol (2023) 22:1059–1091
https://doi.org/10.1007/s11157-023-09674-z

REVIEW PAPER

**Erosion mitigation with biocementation: a review on applications, challenges, & future perspectives**

Anant Aishwarya Dubey · Navdeep Kaur Dhami · K. Ravi · Abhijit Mukherjee

https://doi.org/10.1007/s11440-022-01536-2

RESEARCH PAPER

**Biopolymer-biocement composite treatment for stabilisation of soil against both current and wave erosion**

Anant Aishwarya Dubey[1,2] · Jack Hooper-Lewis[2] · K. Ravi[1] · Navdeep Kaur Dhami[2] · Abhijit Mukherjee[2]

Original Article

WM&R

**Effective method for upcycling construction and demolition waste into concrete: A life cycle approach**

Abhijit Mistri[1,2,3], Venkata Ravi Sankar Cheela[4,5], Brajesh Kumar Dubey[4], Navdeep Dhami[2], Sriman Kumar Bhattacharya[1], Abhijit Mukherjee[2] and Sudhirkumar V Barai[1,6]

# Limitations of MICP

- Extreme conditions such as lower pH conditions
- By-products and Uncontrolled Growth
- Obtaining Uniform Treatment
- Economic



(Phillips et al., 2013, Farah et al., 2016, Zhu and Maria 2016 Hart et al.,2012)

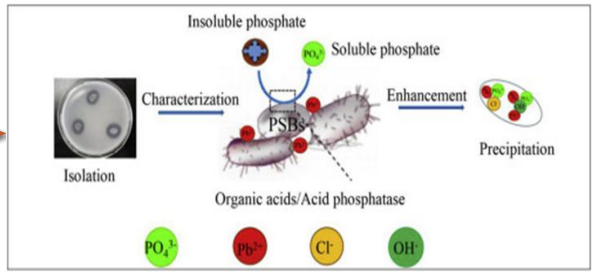
# Microbially induced phosphate precipitation

- Wide range of phosphate compounds can precipitate
- Tricalcium phosphate
- Struvite
- Apatite
- Baricite
- Vivianite
- Variscite

BACTERIAL ENZYMES

Acid phosphatases enzymes

Such as *Bacillus sp. and Pseudomonas sp.*




## Advantages of bio-phosphates as grout material

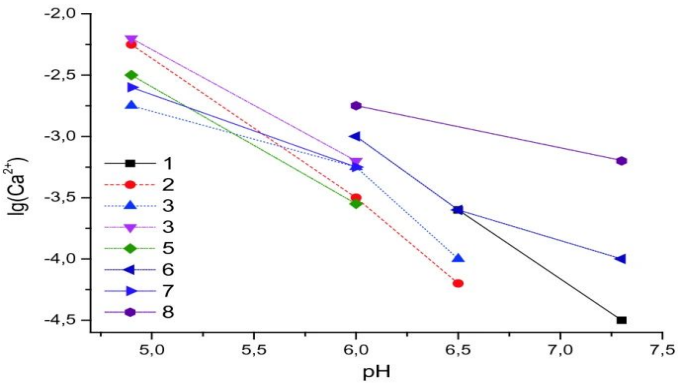
- Nontoxic
- Better performance and stability under low pH conditions
- Can be extracted from natural sources as fertilizers and bones of livestock

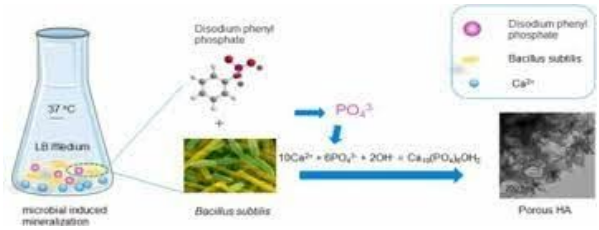
(Qian C, 2018)

**Hydroxyapatite (HAP) $Ca_5(PO_4)_3(OH)$**

$$10\ Ca(OH)_2 + 6\ H_3PO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 18\ H_2O$$

- Thermodynamically stable in its crystalline state
- Similar composition to bone mineral
- Biological sources or wastes such as mammalian bone, marine or aquatic sources, shell sources, and plants and algae and also from mineral sources
- Can be synthesised chemically or microbiologically




