

Modification of surface hydrophilicity of dental materials by ozone

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ABSTRACT

Introduction: Gypsum, Portland and apatite cement have been developed as dental materials since a long time ago. Their similarity leads to some relevance approaches to improve the characteristic of dental material. Water reducing agent is commonly used in detergent or soap and also used as a conventional method in the industrial cement industry to increase the handling and mechanical property. Cement paste mixed with water reducing agent is more flowable (ease handling) and the set mass is harder (mechanical property increased). However, it has a problem with biomaterial cement due to the biocompatibility. This water reducing agent is harmful to living tissue. Therefore, a new approach will be demonstrated in this research. **Methods:** In this study, the hydrophilicity of cement powder was modified by ozone gas treatment. Ozone gas treatment will be applied to modify the hydrophilicity of cement particles; therefore, it can act similar to the water reducing. **Results:** The hydrophilicity of gypsum, Portland and apatite cement powder was significantly increased after ozone gas treatment. The hydrophilicity improvement of cement powder increased the ability of water to interact with the cement powder. The benefit is, it will improve the flowability of cement paste, therefore, the manipulation index would be increased. The mechanical property also would be increased because the water added for manipulation is decreased. **Conclusion:** Ozone gas treatment could improve the hydrophilicity of gypsum, Portland, and apatite cement powder.

Keywords: Gypsum, Portland, apatite cement, hydrophilic, ozone

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INTRODUCTION

Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), Portland (calcium silicates) and apatite cement are categorized as bioactive cement due to its osteoconductive properties.¹ These cement have similarities in calcium as its major component and have self-setting characteristics after mixed with liquid and can be

used as dental materials.²⁻³ Since a long time ago gypsum has been used in bone fracture therapy and showed good characteristics in medical uses.⁴ Portland cement also used in the past to fill the bone defect and has good clinical results similar to MTA.⁵⁻⁷ Apatite cement is a cement formulation that sets to form apatite upon setting reaction.⁸⁻⁹ Apatite cement initially was invented by Professor

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Monma and Kanazawa in 1976 which found that α -tricalcium phosphate (α -TCP; α -Ca₃(PO₄)₂) could set in room temperature to form Ca-deficient hydroxyapatite (cdHAp; Ca₉(HPO₄)(PO₄)₅(OH)).¹⁰ Research and clinical application of all these cement as bone and tooth substitute materials are growing rapidly.¹¹⁻¹⁴

Generally, characteristic of cement powder and liquid formulation is determined the characteristic of its handling property and final product or set cement.¹⁵ More liquid added is requires for handling in low consistency of cement paste. When the powder is mixed with more liquid the set mass will produce porosity which usually decreasing the mechanical property.¹⁶⁻¹⁷ Therefore, the water content has trade-off relationship with mechanical property. In order to have good mechanical property of final product, cement powder should be mixed with less water.¹⁸

Technology to improve the manipulation index of cement without sacrificing the mechanical property has been developed recently.¹⁹⁻²⁰ One of the method is added water reducing agent to reduce water required for handling and increase the mechanical property of harden set cement. This method is usually applied for non-medical material.²¹⁻²⁴

Water reducing is amphiphilic agent with hydrophobic and hydrophilic hand. In soap or detergent, water reducing agent will act to decrease the surface charge of water therefore it can easily remove dirt. Unfortunately, by adding water reducing agent still a problem for biocompatibility of biomaterials when used in the living tissue.

Another method is by modifying the hydrophilicity of materials. In the similar mechanism with water reducing agent, when the hydrophilicity of materials is increases it can be more easily to react with water. In the other word the water reducing agent is not needed.²⁵⁻²⁶ In this study, modification of hydrophilicity of cement powder is applied by ozone gas treatment. Ozone gas has been reported could modify the surface hydrophilicity of materials.²⁷⁻³³

METHODS

Gypsum powder (Kerr, California, USA) and Portland cement (ASO, Japan) obtained commercially were

used without further modification. Apatite cement powder was consist of equimolar mixture of tetracalcium phosphate (TTCP; Ca₄(PO₄)₂O; Taihei Chemicals Inc., Osaka, Japan) and dicalcium phosphate anhydrous (DCPA; CaHPO₄; J.T. Baker Chemical Co., NJ, USA). All cement followed by drying 24h at 40°C in a dry-heat oven (DO-300A, AS ONE, Japan).

