There are a plethora of dental cements that have been used historically in dentistry. The following review will touch on all of those types but will finally focus on the two major ones in current use, resin-modified glass ionomer and composite (or resin) cements. At the outset, consider general conditions under which cements are used and their primary goals.

Cements provide retention and sealing. However, both of these depend on other important resistance and retention form features of the preparation. If less tooth structure is available for resistance form, more complex the stresses will be on the cement and long term retention and sealing will be compromised.
Two principal terms are used to describe retention of cemented prostheses – luting and bonding. [CLICK] As shown above, the prepared surface of tooth structure is actually quite rough and usually appears scalloped from the teeth of the bur or diamond that was used to cut it. Scallops may be 25-100 microns across their width. Several hundred tubules are involved with each scallop at a finer scale. [CLICK] Luting cements take advantage of these scallops to become mechanically locked along the path of draw.

Quite often a dentin tubule sealer, such as GLUMA, is applied first. [CLICK] It’s job is to help occlude the tubules. There is also a very fine smear layer impacted across the entire surface of 1-2 microns. Subsequent etching removes any smear layer and relieves intertubular spaces to prepare for bonding to the intertubular dentin. [CLICK]

Bonding implies fine micromechanical bonding. The smear layer is removed and a 2-3 um hybrid zone is generated. [CLICK] Until the advent of bonding in dentistry, luting was the sole mechanism of retention of dental cements. Polymer-based cements now can include bonding as well.
A large number of different cavity preparation surfaces (adherends) may be encountered (see above) and coupled to an equally diverse number of restorative materials (see above). The combination of adherends, adhesives (or cements), and interfaces comprises a dental joint.

To understand the key properties of cements, it is crucial to examine the variety of interfaces that may be involved between the tooth structure and prosthesis. Luting cements used with casting alloys will have a tooth/cement and cement/prosthesis interface. Adhesive cements used with all-ceramic prostheses will have tooth/bonding-system, bonding-system/composite-cement, composite-cement/silane-coupling-agent, and silane-coupling-agent/ceramic interfaces. Most problems arise at these interfaces where either there are poor wetting or incompatibilities that create weak links and/or defects such as pores. During loading pores permit crack formation. Cracks propagate along weak interfaces.
Imagine a simplified view of the margin of a cast gold crown as shown above. It is tempting at first to concentrate on the large volume of dental cement that occupies the space under the entire crown. However, the most critical portion of any cement is that portion at the margin. While the bulk of the cement contributes to retention, the small portion at the margin is the most important for sealing. If retention persists, but sealing fails, the procedure is a failure.

Sealing includes the prevention of both (1) fluid flow (which causes pain) and (2) microleakage (which causes inflammation). Dentin includes a large number (30,000/mm²) of dentinal tubules filled with odontoblastic processes and/or dentinal fluid. A very tiny movement of fluid in response to osmotic pressure changes (concentrations of sugar or salt in the saliva or shifts in temperature) will be sensed by mechanoreceptors at the wall of the pulp chamber near the odontoblasts as rapid and sharp pain. This is the classic symptom described by patients. “It hurts when I drink cold water, or when I have sweets in my mouth, or when I chew.” Sealing dentin prevents this event and prevents “sensitivity.” Microleakage is the penetration of chemicals called endotoxins (cell wall constituents released from decaying bacteria generally from plaque) from diffusing through dentinal tubules to the pulp and producing pulpal inflammation. Microleakage is a slow and insidious process. Pulpal inflammation may produce a low level dull pain or not even be sensed at all. Both events are eliminated if a cement or adhesive functions well in sealing the tooth. Small breaches in the sealing system lead to problems and failure.

It is probably more helpful to review the key cement facts at the start rather than the end. There is no correlation of laboratory results and clinical properties for cements. The general recommendation for cement use for the last 10 years has been to use RMGI with metal substructures and use composite cements with all-ceramic restorations. Cement failure occurs by fatigue (which is typical of almost all dental materials) in which a crack forms and is propagated. Actual dental cement compositions are not stable but change constantly in the oral environment. Cements are theoretically strong enough, if they would just resist changes over time. Cement effectiveness depends on retention and sealing. Generally enamel margins are more stable than dentin ones because they are supragingival and more well bonded. The highest stresses in cemented restorations occur at cement margins. Stress is transmitted through the crown around the coronal portion of the tooth toward the margin.
All dental cements have a common microstructure (micro-architecture) that is represented as islands of dispersed reinforcing filler particles within a matrix of reaction products. For a traditional dental cement, the mixture is made from a ceramic powder with an acidic liquid. A portion of the powder particles is dissolved in the acid, releasing ions that react with the acid to produce a salt. [CLICK] The reaction leads to either precipitation of a crystalline matrix or crosslinking of a polymer phase to produce an amorphous solid matrix. In either case, the microstructure looks the same. Properties of the set cement are proportion to the quantity of reinforcing filler or powder particles within the set cement. Filler particles lead to good qualities for all properties. Matrix is the weaker and more soluble phase. When dental cements are used as bases, the filler or powder portion is maximized to provide optimal properties. For luting, more matrix occurs because the mixed mass must be lower in viscosity to permit flow and seating of the prosthesis. Therefore, the properties are not as good as they might be.