Experimental data on hydroxyapatite solubility in aqueous solutions at different pH from literature sources: (1) Rootare et al. (1962), (2) Wier et al. (1971), (3) Avnimele et al. (1973), (4) Chuong (1973), (5) McDowell et al. (1977), (6) Bell et al. (1978), (7) Verbeeck et al. (1980), (8) Mahapatra et al. (1982)



# Methodology

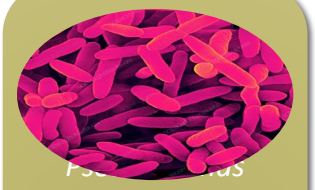
*Sporosarcina pasteurii ATCC 11891*

Gram positive
Ureolytic bacterial culture
Has the ability to precipitate calcite
(Dhami et al., 2012)

*Bacillus subtilis ATCC 6051*

Gram-positive
Biofilm producing
Ureolytic bacterial culture capable of producing nano-hydroxyapatite

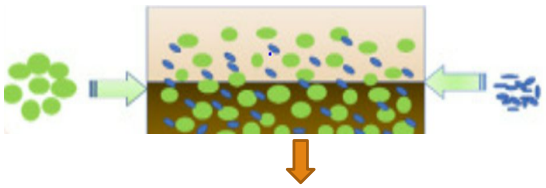
(Yu et al., 2021).



*ATCC13525*

*Gram – negative*
*Strong biofilm producing*
Capable of producing nano-hydroxyapatite
(Turner et al., 2017)

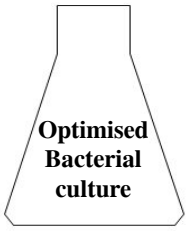
Bacteria + Cementation Fluid



Growth condition optimization
Enzyme activity measurements

Crystal precipitation

Crystal analyses
Scanning Electron Microscopy
X- ray Diffraction
Nanomechanical characterisation
Acid Solubility Test




+

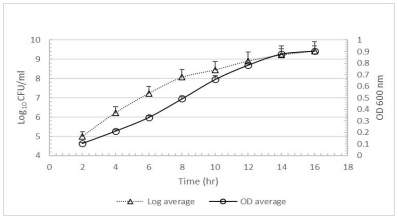
Mine tailings

- Mineral Characteristic
- Hydraulic characterisation
- Service life assessment

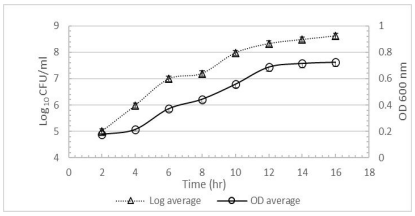


# Results

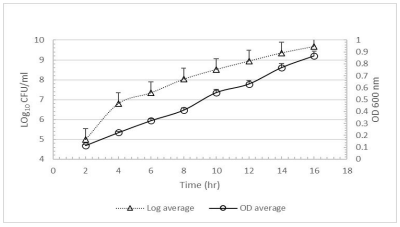
**. Growth curve for 3 different cultures**




*S. pasterurii*



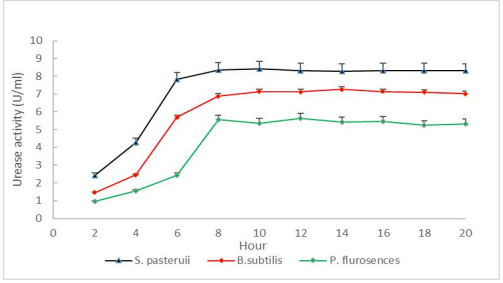

*B. subtilis*

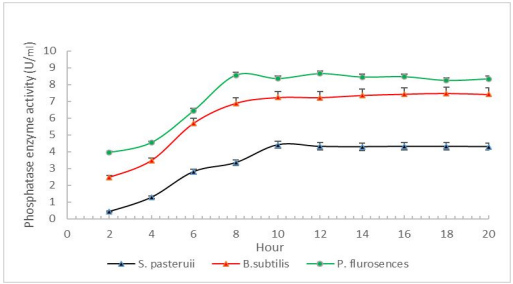



*P. fluorescence*

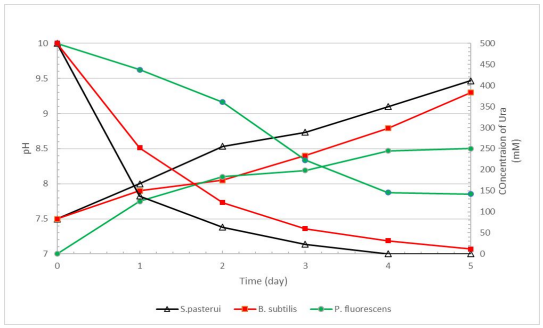
- optical density (OD 600 nm) and the corresponding bacteria concentration (CFU ml ) are plotted vs. time. Data of concentration curves are reported until the stationary phase

