HIGH ALUMINA CEMENTS & CHEMICAL BINDERS

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HIGH ALUMINA CEMENTS AND CHEMICAL BINDERS

1 Prefix

To understand the basics of binders is important as the trend towards monolithic refractories for high performance applications, especially in the steel industry, is increasing all over the world. There has been more research and development on concrete technology, application and testing methods in the past 10 years than in the previous half century. The progress is due to new developments and improvements in several key areas like raw materials (i.e. Spinel), advanced castable technologies (conventional cement, low cement, ultra low cement, no cement), additions (stainless steel needles, organic fibres), or installation techniques (vibration, self flowing, gunning, shotcrete).

Some of today’s concretes represent the most complex refractory formulations, requiring high-quality aggregates, fillers, additives, and binders! To select and apply the best suitable binder is essential for the monolithic product performance.

Today’s most widely used binder systems for monolithic refractories are High Alumina Cements, and Chemical Binders. This talk will review these binder types, how they function, how the bonding effect can be followed up and controlled, and what influence the chosen binder has on the performance of the final product.

2 Definition of Binders

Cold binders gain their important role in monolithic technology by being the backbone, or the skeleton, of the power compound that will finally become a monolithic refractory product.

A binder is bonding a powder compound together, after installation/ demoulding keeping the mix in the given shape, giving strength to the green body, allowing handling of the unfired monolithic product.

Without proper binders the monolithic technology would not be possible.

2.1 Types of Bonding Systems

Binders can be split up in four major groups based on the bonding type:

- Hydraulic
- Chemical
- Organic
- Ceramic bonding (Clay/Sintering).

The first three types, hydraulic, chemical and organic, stand for the bonding of “cold”, unheated systems.

Ceramic bonding represents “hot” bonding, the final bonding type of the monolithic product in its hot stage at the working site. Sintering starts at temperatures of 800°C and above, depending on the chemical composition of the compounds.

Note: the expression “Ceramic bonding” is sometimes also used for cold bonding, referring to bonding by addition of clays.
2.2 Ceramic (Hot) Bonding

<table>
<thead>
<tr>
<th>Bonding → COLD:</th>
<th>Hydraulic - Chemical - Organic - Clay bonding gives strength at RT → 200-600°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>Treatment (T &gt; 800°C)</td>
</tr>
<tr>
<td>Bonding → HOT:</td>
<td>Sintering Reaction (dry/wet) within Powder Particles gives Strength to Compound</td>
</tr>
</tbody>
</table>

We differentiate between dry and wet sintering:

Dry sintering is driven by the principle that a compound is aiming to reach its final equilibrium (stage of lowest energy). It is proceeding via material diffusion processes.

For mono-compound products this is to become a mono-crystal by growing all powder particles together to one big crystal. For multiple components it also includes the formation of new minerals representing an energetic lower stage as the minerals they originate from. These can be minerals with higher melting points, giving an improved product hot performance, such as Mullite or Calciumhexaaluminate CA₆. An example for CA₆ formation will be given later on for Calcium Aluminate Cement bonded systems.

The term wet sintering refers to melting of grains, at grain contact zones, or at grain boundaries, giving a gluing effect between the particles. It is driven either by reaching the melting temperature of a powder particle, or by the effect that two minerals/particles of different chemistry reach an eutectic melting point (particle contact, grain boundary). The viscosity of the melted phases is critical for the product strength at the individual working temperatures. High viscosity stands for thick (honey-like) consistency of the melt, low for being very fluid.

Note that materials with wet sintering (such as chamotte products) will show high strength when tested at room temperature (melt → glass), but will have low strength and creep resistance at the actual working temperatures.

2.3 Refractory Binders for Cold Bonding

The most common Cold Binders and their type of bonding are:

<table>
<thead>
<tr>
<th>BINDER</th>
<th>BONDING TYPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Alumina Cements</td>
<td>Hydraulic</td>
</tr>
<tr>
<td>Alumina Binders (Ca-free)</td>
<td>Hydraulic</td>
</tr>
<tr>
<td>Phosphate Binders</td>
<td>Chemical</td>
</tr>
<tr>
<td>Water Glass</td>
<td>Chemical</td>
</tr>
<tr>
<td>Organic Binders (Sulfite Lye, Tar, Pitch)</td>
<td>Organic</td>
</tr>
</tbody>
</table>

Hydraulic bonding with Cements represents the largest group, followed by phosphate and water glass bonding.
3 High Alumina Cements

The term High Alumina Cements stands for a family of refractory cements for high performance application, the Calcium Aluminate Cements (CAC). The hydraulic strength development is due to a waterbonding reaction of the Calcium Aluminate Minerals to water-resistant hydrate phases (not water dissolvable). It is a cold bonding system.