[CLICK] Included is a picture of zinc phosphate cement at 50,000X magnification. While it is initially hard to identify the phases, the microstructure includes residual ZnO particles [CLICK], tertiary zinc phosphate crystals [CLICK], and pores [CLICK]. Pores seem to be part of all dental materials and have a strong effect on the properties of the final product.
### OVERVIEW OF DENTAL CEMENTS

<table>
<thead>
<tr>
<th>Cement Type:</th>
<th>(Abbr.)</th>
<th>LIQUID</th>
<th>POWDER</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Zinc Oxide Eugenol:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZOE</td>
<td>(ZOE)</td>
<td>Eugenol</td>
<td>ZnO</td>
</tr>
<tr>
<td>Reinforced ZOE</td>
<td>(RZOE)</td>
<td>Eugenol</td>
<td>ZnO, Polymer, Rosin</td>
</tr>
<tr>
<td>ZOE-EBA</td>
<td>(EBA)</td>
<td>Eug, EBA</td>
<td>ZnO, Al₂O₃, Rosin</td>
</tr>
<tr>
<td>HV-EBA</td>
<td>(HV-EBA)</td>
<td>HV, Eug</td>
<td>ZnO, Al₂O₃, Rosin</td>
</tr>
<tr>
<td><strong>Zinc Phosphate Silicate:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(ZP)</td>
<td>H₃PO₄ / H₂O</td>
<td>ZnO</td>
<td></td>
</tr>
<tr>
<td>(SC)</td>
<td>H₃PO₄ / H₂O</td>
<td>F-Al-Silicate glass</td>
<td></td>
</tr>
<tr>
<td>(ZSP)</td>
<td>H₃PO₄ / H₂O</td>
<td>ZnO, F-Al-Silicate</td>
<td></td>
</tr>
<tr>
<td><strong>Polycarboxylate:</strong></td>
<td>(PC)</td>
<td>PAA / H₂O</td>
<td>ZnO</td>
</tr>
<tr>
<td><strong>Glass Ionomer:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conventional</td>
<td>(GI)</td>
<td>PAA / H₂O</td>
<td>F-Al-Silicate Glass</td>
</tr>
<tr>
<td>Resin-Modified</td>
<td>(RMGI)</td>
<td>“ + HEMA, …</td>
<td>F-Al-Silicate Glass</td>
</tr>
<tr>
<td>Compomer</td>
<td>(CM)</td>
<td>(Monomers)</td>
<td>F-Al-Silicate Glass</td>
</tr>
<tr>
<td><strong>Composite (with DBS):</strong></td>
<td>(CC, CP)</td>
<td>(Monomers)</td>
<td>(Silicate glass fillers)</td>
</tr>
</tbody>
</table>

The table above shows the wide range of types of dental cements that have been used over the last 150 years. It is important to appreciate their compositions and properties because this information explains the path to choosing the currently popular compositions. It is divided into traditional ceramic dental cements (top half) and resin-based cements (bottom half). Both have composite structures and can be viewed as a combination of residual powder dispersed in a reaction product matrix.

The table shows the categories, acronyms (abbreviations), major components of the liquids, and major components of the powder portions of the materials. Each will be described in more detail shortly.
The earliest dental cement composition was zinc oxide and eugenol (ZOE). [CLICK] Cast alloys were actually used in dentistry as early as 1850 by grinding up gold coins as a source of material. Their composition is roughly that of a Au-Cu Type III composition used today. Impressions were accomplished with plaster. Once set the impression was fractured carefully along occlusal and facial surfaces so that it could be re-assemble by gluing and poured to generate a working cast. Dies were waxed and invested in plaster. The investment mold was cast by melting gold in a coal or charcoal furnace, pouring it into the mold, and using steam, and centrifugal force from a sling to drive the molten alloy into the detailed portions of the mold space. The finished restoration was then cemented with ZOE. While cemented alloys were not in common use, the indirect fabrication process could be accomplished at least in a primitive way.

[CLICK] Experiments with early versions of zinc phosphate cement occurred at the National Bureau of Standards in the 1900-1920 range. [CLICK] Silicate cements arose during the 1930s as restorative materials but with some application as luting materials. [CLICK] Polycarboxylate cement was invented by Dr. Dennis Smith in 1960. [CLICK] Glass ionomer cements for restorations and luting were introduced into dentistry in 1972 but Alan D. Wilson (who contributed earlier to silicate cement research) as a hybrid cement using silicate cement powder and polycarboxylate cement liquid. [CLICK] Composite cement was introduced about 1980 but not used very often until later. [CLICK] Resin modified glass ionomers and [CLICK] compomers evolved from glass ionomer after 1990. [CLICK] Only some of these appear in a contemporary dental practice and that number has focused on just a couple in recent times.
Which cement do you use or do others use? Quite often the response to this question is based on the type which they were initially trained to use. There is often a direct correlation between the age of the clinician and type of cement preferred. It is common to find that clinicians who are 55-65 years old prefer to use zinc phosphate cement. Clinicians who are 45-55 years old prefer polycarboxylate and glass ionomer. Clinicians who are 25-45 years old prefer resin-modified glass ionomers. As we will see shortly, it is much more important to manipulate the materials properly rather than to choose one type over another.

