

Structural, Chemical Etching and Dissolution Studies on Gel Grown Urinary Crystals

¹Shailesh S Dongare

¹Assistant Professor Department of Physics,
S. G. Arts, Science and G. P. Commerce College, Shivle, Murbad, 421401, India
(Affiliation: University of Mumbai)

Abstract: Most common urinary crystals (calculi) encountered are Brushite and Struvite. These crystals have been grown by single diffusion gel growth technique. Well defined kite shaped struvite crystals suitable for dislocation studies along with cluster shaped brushite crystals were obtained in about 25 days' time. The structural studies show single phase formation with orthorhombic symmetry. On addition of barley extract from the top of the gel, the dissolution /denaturation of crystals occurs which in turn is seen to affect the XRD structure in solid state. The 'a' and 'c' lattice parameters are found to change with least effect on the 'b' parameter. Surface topography reveals clustered- spear shaped brushite crystals, which dissolve on treatment with barley extract. Perforations have been recorded on the well grown struvite crystals treated with barley extract. The crystals are water insoluble and etching studies show well defined, oriented etch pits on the habit face treated with sulphuric acid. Barley extract as well as acidic medium helps in dissolution/ denaturation of urinary calculi (crystals), as recorded in the study.

Keywords: Sodium meta-silicate (SMS), Brushite (B), Struvite (S), XRD, Surface topography

I. INTRODUCTION

Urinary crystals, often seen in medical practice, usually consist of calcium oxalate and calcium phosphate. These crystals significantly contribute to kidney stones, which are a major health concern. In this study, Brushite and Struvite crystals were successfully grown using the single diffusion gel method in sodium metasilicate gel. Brushite crystals formed from calcium chloride with orthophosphoric acid, while Struvite crystals developed from ammonium dihydrogen phosphate and magnesium acetate with acetic acid. Calcium stones are the most common in urinary stones. Calcium oxalate stones are more common than Calcium phosphate, also there is most common crystals are oxalate-calcium phosphate are observed in investigation kidney stone. Also phosphate is present in urinary calculi as either apatite $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$ or Brushite $[\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}]$. There is another urinary calculi crystal observed in kidney stone, in the contamination of ammonium dihydrogen phosphate and magnesium phosphate hexahydrate $[\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}]$ are major crystalline component forms named as Struvite [1-4].

The brushite and struvite stones have been grown and characterized by various researchers. The first attempt to dissolve calcium stone was made by Hellos Tron and Albright in 1930. using combination of sodium citrate and citric acid. In which observed that citrate prevents crystallization, that reduced ionic calcium concentration [5-6]. In our studies we have grown the urinary crystal by single diffusion technique and characterized them by XRD with and without addition of barley extract on the grown brushite and starvite crystals.

The main goal is to examine the structure of newly grown urinary calculi and to see how barley extract affects the structure and dissolution of crystals. In addition, we also performed chemical etching on these water-insoluble urinary stones to understand their surface changes after treatment. The etching process used agents like concentrated sulfuric acid, which helped us observe detailed changes in the surface of the crystals.

II. CRYSTAL GROWTH

Glass test tubes of 2.5 cm diameter and 15 cm in length were used for growing the crystals. Sodium meta-silicate (SMS) gel was prepared from AR grade SMS in distilled water at room temperature by single diffusion method [7,8]. For growing brushite crystals, sodium metasilicate solution of specific gravity 1.06 g/cc was acidified by adding appropriate amount of orthophosphoric acid thereby maintaining pH at 6.5. This mixture is subsequently transferred into different test tubes. After gelation takes place (24 Hrs), 10ml solution of one molar calcium chloride (CaCl_2) was carefully poured on set gel. The crystals were found to be growing very rapidly within 48 hrs from the pouring the solution. Elongated, platelet type and star shaped crystals were are formed at the center of the gel medium. In 15 days' time the crystals achieved a maximum length of 2-5mm. Lower values of pH (= 4.5), few platelet type crystals are seen whereas at higher pH (=7) star shaped crystals together with and platelet type ones have been observed. The density of the brushite crystals was found to be 2.28g/cc. For growing the struvite crystals, sodium meta-silicate solution of specific gravity 1.06 g/cc was acidified by adding appropriate amount of acetic acid. So that pH=7 was maintained. To this, 1.5 molar ammonium

dihydrogen phosphate solution was added after transferring it to a new test tube. The gel is allowed to set for 24 hrs to which 10 ml of 1.5 molar magnesium sulphate solution is gently poured. Transparent, kite shaped struvite crystals of length 6.5-7mm were obtained within 20-25 days' time having density of 1.67g/cc.