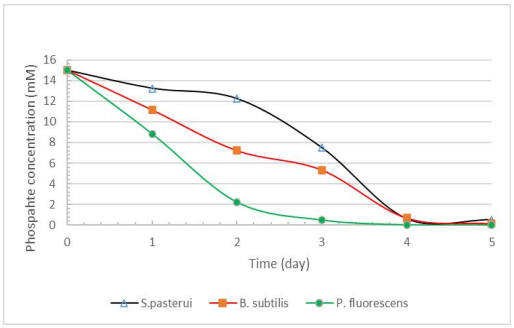
**. Urease and Alkaline Phosphatase Enzyme Activities**



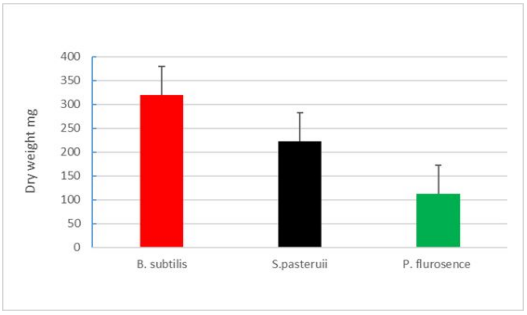



## . Concentration of soluble calcium ions, phosphate and pH over the time



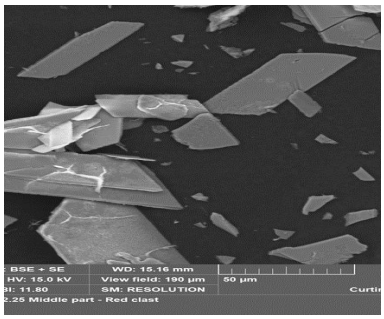



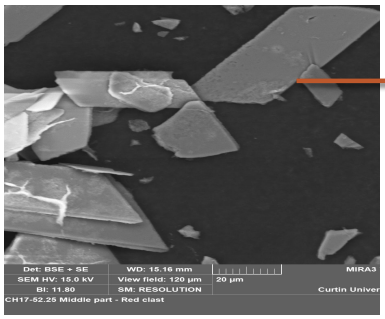

- **Dry weight of insoluble precipitate**



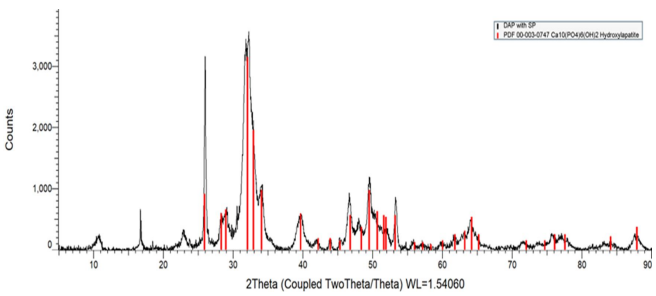



- **Precipitation by *S. pasteurii***

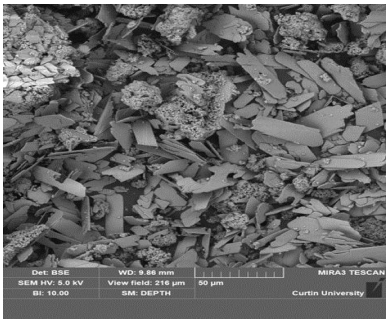


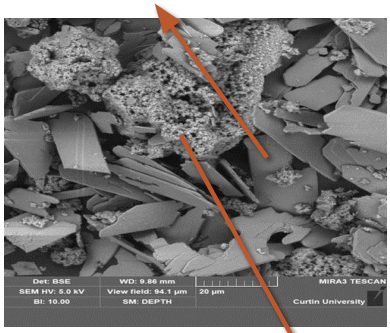