**Dental Cement Use**

<table>
<thead>
<tr>
<th></th>
<th>1990</th>
<th>1995</th>
<th>2001</th>
</tr>
</thead>
<tbody>
<tr>
<td>EBA (ZOE)</td>
<td>1%</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Zinc Phosphate</td>
<td>22%</td>
<td>12%</td>
<td>10%</td>
</tr>
<tr>
<td>Polycarboxylate</td>
<td>33%</td>
<td>17%</td>
<td>5%</td>
</tr>
<tr>
<td>GI, RMGI, Compomer</td>
<td>42%</td>
<td>65%</td>
<td>75%</td>
</tr>
<tr>
<td>Resin (Composite)</td>
<td>2%</td>
<td>6%</td>
<td>10%</td>
</tr>
</tbody>
</table>

The effect of changing preferences is revealed by monitoring some of the professional surveys like those from CRA Newsletters. [CLICK] The information from 1990 and 1995 come directly from published reports. The information from 2001 was extracted from a series of tables from a CRA Newsletter.

[CLICK] In 1990, traditional glass ionomer was just beginning to become popular. There was a notable shift away from zinc phosphate and polycarboxylate use. [CLICK] By 1995, resin-modified glass ionomers (RMGI) were routinely available and this trend was even more noticeable. The rapid rise in the use of all-ceramic restorations also led to increased use of resin or composite (they are the same thing) cements. All-ceramic restorations function best if stress can be effectively transferred across the cemented interface. [CLICK] By 2001, RMGI and composite cements became the most often utilized materials by far.

[CLICK] Now, compomer cements have been slightly refashioned as “universal cements” to replace RMGI and composites” and providing the best of both. The first entry into the “universal cement” market was 3M-ESPE’s UniCem. In addition, these materials have the potential to include self-etching bonding system technologies that allow them to bond at the same time. MaxCem is Kerr’s competitive product. All of the companies are now developing similar products. This may soon be the only cement type in existence.
All dental cements take considerable time to go to completion of all setting reactions. On the graph above, the percentage reaction conversion (y-axis) is plotted versus the log of time (x-axis). Once mixing starts, the reactions start. Traditional ceramic dental cements (which are shown by the red line above) quickly reach a point that they are gelled but do not necessarily complete the reaction very quickly. Consider traditional ceramic dental cements first.

After about 25-50% conversion from reactants to products, [CLICK] the mass is hard. However, the cement does not achieve its final mechanical properties for hours or days afterward. Once setting starts the material should not be disturbed or else cracks will develop. [CLICK] The early reaction is monitored with a penetrometer. [CLICK] At the onset of setting the material is solid but usually only 25% reacted. At the completion of setting a few minutes later, it is 50% reacted but beginning to slow down considerably. The reason is that diffusion is very slow in the solid state.
As we start the discussion of dental cement properties (in a general way), remember that there is a long list of potential properties of interest. The most logical manner to consider them is in terms of physical, mechanical, chemical, and biological ones. Not all properties are important to know or monitor. In many cases, the ones which are reported are the ones that are easiest to measure and not the ones of special importance for understanding clinical success. No single laboratory property predicts success.

In the category of physical properties, [CLICK] the linear coefficient of thermal expansion (LCTE or \( \alpha \), ppm/°C) and thermal conductivity are important and should be close to that of tooth structure. Cements have low coefficients (10-20 ppm/°C). They are generally good insulators. Most dental cements are 100-150 \( \mu \)m thickness and have a modest effect.

[CLICK] While the mechanical properties are generally reported in terms of compressive, diametral tensile, or shear strengths, the more practical information about the retentive properties of a cement is its bond strength. Referring to the list of materials in the next slide, the trend is for strength to increase from the top to the bottom list of cements.

[CLICK] Probably the most intuitive chemical property is resistance to solubility and disintegration. Unfortunately the results of the standard laboratory test that tries to simulate this event is not only not predictive of clinical success but often reports the worst results for the best materials. This will be discussed in detail later. Absorption is important as well but rarely measured.

