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**A Gas Adsorption Porosimetry of Specific Pore Characteristics of Portland Cement
Prepared by Two Placement Methods**

by

Nader Azizi, DDS

THESIS

Submitted in partial satisfaction of the requirements of the degree of

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ABSTRACT

A Gas Adsorption Porosimetry of Specific Pore Characteristics of Portland Cement Prepared by Two Placement Methods

Nader Azizi, DDS

Introduction and Objectives:

Mineral trioxide aggregate (MTA), a hydraulic Portland-cement based dental restorative material, is commonly used in various endodontic and restorative procedures. Numerous methods have been proposed for clinical placement of MTA due to its difficult handling and placement in its paste form. A clear relationship between porosity and compressive strength of hydraulic cements has been established in previous reports. In this study, we used gas adsorption porosimetry to quantify specific pore characteristics of Portland cement samples prepared by two different placement methods. A correlation was made between specific pore characteristics to compressive strength in general.

Methods:

Portland cement paste was placed in cylindrical moulds using either compaction alone (Group 1) or compaction along with indirect ultrasonic agitation (Group 2) of the paste. Visible differences in porosity on surface and in cross sections of specimens were evaluated using a stereomicroscope. Specific pore characteristics and compressive strength were quantified using a gas adsorption porosimeter and an Instron universal testing machine, respectively. Student's t-test was used for statistical evaluation. A regression and correlation analysis was done to compare specific pore characteristics against compressive strength in general.

Results:

Gas adsorption porosimetry provided quantitative values for specific pore characteristics of the set specimens. Microscopic evaluation revealed visibly larger pores both on the surface and in cross-sections of specimens prepared by the indirect ultrasonic activation method. This group also displayed weakened demarcation lines between aliquots of cement paste in each specimen. Based on the limited preliminary data ($n=8$) no significant difference in mean values of specific pore characteristics or compressive strength of specimens may be reported. Regression/ correlation analyses do not show a statistically significant relationship between compressive strength and any specific pore characteristic.

Conclusions:

1. Gas adsorption porosimetry may be used to quantify specific pore characteristics of hydraulic cement based dental restorative materials
2. Ultrasonic agitation of the cement may separate the liquid from the solid component of each aliquot of cement, producing weakened areas at the interface between aliquots of paste placed on top of each other
3. Larger scale studies are needed to evaluate the superiority of one method of placement over the other.

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INTRODUCTION

Cement is a material that binds solid bodies together by hardening from a plastic state. A type of cement which increases strength even when stored under water after setting is said to be a hydraulic cement. Inorganic hydraulic cements, like Portland cement for example, function by forming a plastic paste when mixed with water which sets and then steadily hardens by a chemical reaction termed hydration. The key requirement for the strength and stability of hydraulic cement is that the hydrates formed on immediate reaction with water be essentially insoluble in water. Non-hydraulic cements include such materials as lime and gypsum plasters [1].

Mineral trioxide aggregate (MTA) is an inorganic hydraulic cement used as a restorative material in dentistry. Portland cement (a mixture of tricalcium silicate, dicalcium silicate, tricalcium aluminate and tetracalcium aluminoferrite) is reported to be the main component of this inorganic hydraulic cement. Similar to other inorganic cements, MTA can set and harden in moist environments [2], a property which makes it ideal for use in dentistry. In addition, MTA has been shown to provide a predicable seal against leakage in bacterial and dye leakage studies [3-5]. The calcium hydroxide component released during the hydration of MTA provides alkalinity to this material, which may account for both its antibacterial and hard-tissue growth induction properties [6] [7]. Its clinical use, however, comes with few reported drawbacks. Its slow setting time often demands multiple appointments for completion of treatments (although single visit treatments have been suggested in the literature [8, 9]). Also, the cement paste's difficult handling

properties and placement, along with its high cost, are other reported sources of dissatisfaction by many practitioners who use this material in clinical settings [10] [11]. Numerous methods for handling and placement of MTA have been reported. Some authors advocate the use of ultrasonic devices for agitation of the cement paste during its placement for improvements in both its “flowability” and possibly mechanical properties. Others call for the use of Lentulospiral instruments for placement of the cement paste into root canal spaces [12], and some even suggest “dry-packing” the powder into the moist root canal environment [13] in experimental models.

A few studies have shown that the choice of MTA placement technique may affect some of the structural and material properties of the set cement. These properties range from the cement’s adaptation to its container’s walls, to changes in its resistance to leakage, and variations in its surface and internal porosity. It is now well accepted that pores decrease the mechanical properties of cements [14]. Therefore, any technique that would potentially affect the porosity of MTA may similarly affect its mechanical properties. Selection of handling and placement methods which optimize the physical and mechanical properties of the cement may prove to be beneficial. For instance, commonly observed flexural weakness of cements has been related to presence of large voids in a set material. The removal of macro-defects during preparation, in fact, has been shown to increase the flexural strength of hydraulic cements, despite the large volume of gel pores that may remain in the material [15]. Similar effects may potentially be expected in respect to compressive strength, raising questions such as: would the choice of placement technique affect the porosity of a hydrated cement paste? would changes in

porosity affect the compressive strength of set specimens of a hydraulic cement? and which specific pore characteristic (BET specific pore surface area, pore volume or pore size distribution) affects the compressive strength of the set material in general?

In an attempt to respond to such questions, ideally methods should be used that provide quantitative values representing specific pore characteristics of the set cement while preserving the integrity of the samples for further testing of their other material properties, such as their compressive strength. Such protocols would generate data which allow for comparative statistical analysis of specific pore characteristics of a cement, and provide more powerful correlations between changes in specific pore characteristics and compressive strength.

Pores in hydraulic cements, such as MTA, may stem from a number of sources. They could be either internal in source, such as those created as a result of the material's hydration reaction, or they could have an external source such as those produced as a consequence of preparation, handling and placement techniques. Internal sources of porosity may have a profound impact on its mechanical properties. For instance, powder-to-water ratio is explained as the most important parameter influencing the porosity of hydraulic cements [1]. Selection of the powder-to-water ratio would affect the porosity of a cement mix due to its effect on the size and distribution of its capillary-pores which are inevitably formed during the hydration reactions. Similarly, external sources of porosity may also influence some structural properties of restorative cements. For example, direct ultrasonic activation of MTA cement paste during its placement has been linked to

entrapment of larger sized air-bubbles in the set specimen [16] possibly due to a proposed “whipping” motion of the ultrasonic delivery device. These larger pores, similar to those affecting the flexural strength of the material, may affect the compressive strength of the material.

Although MTA is traditionally used in low pressure bearing areas- such as root end fillings and in areas of root perforation- its use in pressure bearing areas may potentially be indicated (i.e. as bases under other restorative dental materials). Some have proposed the use of Portland cement as an inexpensive alternative to other more expensive dental restorative materials for restoration of coronal defects [10]. When used in such critical locations, both MTA and Portland cement will have to withstand compressive forces that could challenge their functional longevity over time. Porosity is not the only parameter that affects the strength of a cement. Other factors such as liquid to powder ratio, pore size distribution, microcracks, interface, and so on are also important in determining the mechanical properties of cementitious materials [17, 18]. However, porosity, which can be semi-empirically and concisely used to describe the relationship between strength and microstructure of porous material, is still being studied [19, 20]. Porosity has been shown to display an inverse relationship to compressive strength, with reduction of porosity leading to increases in compressive strength of a solid but porous material. Here, we investigated whether the choice of a clinically practiced handling and placement technique would affect the general porosity and specific pore characteristics of a hydraulic cement based dental restorative material, such as MTA, and monitor their potential impact on compressive strength of the set cement. **Our null hypothesis was**

that the addition of indirect ultrasonic energy during placement and compaction of Portland cement paste into cylindrical moulds will not significantly affect the specific pore characteristics and compressive strength of experimentally prepared specimens.

We studied the effect of two common clinically practiced placement techniques on porosity and compressive strength of Portland cement in an in vitro model. We compared the specific pore characteristics of samples of Portland cement placed by either of two methods of compaction alone (Group 1) or compaction in conjunction with indirect ultrasonic activation of the cement paste during its placement (Group 2). Initially, stereomicroscopic inspections of samples were made in an attempt to make visual comparisons between specimens selected from either of the two experimental groups. Later, a gas adsorption porosity method was used to quantify and compare specific pore characteristics of the cement samples – namely their BET specific pore surface area, pore volume, and pore size distribution- from both groups. Compressive strengths of samples were quantified using an Instron universal material testing machine.

Statistical comparisons, using a paired student's t-test, were made to evaluate the effect of the placement technique on specific pore characteristics and compressive strength of specimens from both experimental groups. Correlations between each specific pore characteristic and compressive strength were also investigated.

MINERAL TRIOXIDE AGGREGATE (MTA)

The emergence of MTA as a dental restorative material:

The first published report suggesting the use of mineral trioxide aggregate (MTA) in dentistry was made by Lee et al in 1993 [21] . Amalgam, IRM, and a mineral trioxide aggregate (MTA) were used to repair experimentally created root perforations. In this in vitro model, the investigators showed that MTA provides a superior seal against dye leakage when compared to both amalgam and IRM. Further studies since have unveiled this material's various other properties. Torabinejad et al. suggested the use of this material as a possible alternative to the commonly used amalgam and Super-EBA for retrograde filling of root-end preparations during endodontic surgeries. In their in vitro leakage studies, they confirmed that mineral trioxide aggregate leaks significantly less than amalgam and super EBA, even in blood contaminated root end cavities [5]. Because of its good marginal adaptation [22], MTA provides a superior seal against bacterial leakage compared to other dental restorative materials such as amalgam, Super-EBA, or IRM [23]. A possible explanation for this superior sealing ability of mineral trioxide aggregate has been linked to its slight expansion upon setting. Reports show that on average, MTA may expand as much as 1% throughout its first 24 hours of setting [24]. Other reports confirm that MTA is neither cytotoxic [25] nor mutagenic [26]. Animal studies have also shown favorable biocompatibility between MTA and its animal host surroundings [27, 28] with even appearance of cementum formation on its surface reported as a frequent finding [27]. Furthermore, reports suggest some anti-bacterial

activity related to this material [6], which is most commonly linked to its high alkaline pH (~12).

Many uses of MTA:

Since its introduction, MTA has become an extensively studied material and its use has expanded to other clinical dental procedures, especially in the field of endodontics. Today, MTA is commonly used in repair of perforated pulp chambers and root canals [29-32]; it is successfully used in pulp-capping procedures beneath other types of coronal restorative materials [33-39]; it has rapidly become a widely accepted material for orthograde obturation of root ends during endodontic surgeries [40, 41]; and its use has also been explained in apexogenesis [34, 42, 43] and in formation of artificial apical barriers for treatment of teeth with immature and widely open apices [39, 44]. Such extensive use of MTA has triggered numerous studies to evaluate its physical, chemical, and biologic properties. Few of such studies have evaluated its clinical handling and placement methods.