TTCP and DCPA powders were mixed in a sample mill (Kyoritsu-Rikou SK-M2, Tokyo, Japan). Ozone gas treatment Ozone gas was prepared by discharge method using ozone generator (Keiso ED-OG-R4, Tokyo, Japan). Each cement packed in a Teflon tube was exposed to a level of ozone concentration in O₂ gas at a rate of 4 L/min for 4 h at room temperature and atmospheric pressure. After exposure, all cements were kept in a desiccators using P2O₅ as desiccants at room temperature before characterization and evaluation.³⁴⁻³⁵

Hydrophilicity measurement In the present study, the hydrophilicity of powder was calculated by water capillary penetration rate.³⁶⁻³⁹ In short, the rate of distilled water penetration into 0.3 g powder packed in a glass column (10 mm inner diameter) at the same height was measured by touching the bottom of powder packed column to the distilled water surface.

Water mass was measured by electronic balance connected to a computer. More hydrophilic material could absorb more water. The schematic figure of hydrophilicity measurement of powder was shown in Figure 1.

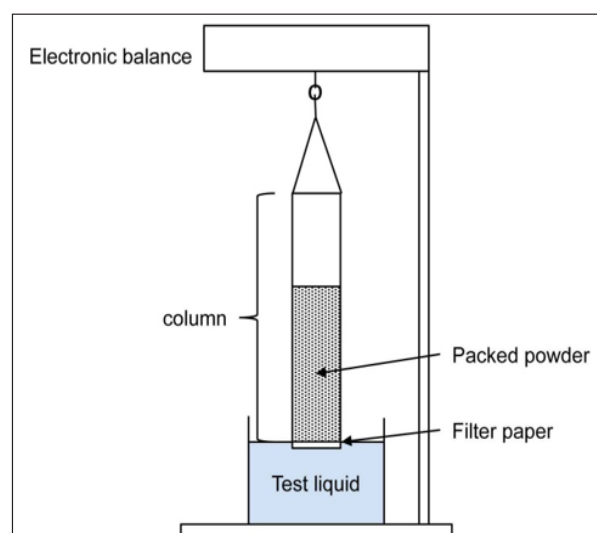


Figure 1. Schematic figure of cement powder hydrophilicity measurement

RESULTS

Figure 2 demonstrated the gypsum treated with ozone at the beginning time could absorb water faster than gypsum without ozone treatment. At the end of time, the gypsum treated with ozone could significantly absorb more liquid mass than gypsum without ozone treatment.

The curve trend in the initial phase is decreasing by times and after that, the state phase was achieved at similar times but at a different mass level. Figures 3 and 4 also demonstrated a similar trend. The Portland and apatite cement powder treated with ozone could absorb water faster and more water than powder without ozone treatment. Each sample when compared with

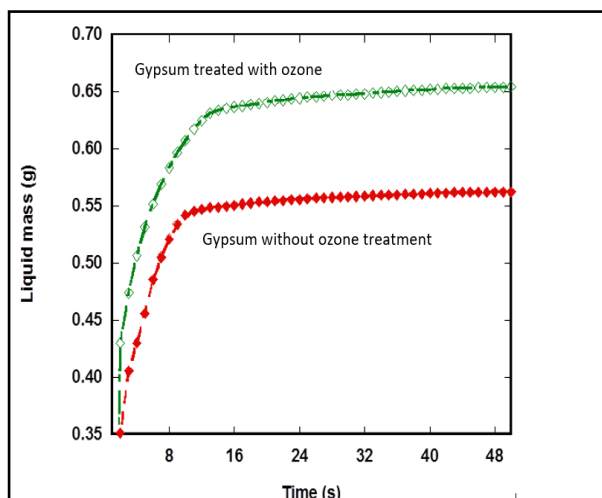


Figure 2. Mass of water absorb to the gypsum powder with and without ozone treatment