[CLICK] The biological properties of the materials are considered for the most part clinically acceptable. This does not mean that dental cements are inert. Rather such small quantities of components are typically released that they do not exert any real biological threat to the body. In addition, most materials that are released tend to diffuse through the tubules toward the pulp where they are cleared. The dentinal fluid with its many ions has a strong buffering potential and tends to neutralize acidic or basic materials being released. As long as there is approximately 0.5 mm of remaining dentin thickness (RDT), buffering is very effective.
## DENTAL CEMENT PROPERTIES

<table>
<thead>
<tr>
<th></th>
<th>Physical Properties</th>
<th>Chemical Properties</th>
<th>Mechanical Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Setting $\Delta l$ (µm/cm)</td>
<td>Solubility (w/o, 37°C, 7d)</td>
<td>CS (psi, 37°C, 7d)</td>
</tr>
<tr>
<td>ZOE</td>
<td>-31 to -85</td>
<td>0.02 to 0.10</td>
<td>2000 to 5500</td>
</tr>
<tr>
<td>R-ZOE</td>
<td>---- to ----</td>
<td>---- to ----</td>
<td>10000 to 15000</td>
</tr>
<tr>
<td>ZOE-EBA</td>
<td>-12 to -24</td>
<td>---- to 0.40</td>
<td>-------- to --------</td>
</tr>
<tr>
<td>HV-EBA</td>
<td>---- to ----</td>
<td>---- to 0.01</td>
<td>-------- to --------</td>
</tr>
<tr>
<td>ZP</td>
<td>+15 to -7</td>
<td>0.05 to 0.10</td>
<td>19000 to 21000</td>
</tr>
<tr>
<td>PC</td>
<td>+50 to +420</td>
<td>0.04 to 0.08</td>
<td>8000 to 18000</td>
</tr>
<tr>
<td>GI</td>
<td>????</td>
<td>????</td>
<td>18000 to 24000</td>
</tr>
<tr>
<td>RMGI</td>
<td>????</td>
<td>????</td>
<td>24000 to 30000</td>
</tr>
<tr>
<td>Composite</td>
<td>????</td>
<td>????</td>
<td>35000 to 45000</td>
</tr>
</tbody>
</table>

Actual laboratory properties of dental cements are not predictive of clinical performance. The test values shown above are used mostly as guidance to monitor the effects of modifications on a material but not as predictive of success. However, the absolute values of the tests do not reflect clinical behaviors.

In a clinical study of three luting cements, 547 bridges and 162 crowns were permanently cemented. Patients were recalled at 6-month intervals and the restorations were examined for looseness. A pattern of retainer type, cement type and retainer success was demonstrable.

<table>
<thead>
<tr>
<th>5-Year Cement Retention:</th>
<th>Crowns</th>
<th>Bridges</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reinforced ZOE, ZOE-EBA</td>
<td>98%</td>
<td>92%</td>
</tr>
<tr>
<td>Zinc Phosphate</td>
<td>100%</td>
<td>98%</td>
</tr>
<tr>
<td>Polycarboxylate</td>
<td>96%</td>
<td>95%</td>
</tr>
</tbody>
</table>

There is only a small handful of dental cement clinical trials ever conducted. This might seem strange at first, but makes sense when one considers the relative profit in the realm of dental materials products. Dental cements constitutes the smallest portion of material and profit. While gross sales of implants, dentifrices, and powered toothbrushes may represent several billions of dollars annually in the marketplace, and while composites and amalgams may represent several hundreds of millions of dollars, the total market for dental cements is not much more than 10 million dollars. Therefore, there is no incentive for manufacturers to develop and test new materials, much less conduct clinical trials.

The only clinical trial of any significance was conducted in the middle 1970s but the University of Michigan using dental students to place and recall fixed restorations (crowns and bridges) cemented with ZOE-EBA, zinc phosphate (ZP), and polycarboxylate cement (PCC). The details of the 5-year recall are shown above. [CLICK] While there were small differences in percentage retention, there were no statistically significant differences among materials. This brings up an important reference point for all clinical evaluations. What is the important time period for testing a cement? Think about what is happening. Do most of the important events for cements show up early during the first few years or do they occur at a much later time, perhaps 10-15 years down the road? Everyone suspects that only long-term clinical research data would ever reveal the true changes taking place.
Dental cements change in composition and properties with time. Unfortunately since there are no long-term clinical trials to measure these effects or recover materials for careful documentation of the chemical alterations, we do not know many details of this process. However, we can see some of this by examining traditional cements such as zinc phosphate that have been stored in water for years.

Set zinc phosphate cement includes residual zinc oxide powder (with small amounts of MgO as well) particles surrounded by a matrix of tertiary zinc phosphate crystals. Within the oral environment, the cement is exposed to saliva (water, lactic acid, Na\(^+\), Cl\(^-\), F\(^-\), Ca\(^{2+}\), and K\(^+\) ions). ZnO and MgO can readily be converted to Zn(OH)\(_2\) or Mg(OH)\(_2\) crystals that are both weaker and more soluble than the parent oxides. In addition, the tertiary zinc phosphate matrix crystals can be altered to less hydrated forms. These represent just a few of the many reactions that can occur to change the mass balance between the cement and environment, either increasing or decreasing the weight in multiple ways.