Method of handling and placement of MTA:

Problems with working and handling of MTA have often been cited among the disadvantages of this cement. Despite MTA's popularity and common usage, there have been concerns about its difficult handling characteristics. It has been reported that the MTA mixture loses consistency in the presence of excessive liquid, even at the proportion recommended by the manufacturers and results in a fluid mix [45]. The long setting time of MTA results in an initial looseness which can make its handling rather

difficult [46]. When MTA powder is mixed with a liquid (deionized water or anesthetic solutions are often used as such) it forms a cement paste with an initial consistency resembling that of “wet-sand”, making its placement and compaction somewhat difficult in clinical situations. Such studies have focused on comparing and contrasting the advantages and disadvantages of those proposed handling and placement techniques in an attempt to optimize those properties, and to improve its material characteristics as a consequence.

Vizgirda et al [12] evaluated the potential use of MTA as a root filling material by comparing its apical sealing ability with that of laterally condensed gutta-percha with sealer and high-temperature thermoplastisized gutta-percha with sealer in extracted bovine teeth. In this study, MTA was placed into the canals using a Lentulospiral instrument until the material reached the canal orifices. Their results suggested that gutta-percha obturation might provide an apical seal that is superior to MTA. However, the possible explanation for this inferior performance of MTA was suggested to be its “difficulty to place and condense in the apical portion of the root canal” [47, 48].

Other investigators have used light microscopy and radiography to examine the adaptability of MTA to walls of plastic tubing simulating root canal walls. In their study, MTA was placed by either manual plugger condensation or by direct ultrasonic activation of the paste- a direct activation here refers to placing the tip of the ultrasonic delivery device in direct contact with the cement paste. The latter practice is often suggested and used by many practitioners to ease the placement of the cement by making the paste flow

more readily into place. After condensation, the samples were evaluated with a light microscope and radiographs for degree of adaptation of the MTA to the tube walls and for the presence of voids within the MTA material itself. The investigators found that manual plugger condensation resulted in better adaptation to the tube walls and fewer voids than the direct ultrasonic method. The suggested reason here was the possibility that the direct ultrasonic technique used may have actually introduced larger air voids into the material and reduced its adaptability to the tube walls by application of an excessive amount of ultrasonic energy [12, 16].

The common method of *compaction alone* has also been applied in experimental studies to evaluate the effect of the applied compaction forces on porosity of MTA samples. In one study, MTA was mixed and packed into cylindrical polycarbonate tubes, and the six test groups were subjected to six different condensation pressures of increasing intensity. The results showed that the magnitude of compaction forces applied to the cement paste during its placement can affect the strength and hardness of MTA, and that higher condensation pressures result in fewer voids and microchannels when analyzed under an SEM. [49]. This may imply that the force used during compaction of the cement paste may affect the observed patterns of void formation along with strength and hardness of the cement during its placement. Therefore, it may be prudent to keep such compressive forces constant and equal in experimental designs which set out to compare the effect of addition of other placement aids, such as indirect ultrasonic agitation, to the compaction forces. Although the use of an SEM for observational purposes of the samples may certainly be an acceptable practice, it often provides only a limited visual field which

may not be an accurate representation of the whole sample in general. More quantitative methods of analysis may provide better options in this regard.

In an attempt to quantify porosity as a function of density, a recent study compared the fill density of MTA produced by manual plugger compaction alone to that produced by indirect ultrasonic assisted compaction of the paste. By this method, the vibrating tip of the ultrasonic unit is placed at some point along the length of the obturation plugger used for the delivery of the vertical compaction force, thereby delivering both compaction and ultrasonic energy to the cement paste at one time. In this study, a distinction between the dry and wet weight of the samples was made in an attempt to relate density to porosity of the samples. However, as already stated, changes in compaction forces alone may affect the porosity and strength of experimental specimens. Since manual compaction methods in experimental studies may result in differential delivery of forces during placement of the paste, some observed variations may be attributed to such un-accounted variable.

A more recent group has even explored the potential obturation of root canals with dry-MTA powder in an in vitro model. They reported that dry MTA can be adequately hydrated by moisture that penetrates the body of the root in an in vitro model when submerged in saline for 72 hours [13], suggesting that the packed powder may similarly be able to obtain its required fluid component from that of the body tissues. This technique has not been tested *in vivo*.

As already mentioned, some clinicians advocate and practice the use of ultrasonic devices to provide a better “flow” to the MTA paste during its placement protocols. In dentistry, the use of flowable materials has become a common practice. Flowable cements are used in prosthodontic procedures (i.e. crown and bridge cements). They are also used as temporary filling materials in provisional restoration of coronally damaged teeth, and as temporary post-operative restorations to seal endodontic access cavities. Many of such flowable restorative materials are also widely used as bases underneath permanent restorations (i.e. glass ionomers), or as other parts of permanent restoration of teeth with coronal deficiencies (i.e. flowable resins). However, recent studies suggest that this “flowable” characteristic may impose some disadvantages to these materials, at least when it comes to their porosity, when compared to the more conventional condensable materials such as amalgam, or more recently, MTA.

A study, based on both radiographic and μ CT findings, has shown that condensable materials such as amalgam or MTA result in less porosity compared to flowable materials such as Fuji-Plus and Geristore which tend to trap air bubbles while setting. These authors suggest that this increase in porosity may influence the overall performance of the materials over time when subjected to thermal, occlusal, and mechanical stresses in the oral cavity as they age, resulting in leakage [50].

At this point, reports suggest various ways of placement of MTA in both experimental and clinical settings. They also suggest that choices in placement method, such as the amount of applied force, or the use of direct or indirect ultrasonic techniques alone or as

an adjunct during compaction of MTA, may affect the porosity or strength of the prepared material. Methods of porosity evaluation in material testing of MTA or Portland cement based dental restorative materials range from observational evaluations (such as stereomicroscopy, SEM analysis, radiography, or μ CT analysis) to the more quantitative methods of analysis by relating the changes in density to porosity of samples.

In an attempt to better understand the micro- and macro-structural entities that govern the characteristics of inorganic hydraulic cements, such as the Portland cement based MTA, we will allude to some chemical and compositional parameters that relate to some observed patterns of change in mechanical properties of the cement during its setting and maturation.

Compositions, variations, and chemical reactions of MTA:

MTA goes through different phases during its setting maturation. These phases often times correspond to chemical reactions which may affect the material properties of the set cement, and vice versa. Therefore, an overview of such chemical reactions and physical parameters is necessary in order to isolate and identify factors which may influence those parameters.

Commercial MTA powder is a mixture of two or three main inorganic components and a number of other trace elements. ProRoot MTA (sometimes referred to as “grey-MTA” or GMTA) is a mixture of three main components which together constitute close to one-

hundred percent of its parts. The three main components of GMTA are Portland cement, Bismuth Oxide, and Gypsum (calcium sulfate) [51].

Portland cement, the main constituent of MTA, comprises about 75 percent of the dry weight of this material. Portland cement is an inorganic hydraulic type of cement which is made primarily from limestone, certain clay minerals, and gypsum in a high temperature process that drives off carbon dioxide and chemically combines the primary ingredients into new compounds. Portland clinker is composed largely of four types of minerals: alite (Tricalcium Silicate), belite (Dicalcium Silicate), aluminate and a ferrite phase. Tricalcium silicate is the major compound of clinker and the one which determines, to a great extent, the progress of setting and hardening. The effectiveness of dicalcium silicate is lower compared to the one of tricalcium silicate [1].

Setting and hardening of hydraulic cements is caused by the formation of water-containing compounds, which form as a result of reactions between cement components and water. The reaction and the reaction products are referred to as hydration and hydrates or hydrate phases, respectively. As a result of the immediate start of the reactions, a stiffening can be observed which is very small in the beginning but increases with time. The point at which the stiffening reaches a certain level is referred to as the start of setting. Further consolidation is called setting, after which the phase of hardening begins. The compressive strength of the material then grows steadily, over a period that ranges from a few days in the case of "ultra-rapid-hardening" cements to several years in

the case of ordinary cements. Hydration of Portland cement, the main component of MTA, involves four principal phases [1].

The first phase is governed by the tricalcium silicate. This is the principal strength generating phase in cement which gives the cement its early and long-term strengths. Products of hydration of this phase are calcium silicate hydrate and crystalline calcium hydroxide $[\text{Ca}(\text{OH})_2]$ (portlandite). The calcium silicate hydrate formed in this reaction is poorly crystalline, and has been described as gel-like due to its high specific surface area. This high specific surface area is a reflection of the porous nature of this reaction product. The product of hydration at ambient temperature is an amorphous phase of hydrated calcium silicate and crystalline calcium hydroxide $[\text{Ca}(\text{OH})_2]$. The calcium hydroxide $\text{Ca}(\text{OH})_2$ formed here is responsible for the high alkaline nature of the cement ($\text{pH}=12.5$) [1].

The second phase is controlled by the Dicalcium silicate. The products from hydration of Dicalcium silicate are similar to the ones of tricalcium silicate with the only difference being the lower percentages of calcium hydroxide $\text{Ca}(\text{OH})_2$ produced. Dicalcium silicate is responsible for the long term strength of the cement [1].

The third phase in this reaction is that of tricalcium aluminate with water. This reaction would have been very fast and would have resulted in rapid setting of all the cement, but due to gypsum that exists in the cement, it is hydrated differently from the pure compound. The reaction of tricalcium aluminate with gypsum gives a hydrated sulfate tricalcium aluminate called ettringite. Ettringite is present as rod-like crystals in the early

stages of cement hydration. The retarding impact of gypsum is attributed to the formation of a coating of ettringite on the surface of the grains of tricalcium aluminate, which delays its hydration, making the setting of cement dependent mainly on the hydration of tricalcium silicate. When gypsum is consumed, the reaction of tricalcium aluminate with the ettringite takes place and hydrated monosulfate is produced while at the same time an increase of the hydration rate is achieved. Monosulfate tends to occur in the later stages of hydration, after a few days. Usually, it replaces ettringite, either fully or partly. At ambient temperature, the hydration of tricalcium aluminate can be completed after several months period. Tricalcium aluminate gives rise to the cement early strengths [1].

The final phase of the reaction is under the influence of Tetracalcium aluminoferrite. The hydration of the ferrite phase is substantially retarded with the presence of gypsum.