On addition of Barley extract the clusters in the brushite are found to separate and become whitish whereas, the barley extract is found to produce perforations on the well-defined struvite crystals, which turn little pinkish on reaction. Whereas the brushite crystals are soft and attain saturation in growth immediately after their formation [11-12], the struvite crystals are hard and continue to grow further with time attaining a maximum length of about 7mm.

III. XRD STUDIES

The powder XRD studies were performed using characteristic Cu-K α radiation, confirming the single-phase formation of the crystals [9,10], which belong to orthorhombic symmetry. Table 1 presents the lattice parameters before and after the addition of barley extract. The corresponding XRD profiles are depicted in Figure 1. For both brushite and Struvite crystals, the 'a' parameter increased with the addition of barley extract, while the 'c' parameter decreased. The 'b' parameter remained largely unchanged. Specifically, for brushite crystals, the addition of barley extract led to an increase in the 'a' parameter from 13.770 to 14.884 (A.U.) and a decrease in the 'c' parameter from 8.136 to 5.146 (A.U.), resulting in a significant reduction in cell volume from 1735.10 to 1389.12 (A.U.)³. Similarly, for struvite crystals, the 'a' parameter increased from 7.988 to 16.510 (A.U.), and the 'c' parameter decreased from 11.913 to 6.199 (A.U.), with a corresponding increase in cell volume from 1745.02 to 1876.81 (A.U.)³. These findings suggest that barley extract induces notable structural changes in urinary crystals, impacting their dissolution properties.

Table 1: Lattice Parameters for Brushite & Struvite Crystals

Crystal	a	b	c	Volume
Brushite (B)	13.770	15.488	8.136	1735.10
Brushite with Barley (WB)	14.884	18.136	5.146	1389.12
Struvite (S)	7.988	18.338	11.913	1745.02
Struvite with Barley (WB)	16.510	18.338	6.199	1876.81