These changes tend to lead to a porous cement that is mechanically much weaker.
Imagine the typical cement margin that is about 100-150 \( \mu m \) in thickness. The dental cement literature is confounded by a mis-perception that an ideal dental cement thickness is 25 \( \mu m \) but that is not true. An old ADA test for ZP flowability used 25 \( \mu m \) as the target value for success, but the test had nothing to do with an ideal film thickness. Unfortunately, that information has been misquoted for about 50 years. A good cement margin is typically about 110 \( \mu m \) and may vary from 50 to 350 \( \mu m \). The actual image of the cement is probably much different than you originally imagined.

Now let's magnify a small section of the margin near the dentin surface of perhaps 5 \( \mu m \) (as shown in the SEM image above at 2000X). Some residual powder particles are exposed along the surface. Small pores are evident that are either from reaction shrinkage or powder particle erosion. Cracks are evident that connect small and large pores. A large pore is exposed that contains new phases formed from dissolved cement phases and/or materials that have diffused into the cement from saliva along the crack channel system.

Now ask the question about whether this 10-year old cement is still providing clinical retention and sealing. Despite the chemical and mechanical changes in the cement, it appeared to be providing retention. It is questionable whether it was still providing sealing. As the crack channels become larger, there is more opportunity for both fluid flow (leading to sensitivity) and endotoxin diffusion (leading to pulpal inflammation). If cement is lost or disintegrated at the margin during this time, then both fluid flow and leakage will become dramatically increased due to the uncovering of dentin.
The formation of pores during setting and disintegration events causes a **significant decrease in strength**. The curve above is a generalized summary of the effect of porosity (horizontal axis) on strength (% of theoretical strength without pores).  

[Dental cements typically contain from 3 to 15% porosity. There is an exponential decrease in strength. At 10% porosity the strength is only 55% as great. At 20% porosity it is only 28% as great. It is readily apparent that it is much more effective to increase the strength (bulk strength or bond strength) by eliminating porosity rather than trying to redesign the systems. This is one of the important reasons that precapsulated products are preferred. There is less chance for porosity to occur during mixing. However, reaction shrinkage still causes pores and disintegration leaves porosity.](#)
The figure above emphasizes this point about the effects of operator variability on properties. This is particularly true for traditional ceramic dental cements such as ZP that are hand mixed. [CLICK] There is the variation in compressive strength observed for zinc phosphate cement mixed by varying, well-trained, experienced dental assistants. Despite the attempt to produce equivalent results, a large spread in strengths still occurred from 40 to 80 MPa. If this is the result for well-controlled conditions with experienced personnel, imagine the spread for more challenging clinical conditions with quite variable efforts of the personnel.

For all restorative dental materials, [CLICK] the keys to clinical performance involve 5 factors: operator (folks do things differently), design (preparation design, retention features, etc.), materials (of the many choices), intraoral location (anterior-posterior, maxillary-mandibular, etc.), and patient (dental IQ, diet, F history, ...). [CLICK] The most important of these is the operator (>50% of risk factors). [CLICK] The least important is the materials (~15% of risk factors). Therefore, dental materials manufacturers are constantly trying to package products to remove the potential for operator variations.
ZOE can be improved by replacing small amounts of the eugenol with a co-acid called ethoxy benzoic acid (EBA). [CLICK] Its acid groups react with Zn$^{2+}$ in a similar fashion producing chelate reaction products that precipitate into the matrix. This combination of crystals is stronger and much more water resistant. However, these cements are still not very strong overall.

Both ZOE and ZOE-EBA cements may be doped with PMMA, rosin, and/or Al$_2$O$_3$ to further strengthen them. Clearly they are better with these additions, but yet not as good as materials such as zinc phosphate cement. Therefore, all ZOE types are usually relegated as temporary cements only.
Zinc phosphate cement was the first dental cement which generated good mechanical strength. It is very similar to the microstructure of ZOE cement. The actual reaction is quite complex and proceeds through a series of intermediates to the final tertiary zinc phosphate.

While matrix crystals are strong, they still permit relatively rapid diffusion at their grain boundaries. Therefore, dyes or other leakage markers can penetrate quickly through set ZP cement by following these channels at grain boundaries. While this prevents perfect sealing, it is still good enough to exclude fluid flow and endotoxin penetration. However, in laboratory studies of cement leakage, this material is poorly ranked. This is the first evidence you have that laboratory properties do not predict clinical behavior for cements.

Zinc phosphate cement was the major luting material in dentistry for almost 50 years (1920 to 1970) until polymer-based cements began to emerge (e.g., PCC, GI, RMGI, CC). It is still used to a limited degree today. It is generally considered the gold standard for comparison of everything else, although it is clearly not the best dental cement.
To mix zinc phosphate, it is important to carefully manage the reaction.