Alumina contents of high performance CAC equal or exceed 70%, CaO content is 28% or less. Purity is very high. Target can be set at Sum (Na₂O, SiO₂, Fe₂O₃, TiO₂) < 2%. The purity gives a high refractoriness to the cement and therewith to the final product.

![Diagram of the phase diagram of cementitious materials](image)

constituent, for CAC exceeding 70% Alumina plus CA₂

3.1 Raw Materials & Production Process

Raw material sources for High Alumina CAC are
- further purified alumina from the Bayer process,
- high purity Limestone.

The quality consistency of the cement depends to a great extent on the amount and variations of impurities inherent in the raw materials.

Compounds formed during sintering generally proceed dynamically in a non-equilibrium manner. Calcium aluminates high in lime form initially (together with ferrites, silicates, and titanates for high impurity cements).

The difference in mineral constitution between CAC and Portland Cement can be seen in the CaO- Al₂O₃ - SiO₂ Equilibrium Phase Diagram. Portland Cement occurs in the relatively high CaO region, with C₂S and C₃S as its main constituents.

CAC, on the other hand, occurs in a region with high Al₂O₃ (and low CaO and SiO₂), a factor that accounts for their higher melting point and use as a refractory cement. CA is generally the main con-
In sintering, the raw mix combinations generally progress into higher alumina phases as the material temperature increases in the kiln. Both lime/alumina ratio and temperature will determine the amount and type of calcium aluminate phases formed in the clinker.

\[
\begin{align*}
& \text{C + A} \\
& \downarrow \\
& \text{C}_3\text{A} > \text{C}_{12}\text{A}_7 > \text{CA} > \text{CA}_2 > \text{CA}_6
\end{align*}
\]

*Note: C=CaO, A=Al_2O_3*

The major hydrating phase present in all commercial CAC cements exceeding 70 wt% Al_2O_3 (<28% CaO) is CA, followed by CA_2. C_{12}A_7 and CAO (free lime) are the fastest setting phases in a CAC. Their content is kept at low (<10% for 80% alumina cements, >4% for 70% alumina cements) or zero in order to be able to control the cement setting properties. C_3A is not or only very rarely occurring as the clinker alumina level is too high for its formation.

Tight control of the reactive clinker phase formation (CA_2, CA, C_{12}A_7) is essential for the consistent performance of a cement.

### Setting behavior of Clinker Phases
- **Fast Setting:** C_{12}A_7, C, C_3A
- **Moderate Setting:** CA
- **Slow Setting:** CA_2, C_4AF
- **Minimal or Non-Setting:** CA_6, α-Al_2O_3, C_2AS, CT, C_F

### Reactivity of Calcium Aluminate Phases

\[ \text{CA}_2 < \text{CA} <\!< \text{C}_{12}\text{A}_7 \]

### 3.2 Effect of Impurities during Clinker firing

Silica, Iron Oxide, Titania, and Alkalis can affect the types of hydration-reactive clinker compounds formed in the sintering process, and with this of the final CAC performance.

For example, high SiO_2 amounts in the CaO-Al_2O_3 raw mix lead to the formation of the non-hydrating Gehlenite, C_2AS, a mineral using up CaO which is then not available for the formation of the desired CA. Ferrites lead to formation of slow setting C_4AF or nonsetting C_F. TiO_2 is forming nonsetting CT.

Sum up: Impurities in the clinker can lead to inconsistent CAC mineral composition, resulting in varying setting times, which are influencing strength development. The impact on the refractory product manufacturing and its properties can be immense.

Additional, impurities such as silica or ferrites decrease the Hot Properties of the CAC and therewith of the total refractory compound. High purity raw materials (i.e. as a target for 70% alumina CAC: Na_2O, SiO_2, Fe_2O_3 total < 0.5%) are therefore the best choice for the production of consistent, reliable, high performance CAC.

