

Cement



Introduction & Evolution of Cements



- **Historical Context:**
 - For most of the 20th century, only **Zinc Oxide–Eugenol** and **Zinc–Phosphate** cements were available.
 - The term "cementation" was appropriate for fixing restorations.
- **Modern Revolution:**
 - Introduction of **adhesive materials** and procedures.
 - Now a wide variety: **Zinc–Polycarboxylate**, **GIC**, **RMGIC**, and **resin-based** cements.
 - Rise of '**Universal Adhesives**'.
- **Chapter Goal:** To demystify common materials, look beyond marketing, and help clinicians choose the best material for each specific situation.

Terminology: Cementation vs. Luting



- **Cementation:** Still a commonly used term, but it doesn't fully describe modern materials.
- **Luting / Luting Agent:** A more accurate term for materials that act as a protective, airtight seal (e.g., resins).
- **In practice,** both terms are used.

General Requirements for Cements



- **Biocompatibility:**
 - Direct contact with dentin → Must prevent **post-operative sensitivity** and **pulpal inflammation**.
 - Acts as a barrier → **Antibacterial properties** are beneficial.
- **Retention:**
 - **Primary Role:** To retain the restoration.
 - **Water-based cements** (e.g., Zn-phosphate): act as a "space filler," relying on mechanical locking.
 - **Resin adhesives:** Create a chemical bond → **Significantly enhance retention**.
- **Mechanical Properties:**
 - Must withstand high forces → Requires **high tensile strength, fracture toughness, and fatigue strength**.
 - A good marginal fit minimizes cement layer → improves performance

General Requirements for Cements



- **Marginal Seal:**
 - **Key Goal:** Prevent **recurrent caries**.
 - **Low solubility** in oral environments is crucial for long-term seal.
 - Adhesive bond to tooth and restoration helps maintain seal integrity.
- **Low Film Thickness:**
 - Essential for proper **seating of the restoration** without occlusal problems.
 - Thick film → poor marginal fit → more exposed cement → dissolution, staining, and plaque accumulation.

General Requirements for Cements



- **Ease of Use:**
 - **Powder/Liquid systems:** Critical to follow mixing ratios. Altering ratios affects working/setting times.
 - **Preferred systems: Encapsulated or resin-based** cements with dual-cure (light/chemical) mechanisms for adequate working time.
- **Radiopacity:**
 - Must be **more radiopaque than dentin** to:
 - Distinguish cement from **recurrent caries**.
 - Detect **excess cement** and **marginal overhangs**.
- **Aesthetics:**
 - Crucial for **all-ceramic restorations** (e.g., veneers).
 - Cement must match the restoration's **color, translucency, and stability**.

Key Conclusion & Clinical Significance



- No single material can meet all the stringent requirements for a cement.
- This is the fundamental reason why there is such a wide choice of materials available.
- Selection must be based on scientific understanding and the specific clinical circumstance.

Choice of Cements - Overview



- **Two Main Categories:**
 - **Water-based Cements**
 - **Resin-based Cements**
- **Evolution of Adhesion:**
 - **Zinc-Phosphate:** A simple "space filler" or "grout" with **no adhesive properties**.
 - **Zinc-Polycarboxylate, GIC, RMGIC:** Can **bond to enamel and dentine**.
 - **Resin Cements:** The biggest impact, providing strong **adhesive bonding** to various surfaces

Water-Based Cements: Zinc-Phosphate



- **Overview:** One of the oldest cements, popular due to long clinical history and handling.
- **Composition:**
 - **Powder:** Zinc Oxide, Magnesium Oxide (for whiteness & strength).
 - **Liquid:** Phosphoric Acid solution.
- **Key Properties:**
 - **Working Time:** 3-6 min. **Setting Time:** 5-14 min (affected by mixing technique and slab temperature).
 - **Biocompatibility:** **Low initial pH (1.3-3.6)** can cause pulpal irritation. **No antibacterial** properties.
 - **Mechanical:** Compressive strength: 40-140 MPa (depends on powder/liquid ratio). **Brittle** (low tensile strength).
 - **Solubility:** High in first 24 hours, then reduces. Highly dependent on powder/liquid ratio.