The 50% aqueous phosphoric acid solution has an initial $pH = 1.0$ and is extremely reactive toward ZnO powder. [CLICK] To control and stage the reaction, the cement components are cooled, mixed on a chilled glass slab, and powder is added slowly to the liquid. [CLICK] A glass mixing slab is chilled by exposing it to cold running water for 1-2 minutes. After careful drying of the slab with a paper towel, the powder and liquid components are dispensed onto the slab. [CLICK] The powder is sectioned into 6 to 8 increments and [CLICK] slowly added in 15 second mixing intervals into the liquid. This allows some reaction to occur and causes the $pH$ to rise from 1.0 to around 3.0, slowing the overall reaction. As with all water-based cements, it is critical to insure that any other water is not inadvertently gained or lost from the mixed materials, or else the reaction will not occur as planned. To minimize moisture contamination effects, these cement liquids are buffered. The reaction progress can be seen in the next slide.
The figure above shows the same logarithmic time line that was used in the reaction conversion graph earlier.

Now examine the reaction acidity with time. The vertical axis here is pH. Remember that each step along the pH scale represents a 10-fold change in acidity. Going from pH 7.0 to 6.0 is an increase in acidity of 10 times. Going from a pH of 7.0 to 1.0 (6-fold) is an increase in acidity of 1,000,000 times. [CLICK] During the mixing phase, the pH changes from 1.0 to almost 4.0 and thus the acidity is 1000 times less and the reaction is significantly slower beyond this point. [CLICK] That is why it may take several days or weeks for the reaction to be 95% complete.
Silicate cement gained fame because of its initial esthetics and fluoride-releasing capability. However, it was used for direct restorations much more than as a luting cement. It deserves some passing comments, because it was one of the bases for the evolution later of glass ionomer cement.

Silicate cement (SC) is based on silicate glass powder particles. In addition to predominantly silica, the glass contains alumina and sodium or calcium fluorides. On reaction with the 50% aqueous phosphoric acid solution, a range of ions are released (Si$^{+4}$, Al$^{+3}$, Ca$^{+2}$, and F$^{-1}$) from the perimeter of the powder particles. [CLICK] These ions generate a number of reaction products, but primarily calcium and alumino phosphates that form the cement matrix. [CLICK] The powder particles and reaction products are almost clear, so the cements have good esthetics. ZnO-based cements are much more opaque. ZnO and TiO$_2$ are generally used as reflective pigments (in paints, porcelain opaquing agents, and as sun-blockers in suntan lotions).

Unfortunately, the cement matrix in SC is relatively soluble. The good part is that fluoride ions are rapidly released for potential resistance to secondary caries. However, at the same time, the cement is losing volume, becoming rougher, and collecting stain. Therefore, the esthetic properties are extremely limited. Most of the cements had to be repaired or replaced in 3-8 years.
The revolution toward polymer-based cements started in 1960 when Dr. Dennis Smith invented polycarboxylate cement (PC or PCC). The easiest way to imagine this particular composition is simply as ZOE or ZP cement in which the liquid is now replaced by a 50% solution of polyacrylic acid polymer in water. [CLICK] The polymer contains carboxylic acid side groups, many of which are ionized in water, and which react with zinc ions released from the periphery of the ZnO particles. Polyacrylic acid solution is still acidic (pH = 1), but the large polymer molecules are much less likely to diffuse very far into dentin. Therefore, this material was hailed originally as a much more biocompatible dental cement.

The final cement microstructure is very similar to that of ZOE or ZP. Residual ZnO particles are surrounded by a zinc polyacrylate gel. [CLICK] Generally the ZnO powder is more uniform in these cements and [CLICK] thus the matrix appears to be more uniform in thickness as seen in the SEM photograph above.
Mixing Procedure and Precautions
Polycarboxylate Cement

Dispensing P and L. → Folding P into L. → Stropping.

There is not much PC cement still being used. However, it is still important for you to understand the challenges for mixing it, in case you encounter an office that is still using it.

[CLICK] One of the most popular products representing PC cements is called Durelon.

During the reaction, it takes very few Zn$^{2+}$ ions to crosslink this system (i.e., one ion can connect two chains) so the initial setting time is very short. The cement cannot be slowed by incremental powder additions (like for ZP cement). Therefore, to control the reaction the components are chilled and mixed on a paper pad very quickly. Polycarboxylate is reactive toward almost all positive ions or surfaces that contain them, so it will chemically bond to a glass slab, tooth structure, or the protective oxide on a stainless steel spatula. Either an agate or plastic mixing instrument is substitute for a stainless steel spatula or else the spatula must be quickly cleaned before the cement sets.