Generally speaking, with the addition of water to Portland cement based materials, its compounds are hydrated mainly towards calcium silicate hydrate (C-S-H) gel and calcium hydroxide, with the remaining products being aluminous and ferrites [1].

Bismuth oxide, the other major component of MTA, makes up about 20 percent of the dry weight of this material. Bismuth oxide is added to commercial variations of MTA because of its radiopacity. This radiopacity is needed to facilitate accurate placement and follow-up of the MTA over time. The bismuth oxide additive in all commercially available variations has little or no effect on the biocompatibility of the cement, however the addition of Bi_2O_3 to a Portland cement dramatically changes the material constants of

the cement by acting as flaws within the cement matrix. The addition of Bi_2O_3 radioopacifier decreased mechanical stability by introducing flaws and increased porosity by leaving more un-reacted water within the Portland cement-based (MTA-like) endodontic model system. Flaws in the set cement matrix might exacerbate existing cracks (which inevitably exist as a result of the stress of initial setting in a Portland cement-based system); moreover, increased porosity is known to increase the solubility and thus the degradation of the material. This might potentially affect the longevity of the material, compared to that of pure Portland cement, because the set material is more likely to degrade and is thus more likely to be compromised as a sealant [52, 53]. In fact, in one study bismuth affected the hydration mechanism of MTA; it formed part of the structure of the calcium silicate hydrate and also affected the precipitation of calcium hydroxide in the hydrated paste. Hydrated MTA with Bi_2O_3 would likely be weaker when compared with that of Portland cement without this additive [54].

Gypsum (calcium sulfate), makes up the remaining 5% of grey-MTA (GMTA). Because the gypsum from the quarries of the Montmartre district of Paris has long furnished burnt gypsum used for various purposes, this material has also been called plaster of Paris. Gypsum is a water soluble mineral. It has a long history of use in physical filling of bone defects when used in surgical procedures. However, it does not appear to stimulate osteogenesis per se. In such procedures, its chief effect has been described as a mechanical one of preventing the collapse of periosteum and favoring regeneration in this way. Therefore, this component does not appear to prejudice wound healing nor does it provoke a foreign body reaction [55]. As described previously, the addition of gypsum to

MTA tends to affect its setting reaction, but it does not appear to add any other therapeutic benefits. Gypsum was first added to Portland cement materials to retard the rate of setting sufficiently to allow the proper placing of mortar and concrete. It is not known when and by whom this property of gypsum was discovered, but it appears likely that it was discovered accidentally by workmen mixing cement and mortar in uncleaned equipment that had been used for mixing of plaster of Paris [56]. Addition of gypsum to Portland cement based materials tends to prevent flash setting of the cement material [57].

Concerns about setting time and the discolored appearance of visible areas of the tooth repaired by grey-MTA have led to development and manufacture of its other formulations. A mixture of grey-MTA with water goes through a hydration reaction with an initial stiffening phase followed by a setting phase that may take up to 4-6 hours. This long setting time limitation at times forces the operators to complete a procedure that may normally take only one visit for the patient in two separate appointments. In an attempt to address this limitation, MTA-Angelus was introduced. MTA-Angelus is not yet available in the United States markets for clinical use. MTA-Angelus, is composed of 80% Portland cement and 20% bismuth oxide and no calcium sulfate (gypsum). The absence of calcium sulfate is advertised to reduce the setting time to 10 min. Studies have shown that setting time of Portland cement can be reduced by excluding the gypsum during the last stage of the manufacturing process without affecting its other properties [53].

In an attempt to limit or prevent discoloration of exposed dentin near MTA repaired sites in esthetic areas, a white-MTA (WMTA) variation has been introduced. White-MTA is similar to grey-MTA when comparing its main constituents, however the observed concentrations for Al_2O_3 , MgO , and particularly FeO in white-MTA are considerably lower than those found in grey-MTA. Differences in the observed FeO concentration are thought to be primarily responsible for the variation in color of the white-MTA (off-white) in comparison with grey-MTA [53].

Other additives (including saline, 2% lidocaine, 3.0% NaOCl gel, chlorhexidine gluconate gel, K-Y Jelly, 3% and 5% CaCl_2), and classic Portland cement accelerants (calcium chloride, calcium nitrite/nitrate, and calcium formate) have also been shown to affect various properties of MTA [58, 59]. These reports suggest that addition or manipulation of chemical constituents of MTA may potentially affect its physical and mechanical properties.

In summary, hydration of an inorganic hydraulic cement, such as the Portland cement based MTA, leads to chemical reactions during its setting and maturation. The resulting mechanical properties that correspond to each phase of reaction may be affected by both internal and external variables. Changes in water-to-powder ratios along with introduction or removal of physical additives, for instance, may account for many of the observed changes in mechanical properties of the cement.

As previously mentioned, MTA and Portland cement share many common characteristics due to their close chemical compositions. To further underline these similarities and to justify the rationale for use of Portland cement in lieu of MTA in both experimental and clinical settings, a more detailed comparison of the two inorganic hydraulic cements will be provided.

A comparison between MTA and Portland cement:

Portland cement is historically and widely used in building construction. It is also the main ingredient of all available varieties of MTA in clinical use today. MTA materials are essentially a refined Portland cement [60] mixed with a fraction of other biologically inert additives. Except for the bismuth oxide, MTA and Portland cement have similar constituent elements[61]. Funes et al. have reported that there is no difference in the presence of 14 elements between ProRoot MTA and Portland cement except for the bismuth that is added to the MTA for its radiopacity [45]. Saidon et al. have reported that both MTA and Portland cement have similar physical, chemical, and biologic properties, and the biocompatibility of both materials is due to the similarity in their constituents [62]. Numerous other reports on MTA and Portland cement's similarities can be found in the dental literature. Portland cement and MTA present similar resistance to leakage in experimental models [63-66]; they express similar genotoxicity and cytotoxicity in tissue culture studies [62, 67, 68], and are reported to have comparable biocompatibility in animal studies [62]. One study evaluated and compared the pH, radiopacity, setting time, solubility, dimensional change, and compressive strength of ProRoot MTA (PMTA= grey-MTA), ProRoot MTA (tooth colored formula) (WMTA), white Portland

cement (WP), and ordinary Portland cement (OP). Their results showed that PMTA and Portland cement have very similar physical properties [69].

MTA is similar to commercial Portland cement [70-72], and as far as composition is concerned, there is support for its possible clinical use as an option to MTA [10]. Due to its similarity in composition to commercial MTA, Portland cement has also been used as a model system for material testing [52].

POROSITY OF HYDRAULIC CEMENT MATERIALS

Differentiation of pore types:

Porosity is a character of all hydraulic cements. Intrinsic pores produced in cement hydration vary in size, shape and origin and can be divided into gel pores, capillary pores, hollow-shell pores, and air voids. The calcium silicate hydrate gel formed during hydration of Portland cement is a colloidal amorphous gel, which contains pores of approximately a few nanometers in size that are called gel pores. The initially water-filled spaces in the hardened paste as interconnected channels, or if the cement is dense enough, as interconnected gel pores, are called capillary pores. The capillary porosity of the cement depends on the amount of the original water-to-powder ratio and on the amount of cement that has become hydrated. Capillary pores are highly irregular in shape and their size could range from small to large values (2nm to 10 μ m). Capillary pores are assumed to have a major effect on transport processes, but only a minor role on hydration rate. Hollow-shell pores are closed, very distinct pores and generally have the shape of

the relicts of cement particles. When stable hydrates do not form within the original cement grain boundaries, a void can develop within the boundary of the original cement grain as the cement grain recedes on continued hydration. Entrapped-air voids (air-bubbles) in hardened cement may occur inadvertently during mixing and placement of the cement. Entrapped air voids come in many sizes [73-76]. Table-1 presents the classification of pores in hardened cement pastes [1]:

Designation	Diameter	Description	Properties influenced
Capillary Pores	10- 0.05 μm	Large capillaries	Strength, permeability
	50-10 nm	Medium capillaries	Strength, permeability, shrinkage at high humidity
Gel Pores	10-2.5 nm	Small (gel) capillaries	Shrinkage to 50% rh
	2.5-0.5 nm	Micropores	Shrinkage, creep
	< 0.5 nm	Micropores	Shrinkage, creep

Table 1. Classification of pores of hardened cement pastes (Modified from *Portland Cement. 2nd Edition*, G.C. Bye and Thomas Telford Limited, 1999)

Relationship between porosity and mechanical properties:

Pore structure is an important micro-structural characteristic in a porous solid material because it influences its physical and mechanical properties, and controls the durability of the material. Materials with the same total pore volume can exhibit entirely different characteristics, depending on whether the material has a small number of large pores or a greater number of small pores. Pore size distribution, total pore volume, specific surface area, gas and liquid permeability, and pore tortuosity are examples of important

properties of porous materials [77]. Pores can exert their influence on the properties of cement based materials in a number of ways. Compressive strength and elasticity are primarily affected by total number of pores; however, they can also be influenced by size and spatial distribution of pores, maximum pores size, pore shape and connectivity. Permeability and diffuseability are influenced by the total volume, size, shape, and connectivity of the pores. Many of deteriorating mechanisms of Portland cements are linked to migration processes. For example, absorption of water and salt solutions is a migration process which limits the service life of concrete structures and is controlled by porosity and pore size distribution. The pore size of concrete is key for its durability [78].

Factors that affect porosity:

Many factors are known to influence the porosity of a setting or set hydraulic cement. Porosity in hydraulic cement systems mainly stems from two sources. First, from water added to form the cement paste, which is not consumed in the setting reaction and, second, from entrapped air in the cement paste resulting from partially dry powder agglomerates (dry spots) and air bubbles [52]. Water to powder ratio is the most important factor affecting the porosity of hydraulic cement based materials. This important ratio can affect the amount of bound and available water in cement paste mixtures. As the volume of the available water increases after a critical ratio, so does the porosity of the setting cement paste. This may be reflected by potential increases in both the surface area and volume of intrinsic micropores in the samples. Other factors that affect the porosity of the samples may be related to placement techniques. For example,

higher compaction pressures or use of ultrasonic devices may also affect the porosity of such materials by reducing the over-all size of smaller pores, such as gel-pores or capillary pores, while inadvertently introducing pores of larger sizes as a consequence of mixing or obturation protocols.

A number of methods are available for analysis of general porosity and specific pore characteristics of solid materials. A general understanding of these methods may help in selection of an appropriate method of pore analysis for evaluation of changes in porosity of samples in experimental models.