Zinc-Phosphate: Clinical Significance



- **Advantages:**
 - Easy to mix
 - Well-defined set
 - Adequate strength
 - Low cost
- **Disadvantages:**
 - Potential for pulpal irritation (low pH)
 - No antibacterial action
 - No adhesion
 - Relatively soluble
- **Conclusion:** A reliable, long-standing option for metal and metal-ceramic restorations, despite its limitations

Water-Based Cements: Zinc-Polycarboxylate



- **Overview:** Introduced in 1968; the **first cement to bond to enamel and dentine.**
- **Composition:**
 - **Powder:** Similar to Zinc-Phosphate (Zinc Oxide).
 - **Liquid:** Polyacrylic Acid solution (or water if acid is in powder form).
- **Key Properties:**
 - **Working/Setting Time:** Short working time (2.5-3.5 min). Cooled slab can extend it.
 - **Biocompatibility: Much milder** on the pulp than Zinc-Phosphate, despite a low initial pH. Has some
 - **antibacterial** properties.
 - **Mechanical:** Lower compressive strength (55-85 MPa) but higher tensile strength than Zinc-Phosphate.
 - **Adhesion:** Bonds to enamel, dentine, and some base metal alloys (via oxide layer). Bond strength is limited by the cement's own low cohesive strength.

Zinc-Polycarboxylate: Clinical Significance



- **Advantages:**
 - Adhesion to tooth structure.
 - Low irritancy to the pulp.
 - Some antibacterial action.
- **Disadvantages:**
 - Short working & long setting times.
 - Difficult clean-up (timing is critical).
- **Conclusion:** A viable adhesive alternative to Zinc-Phosphate, but its use has declined in favor of GICs, which are perceived as easier to use.

Introduction to Glass Ionomer Cements (GICs)



water-based, self-adhesive restorative materials

- Filler: Fluoroaluminosilicate (FAS) glass
- Matrix: Polymer/copolymer of carboxylic acids
- Setting mechanism: Acid–base reaction
- Ideal when moisture control is difficult and fluoride release is beneficial

Types of glass ionomers



- Conventional Glass Ionomers (GI)
- Resin-Modified Glass Ionomers (RMGI)

Background & Rationale



- Invented in the 1970s
- Combined advantages of **silicate cements** and **zinc polycarboxylate cements**
- Used FAS glass for ion release without dissolving like silicates
- Polycarboxylic acids replaced phosphoric acid to improve durability

Composition of Conventional GI



Essential components:

- Polycarboxylic acid (usually acrylic acid copolymers)
- FAS glass powder
- Water
- Tartaric acid (controls working & setting time)

Powder & Liquid System



- **Powder:** Acid-reactive FAS glass containing Ca, Sr, Al Heavy-metal ions → radiopacity
- **Liquid:** Concentrated solution of polyacrylic acid copolymers
- Mixing initiates **acid–base reaction** between polymer and glass

Acid–base reaction mechanism



- COOH groups partially ionize \rightarrow **COO⁻ + H₃O⁺**
- H₃O⁺ attacks glass \rightarrow releases **Ca²⁺ and Al³⁺ ions**
- These ions cross-link polymer chains \rightarrow **salt bridges**
 \rightarrow gelation
- Silicic acid forms \rightarrow polymerizes into **silica hydrogel**

Role of Calcium and Aluminum



- **Ca²⁺** binds rapidly → early set
- **Al³⁺** binds later → long-term strength
- Crosslinking increases mechanical stability during maturation

Long-term stability



- No reduction in strength after **years in water storage**
- Fluoride release does **not** compromise structural integrity
- Silica hydrogel + metal-polyacrylate network ensures durability