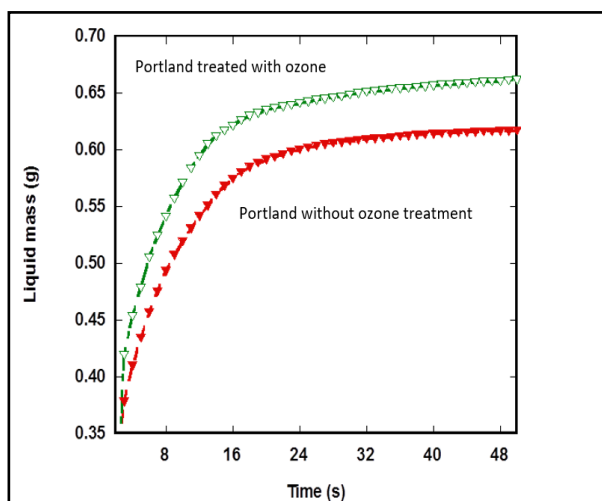


Figure 3. Mass of water absorb to the Portland powder with and without ozone treatment

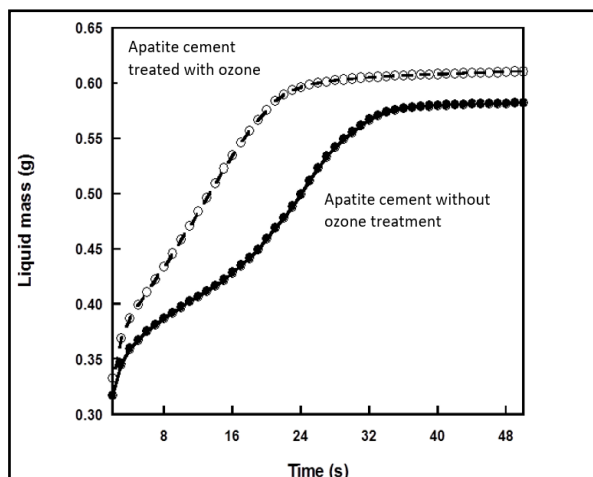


Figure 4. Mass of water absorb to the apatite cement powder with and without ozone treatment

ozone and without ozone treatment statistically significantly different ($p < 0.05$).

DISCUSSION

The ability of the powder to absorb water is related to the hydrophilicity of the powder surface.³¹⁻³² On the contrary, the hydrophobic surface could repel the water. In this study, cement powder treated with ozone could gain more water mass than cement powder without ozone treatment. It was indicated the ozone treatment could modify the hydrophilicity of dental cement material. This water mass is needed for cement reaction and handling property.

Cement paste with more water can flow easily than added less water. In this case, the clinician would be adding less water to the ozone-treated dental cement than without ozone treatment because the ozone treatment dental could show better flowability and more easily to mix (handling property improved). On the other hand, when the clinician mixed the same quantity of water with dental cement powder treated with ozone gas treatment, the handling property could be better than without ozone gas.

Actually, liquid demand which is mixed with dental cement powder depends on the requirement of clinical application. In the case of dental cement powder used for pulp capping or to fill a bone or tooth socket, it requires thicker and moldable paste, therefore, less water is added. On the contrary, when dental cement paste is using for minimally invasive surgery and limited

access in example for intracanal medication, it requires low consistency of paste. Furthermore, it requires a syringe to transfer the cement paste to the target site. However, adding more water is lower the mechanical property of cement.¹⁸ Therefore ozone gas treatment could solve the trade-off problem of adding more water to the dental cement because the hydrophilicity of cement powder could increase the performance of handling property of dental cement paste. In the simple illustration, wet cloth fabric more slippery than a dry one.

The good fact of ozone gas treatment is the safety and biocompatibility of cement powder. This dental cement has superior biocompatibility as biomaterial when it was not mixed with a possible harmful additional agent in the case of the same ingredient with detergent or soap for water reducing agent. The ozone gas treatment environmentally saved treatment when reacted in its chamber for the reaction.²⁸

After reactions, the ozone gas would be decomposed directly to the atmosphere and release the oxygen. Nowadays, ozone gas treatment has been widely used as many purposes for water or air purification, for sterilization and so on.^{29,30,40,41} Therefore ozone gas treatment for dental cement would be applicable in dental practice.