[CLICK] A great challenge for mixing any powder with a liquid is trying to get the particles well wetted before the powder is inadvertently dispersed as an airborne dust. A simple approach for PC cement is to use the spatula to draw the liquid into a thin film. Use the opposite side of the spatula blade to comb the powder onto the liquid film. [CLICK] Scoop and roll half of the film over onto itself (like you are producing a sandwich or omelet). This traps the powder particles within the liquid film. [CLICK] Mix the mass with the spatula tip for 3-5 seconds quickly and then strop it 5-10 times to complete the mixing. Manufacturer’s instructions explain the need to complete the mixing in no more than 30 seconds, leaving only about 60 additional seconds for working time. Using this method, the mixing can be accomplished in about 10 seconds, leaving 20 additional seconds for working time.
Dr. Alan D. Wilson (U.K. government scientist) is generally credited with the development of glass ionomers (GI). This class of cements is a hybrid of silicate (powder particles) and polycarboxylate (liquid) technologies. The first commercial product was offered by Dentsply in 1972 under the acronym of A.S.P.A. (alumino-silicate-polyacrylic-acid). The actual chemical reactions that produce setting are numerous and complicated. These will be discussed shortly. For the time being, consider the main features of this cement. This material is a hydrogel. Water is necessary to dissolve the polyacrylic acid and to stabilize the crosslinked matrix. As such it has certain advantages and disadvantages. The water channels permit rapid ion exchange with the environment, such as F ion release. The water also plasticizes the matrix and limits its overall strength. The water also makes the material appear more opaque than one might like. Therefore, bonded composites are almost always better in terms of esthetics and mechanical properties. However, GI cements still have some important uses.
Imagine tooth structure as an adherend portrayed to the left in the slide above. [SLIDE] A single alumino-silicate particle is shown at the top. [SLIDE] A couple of polyacrylic acid polymer chains are revealed as partly ionized in the watery matrix. [SLIDE] A variety of ions are released from the particle as its surface dissolves. [SLIDE] Released calcium ions form divalent crosslinks between chains at first. [SLIDE] These are replaced by more and more trivalent crosslinks from aluminum ions later on. At the same time, the pendant carboxyls that are reacting with ions, may also react with partially ionized calcium ions on the surfaces of the powder particles and on tooth structure to create chemical bonds. [SLIDE] Long after these processes have been completed, the siliceous network develops within the hydrogel. The primary focus for many years of this set structure has been the presence of releasable fluoride ions in cements.
Glass ionomers have evolved in most cases to become more and more like composites. Starting at the middle of the bottom of this map, we can trace the evolution of the materials from a traditional hydrogel toward the upper right-hand corner that represents a standard hydrophobic composite. [SLIDE]

The first substantive modifications to glass ionomers were made by adding reinforcing fillers. Amalgam alloy powder was admixed with conventional GI to produce metal-modified GIs (MM-GI or MM-GIC). However, since the Ag-Sn alloy particles were not well-bonded to the matrix, the admixture was actually weaker. This was promoted at a time that dental amalgam was first coming under fire in the U.S. (about 1982) due to its Hg content. The admixture was called the “miracle mixture” and substituted for dental amalgam in some practices. Unfortunately its poor properties were quickly revealed and all such restorations had to be replaced. Yet, this mixture is still sold today as an alternative for build-ups or cores. Another version of MM-GICs was developed by adding metallic particles with ceramic coatings (cermets) as reinforcing fillers. These have continued to be used as cores.

A major hurdle for GI acceptance was overcome when water soluble acrylic monomers (predominantly HEMA) were added along with double bond functional polyacrylic acid chains and initiators. These were called resin-modified glass ionomers (RMGI). It was now possible to visible light (VL) cure the materials to achieve high early strength and more protection of the hydrogel. The same GI reactions still took place but were more secondary for the performance of the materials.

Compomers eliminated the use of GI chemistry altogether. They are simply composites with the inclusion of fluoride releasing alumino-silicate glass filler particles. Another way of thinking of these materials is as GI powder particles substituted into composites. They are truly composites. Currently, compomers are being formulated to replace both RMGI and composite cements. These new designs are called “universal cements” and 3M-ESPEs UniCem is the first example of this. [SLIDE]

In response to the criticism that compomers are not really glass-ionomer-like at all, pre-cured glass ionomer particles have been blended into compomers to create giomers. However, these are not really competitive with standard composites as filling materials or cements.

[SLIDE] Finally, in the early 1990s, a version of traditional glass ionomer was targeted at a market called A.R.T. (atraumatic restorative technique). In second and third world regions in which dentistry is not readily available, it is important to halt caries before it completely destroys a tooth and leads only to extraction. ART materials were designed to be placed by non-dental personnel as a holding procedure to stop caries until the individual could be treated in a dental office. Caries was liltter scooped out and the hole filled with a powder/liquid GI cement that was mixed between your thumb and first finger and pressed into place. This has become extremely popular as well with pediatric dentists for treating primary teeth that were once restored with amalgam. To increase the longevity, these products have a small amount of polymer added for improved toughness and so they are called resin-reinforced glass ionomers (RR-GICs). The market for these materials is incredible expansive. This is the largest volume of GI sold today.
A small picture of a glass ionomer cement is shown inset on a graph for fluoride release versus time.