Structure of the Set Cement



- Final material = **hydrogel matrix** of
- Calcium polyacrylates
- Aluminum polyacrylates
- Fluoroaluminum polyacrylates
- Unreacted glass particles are surrounded by a **siliceous hydrogel layer**

Glass Dissolution & Hydrogel Formation



- **20–30%** of the glass dissolves during setting
- Small particles may dissolve completely
- Replaced by **silica hydrogel containing fluorite crystallites**

Matrix stability comes from:

- Polymer chain entanglement
- Weak ionic cross-links
- Hydrogen bonding

Introduction to RMGIs



- developed in the **late 1980s**
- Goal: **Longer working time + quick set** for immediate finishing
- Combine **acid–base reaction** of conventional GIs with **methacrylate polymerization**

Essential Components of RMGIs



- Polycarboxylic acid polymer
- FAS glass
- Water
- **Hydrophilic methacrylate monomer**
- **Free-radical initiators** (light-cure or redox)

Dual-Cure Mechanism



Two simultaneous reactions:

- **Acid–base reaction** (GI-style)
- **Methacrylate polymerization** (light-activated and/or chemical)

Methacrylate reaction is **much faster**

Balance between the two depends on water and monomer content

Two Parallel Setting Reactions



1. GI Acid-Base Reaction

- Can be monitored via IR spectroscopy (carboxylate peaks)

2. Methacrylate Polymerization

- Chain-reaction → extremely fast
- Dominates when:
 - Water content is **low**
 - Methacrylate content is **high**

Influence of composition



- High water → stronger acid–base reaction
- High methacrylate → more resin-like behavior

Performance and balance of reactions vary **by product and formulation**

Glass Ionomer Cements (GICs) & RMGICs for Luting



- **Key Difference from Restorative GICs:**
 - **Smaller particle size for thin film thickness** (20-50 μm).
 - **Do NOT** use restorative GICs and alter the powder/liquid ratio for luting, as this ruins the properties.
- **Handling:**
 - **Working Time:** Critical. Must mix and place within **2-2.5 minutes** to avoid a thick film.
 - **RMGIC Advantage:** Dual-cure mechanism (light + chemical) reduces time.
- **Solubility:** Newer formulations set faster and have lower solubility, but initial protection from moisture is still recommended.
- **Clinical Significance:** Always use a **purpose-made luting cement**, not a modified restorative material.

Resin-Based Cements



They are based on **methacrylate resin systems**, similar to composite resins, but are formulated specifically for **high bond strength, low film thickness, and good optical properties**.

They chemically bond to:

- Tooth structure (via bonding systems)
- Ceramic restorations (via silane or primers)
- Metal restorations (via MDP primers)
- Composite and polymer-based restorations

Where Resin Cements Are Used



They are most commonly used for bonding:

Indirect Restorations

1. Ceramic crowns (lithium disilicate, feldspathic, zirconia with primer)
2. Veneers (ultra-thin restorations → need strong light-cured resin cement)
3. Inlays / Onlays
4. Fiber posts
5. Maryland bridges
6. CAD/CAM restorations

Types of Resin Cements



1. Light-Cured Resin Cements

- **Characteristics**

Polymerize only when irradiated (~450–500 nm)

No amine/peroxide → very **color stable**

Unlimited working time until light activation

Thin film (< 25 μm)

High esthetic quality

Types of Resin Cements



1. Light-Cured Resin Cements

- **Advantages**

Zero discoloration (no amine oxidation)

Best control during veneer placement

Excellent polishability

Perfect shade matching

Types of Resin Cements



1. Light-Cured Resin Cements

- **Limitations**

Light cannot penetrate thick ceramics, so NOT used for:

Zirconia crowns

Thick lithium disilicate crowns

Metal restorations

- **Examples**

Variolink Esthetic LC (Ivoclar)

RelyX Veneer Cement (3M)

Choice 2 (Bisco)