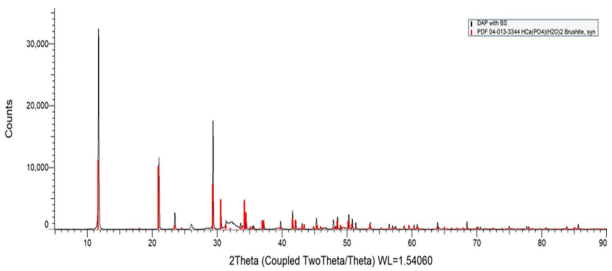
- XRD results




- **Precipitation by *B. subtilis*** Hydroxyapatite

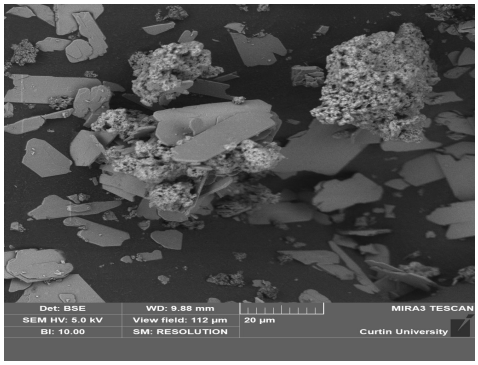




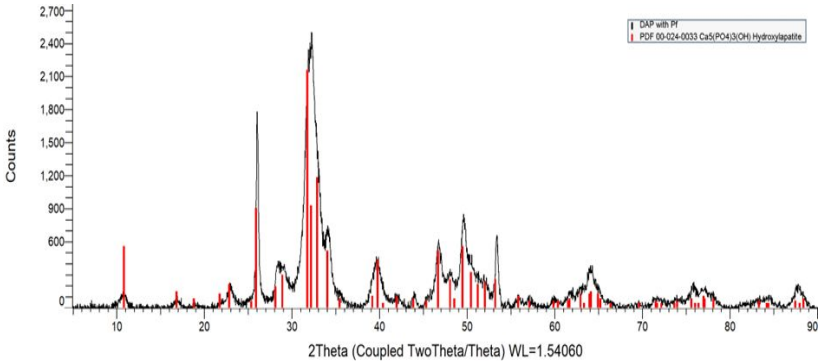



Brushite

## Precipitation by *P. flurosence*

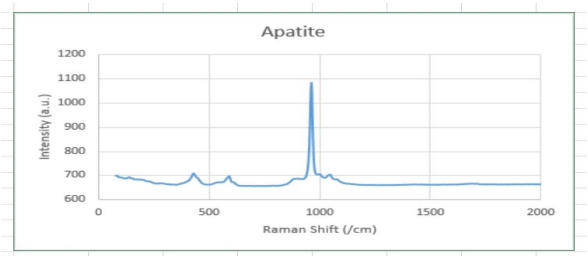


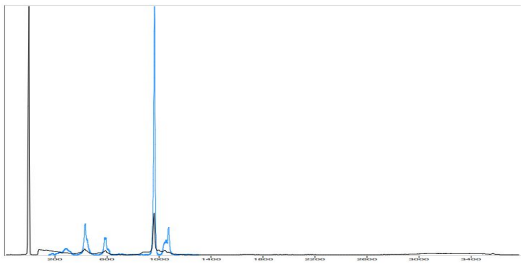

XRD results



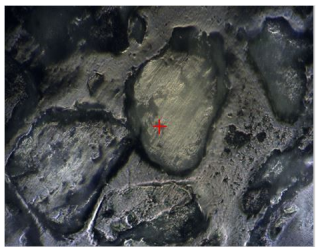


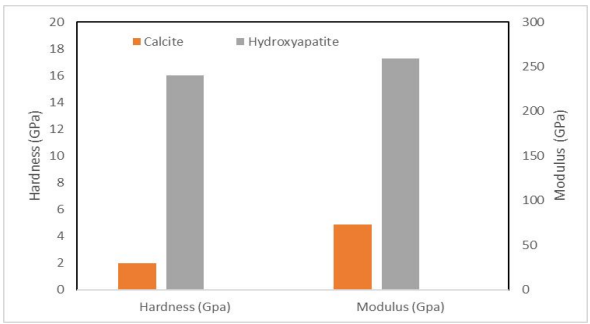

## Raman Analysis For HAP Precipitation



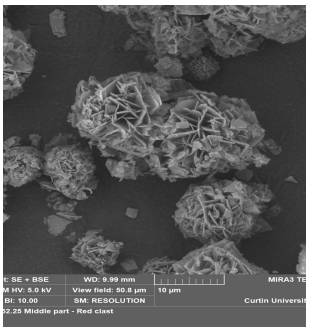



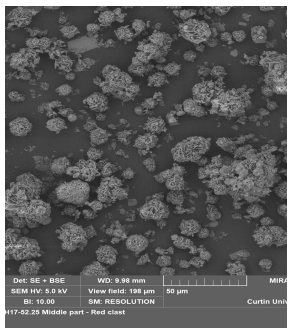