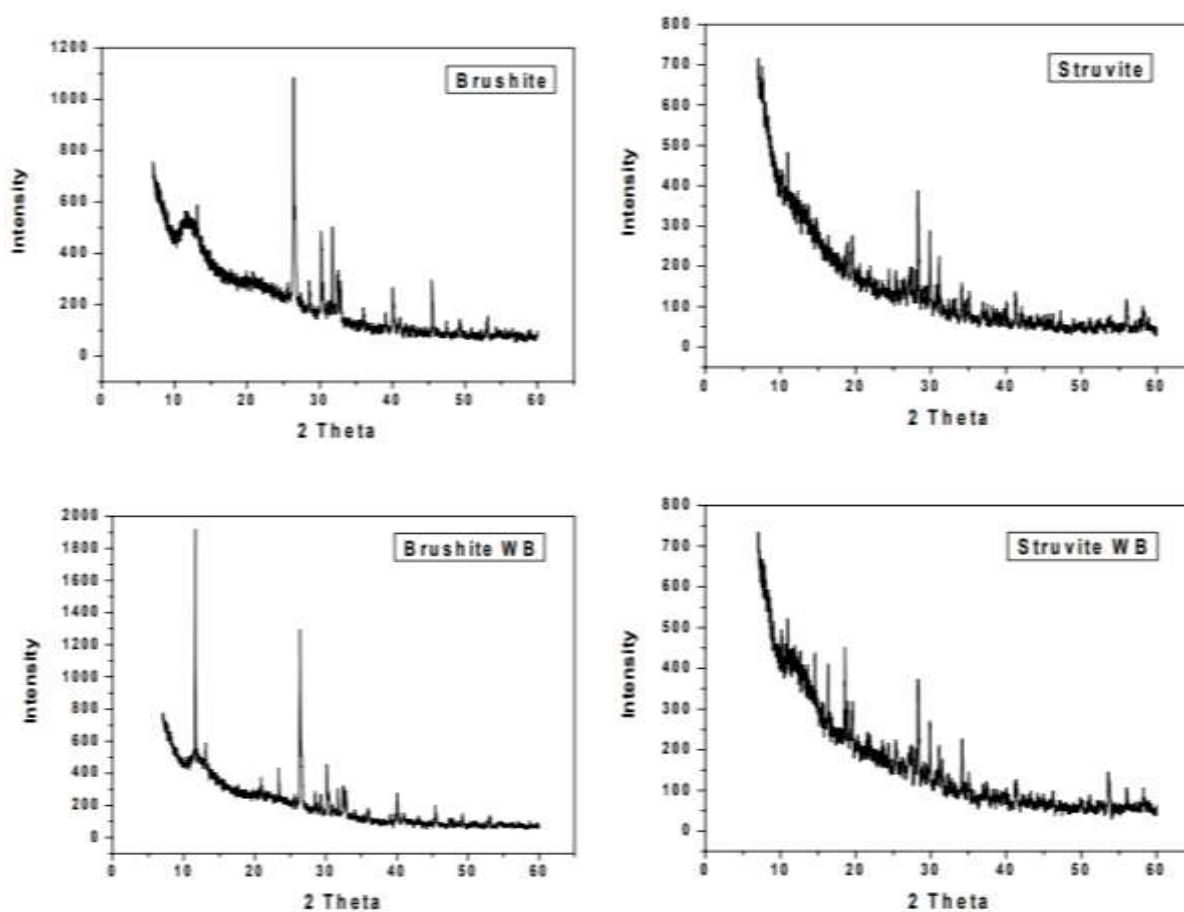


Figure 1 : XRD profiles of Brushite and Struvite crystals

IV. TOPOGRAPHICAL STUDIES

The topographical studies of Brushite and Struvite crystals revealed distinct morphological features and the effects of barley extract and chemical etching [11-12]. Figure 2 illustrates the clustered nature and spearhead shape of Brushite crystals at 300x magnification. Adjacent to these clusters, a typical biological growth pattern is depicted in Figure 3 at 200x magnification. Figure 4 presents transparent, kite-shaped Struvite crystals at 200x magnification. Figures 5 and 6, also at 200x magnification, show the development of boat-shaped features and surface perforations on Struvite crystals following the addition of barley extract. These features indicate the extract's impact on the crystal structure, promoting dissolution.

Pits formed on the crystal surfaces, concentrating in specific areas, as highlighted in Figure 8 at 400x magnification. Due to the water insolubility of these crystals, various chemical etching agents were tested. Concentrated sulphuric acid was particularly effective, producing well-defined, oriented etch pits within just 2 seconds, as shown in Figure 9 at 400x magnification. These etched surfaces were observed under a metallurgical microscope, providing detailed insights into the surface morphology. Overall, these studies demonstrate the significant effects of barley extract and sulphuric acid on the structural integrity and surface morphology of Brushite and Struvite crystals, suggesting potential applications in the treatment of urinary calculi.

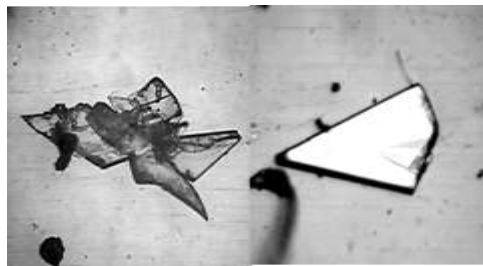


Figure 2. Geometry of Brushite crystals (x300)



Figure 3. Biological growth pattern of Brushite crystals (x200)

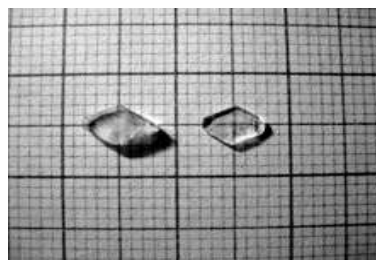


Figure 4. External geometry of Struvite crystals (x200)

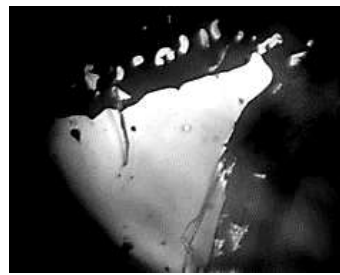


Figure 5 and 6. On Brushite crystal, Boat shaped features and perforations developed on addition of barley extract (x 200)