Methods of Porosity determination:

Numerous methods have been proposed for measurement and characterization of pore structures. Each of the various methods is most suitable for a specific pore size range. Some methods only have access to open pores (penetration and adsorption methods) while others have access to both open and close pores (radiation methods). In indirect methods, an external stimulus is applied to the material and the material's response is measured using a suitable detector. The indirect methods most commonly used for pore structure characterization and analysis include the following [78]:

- Mercury intrusion porosimetry
- Gas adsorption porosimetry
- Displacement methods
- Thermoporometry
- NMR
- Small-angle scattering

Mercury intrusion porosimetry and gas adsorption porosimetry, essentially, operate on the same principle. Initially, samples are prepared to remove all the available water and impurities. This is followed by infusion of either mercury or a specific gas into the solid

sample. A detection mechanism measures the amount of mercury or gas taken up by the sample at various time frames, providing information about the surface area of the pores at first, followed by volume of pores and consequently the size distribution of pores in the sample. The main difference in the two methods is in the size of the molecules used for this purpose, and the reversibility and preservation of the sample provided by the gas adsorption method of porosity determination. The method of gas adsorption porosimetry will be discussed in more detail later on.

Displacement methods are based on the Archimedean principle. Liquids such as water, toluene and alcohol are usually used with this method. Mean weight of a dry sample (W_1), weight of a sample put in liquid (W_2) and weight of a wet sample (W_3) are placed in the following equations to calculate density (d) and open (P_o) and closed (P_c) porosities of the sample [79]:

$$\rho_{bulk} = W_1 \rho_{liquid} / (W_3 - W_2)$$

$$\left(d = \rho_{bulk} / \rho_{th} \right)$$

$$P_o = (W_1 - W_2) / (W_3 - W_2)$$

$$P_c = 1 - d - P_o$$

Thermoporometry is based on the fact that conditions of the equilibrium of the solid, liquid and gaseous phases of a pure substance depend on the curvature of the solid-liquid interphase. In the case of a liquid contained in a porous material the solid-liquid interphase curvature is closely related to the dimensions of the pore. By recording a

solidification thermogram of a pure condensate inside a porous material the pore size can be determined from the temperature at which the condensate solidifies and the pore volume can be determined from the amount of energy involved. An important advantage of this method is that information is obtained about the internal size of the pores and not of their entrances [80].

Nuclear magnetic resonance (NMR) measurements have exhibited their capability to probe a variety of shapes and sizes of pores in porous media filled with fluid. For instance, a low field NMR well logging technique based on these principles has been used to detect the porosity, pore size distribution and permeability of rock structures in oil reservoirs where the fluids (oil and water) are stored in pores [81].

Small-angle X-ray (SAXS) scattering is a technique where the elastic scattering of X-rays by a sample which has inhomogeneities in the nm-range is recorded at very low angles. This angular range contains information about the shape and size of macromolecules, characteristic distances of partially ordered materials, pore sizes, and other data. SAXS is used for the determination of the microscale or nanoscale structure of particle systems in terms of such parameters as averaged particle sizes, shapes, distribution, and surface-to-volume ratio. The materials can be solid or liquid and they can contain solid, liquid or gaseous domains of the same or another material in any combination. [82].

On the other hand, direct methods produce a direct physical image of the microstructure examined, revealing the size and shape of the phases, and extrapolating the relationship

of the phases in space by using mathematical analysis techniques. The most common direct methods include the following [78]:

- Optical microscopy
- Scanning electron microscopy

Each of the above methods can be used for evaluation of pores in solid porous materials. Some may shed light on the generally porosity of specimens, while others may provide data that represent specific pore characteristics of the porous object. Such specific pore characteristics may be of interest to investigators and will be defined in the upcoming section.

SPECIFIC PORE CHARACTERISTICS OF SOLID MATERIALS

Pore volume:

Pore Volume (P_V) is defined as the ratio of a porous material's air volume to a porous material's total volume. The total volume of a part is described by the amount of space contained within an imaginary film that has been tightly shrunken around the outside of the porous part's exterior geometry. We can designate the total volume within this film as V_T . Inside the tightly wrapped film and within the cavities of the porous part exists a certain volume of air. We can designate this volume of air as V_A . Pore Volume is, hence, equal to the ratio of a porous material's air volume to total volume ($P_V = V_A / V_T$).

Pore size distribution:

Pore size distribution is a measure of the range of pore sizes. The range of pore sizes can be normally distributed, and the spread can be quite narrow. On the other hand, pore size distribution can be very heterogeneous. In the case of large spreads and heterogeneity, the pore size will be far less predictive of flow rate (either filtration or capillary) than it will be for a membrane with a narrow pore size distribution. It is important to note that the pore size corresponding to the bubble point is not at the middle of the distribution, but is the largest pore.

BET Specific Surface Area:

The determination of specific surface by means of the BET theory is based upon the phenomenon of physical adsorption of gases on the external and internal surfaces of a porous material. BET theory describes the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of a material. The BET method is widely used in surface science for the calculation of surface areas of solids by physical adsorption of gas molecules [83, 84].

GAS ADSORPTION POROSIMETRY

Gas adsorption has been one of the most popular techniques used for the study of pore structure in materials that contain micropores and mesopores. Gas adsorption methods are based on measurements of the amount of gas adsorbed on the surface of a powder at monomolecular depth on the particle's surface [85]. When a porous solid is exposed to gas of a certain volume and pressure, it begins to adsorb the gas molecules on its outside surface and inside its pores. First, the surface of the solid's pores adsorb gas molecules forming a monolayer on the surface (Figure 1). The monolayer of gas then attracts other molecules and becomes a multilayer. Eventually, the thickness of the adsorbed layers approximates the size of the pore, and capillary condensation takes place.

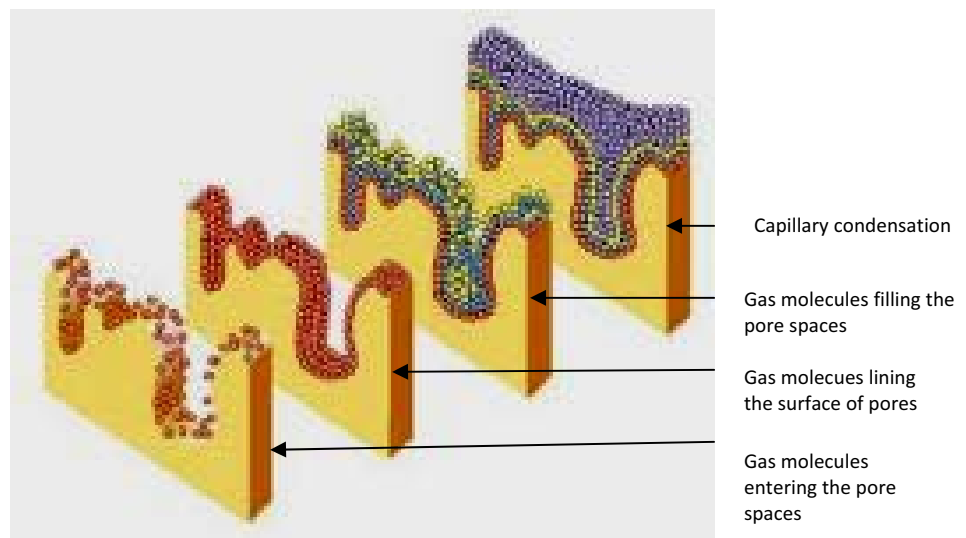


Figure 1. Progressive lining and filling of micro-pores by gas molecules during gas adsorption porosimetric analysis (Image courtesy of Micromeritics, Norfolk, GA, USA)

From the amount of gas adsorbed and the corresponding relative pressure recorded during the experiment, a great number of methods are developed for analysis which include methods for determining the pore volume, pore size distribution, and the BET specific surface area of the material. The first steps of analysis include obtaining the adsorption isotherm, determining the thickness of adsorbed film on the pore walls, and determining the pore size from the values of relative pressure measured during the experiment. The total pore volume of the specimen may be calculated from the gas adsorbed at saturated vapor pressure. Gas adsorption will measure pore size by recording isotherms from low pressures to saturation pressure. The pressure range is determined by the size range of the pores to be measured. Isotherms of microporous materials are measured over a pressure range of approximately 0.00001 mmHg to 0.1 mmHg. Isotherms of mesoporous materials are typically measured over a pressure range of 1 mmHg to approximately 760 mmHg. Once details of the isotherm curve are accurately expressed as a series of pressure vs. quantity adsorbed data pairs, a number of different theories or models can be applied to determine the pore size distribution [78, 86]. After converting the relative pressure to pore radius, it is possible to obtain a pore size distribution, which is a plot of the cumulative pore volume vs. the pore radius. Specific surface area can be determined by either analytical or graphical methods. Surface area measurements are the most widely used means for characterization of porous materials. Since the surface corresponds to the roughness of the solid and its porous interior, gas adsorption is the preferred technique [78, 87].

For accurate surface area measurements, the temperature and pressure of an inert gas are adjusted to cause a single layer of gas molecules to be adsorbed over the entire surface of a solid. Pressure transducers or other sensors respond quantitatively to the amount of gas adsorbed. Using these data, and by means of a simple well-known calculation (the B.E.T. equation), it is easy to compute the surface area of a sample which is usually reported as the specific surface area (i.e. surface area per unit mass, usually m^2/g) [87].

Most techniques used in pore structure studies require that the hardened cement paste be treated to remove water and evacuated before the testing. Non-evaporated water is lost during the heating process. Hydrate water from the C-S-H gel is held inside the gel pores, and can be removed by heating, desiccation, evacuation or a combination of these methods [78].

COMPRESSIVE STRENGTH

The most important test of cement quality involves the determination of its compressive strength. Compressive strength is the maximum stress a material can sustain under a crushing load. It is calculated by dividing the maximum load by the original cross-sectional area of a specimen in a compression test [1, 88]. The compressive strength developed depends on the materials used, the mix proportions, the procedure employed in mixing and the efficiency with which the mix is compacted into a mould, as well as the temperature, humidity, and time of curing [1]. The compressive strength behavior can be correlated exponentially with pore volume [89]. The volume of air present in a sample depends on the degree of compaction achieved. A correlation between an increase in strength of a cement and an increase in the degree of hydration is also observed. At a high degree of hydration, an increase in bound water contributes to the reduction of porosity. So, compressive strength can be viewed as a function of curing time and water-to-cement ratio, and these variables are the principle influences on the porosity of a hardened cement [1].