The constituents in a high purity CAC have quite well refractoriness, see melting points shown in the following table.
But, in a castable the cement will react with the surrounding compounds. In a high alumina castable this is leading to the formation of CA₆, Calciumhexa-Aluminate, a high refractoriness phase, superior to the original cement phases (see chapter 3.4.3).

This shows that the cement has to be seen in the total system. To give pyrometric cone equivalents (PCE) for a cement is not useful. The product compound determines which effect the cement can give to the total system such as the positive CA₆ formation.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>CaO</th>
<th>Al₂O₃</th>
<th>Melting point (°C)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>99.8</td>
<td>51.4</td>
<td>2570</td>
<td>3.25/3.38</td>
</tr>
<tr>
<td>C₁₂A₇</td>
<td>48.6</td>
<td>51.4</td>
<td>1360-1390</td>
<td>2.69</td>
</tr>
<tr>
<td>CA</td>
<td>35.4</td>
<td>64.6</td>
<td>1600</td>
<td>2.98</td>
</tr>
<tr>
<td>CA₅</td>
<td>21.7</td>
<td>78.3</td>
<td>1750-1765 (decomposition)</td>
<td>2.91</td>
</tr>
<tr>
<td>CA₆</td>
<td>8.4</td>
<td>91.6</td>
<td>1830</td>
<td>3.38</td>
</tr>
<tr>
<td>α-A</td>
<td>99.8</td>
<td></td>
<td>2051*</td>
<td>3.98</td>
</tr>
</tbody>
</table>

3.3 Compositions of High Purity CAC

CAC can be separated in 80% and 70% alumina cements grades.

For 70% alumina cements usually the clinker can be directly ground to cement as the clinker has about 70% Al₂O₃ content. Additives can be added to steer setting times, or to cover up inconsistencies.

For 80% CAC’s the clinker is co-ground with calcined alumina to reach the targeted alumina level. Additives can be added to assist alumina dispersion (about 50% alumina) in order to give the CAC a proper water demand and flow behaviour, often also to control its setting.

Both grades are ground to specific fineness.

3.4 CAC in Castables

The refractory concretes are divided into 4 main groups:

1. Conventional Cement castables, CCC, high cement contents (>20% CAC)
2. Low Cement Castables, LCC (6-15%)
3. Ultra Low Cement Castables, ULCC (<6%)
4. Cement Free Castables/ No Cement Castables, NCC (<1.5%)

80% CAC’s are mainly used in conventional castables. 70% CAC’s are the major grade used for LCC and ULCC. This is i.e. reasoned in their lower shrinkage and higher strength development, and flow behaviour in the castable.

When used in Monolithics, CAC’s are subjected to three main stages of dynamic reactions:

- **Curing** - As soon as possible after placement curing for 24 h or more at ambient temperatures (Hydration).
- **Drying** - Drying of the concrete at 104° to 110°C is necessary to remove all superficial or free water. This also fully converts any metastable phases into the cubic hydrate and crystalline Gibbsite, and provides a higher compressive strength development for the binder/aggregate system cured 24 hours at higher temperatures.
• **Firing** - Heating rates depend on the thickness of the concrete structure. A rate of 28 to 55 K/h to the expected operating temperatures is usual. This will enable the hydration products to dehydrate completely and eventually react with the aggregates to form ceramic bonds at higher temperatures.

### 3.4.1 CAC Curing - Hydration

A castable is made by mixing and homogenising Grog, CAC, additives, and water, and to install it by gunning, ramming, vibration, or by self-flowing properties of the mix. The term curing refers to the full hydration of the mix, including setting & strength development of the green body, at ambient temperatures for about 24h, with moisture contents as of the ambient environment up to saturation.

How does the hydration work?

The hydration process commences on initial contact of binder with water. The clinker minerals start to dissolve in water as Calcium ions Ca$^{2+}$ and Aluminium hydroxide Al(OH)$^{3-}$. This continues until the saturation level is reached. The pH of the liquid phase rises up (~12).

Saturation level and high form the condition for nucleation & precipitation of Calcium Aluminate Hydrate crystals together with alumina hydroxide gel (AH)$_3$ or crystalline Gibbsite (AH$_3$). At start this will first take place close to the clinker surface, where the dissolution rate is highest. It results in a stiffening (setting) of the mix. Dissolving, nucleation and precipitation is an ongoing, continuous process as long as enough water is available for clinker dissolution. As the hydration crystals multiply and grow, around the clinker and between the mix particles, bonding them together, the compound is gaining increasing strength.