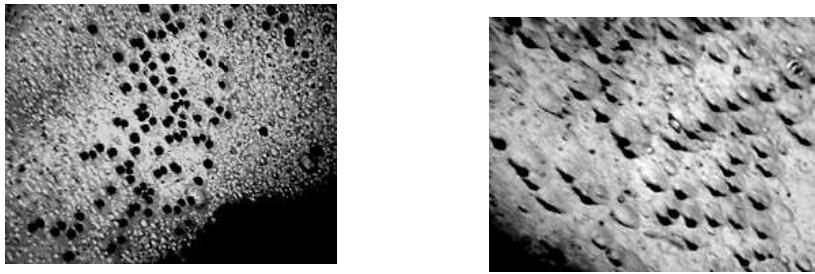


Figure 7 and 8. Concentration of pits and etch pits produced on Struvite crystal on etching in H_2SO_4 for 2 seconds (x 400)

V. CONCLUSION

Urinary calculi, commonly known as kidney stones, are frequently composed of Brushite and Struvite crystals. These crystals have been successfully cultivated using the single diffusion gel growth technique. Over a period of approximately 25 days, well-defined kite-shaped Struvite crystals and cluster-shaped Brushite crystals were formed, suitable for detailed dislocation studies. Structural analyses revealed that these crystals exhibit a single-phase formation with orthorhombic symmetry.

The introduction of barley extract to the gel resulted in notable dissolution and denaturation of the crystals, which was evidenced by alterations in their infrared spectra and X-ray diffraction (XRD) patterns. Specifically, the lattice parameters 'a' and 'c' showed significant changes, whereas the 'b' parameter remained largely unaffected. Surface topography studies highlighted that Brushite crystals, initially spear-shaped and clustered, dissolved upon treatment with barley extract. Similarly, Struvite crystals displayed perforations after exposure to the extract. These findings suggest that barley extract induces notable structural changes in urinary crystals, impacting their dissolution properties.

The crystals, which are insoluble in water, exhibited distinct etching patterns with the effect sulphuric acid, this revealing well-defined, oriented etch pits on their habit faces. These findings indicate that both barley extract and an acidic environment can effectively facilitate the dissolution and denaturation of urinary calculi.

VI. Acknowledgment

Thanks are due to the Department of Material Science at TIFR Mumbai, IIT Mumbai, UICT Mumbai, Material Research Lab in Kaylan and the Indian Institute of Science, Bangalore, for kindly providing access to their experimental facilities. Without their support and resources, this research would not have been possible. We are grateful for their collaboration and commitment to scientific advancement.

REFERENCES

- [1] T. Chacko, T Asaithambi and C K Mahadevan, *Ind. J Phys*, vol **79**, pp.1363-1367, 2005.
- [2] B. B Parekh and M. J. Joshi, *Ind. J. Pure Appl. Phys*, vol **43**, pp.675-678, 2005
- [3] E. Ramachandran and S Natarajan, *Indian J. Phys.*, vol **79**, pp.77-80,2005
- [4] I. Paul, G.Varghese & M A Ittiyachan, *Ind. J. Pure &Appl. Phys*, vol **40**, pp. 664-669, 2002.
- [5] R. Z. Le Geros and J. P. Le Geros, *J.Cryst.Growth*, vol **13**, pp.476-481,1972
- [6] F. Lefauchaux, M. C. Robert and H. Arend, *J. Cryst. Growth*, vol **47**, pp. 313-318,1979
- [7] T. Iruzan, D. Arivuoli and P. Ramasamy, *Cryst. Res. Tech.*, vol **25**,104-109,1990.
- [8] R. H Plovnick, *J. Cryst.Growth*, vol **114**, pp.22-27,1991.
- [9] T. Iruzan, S. N. Kalkurs, D. Arivuoli and P. Ramasamy, *Cryst. Res. Tech*, vol **29**, pp.71-75,1994.
- [10] K. C.Joseph and M. J. Joshi *Indian J. Phys.*vol **76A** pp.159-163, 2002.
- [11] I Paul, C Joseph, M A Ittiyachan, P A Varghese, J George and G Varghese *Indian J. Phys.* Vol **77A**, pp. 37-41 (2003).
- [12] V. S. Joshi and M. J. Joshi *Indian J. Pure Appl.Phys*, vol **41**, pp.183-192, 2003.
- [13] B. K. Sharma, *Spectroscopy*, Goel publ. House, New Dehli 1997-98.
- [14] L. J. Bellamy, *The infrared Spectra of complex molecules*, Chapman and Hall,1975.
- [15] J. W. Mallin, *Crystallization*, Butterworth's, London 1972.