In set glass ionomer cements, the initial dissolution of the edges of fluoro-alumino-silicate particles also releases fluoride into the matrix of the setting cement. These levels are initially very high but are quickly released by diffusion into the oral environment. Typically the levels drop from about 20 ppm down to 1-2 ppm in 24-72 hours. At that point, the remaining reservoir of fluoride ions is the residual powder particle phase. Only slowly, does fluoride ion come out of the particles into the matrix and then get released. So the slow long term release of fluoride is limited by that diffusion rate. In the figure above, the overall process is described by the red curve. After the first day or so the fluoride release rates are very low and questionable in efficacy.
Despite the fact the glass ionomers release fluoride, the levels are very low and not considered efficacious. Over the last few years there have been efforts to "recharge" (add fluoride back into the restorations for subsequent release) by exposing the surfaces to fluoride ion sources. [SLIDE] Quite a few things can push fluoride back into cements or restorations. This is simply a way of changing the osmotic pressure. If the concentrations on the outside are higher than the inside, then fluoride ion moves in rather than out. The best way to make this happen is with fluoride containing toothpastes, fluoride mouth rinses, or topical fluorides. This temporarily boosts the fluoride concentration. [SLIDE] However, quickly this falls back to original levels again. [SLIDE] Unfortunately, the boosted levels are not high enough for even a short time to be considered clinically efficacious as an anti-caries therapy.
Finally we arrive at composite cements which are used for all-ceramic restorations. Enamel and dentin are etched, primed, and bonded. [CLICK] The ceramic inlay is etched with hydrofluoric acid and bonded with silane coupling agent. [CLICK] Composite cement is used to attach the bonded dental surfaces to the silanated ceramic surfaces.

While some the enamel/dentin bonding system can be visible-light cured, the composite cement is generally self-cured or dual cured. It is important not to mix the chemistry of VLC and self-cured or dual-cured materials. The accelerator for self-cured or dual-cured systems (which is basic) can neutralize the photo-sensitizer (photoinitiator) for VL systems that is acidic. The interfaces between the materials are therefore not cured and bonding fails.

Successful bonding to ceramic interfaces requires that HF etching [CLICK] preferentially dissolve a component in the ceramic surface. This occurs with silicate ceramics but not with alumina or zirconia which are single phase. Silane coupling only works if silica is available for bonding on the ceramic surface. Again, this is true for silicate ceramics but not with alumina or zirconia. The latter depend solely on cement luting from surface roughness created by sandblasting the surfaces of the ceramic restoration.
DENTAL CEMENT EXAMPLES

A. Zinc Oxide Eugenol Cements:
- ZOE 2200 (LD Caulk)
- ZOE (J. Bird Moyer Co.)
- ZOE Temporary (LD Caulk)
- IRM (LD Caulk)
- FynaL (LD Caulk)
- ZEBACEM (LD Caulk)

B. Hexyl Vanillate Cements (HV):
- (None currently marketed)

C. Zinc Phosphate Cements (ZP):
- MODERN TENACIN (LD Caulk)
- FLEX'S EXTRAORDINARY (Mizzy)
- SMITH'S ZINC CEMENT (Teledyne)
- AMIES ZINC CEMENT (Teledyne)
- KENT ZINC CEMENT (Stratford Cookson)
- LANG-C+B Only (Lang)
- S-C (Stratford Cookson)
- DROPIN (Atwood Industries)
- ELITE (I.D.T. Corp)

D. Silicate Cements (SC):

E. Zinc Silico-phosphate Cements (ZSP):
- AMIES PC GLASS CERAMIC (Teledyne)
- ASTRALIT (Premier)
- SYNTREX F (Premier)
- SILICAP (HD Justi)

F. Polycarboxylate Cements (PC):
- TYLOK (LD Caulk)
- DURELON (Premier)
- CHEMIT (Harry J. Bosworth)
- CARBOXYLON (3M)
- POLY-F (DeTrey)

G. Glass Ionomer (GI):
- ASPA-LD (Herrmann)
- Ionomer (Denmat)
- Fuji II (GC America)
- KETAC-CEM (ESPE)
- BISBOND LUTING (Harry J. Bosworth)
- AQUACEM (DeTrey)
- BASELINE (DeTrey)

H. Resin Composite Cements (CC):
- COMSPAN (LD Caulk)
- PANAVIA F (Kuraray)
- PANAVIA 21 (Kuraray)
- ENFORCE (LD Caulk)
- RESIN CEMENT (3M)
- NEXUS (Kerr)
- MEGABOND (Harry J. Bosworth)
- DUO-CEMENT (Collane)
- CALIBRA (LD Caulk)
- OPAL LUTING (3M)
- COMPOULITE (ESPE)
- CEMENT-IT (Jeneric/Pentron)
- LUTE-IT (Jeneric/Pentron)
- BUILD-IT (Jeneric/Pentron)

There are many examples of each category of dental cements. While a few are extremely popular and have major market shares, numerous versions are available as shown in the list above. It is key to recognize the commercial names of the few which are popular and remember their classification. A few are highlighted in yellow for your reference.
Perhaps more importance will be placed on dental cements as we shift into a patient population that survives into their 90s. Instead of assuming that cements need to survive 10-20 years, we are now facing a requirement of 40-60 years for patients with fixed restorations being placed when the individuals are 35-40 years old.

Remember, above all, the clinical performance depends primarily on the operator. If more discriminating information were known about the details of long-term clinical performance, then perhaps cement modifications could be made dramatically improve cements. THANK YOU.