The hydration development in the mix is demonstrated in the below picture.

- Initial crystals form on the clinker grain surfaces, as the saturation levels for CAH formation are reached first close to the surface. The mix still shows plasticity at this point, but has lost its good initial flow properties.
With the continuous dissolving/precipitation progress the crystals grow further, bond with one another and include surrounding mix particles. The individual grain movement is stopped, the mix is stiff & set.

As the hydration process continues more and more crystals are developed and grow, interweaving with one another, giving strength to the structure.

The final stable structure is reached when the water is used up, no more crystals are formed, and the stable crystal phases (C₃AH₆/AH₃) have developed. The concrete has reached its final strength.

3.4.2 Calcium Aluminate Hydrates Modifications

Calcium Aluminate Hydrates have specific crystal modifications with individual crystal water contents, depending on temperature and time progress. Ambient temperatures during mixing, installation & curing determine the mix property development. It can be differentiated between low and high temperature formation of hydrates:

- At low temperatures (<20°C) metastable CAH₁₀ will form, having the highest water content, plus AH₆ gel.
- At high curing temperatures (>35°C) stable modifications C₂AH₆ and Gibbsite AH₃ will form, having the lowest water content. Metastable C₂AH₆ forms in the temperature/time range in-between.

Metastable CAH₁₀/AH₆ gel will convert to stable C₂AH₆/AH₃ with time at 20°C, or with increasing temperature. This process is called conversion. The hydrate volume decreases 53%. The volume change and the crystal restructuring is resulting in a lower strength development. Therefore a newly placed concrete should be subjected to a curing temperature suitable to prevent formation of CAH₁₀/AH₆ gel.

Below see picture & table on Hydration crystal development, crystal form and data:

<table>
<thead>
<tr>
<th>Chemical Composition [%]</th>
<th>Crystal Form</th>
<th>Density [g/cm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO 16,6</td>
<td>metastable</td>
<td>1,72</td>
</tr>
<tr>
<td>Al₂O₃ 30,1</td>
<td>Hexagonal Prisms</td>
<td></td>
</tr>
<tr>
<td>H₂O 53,3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂AH₆ 31,3</td>
<td>metastable</td>
<td>1,95</td>
</tr>
<tr>
<td></td>
<td>Hexagonal Plates</td>
<td></td>
</tr>
<tr>
<td>C₃AH₆ 44,4</td>
<td>stable Cubic</td>
<td>2,52</td>
</tr>
<tr>
<td></td>
<td>Trapezohedrals</td>
<td></td>
</tr>
<tr>
<td>AH₃ - 65,4</td>
<td>Gibbsite - stable</td>
<td>2,42</td>
</tr>
<tr>
<td></td>
<td>Monoclinic Prisms</td>
<td></td>
</tr>
</tbody>
</table>
3.4.3 CAC Hydration - Exothermic Reaction

The hydration is an exothermic reaction: with the formation of hydrates heat is created. The heat evolution in the first hours/day is high compared to Portland cement hydration, due to the much faster and more concentrated hydration reaction.

The amount of heat generated and its time frame is dependent on various factors, such as CAC reactivity, ambient temperature, pH, and additive addition to accelerate/retard setting.

To check on the Hydration Heat Development is a good and easy tool to control the CAC hydration, setting and strength development performance in a concrete. The recording of the Exothermic Heat Development is done by a thermocouple stuck into a freshly mixed concrete. The temperature inside the mix is recorded with the help of a data logger connected with to thermocouple. The collected data base can be monitored in the connected PC workstation.

In the first example, the heat development versus time is recorded for a Tabular concrete with 20% CAC, 9% H₂O, no calcined alumina fines, no additives). The starting temperature was 20°C (=ambient lab temperature)

The **exothermic curve** shows the start of temperature increase after a longer incubation period. But once exothermic heat starts to developed, the mix temperature is rapidly rising to a maximum of 45°C (+25°C). Afterwards the mix temperature is slowly decreasing back to ambient temperature.
Parallel to temperature recording, part of the mixture was used for flow and strength development tests. Looking at the vibration flow decay over time, a slow but steady flow decay (→ stiffening of the mix) can be seen. The flow stops fully with the begin of noticeable heat development.