Types of Resin Cements



2. Dual-Cured Resin Cements

characteristics

- Polymerize by **light + chemical cure**
- Reliable in deep areas where light doesn't reach
- Strong mechanical properties

Types of Resin Cements



2. Dual-Cured Resin Cements

Indications

- Lithium-disilicate crowns and bridges
- Zirconia crowns (with MDP primer)
- Fiber posts
- Metal ceramic restorations
- Onlays, inlays

Types of Resin Cements



2. Dual-Cured Resin Cements

- **Advantages**

Strongest bonds to both tooth & ceramic

High color options

Compatible with adhesive system

Types of Resin Cements



2. Dual-Cured Resin Cements

- **Limitations**

Some older dual-cure systems discolor if light does not reach deeply (due to tertiary amines)

→ Newest systems use more stable initiators (Ivocerin)

- **Examples**

Panavia V5 (Kuraray)

RelyX Ultimate (3M)

Multilink Automix (Ivoclar)

NX3 Nexus (Kerr)

Types of Resin Cements



3. Self-Cured (Chemical-Cured) Resin Cements

Polymerize without light.

Characteristics

Benzoyl peroxide + amine chemical initiation

Used where no light reaches at all (deep canals)

- **Indications**

Metal post cementation

Fiber posts in deep canals

Thick opaque zirconia crowns (rarely)

Types of Resin Cements



3. Self-Cured (Chemical-Cured) Resin Cements

- **Advantages**

Independent from light

Good for completely dark areas

- **Limitations**

Lower color stability than light- or dual-cure

More bubbles

Short working time

Higher porosity risk

Types of Resin Cements



3. Self-Cured (Chemical-Cured) Resin Cements

- Examples

C&B Metabond (Parkell)

ZOP-resin hybrid

Composition



Typical composition includes:

- **Resin matrix:** Bis-GMA, UDMA, TEGDMA
- **Fillers:** Silica, barium glass, etc.
- **Photoinitiators:** Camphorquinone
- **Self-cure initiators:** Benzoyl peroxide + tertiary amines
- **Adhesion promoters:** MDP for zirconia, silane for glass ceramics

Film thickness typically < **25 μm** (ISO requirement)

Bonding Mechanism



1. Micromechanical Retention

Etching enamel → microporosities

Etching ceramics (HF acid)

Sandblasting zirconia

2. Chemical Bonding

MDP → zirconia, metal oxides

Silane → glass ceramics

Carboxylate groups → dentin

Advantages



1. Highest bond strength among all dental cements
2. Excellent esthetics
3. Low solubility
4. Strong retention even for short/over-tapered preparations

Disadvantages



1. Technique sensitive
2. Moisture control required
3. Pulpal irritation possible
4. Requires bonding agent (unless self-adhesive type)
5. Some dual-cure systems suffer from color instability if light cannot reach them fully

Composition



Resin Matrix

Usually a mixture of:

- **Bis-GMA** (high viscosity, rigid backbone)
- **UDMA** (lower viscosity than Bis-GMA)
- **TEGDMA** (diluent monomer, improves flow)
- **HEMA** (sometimes used to enhance wetting, increases water sorption)

These monomers polymerize via a **free-radical chain-growth reaction**

Composition



Inorganic Fillers

- Silica nanoparticles
- Barium/strontium glass (radiopacity)
- Aluminosilicate
- Zirconia fillers

Fillers provide:

- Strength
- Low polymerization shrinkage
- Radiopacity
- Reduced solubility

Composition



Adhesion Promoters

- **MDP monomer** (10-methacryloyloxydecyl dihydrogen phosphate)
→ Bonds to **zirconia, alumina, metal oxides**
- **Silane**
→ Bonds to **glass ceramics (feldspathic, lithium disilicate)**
- **Polyalkenoic acid copolymers**
→ Bond to **calcium in enamel/dentin**
- **Functional acid monomers** (GPDM, PENTA)
→ Dentin bonding