

MONETITE CEMENT

(Dicalcium phosphate anhydrous, DCPA, CaHPO_4)

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The very first monetite cement, having only one phase in its powder component, for skeletal repair / oral surgery was conceived by A. Cuneyt Tas while he was working between May 2003 and May 2006, as a research assistant professor, on a temporary faculty basis, at the School of Materials Science and Engineering of Clemson University, Clemson, South Carolina, USA.

The proposal to develop a novel calcium phosphate cement whose only setting product shall be monetite (instead of hydroxyapatite or brushite) was actually inspired by the previous experience of A. C. Tas (*i.e.*, patent- and publication-based experience he possessed before he joined the Clemson University in May 2003) on developing new orthopedic and dental cements:

- 1.) "A New Calcium Phosphate Cement Composition and a Method for the Preparation Thereof," Sole Inventor and Proprietor: A. C. Tas, US Patent No: 6 929 692,
- 2.) A. C. Tas and F. Aldinger, "Formation of Apatitic Calcium Phosphates in Na-K-Phosphate Solution of pH 7.4," *J. Materials Science: Materials in Medicine*, 16 (2005) 167-174.

The powder component of the monetite cement is a single-phase powder, *i.e.*, Ca(OH)_2 , calcium hydroxide. Nothing else! The powder does not contain phosphorus. The powder is the sole calcium source. The setting solution, on the other hand, consists of an aqueous solution of phosphoric acid (H_3PO_4) and NaHCO_3 (sodium bicarbonate). The setting solution may also contain small amounts of citric acid monohydrate ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$), if desired and as shown in the below MSc thesis.

(The above cited reference 2 of Dr. Tas shows previous usage of an aqueous solution comprising both sodium phosphate and sodium citrate as a setting solution again with a cement having single-phase powder component.)

The monetite cement, upon mixing calcium hydroxide powder with the setting solution of phosphoric acid-sodium bicarbonate, represents a robust and simple-to-pursue example of an acid-base neutralization reaction, and by kneading appropriate amounts of powder with the setting solution one

automatically stops the reaction at the moment of the formation of single-phase monetite crystals as the cement product.

This monetite cement presented a case of perfect separation of Ca and P into the powder and setting solution, respectively. This was the novelty of this calcium phosphate cement yielding only monetite (CaHPO_4) as its setting product in a short time.

The experiments leading to the development of the monetite cement were performed by Dr. Tas and the MSc student Tarang Desai over the period of January 2005 and April 2006, and Mr. Tarang Desai received his MSc degree with the thesis on the same topic at Clemson University.

The below link allows the readers to see the MSc thesis of Tarang Desai:

<https://www.cuneyttas.com/Monetite-cement-MSc-thesis-2006.pdf>

The novelty and the amount of work included in the above MSc thesis was actually close to the caliber of that of a PhD thesis, and it also contained a compartment of testing the monetite cement samples by using both rat osteoclasts and osteoblasts. Especially, the “osteoclastic resorption testing of calcium phosphate-based biomaterials” is very difficult to come by in the literature.

For some of the high resolution microscope images of the above MSc thesis, follow the below links:

[Fig. 3.1](#), [Fig. 3.4](#), [Fig. 3.10](#), [Fig. 3.11](#), [Fig. 3.15](#), [Fig. 3.23](#), [Fig. 3.24](#), [Fig. 3.25](#), [Fig. 3.26](#), [Fig. 3.28](#), [Fig. 3.29](#), [Fig. 3.30](#)

(Figure captions are available in the above-mentioned MSc thesis.)

There has been one publication resulting from this work, which summarized the above-mentioned MSc thesis:

Tarang R. Desai, Sarit B. Bhaduri and A. Cuneyt Tas, “A Self-setting, Monetite (CaHPO_4) Cement for Skeletal Repair,” in *Advances in Bioceramics and Biocomposites II, Ceramic Engineering and Science Proceedings, Vol. 27, Issue 6*, pp. **61-69**, Wiley & Sons, Inc., 2007, USA.

The below link will let the readers of this web-page to access the above publication:

<https://www.cuneyttas.com/Monetite-cement-ACerS.PDF>

Researchers who would like to further develop this monetite cement is more than welcome to do so, as long as they properly cite the above-mentioned MSc thesis (Tarang Desai, “Development of Monetite (CaHPO₄)-based Orthopedic and Dental Cements of High Resorbability,” MSc Thesis, Clemson University, August 2006) and the resulting publication:

T. Desai *et al.*, *Ceramic Engineering and Science Proceedings*, **27(6)**, 61-69 (2007). Its full citation information was given above.

It is quite **unethical** to reproduce and publish this cement formulation and the preparation method in further articles or patent applications without citing the above-mentioned MSc thesis and the above article.

The below researchers, who apparently decided to bluntly **steal** this monetite cement preparation method I invented, seemed to consistently forget to cite the above article and its parent MSc thesis:

- 1.) A. H. Touny and S. B. Bhaduri, “A reactive electrospinning approach for nanoporous PLA/monetite nanocomposite fibers,” *Materials Science and Engineering C*, 30, 1304-1312 (2010),
- 2.) A. H. Touny, H. Dawkins, H. Zhou, and S. B. Bhaduri, “Hydrolysis of monetite/chitosan composites in α -MEM and SBF solutions,” *Journal of Materials Science: Materials in Medicine*, 22, 1101-1109 (2011).
- 3.) N. M. Boroujeni, H. Zhou, T. J. F. Luchini, and S. B. Bhaduri, “Development of multi-walled carbon nanotubes reinforced monetite bionanocomposite cements for orthopedic applications,” *Materials Science and Engineering C*, 33, 4323-4330 (2013).
- 4.) N. M. Boroujeni, H. Zhou, T. J. F. Luchini, and S. B. Bhaduri, “Development of monetite/phosphorylated chitosan composite bone cement,” *J. Biomed. Mater. Res.*, 102B, 260-266 (2014).
- 5.) B. Lin, H. Zhou, D. W. Leaman, V. K. Goel, A. K. Agarwal, and S. B. Bhaduri, “Sustained release of small molecules from carbon nanotube-reinforced monetite calcium phosphate cement,” *Mater. Sci. Eng. C*, 43, 92-96 (2014).
- 6.) H. Zhou, T. J. F. Luchini, A. K. Agarwal, V. K. Goel, and S. B. Bhaduri, “Development of monetite-nanosilica bone cement: A preliminary study,” *J. Biomed. Mater. Res.*, 102B, 1620-1626 (2014).
- 7.) H. Zhou, T. J. F. Luchini, N. M. Boroujeni, A. K. Agarwal, V. K. Goel, and S. B. Bhaduri, “Development of Nanosilica bonded Monetite Cement from Egg Shells,” *Mater. Sci. Eng. C*, 50, 45-51 (2015).
- 8.) S. B. Bhaduri *et al.*, “Injectable, Biodegradable Bone Cements and Methods of Making the Same,” United States Patent Office, Patent application No. 20150005392, Application filed on January 10, 2013, Patent Application published by USPTO on January 1, 2015.

- 9.) N. Koju, P. Sikder, B. Gaihre, and S. B Bhaduri, "Smart injectable self-setting monetite-based bioceramics for orthopedic applications," *Materials*, 11, 1258 (2018).