CONCLUSIONS

Ozone gas treatment on dental cement: gypsum, Portland and apatite cement could improve the hydrophilicity of cement powder. It would improve the handling property and mechanical property of this dental cement.

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REFERENCES

1. Ishikawa K. Bone substitute fabrication based on dissolution-precipitation reactions. *Materials* 2010; 3: 1138-1155.
2. Lewry AJ, Williamson J. The setting of gypsum plaster. *J Mater Sc* 29(1994)5279-5284.
3. Lewry AJ, Williamson J. The setting of gypsum plaster part I the hydration of calcium sulphate hemihydrates. *Journal of Materials Science* 1994;29:5279-5284.
4. Lautenschlager EP, Harcourt JK, Ploszaj LC. Setting reactions of gypsum materials investigated by x-ray diffraction. *Journal of Dental Research* 1969;48:43-48.
5. Morais CAH, Bernardineli N, Garcia RB, Duaerte MAH, Guerisoli DMZ. Evaluation of tissue response to MTA and portland cement with iodoform. *Oral Surg Oral Med Oral Pathol Oral Radiol Endod* 2006;102:417-21.
6. Monezes R, Bramante CM, Letra A, Carvalho VGG, Garcia RB. Histologic evaluation of pulpotomy in the dog using two types of mineral trioxide aggregate and regular and white portland cement as wound dressings. *Oral Surg Oral Med Oral Pathol Oral Radiol Endod* 2004;98:376-9.
7. Dokami S, Raofi S, Ashraf MJ, Khorsidi H. Histological analysis of the effect of accelerated portland cement as a bone graft substitute on experimentally created three-walled infrabony defect in dogs. *JODDD vol 1 No 3 Autumn* 2007.
8. Brown WE, Chow LC. Pastes mineralizers and cements, US Patent No.4612053 (1986).
9. Brown WE, Chow LC. In: Brown PW, editors. *Cements research progress*. American Ceramic Society, Westerville, OH.1987.p.351-379.
10. Monma H, Kanazawa T. The hydration of α -tricalcium phosphate. *Yogyo-Kyokai-Shi* 1976;84:209-213.
11. LeGeros RZ. Calcium phosphate materials in restorative dentistry: A review. *Advances in Dental Research* 1988; 2: 164-180.
12. Chow LC, Takagi S. A natural bone cement-a laboratory novelty led to the development of revolutionary new biomaterials. *Journal of Research of the National Institute of Standards and Technology* 2001; 106:10029-1033.
13. Chow LC. Next generation calcium phosphate-based biomaterials. *Dental Materials Journal* 2009;28:1-10.
14. Bohner M, Gbureck U, Barralet JE. Technological issues for the development