## Nanoindentation Results For HAP

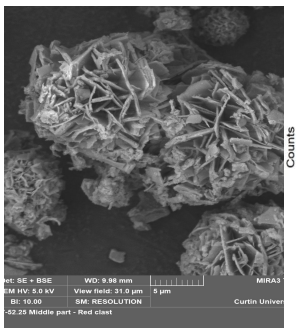




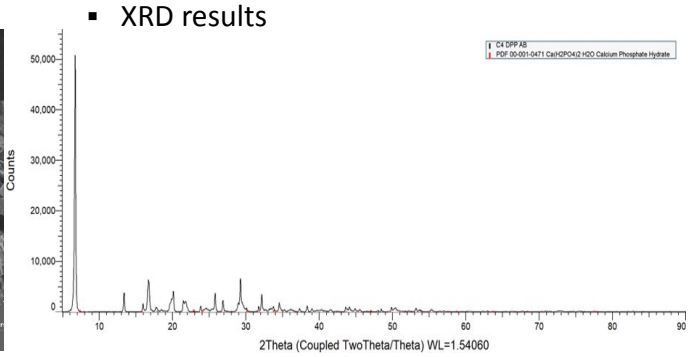
- **Abiogenic precipitation**



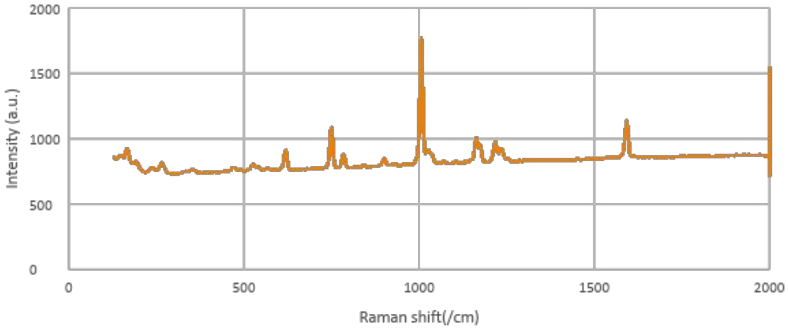


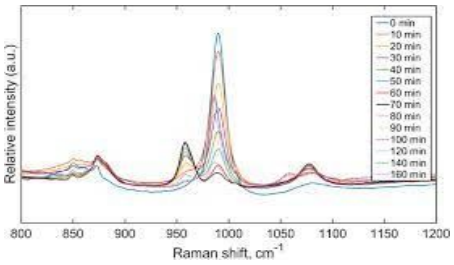


- XRD results




- Raman result



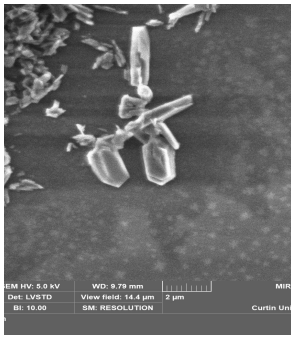



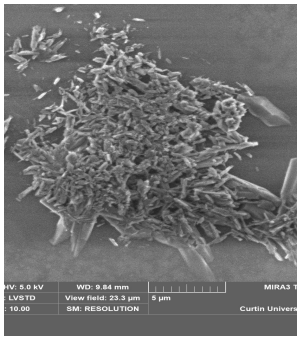

Hang, B. 2018



**. The impact of biofilm production on mineral precipitation**

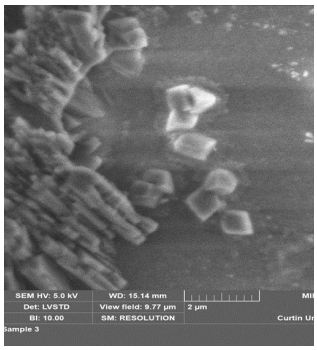
***B.subtilis*** **vs** ***S.pasteurii***