The Instron Universal Testing Machine:

Various methods may be used for evaluation of compressive strength of solid materials. One such method may use an Instron universal testing machine. This laboratory testing equipment is capable of delivering vertical compressive loads to a test sample at specified rates. Recording devices measure the amount of force applied to the sample up to its mechanical failure (the point where the material is crushed under a certain amount of

applied vertical load). The peak amount of force applied prior to point of failure may be used for determination of compressive strength of the material.

MATERIALS AND METHODS

Cement mix preparation:

In a clean glass dappen dish, 1.0 g of Portland cement was mixed with 0.32 ml of deionized water using a metal mixing spatula. Care was taken to gently mix the two components to avoid introduction of large air bubbles into the cement paste. Mixing was done for 30 seconds until the material took a consistency which allowed for easy transfer and placement of its aliquots by an amalgam carrier into metallic moulds (Figure 2)



Figure 2. Disassembled mould apparatus displaying the two halves of the metallic mould used for confinement of cement samples during placement and setting

The metallic moulds:

Split metallic moulds were used as compartments to contain the cement paste through its placement protocol and setting duration (Figure 2). Juxtaposition of the two half portions of the mould, each with a half-cylinder cut out of one edge, made up the cylindrically shaped space that contained the cement paste. Tightening of screws holding the two halves of the mould formed a solid structure that provided resistance to expansion upon compaction and along the setting and hardening duration of the cement. Each cylinder formed by placing the two halves together measured 12 mm in height and 6 mm in diameter.

Preliminary trials of our experiments presented an initial challenge of removing the set cement from the cylindrical moulds, with the cement breaking in half following

disassembly and splitting of the two halves of the cylindrical moulds. In an attempt to overcome this challenge, a thin layer of petroleum jelly was applied to the interior walls of the moulds prior to placement of the cement paste. Again, removal of whole cylindrical cement specimens proved problematic as they continued to break in half during our attempts at their removal. To rectify this situation, a small cylindrical tube was cut out from a polycarbonate water line which measured 6 mm in its cross-sectional diameter, assuring a tight fit inside of each assembled mould. The cylindrical tube was inserted into the mould to separate the metallic walls of the mould from the cement paste during its placement and setting (Figure 3). However, due to the tube's thickness, the diameter of the cylindrical mould was reduced to 4.5mm while keeping the height of the cement cylinders still at 12mm. Utilization of these separators proved successful, as we were able to easily push out whole cylindrical specimens of set cement without any damage.

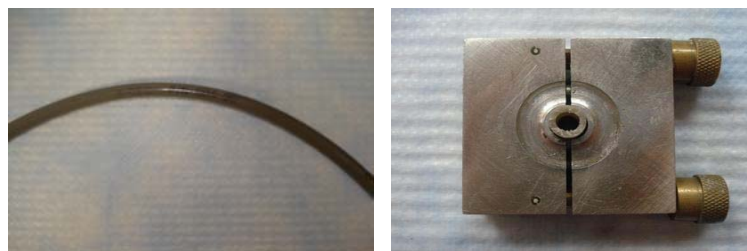


Figure 3. Polycarbonate water tube (left); Small piece of cylindrical Tubing cut to size and placed inside the mould, acting as a separator

Transfer of mixed cement paste to the assembled moulds:

After mixing of the cement into a paste, the large end of an amalgam carrier was used to transfer three aliquots of the cement paste into the cylindrical moulds. Transfer of each aliquot was followed by 10 seconds of treatment by either of the two methods of obturation to be evaluated. This protocol was repeated until the cylindrical moulds were filled flush to their top. At completion of obturation, the metallic moulds, containing the Portland cement paste, were stored in 100% humidity at room temperature and left to harden for one week.

The two methods of obturation:

A total of eight ($n=8$) specimens were made in two groups according to two different placement protocols. In one group (Group 1, $n=4$), aliquots of cement paste were obturated into the moulds using a 10 second application of an equal and constant amount of vertical load to the cement paste. A 5 pound weight placed on top of a piston connected to a custom made metallic obturator delivered the vertical component of the obturation load (Figure 4). The metallic obturator was made to closely fit into the cylindrical moulds (Figure 4). This protocol was repeated during placement of each of the three aliquots of cement paste that made up a whole cylindrical specimen. The second group of samples (Group 2, $n=4$) was prepared similarly, with the difference of addition of indirect ultrasonic energy to the cement paste during its placement. The tip of a vibrating ultrasonic instrument (BUC-2) was placed along an area about one inch above the tip of the obturator to transfer a 10 second burst of ultrasonic energy to the metallic

instrument (Figure 4). The obturator, in turn, propagated the ultrasonic energy to the paste along with delivering its vertical compaction load.

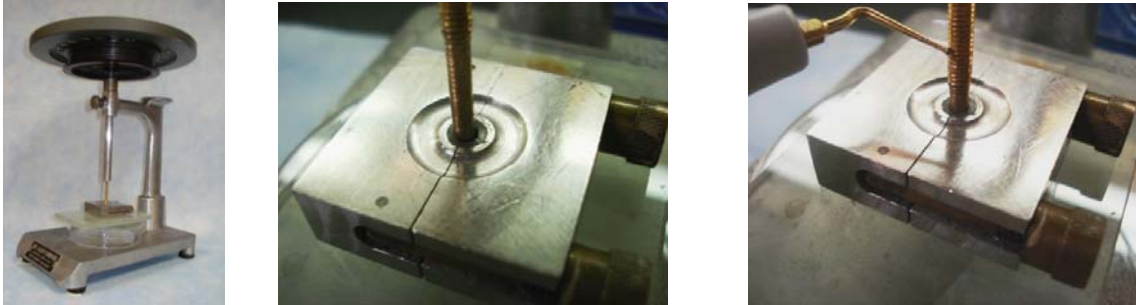


Figure 4. Compaction apparatus with the vertical piston connected to custom plunger, and a 5lb weight on top (left); “Compaction alone”: plunger delivering the vertical compaction force to the cement (middle); “Compaction with indirect ultrasonic activation”: BUC-2 ultrasonic tip placed on an area along the length of the metallic plunger delivering the vertical force on the cement paste

Setting of cement paste:

Samples contained in moulds were stored at 100% humidity at room temperature for one week. A thin layer of deionized water was placed at the bottom of a sealed plastic container. A gridded plastic separator was placed over a thin pool of water at the bottom of the container with the moulds placed on top (Figure 5). The plastic separator was used to prevent the samples from directly coming in contact with the water reservoir, while still setting at nearly 100% humidity and at room temperature. After one week, setting of samples was confirmed. Samples were then pushed out of each mould, and prepared for porosity and compressive strength evaluations.

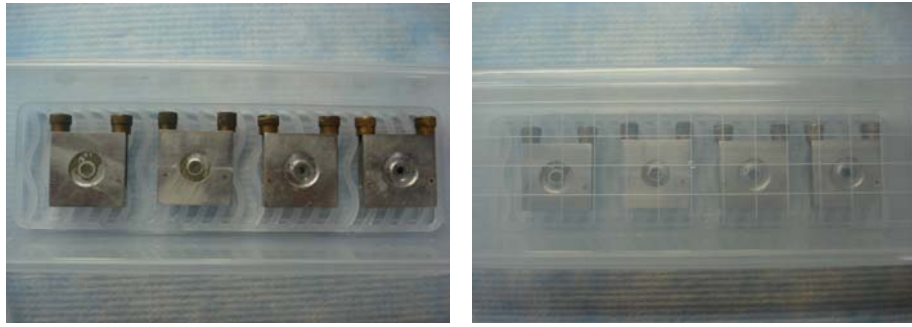


Figure 5. Cement filled moulds placed on perforated plastic separator in the plastic container (left); Water placed under the perforated separator and the lid placed on tightly (right)

Microscopic evaluation of samples:

Randomly selected samples from each group were prepared for stereomicroscopic evaluation. Evaluations were done under 5, 6, and 20X magnifications. The external surfaces of samples were initially evaluated for presence of visibly larger surface pores. Later, samples were ground down using varying grades of sand paper under running water, to make half-cylinders of samples and exposing their internal appearance. Stereomicroscopic evaluations of internal surfaces were also done for presence of notably visible pores in the internal portions of the specimens.

Gas adsorption porosimetry evaluation:

For this purpose, cement samples were sent to Micromeritics (Micromeritics, Norfolk, GA, USA) for evaluation by a gas adsorption porosimetry method. The porosimetric studies required different steps for their sample preparation. In order to obtain a more homogenous sample, initially we attempted to use the middle third portion of the set cylindrical samples for processing and evaluation in the gas porosimeter. However, the

size of our sample was limited by the weight of the sample required for processing by the porosimeter. The measuring device required a sample of at least 0.2 mg in weight. A 4mm middle section of the cylinder yielded a sample of only 0.1 mg. To rectify this obstacle, 2 mm from each end of every 12 mm cylindrical sample was ground away, leaving cylinders of 8mm in height and 4.5 mm in diameter. These samples weighed almost precisely 0.2 mg, and also satisfied our desire to obtain more homogeneous samples of set cement. Prepared samples were subsequently sent for appropriate evaluations.

Samples were processed and evaluated after varying durations of setting time. Briefly, specimens are de-gassed at 40°C for 16 hrs prior to being analyzed. Samples are then placed in a sample tube and heated under vacuum or flowing gas to remove contaminants on the surfaces of the samples. The sample tube is then placed in the analysis port of a 2420 Accelerated Area and Porosimetry System (Micromeritics, Norfolk, GA, USA) for automatic analysis. The krypton adsorption isotherm is recorded at 120 K.

Compressive strength analysis:

As a method, gas porosimetry leaves the samples intact and mainly unaffected. Compressive strength of each sample after porosity evaluation was measured by determining the load required to fracture the samples by an Instron universal testing machine. Cylindrical samples from each experimental group were carefully placed on their vertical axes to stand perpendicular to the two horizontal plates of the Instron testing machine. The mobile upper plate was set to advance at a uniform speed of 1mm per second to deliver the crushing vertical forces to the samples. Increasing vertical forces

were applied to each sample until structural failure was achieved, at which point this maximum weight was recorded.

Statistical analyses:

Statistical analysis comparing the average values of specific pore characteristics and compressive strength of samples was done using a paired student's t-test. Correlation and regression tests were used to look for any relationship between each specific pore characteristic (BET specific surface area of pores, pore volume, and pore size distribution) and compressive strength in general.

RESULTS

BET Specific Pore Surface Area

The average BET pore surface area of samples in Group 1 is calculated to be 6.175 m²/g with a standard deviation value of 4.88. The average BET pore surface area of samples in Group 2 is calculated to be 5.172 m²/g with a standard deviation of 4.07. The two-tailed P value equals 0.1122 (t = 2.2276, df= 3, standard error of difference= 0.450). Despite an apparent trend in BET pore surface area values of samples in Group 1 being larger than those in Group 2, by conventional criteria (p= 0.05), this difference is considered to be not statistically significant. (Figure 6).