- of more efficient calcium phosphate bone cements: a critical assessment. *Biomaterials* 2005;26:6423-6429.
15. Sereda PJ, Soroka I. Interrelation of hardness, modulus of elasticity and porosity in various gypsum systems. *Journal of American Ceramic Society* 1967;51:337-340.
16. Fukase Y, Eanes ED, Takagi S, Chow LC, Brown WE. Setting reactions and compressive strength of calcium phosphate cements. *Journal of Dental Research* 1990;69:1852-1856.
17. Bermudez O, Boltong MG, Driessens FCM, Planell JA. Compressive strength and diametral tensile strength of some calcium-orthophosphate cement: a pilot cement. *Journal of Materials Science: Materials in Medicine* 1993;4:389-393.
18. Ishikawa K, Asaoka K. Estimation of ideal mechanical strength and critical porosity of calcium phosphate cement. *Journal of Biomedical Materials Research* 1995; 29:1537-1543.
19. Sanad MEE, Combe EC, Grand AA. The use of additives to improve the mechanical property of gypsum product. *J Dent Res* 61(6):808-810.
20. Zhang DF, Ju BZ, Zhang SF, He L, Yang JZ. The study on dispersing mechanism of starch sulfonate as a water-reducing agent for cement. *Carbohydrate Polymers* 70(2007)363-368.
21. Beaudoin JJ, MacInnis C. The effect of admixture on the strength-porosity relationship of Portland cement paste. *Cement and Concrete Research* 1971;1:3-11.
22. Peng J, Qu J, Zhang J, Chen M, Wan T. Adsorption characteristics of water-reducing agents of gypsum surface and its effect on the rheology of gypsum plaster. *Cement and Concrete Research* 2005;35:527-531.
23. Jolicoeur C, Simard MA. Chemical admixture-cement interaction: phenomenology and physic-chemical concepts. *Cement Concrete Composition* 1998;20:87-101.
24. Mulligan CN, Yong RN, Gibbs BF. Surfactant-enhanced remediation of contaminated soil: a review. *Engineering Geology* 2001; 60: 371-380.
25. Jönsson AS, Jönsson B. The influence of nonionic and ionic surfactants on hydrophobic and hydrophilic ultrafiltration membranes. *Journal of Membrane Science* 1991; 56: 49-76.
26. Lu W, Fu X, Chung DDL. A comparative study of the wettability of steel, carbon, and polyethylene fibers by water. *Cement and Concrete Research* 1998;28:783-786.
27. Fu X, Chung DDL. Improving the bond strength between steel rebar and concrete by ozone treatment of rebar and polymer addition to concrete. *Cement and Concrete Research* 1997;27:643-648.
28. Suzuki S, Hori Y, Koga O. Decomposition of ozone on natural sand. *Bulletin of the Chemical Society of Japan* 1979;52:3103-3104.
29. Bocci VA. Scientific and medical aspects of ozone therapy. State of the art. *Archives of Medical Research* 2006;37:425-435.
30. Bocci VA, Borrelli E, Travagli V, Zanardi I. The ozone paradox: ozone is a strong oxidant as well as a medical drug. *Medical Research Review* 2009;29:646-682.
31. Thomas K, Hoggan PE, Mariey L, Lamotte J, Lavalley JC. Experimental and theoretical study of ozone adsorption on alumina. *Catalysis Letters* 1997;46:77-82.
32. Fukuzaki S, Urano H, Yamaguchi T. Effect of modification of alumina surfaces by ozone on adsorption behavior of bovine serum albumin at alumina-water interfaces. *Journal Fermentation and Bioengineering* 1997;84:407-413.
33. Sullivan RC, Thornberry T, Abbat JPD. Ozone decomposition kinetics on alumina: effect of ozone partial pressure, relative humidity and repeated oxidation cycles. *Atmospheric Chemistry and Physics* 2004;4:1301-1310.
34. Ezerskii ML. Methods of determining the physicochemical characteristics of pharmaceutical powders. I. dispersity, wettability. All Union Scientific Research Institute of Antibiotics, Moscow. Translated from *Khimiko-Farmasevticheskii Zhurnal* 1976;10:91-101.
35. Tanaka I, Koishi M, Shinohara K. Evaluation of the wettability of spherical cement particle

- surfaces using penetration rate method. *Cement and Concrete Research* 2002; 32:1161-1168.
36. Washburn EW. The dynamics of capillary flow. *Physic Review* 1921;17: 273-283.
37. Lazghab M, Saleh K, Pezron I, Guigon P, Komunjer L. Wettability assessment of finely divided solids. *Powder Technology* 2005;157:79-91.
38. Dang-Vu T, Hupka J. Characterization of porous materials by capillary rise method. *Physicochemical Problems of Mineral Processing* 2005;39:47-65.
39. Yang BW, Chang Q. Wettability studies of filter media using capillary rise test. *Separation and Purification Technology* 2008;60:335-340.
40. Camel V, Bermond A. The use of ozone and associated oxidation processes in drinking water treatment. *Water Research* 1998;32:3208-3222.
41. Arpagaus C, Rossi A, Rohr PR. Short-time plasma surface modification on HDPE powder in plasma downer reactor-process, wettability improvement and ageing effects. *Applied Surface Science* 252 (2005) 1581-1595.