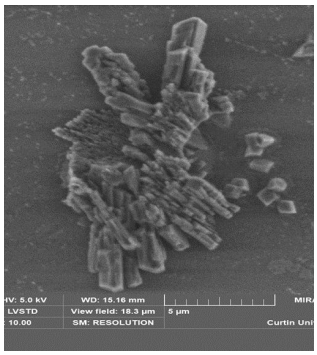




6hr after treatment

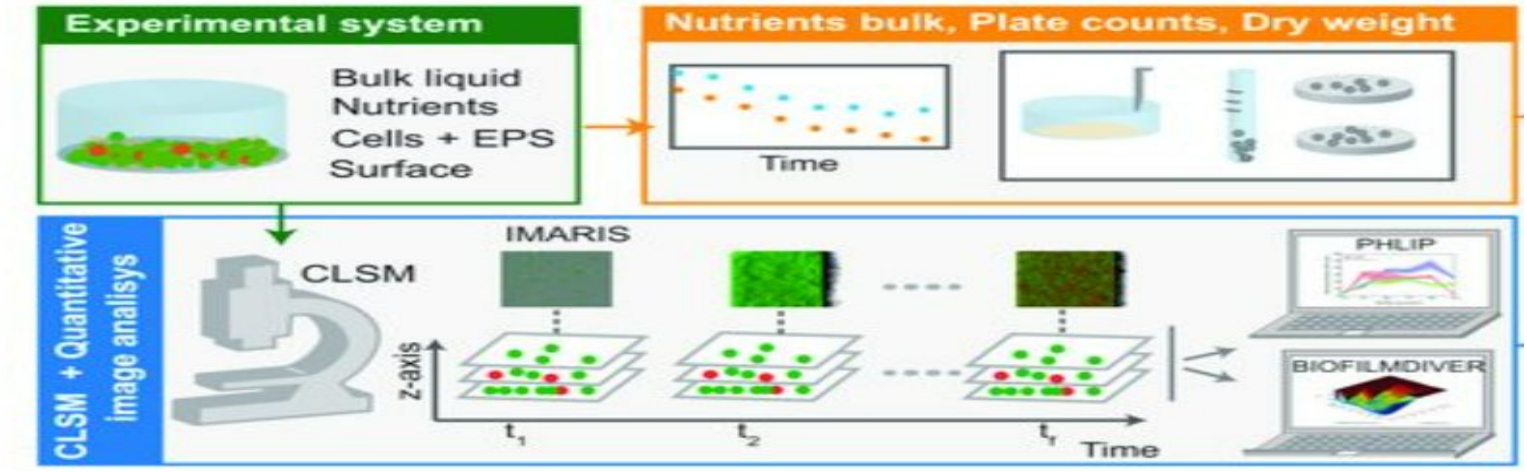
12hr after treatment

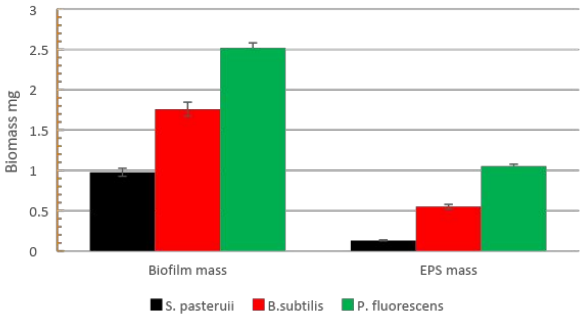


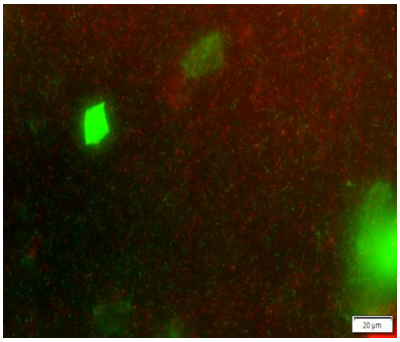


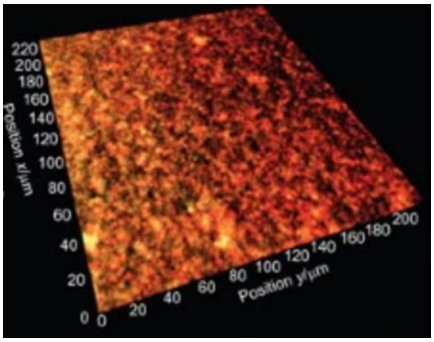
6hr after treatment

12hr after treatment



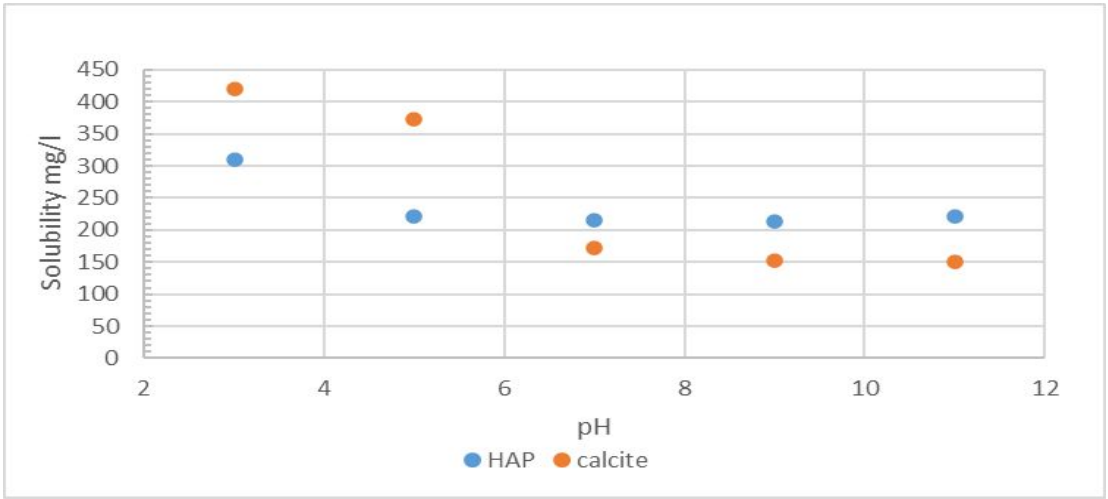



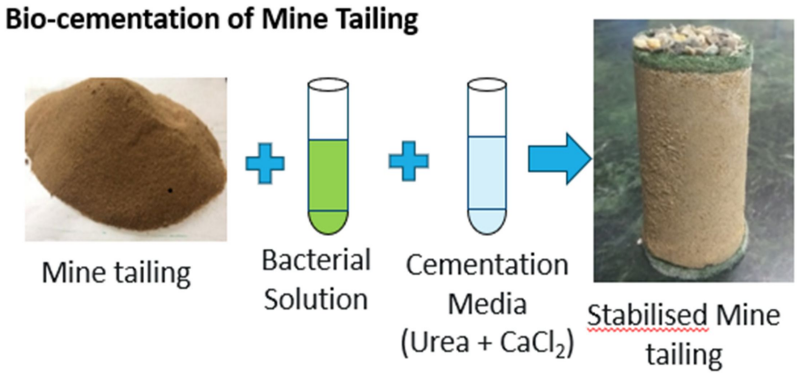


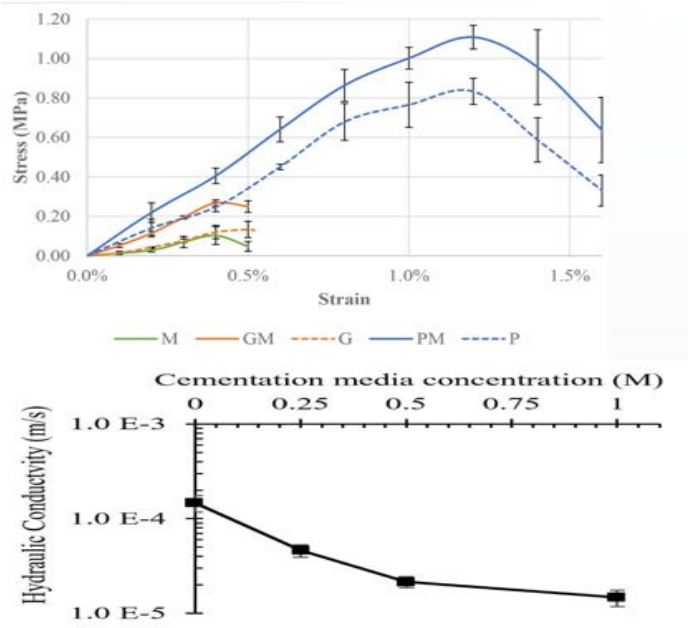



**. Acid solubility of Biogenic Hydroxyapatite/ Calcite**



# Ongoing Experiments







ALTA 2024

# Findings

- Successful production of phosphate biocement as hydroxyapatite achieved
- Bacterial culture plays a crucial role in determining the morphological-mineralogical-nanomechanical properties of precipitated hydroxyapatite
- Biofilm and extrapolymeric substance producing cultures can create uniformity in HAP crystal orientation and pattern
- Biogenic hydroxyapatite demonstrates higher stability in pH environments (>5)
- Co-precipitation of carbonate and phosphate biocement offers promising solution for sustainable barriers
- Further studies to be conducted to investigate the efficacy of biocement barriers under simulated subsurface conditions over longer durations