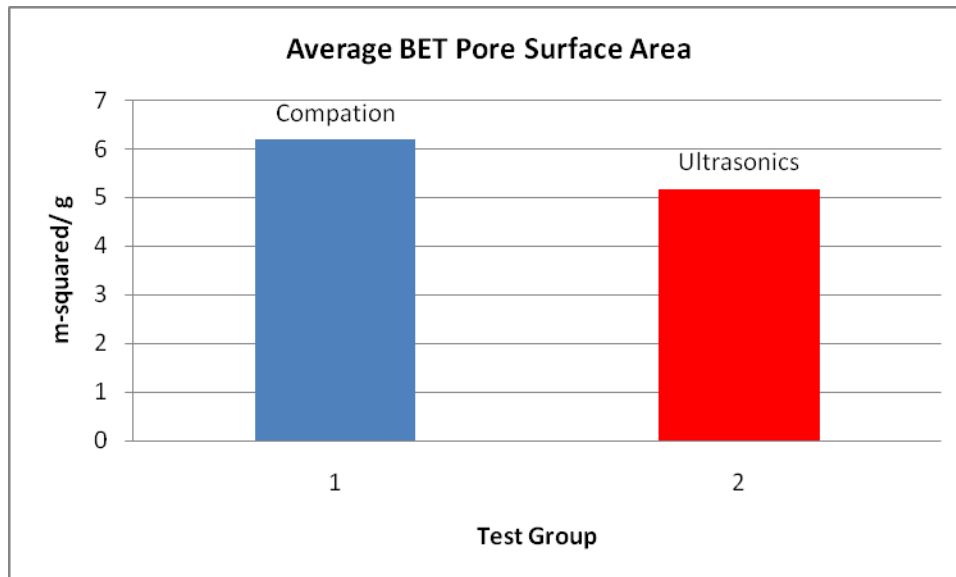


Figure 6. Graph showing the average values of BET specific surface area quantified by the gas adsorption porosimetry

Pore Volume

The average pore volume of samples in Group 1 is calculated to be 0.0257 cm³/g with a standard deviation value of 0.020. The average pore volume of samples in Group 2 is calculated to be 0.0241 cm³/g with a standard deviation of 0.02. The two-tailed P value equals 0.6794 (t = 0.4560, df= 3, standard error of difference= 0.003). Despite an apparent trend in pore volume values of samples in Group 1 being larger than those in Group 2, by conventional criteria (p= 0.05), this difference is considered to be not statistically significant. (Figure 7).

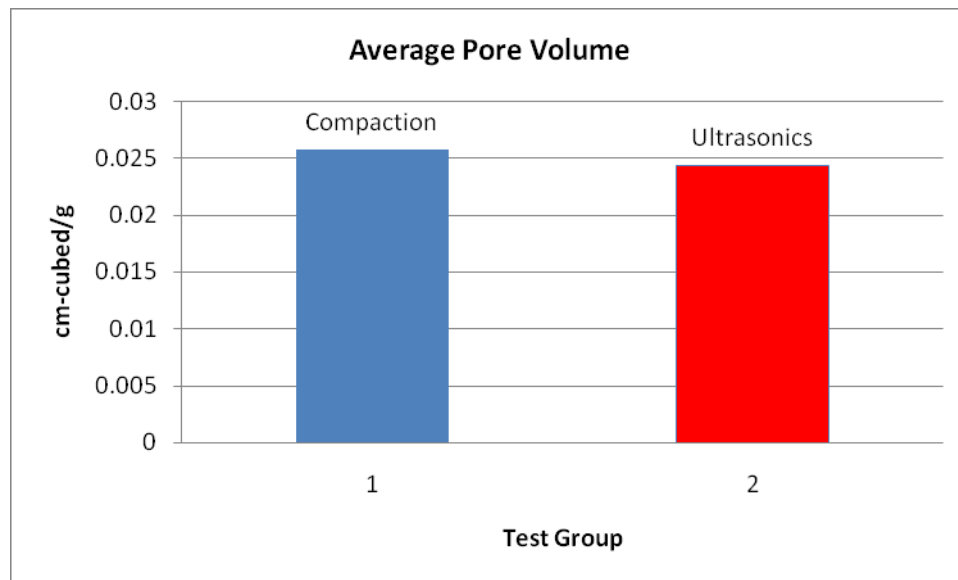


Figure 7. Graph showing the average values of volume of pores quantified by the gas adsorption porosimetry

Pore Size Distribution

The average pore size of samples in Group 1 is calculated to be 239.886 Å with a standard deviation value of 144.27. The average pore size of samples in Group 2 is calculated to be 318.09 Å with a standard deviation of 162.27. The two-tailed P value equals 0.3920 ($t=0.9975$, $df=3$, standard error of difference= 78.399) Despite an apparent trend in pore size values of samples in Group 2 being larger than those in Group 1, by conventional criteria ($p= 0.05$), this difference is considered to be not statistically significant. (Figure 8).

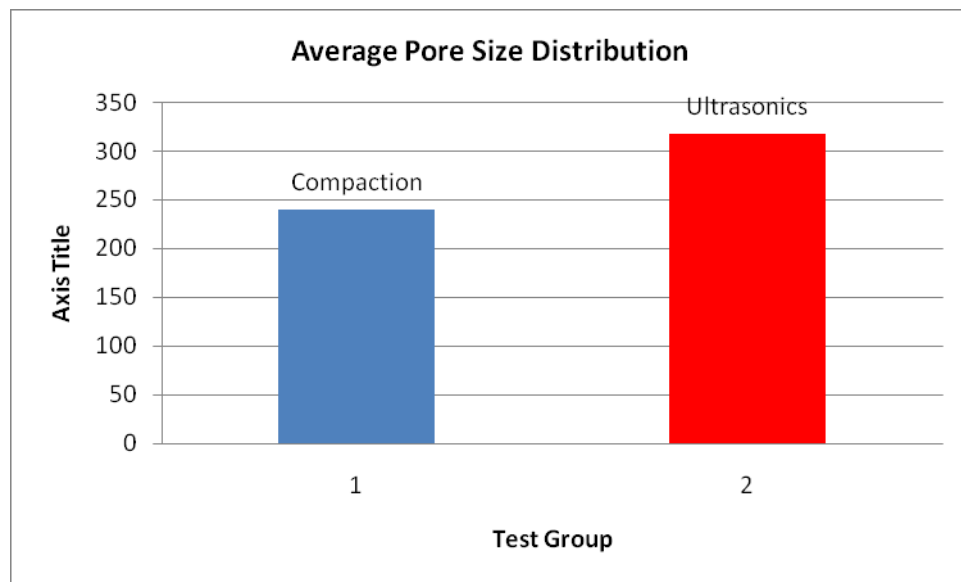


Figure 8. Graph showing the average distribution of size of pores quantified by the gas adsorption porosimetry

Compressive Strength

The average compressive strength of samples in Group 1 is calculated to be 0.543 GPa with a standard deviation value of 0.152. The average compressive strength of samples in Group 2 is calculated to be 0.564 GPa with a standard deviation of 0.212. The two-tailed P value equals 0.4650 ($t = 0.895$, $df=2$, standard error of difference= 0.045). Despite an apparent trend in compressive strength of values of samples in Group 2 being larger than those in Group 1, by conventional criteria ($p= 0.05$), this difference is considered to be not statistically significant. (Figure 9)

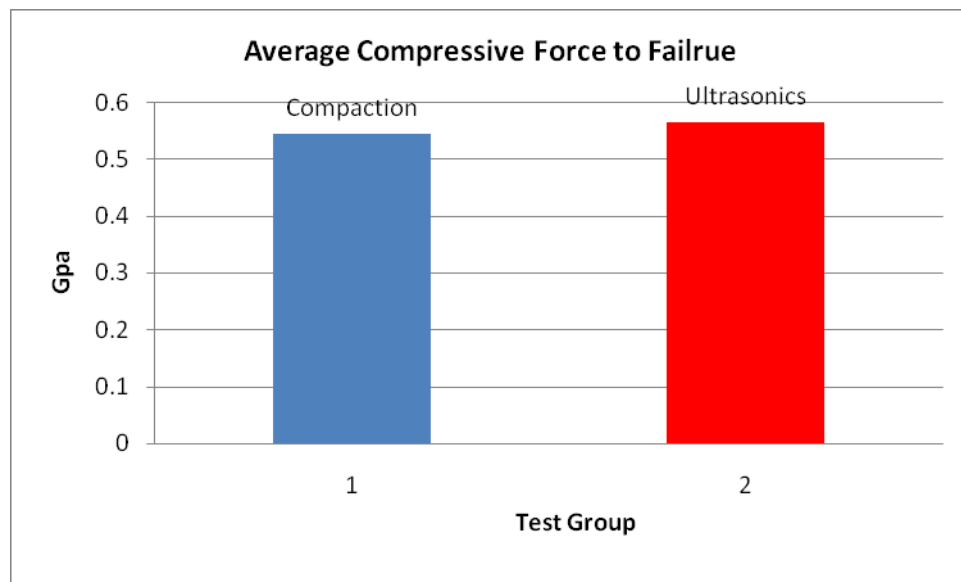


Figure 9. Graph showing the average force applied by the Intron to failure of samples

Regression/ Correlation Analysis

A regression and correlation analysis was done to evaluate the relationship between each specific pore characteristic and compressive strength of combined samples from both groups in an attempt to investigate which, if any, of the pore characteristics would possibly affect the compressive strength.

Compressive strength vs. BET specific pore surface area:

A regression analysis of compressive strength of samples against the BET pore surface area reveals a negative regression with a correlation coefficient of -0.0995 (P value= 0.736). Given the limited number of samples, no statistically significant correlation may be drawn between compressive strength and BET specific pore surface area of samples. (Figure 10, Top).