ALTA 2024

# Acknowledgments


# References

Gat D, Ronen Z, Tsesarsky M. Soil Bacteria Population Dynamics Following Stimulation for Ureolytic Microbial-Induced CaCO3 Precipitation. Environmental Science & Technology. 2016;50(2):616-624. doi:10.1021/acs.est.5b04033

Whiffin VS, van Paassen LA, Harkes MP. Microbial Carbonate Precipitation as a Soil Improvement Technique. Geomicrobiology Journal. 2007;24(5):417-423. doi:10.1080/01490450701436505

1Dejong JT, Mortensen BM, Martinez BC, Nelson DC. Bio-mediated soil improvement. Ecological Engineering. 2010;36(2):197-210. doi:10.1016/j.ecoleng.2008.12.029

14. Hammes F, Verstraete* W. Key roles of pH and calcium metabolism in microbial carbonate precipitation. Reviews in Environmental Science and Biotechnology. 2002;1(1):3-7. doi:10.1023/A:1015135629155

Yu X, Jiang J. Mineralization and cementing properties of bio-carbonate cement, bio-phosphate cement, and bio-carbonate/phosphate cement: a review. Environmental Science and Pollution Research. 2018;25(22):21483-21497. doi:10.1007/s11356-018-2143-7

Qian C, Yu X, Wang X. Potential uses and cementing mechanism of bio-carbonate cement and bio-phosphate cement. 2018;8(9):095224. doi:10.1063/1.5040730

Maxwell RF, Krista G, David F, Melanie JF. Physiological and genetic characterization of calcium phosphate precipitation by Pseudomonas species. Scientific Reports. 2018;8(1):1-14. doi:10.1038/s41598-018-28525-4

Sassoni E, Naidu S, Scherer GW. The use of hydroxyapatite as a new inorganic consolidant for damaged carbonate stones. Journal of Cultural Heritage. 2011;12(4):346-355. doi:10.1016/j.culher.2011.02.005

Naidu S, Blair J, Scherer GW. Acid-Resistant Coatings on Marble. American Ceramic Society. Journal of the American Ceramic Society. 2016;99(10):3421-3428. doi:10.1111/jace.14355

.Sassoni E. Hydroxyapatite and Other Calcium Phosphates for the Conservation of Cultural Heritage: A Review. Materials (Basel, Switzerland). 2018;11(4) doi:10.3390/ma11040557

Cardew PT, Davey RJ. The Kinetics of Solvent-Mediated Phase Transformations. Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences (1934-1990). 1985;398(1815):415-428. doi:10.1098/rspa.1985.0043

Putnis A, Putnis CV. The mechanism of reequilibration of solids in the presence of a fluid phase. Journal of Solid State Chemistry. 2007;180(5):1783-1786. doi:10.1016/j.jssc.2007.03.023

Wang L, Ruiz-Agudo E, Putnis C, Menneken M, Putnis A. Kinetics of calcium phosphate nucleation and growth on calcite: Implications for predicting the fate of dissolved phosphate species in alkaline soils. 2012

Pedrosa ET, Putnis CV, Putnis A. The pseudomorphic replacement of marble by apatite: The role of fluid composition. Chemical Geology. 2016;425(C):1-11. doi:10.1016/j.chemgeo.2016.01.022

Turner RJ, Renshaw JC, Hamilton A. Biogenic Hydroxyapatite: A New Material for the Preservation and Restoration of the Built Environment. ACS Appl Mater Interfaces. 2017 Sep 20;9(37):31401-31410.

doi: 10.1021/acsami.7b07927. Epub 2017 Sep 5. PMID: 28737897.

Hart, Peter & Colson, Gary & Burris, Jeffery. (2012). Application of Carbon Dioxide to reduce water side lime scale in heat exchanges. J. of Science and Technology for Forest Products and Processes. 1. 67-70.