Compressive strength vs. Pore volume:

A regression analysis of compressive strength of samples against the pore volume reveals a negative regression with a correlation coefficient of -0.067 (P value= 0.823). Given the limited number of samples, no statistically significant correlation may be drawn between compressive strength and pore volume. (Figure 10, Middle)

Compressive strength vs. Pore size distribution

A regression analysis of compressive strength of samples against the pore size reveals a negative regression with a correlation coefficient of 0.279 (P value= 0.334). Given the limited number of samples, no statistically significant correlation may be drawn between compressive strength and pore volume. (Figure 10, Bottom)

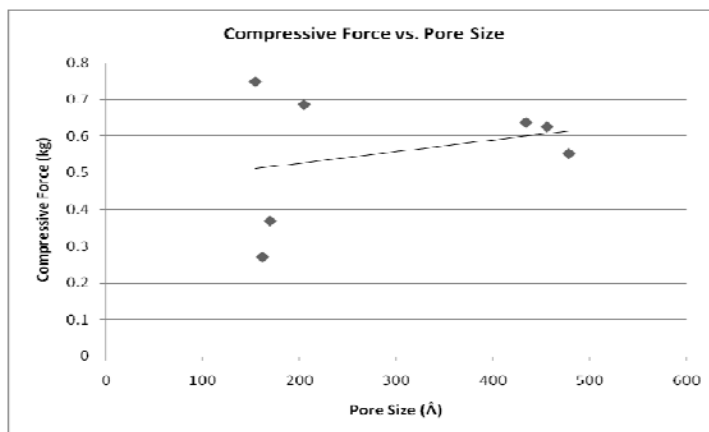
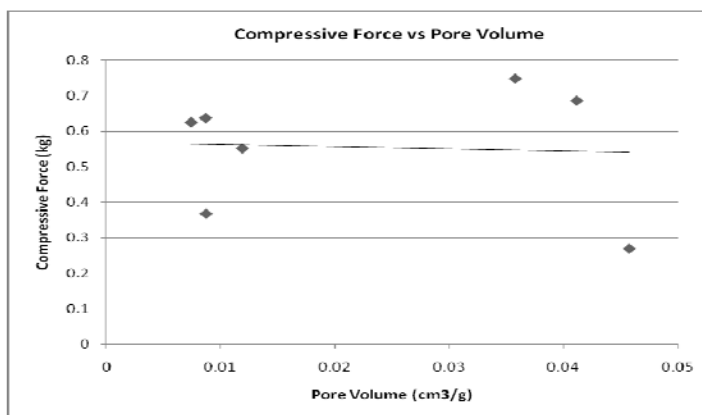
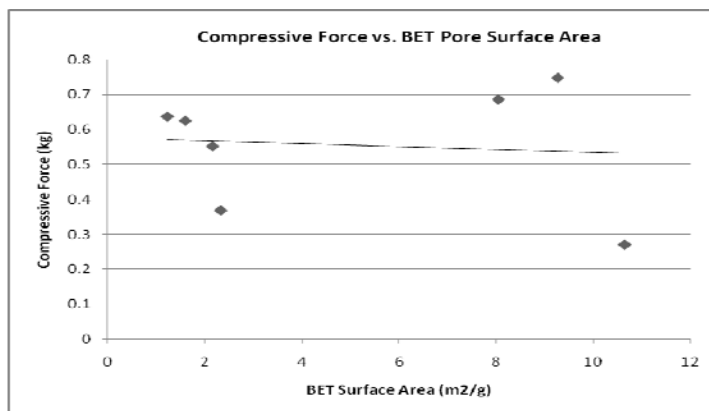


Figure 10. Best fit line through intercepts of specific pore characteristics and compressive strength of samples. The top and middle graphs show a slight positive correlation; The bottom graph shows a slight negative correlation.

Stereomicroscopy

A visual inspection of samples was done through a stereomicroscope to look for any observable differences between samples prepared by either of the two compaction methods. Figure-11 shows a 5x magnification of randomly selected samples from each group placed side by side. The specimen on the left hand side was prepared by a vertical compaction force alone (Group 1). The specimen on the right hand side was prepared by the same vertical compaction force along with ultrasonic activation of the paste during placement (Group 2). Initially we noticed visible differences in the surface appearance of the two cylindrical specimens. The sample on the left presents a more uniform appearance of its outside surface area. No obvious large porosities or transition lines is seen on the outside surface of this sample. On the other hand, the specimen on the right hand side presents numerous larger porosities and a number of transition lines which correspond to the junction between aliquots of cement paste placed on top of each during the segmental compaction of the cement (Figure 11 : A and B arrows, respectively).

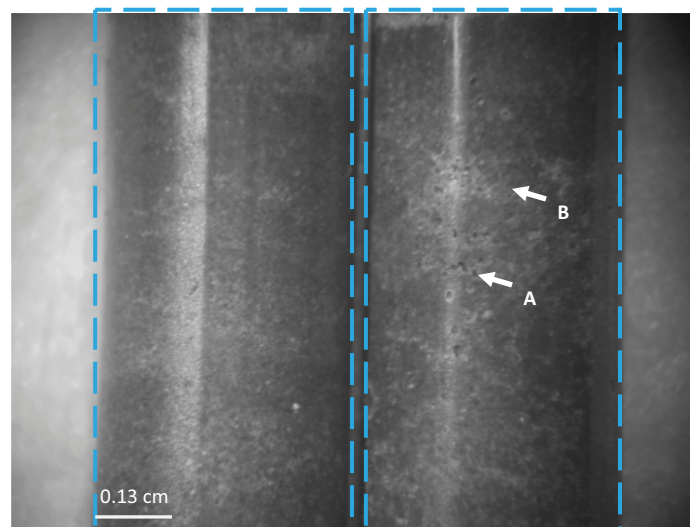


Figure 11. Samples of set cement placed side by side under 5x magnification. Note the presence of visible pores on the surface of specimen from the indirect ultrasonic activation group (A); Slight variation in color marks the border between aliquots of cement placed to make up the whole sample in the indirect ultrasonic group (B).

Each cylindrical specimen was then ground down to half-cylinders to expose a surface cross section through the middle portion of each sample. The same side by side comparison of cross sections of samples arranged as before, but at 6 times magnification, reveals similar arrangement of larger pore sizes and transition lines present throughout the interior bulk of the sample prepared by compaction in conjunction with ultrasonic activation (Figure 12).

A closer look at transition lines visualized at 6 times and 20 times magnification reveals weak faults created between aliquots of cement samples placed by the combined compaction and ultrasonic activation method (Figure 13)

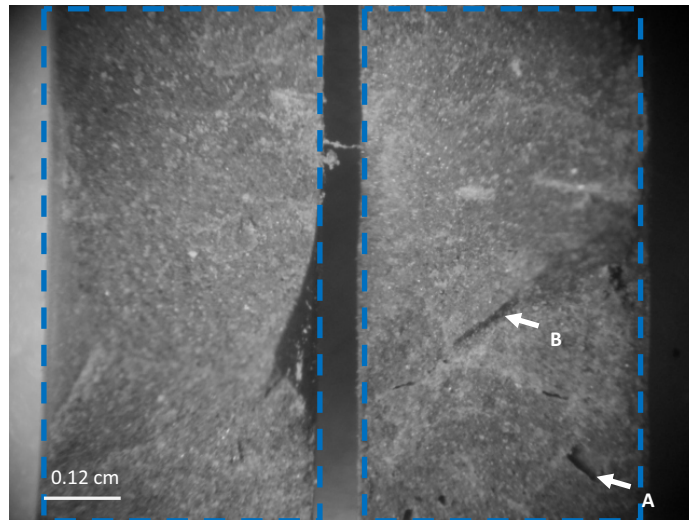


Figure 12. At 6x magnification, large internal pores (air-bubbles) could be seen in cross sections of samples from the indirect ultrasonic activation group (A); Transition areas between aliquots of cement presenting as “watered-down, weak fault-lines

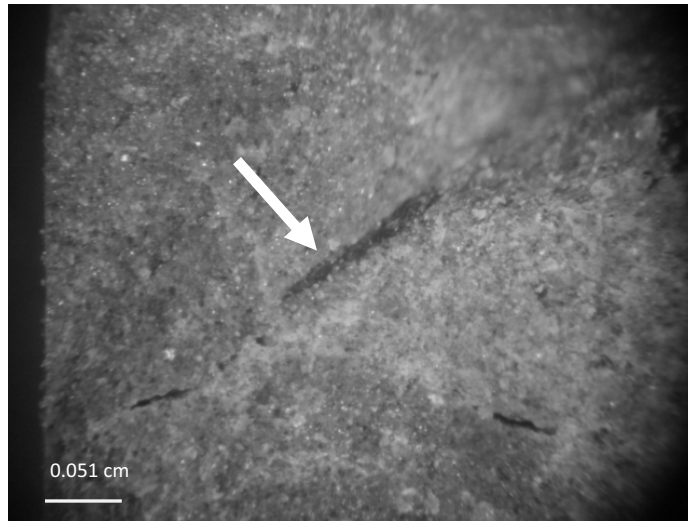


Figure 13. At 20x magnification transition areas between aliquots of cement presenting as “watered-down, weak fault-lines are even more clearly apparent

DISCUSSIONS

In this study, we introduced gas adsorption porosimetry as an acceptable method for evaluation and distinction of specific pore characteristics of a dental restorative material, namely its BET specific surface area, pore volume and pore size distribution. This method of analysis generates quantitative data with values that reflect on those specific pore characteristics of solid but porous materials. This data may be used for comparative evaluation and statistical analysis of pore characteristics of different materials in addition to evaluating the effects of chemical or physical manipulations on the materials' specific pore characteristics.

Gas adsorption porosimetry may be used in numerous ways for analysis of dental restorative materials. It may be used to compare the porosity of different types of solid but porous restorative materials. For example, one may use this method for comparing the general porosity and pore characteristics of two different dental restorative materials. It may similarly be used to evaluate the effect of various additives or clinical methods of application on porosity of otherwise similar restorative materials. For instance, one may use this method to evaluate the effect of addition of a new component to an already existing material, or the effect of a clinically applicable placement method on the general porosity or pore characteristics of a specific material tested against a control group.

Gas adsorption porosimetry also provides the added benefit of “reversibility”, meaning that samples that have endured the evaluation process remain virtually un-damaged and

intact. Therefore, the same specimens tested by this method of pore analysis may be used for further analysis of their other physical parameters. This could potentially strengthen the value of any correlation between the porosity and specific pore characteristics of a material to its other material characteristics, such as flexural and compressive strength.

However, similar to other methods of analysis, gas adsorption porosimetry does not come without its own subtle limitations or drawbacks. One such limitation is the optimal range of pore sizes that can most accurately be evaluated by this method. Gas adsorption porosimetry is a popular technique for the study of pore structure in cement pastes with radii between 1nm to about 60nm. Therefore, gas adsorption techniques can more accurately characterize gel pores and small and medium sized capillary pores, still making this method ideal for evaluating the pore characteristics of dental restorative materials.

Another limitation is vested in its core theoretical assumptions which, at best, provide the closest estimate of the pore characteristics of a porous material which may not necessarily be reflective of the exact and actual interpretation of the porosity and pore characterization in that object. However, the accuracy of this method is comparable to other methods used in quantitative evaluation of pore characteristics of porous materials, such as mercury infusion porosimetry, with the added benefit of reversibility as was stated before.

An additional variable that should be kept in mind is the type of material that is selected for testing by this method. In preparation for testing, all samples are heated and placed in a vacuum chamber for removal of all residual moisture and gaseous impurities before infusing the chamber with the desired test-gases. Therefore, all experimental materials selected for testing by this method must be able to withstand such procedural necessities. For example, the possibility of premature removal of residual liquid from a sample that relies on a hydration-reaction for its setting and hardening may potentially affect the compressive strength of that material. In fact, this has been previously shown by other investigators who have reported that the compressive strength of a Portland cement specimen would increase over time as the slow hydration-reaction takes its course to completion. Disturbances in this slow chemical conversion over time may potentially affect some mechanical characteristics and physical parameters of the hardening cement. In our study, to compensate for such a potential source of discrepancy in compressive strengths of specimens, all samples were prepared and tested by the gas adsorption porosimeter following an equal interval of seven days time allowed for their initial hardening.

When comparing the pore characteristics of samples placed by either of the two tested placement methods, our overall preliminary results showed no significant differences between the BET pore surface area, pore volume, and pore size distribution of samples from either of the two groups. The numbers of specimens tested in this study were limited by the high cost of a larger scale analysis. Furthermore, the large values of observed standard deviations would not make any conclusive remarks possible. However, these

preliminary data display a number of observed trends which will be discussed later. Future investigations using larger numbers of specimens will be needed to either support or refute these empirical findings.

Surface and cross sectional stereomicroscopic inspection of the samples from each group led us to a number of initial impressions related to structural differences between the two. At least visually, it appeared that a sample prepared by compaction alone had a more uniform outer surface (the surface in contact with the walls of the mold) which was devoid of any noticeably large sized air-entrapped pores (air-bubbles) that were more readily observed on the outer surface of the sample prepared by the indirect ultrasonic activation of the paste during its placement. A similar pattern was also observed in midline cross sectional preparations of samples from both groups. These cross sectional preparations also revealed the presence of more numerous air-entrapped pores in samples prepared by ultrasonic activation. Similar observations have also been reported in other investigations where a “direct” activation of the cement through insertion of the vibrating ultrasonic tip into the paste is thought to create a “whipping” motion in the paste, leading to introduction of larger air bubbles into the paste [16]. Another explanation for this observation may be related to a phenomenon of the action of ultrasonically vibrating instruments in liquid media, called “acoustic cavitation”. When the file vibrates in a liquid medium, the acoustic energy is carried through the liquid by the back and forth motion of the molecules along the direction of propagation. This produces alternate compressions and rarefactions in pressure. At a certain threshold displacement amplitude of the file and at a critical value of the negative acoustic pressure amplitude, dependent

on the liquid's local conditions of temperature, viscosity, dissolved gas content, and microscopic particulate content, the tensile strength of the liquid is exceeded and a vapor cavity forms. The subsequent positive pressure phase of the acoustic field then forces this vapor filled cavity to implode, thereby converting the potential energy gained in growth into a concentrated region of kinetic energy as the cavity collapses [90]. This phenomenon may potentially introduce larger bubbles into a more viscous medium, such as that of our Portland cement paste specimens. Although through an indirect route in our experimental model, ultrasonic energy may have similarly propagated through the plugger delivering the vertical force on the cement to create a similar “whipping” motion or cavitation that resulted in the observed air-entrapped pores in our samples. Further studies are needed to evaluate and analyze the physical impact of various levels of ultrasonic or sonic energy applied during preparation of such samples. Data from such studies may lead to recommendations for an optimal range of vibration energy that would maximize the physical characteristics of a prepared paste.

Another noteworthy observation that was made only in the sample prepared by the indirect ultrasonic activation was the presence of horizontal demarcation lines between aliquots of cement placed during obturation of the mould. Each aliquot of cement was carried to the mould by the large end of an amalgam carrier, packed into the mould under a constant and equal force along with simultaneous ultrasonic activation of the plugger for ten seconds. This protocol was repeated until the cement pate filled the mould to the top. Higher magnification inspection of a cross sectional surface of the indirectly ultrasonically activated sample visually verified these demarcations as weak “fault-lines”

in structural make-up of the sample. A plausible explanation for formation of such weak demarcations may be that the agitation provided by the ultrasonic energy may have potentially forced the solid particles of Portland cement to stack-up more closely against each other by forcing any unbound water out of the spaces between those particles, and essentially, causing sedimentation of the solid entities in the water-cement paste mixture. Consequently, this may have resulted in formation of a thin layer of water on top of a more densely-packed aliquot of cement, and effectively change the water-to- powder ratio of the next aliquot of cement paste placed at that defined interface. Other reports have shown that a critical increase in the liquid component of a hydraulic cement would lead to a decrease in the strength of the material. These “watered-down” interfaces may ultimately present as those weak “fault-lines” seen in the indirect ultrasonically prepared samples in our magnified images.

Such observations alone suggest that the indirect ultrasonic activation of the cement paste during its placement may have both micro-structural and macro-structural effects that are reflected on the general porosity and potentially the specific pore characteristics of the sample. Although a “whipping” motion or acoustic cavitation may be suggested as possible sources for inclusion of larger sized air-bubbles in samples placed with the aid of ultrasonic energy activation, a more general reduction in the size, surface area, and volume of smaller pores may be expected due to the observed sedimentation and separation of unbound water particles from the total sample. In an attempt to support or refute these initial findings and impressions, we used a gas adsorption porosimetry

method to quantify and analyze specific pore characteristics of our Portland cement samples, and to evaluate the differences for statistical significance.

Overall, based on the limited number of samples tested, no statistically significant differences in either the average BET specific surface area, pore volume or pore size distribution of samples from either of the two groups may be reported. The observed large values of standard deviations also make the difference between the two groups hard to define. Use of larger sample sizes in future studies may challenge or support the statistical significance of our reported results. However, from these preliminary data, trends may be observed which give support to interpretations of our initial visual observations. First, we searched for differences in BET specific pore surface area of samples from the two groups. Our data showed a *trend toward larger average surface area of pores in those samples prepared by compaction alone*. In contrast, there was a trend toward smaller average surface area of pores in those samples prepared by compaction in conjunction with ultrasonic activation of the paste during its placement. Second, we looked at the average pore volume of samples from the two test groups. Again, we observed similar results with *samples prepared by compaction alone showing a trend toward larger average pore volumes compared to those prepared by the indirect ultrasonic activation method*. Last, we looked at the average size distribution of pores in samples from each group. These data revealed a *trend which showed smaller average pore size distributions in samples prepared by compaction compared to those made using the indirect ultrasonic activation method*. Such observations tend to also relate intuitively. In solid but porous materials of similar dimension, one would expect to see

an increase in both pore surface area and pore volume with decreasing pore sizes. To draw a parallel, consider the anatomic makeup of a human lung. The presence of increasingly smaller compartments in the lungs is considered to increase both the surface area and volume of available air-spaces while decreasing the size of pores in the lungs. A similar relationship may be drawn here from the observed data, expecting samples prepared by compaction alone to have a larger number of smaller pores compared to those prepared by the indirect ultrasonic activation method.

These claims may also be supported by our report of presence of visually larger pores (air-bubbles) in samples placed by the indirect ultrasonic activation method. Such observations concur with our report of larger values for average pore sizes along with the expected correspondingly smaller average pore volume and average pore surface area of samples prepared with the aid of an indirect ultrasonic activation method. However, such findings are in contrast with our report, based on visual evaluations, of possibly more sedimentation of solid Portland cement particles in the paste prepared by the indirect ultrasonic method. This conclusion was based on the pooling of water observed on top of each aliquot of cement paste placed to make up a whole sample. This would suggest that samples prepared by the indirect ultrasonic activation method would expectedly have smaller pores sizes, while presenting larger pore surface areas and pore volumes. Yet, this was not supported by our quantitative evaluation. In an attempt to explain these results, we may relate these findings to “out-liers” in our data. In reality, the indirect ultrasonic activation may have created more densely packed specimens with smaller pores and potentially larger pore surface areas and pore volumes, but the visibly larger

pores, as visualized in stereomicroscopic evaluations, may present as “out-liers” that skew the data enough to support results reporting larger *average* pore size distributions and smaller *average* pore surface areas and pore volumes that contradict the visually observed signs of sedimentation in the indirectly activated ultrasonic method. Excluding these “out-liers”, therefore, we may report that samples prepared by indirect ultrasonic activation are indeed more densely packed at a more microstructural level when compared to those placed by compaction alone.

Based on our limited preliminary data, we also report that the placement method did not have a statistically significant effect on the average compressive strength of the samples from the two groups. *However, there was a trend toward samples in the ultrasonically activated group having a higher average compressive strength values than those samples placed by compaction alone.* As we discussed above, our impression of the pore characteristics of samples from the two groups is that those samples from Group 1 have less pronounced air-bubbles while containing mainly larger microstructural pores, while those samples prepared by ultrasonic activation tend to have larger air-bubbles along with a core of Portland cement particles that is more densely packed. This overall higher density of samples in Group 2 may be translated into their higher average compressive strengths supported by the quantitative data. Presence of few air-bubbles, as seen in visual evaluation of samples, may had been compensated by the more densely packed cement particles at a microstructural level. This density may be related to the observed higher average compressive strength of samples from the group placed by the indirect ultrasonic activation method.

Correlations between compressive strength of samples and their corresponding specific pore characteristic values did not show any significant relationships. This may mean that each specific pore characteristic by itself does not have a strong influence on compressive strength of the specimens. A combination of evaluated specific pore characteristics may be more predictive of a relationship between general porosity and compressive strength in general. A small sample size, as was the case in this study, would not permit making conclusive remarks about those relationships. These findings may be challenged based on larger-scale studies in the future.

CONCLUSIONS

1. Gas adsorption porosimetry may be used to quantify specific pore characteristics of dental hydraulic cement based dental restorative materials
2. Ultrasonic agitation of the cement may separate the liquid from the solid component of each aliquot of cement, producing weakened areas at the interface between aliquots of paste placed on top of each other
3. Larger scale studies are needed to evaluate the superiority of one method of placement over the other.

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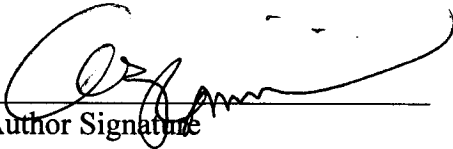
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