A first measurable strength development is noted parallel to the heat development start. The strength first increases steadily in a linear manner, then with reaching the (high!) maximum strength it stays at that level.

These findings can be correlated with the earlier shown hydration progress in a mix:

- The initial hydration decreases plasticity of the mix, with start of strength development the flow is nil.
- The temperature reached during heat rise of >30 °C brought the mix in the range of stable C₃AH₆/AH₃ hydrate formation, giving high strength development.

A Tabular CCC (calcined alumina fines, no additives), 15% CAC, 8.5% H₂O, was tested at ambient temperatures of 10°C up to 50°C in 10°C interval steps.

With the exception of 30°C the following can be noted: The time needed for start of exothermic reaction is steadily decreasing with increasing ambient temperature. Total mix temperature increase from ambient temperature to max. hydration heat is about Δ13-20°C. The maximum strength is slightly increasing with increasing ambient temperature.

**Kinetics at 30°C** ambient temperature are different from the others. The exothermic reaction is only very slowly developing, the mix temperature rises just about 6°C. The strength is low compared to the other.

An explanation for this exceptional behaviour could be the turning point between low and high temperature hydration phase formation, CAH₆/AH₆ gel and C₂AH₆/C₃AH₆/AH₃ formation. Interactions between those two reactions can retard the crystallisation and therewith exothermic/hydration reaction and parallel strength development.

(Note: not shown in the above graph: the flow decay is also in correlation to the starting time of exothermic reaction. The flow is decreasing faster with higher ambient temperatures, decreasing starting times. Surprisingly, the initial flow after 10 min. are in all of the above test castables very well & similar.)
The data shows that the recording of the exothermic reaction/heat of hydration development in a mix can give a very good indication of the setting and strength development of a castable. Furthermore, it allows to check on the additive influence on the setting time and strength development.

EXO recordings are a reliable and easy to handle tool. With a little bit of experience they give a good insight look to what is happening in a mix once the material is put in place and set to curing conditions.

3.4.4 Kinetics during castable heat up/firing

The example shows the curing/dehydration/firing kinetics of a high purity Tabular CCC. The hydration up to the stable $C_3AH_6/AH_3$ formation has been discussed previously. Drying at 105-110°C is necessary to remove all superficial or free water. It also fully converts any left metastable phases to the stable state.

As temperature increases, dehydration continues until all phases lose their water of crystallisation. Lime and alumina reappear and recombine similar to the original sintered raw materials in the kiln to form Calcium Aluminates.

They continue to react with each other until ceramic reaction occurs between the binder components and the aggregate. In the example of a high purity CAC-Tabular castable this will be finally resulting in Calciumhexaaluminate formation. $CA_6$ is a high refractoriness phase, very low in further reactivity.

3.4.5 CAC Application Properties in Castables

For all castables in their specific applications, some important parameters are necessary to know. They are sometimes different for each individual application and concrete compositions. These are:

A. Flow properties  
B. Setting Properties  
C. Strength Properties (Hot)

The used CAC has a high influence on this properties. It can be traced back to its particle size distribution, water demand, composition (additives), consistency, degree of sintering-hydration reactivity, purity, etc.

The following graph shows the vibration flow decay tests results of 4 different commercially available 70% alumina types (CAC A - D) in a Chamotte Castable. The mix contains 7% CAC and 5% Microsilica. Microsilica is known to improve the flow prop-
erties of a castables. But, as the data shows, the used CAC has still a very high influence on the water demand, initial flow, and on the flow decay over time. Vibration flow properties are tested by filling 5 conical Vicat moulds (large inner Ø = 7.5 cm) with mix, cover, and let sit until testing time of 10, 30, 60, 90, or 120 min after mixing is reached. At the given time the sample is set on a vibration table, demoulded and vibrated at 0.5mm/50Hz for 30sec. The sample diameter is noted.

CAC A and CAC C need 0.5% less water (5.5 vs. 6%) for initial flow of 16-19 cm compared to CAC B & D. All mixes have about the same starting flow diameter. The flow decay is very slow for B and C, while D is “flash” setting. D’s flow is already stopped after 30 min. Only A shows good initial flow with a steady vibration flow decay over time.

**Exothermic Reaction** time recordings confirm the vibration flow results. EXO starting times for B and C are the longest, for D the fastest (see its flash set at flow). A is in-between B/C and D with its 257min/4.2h. This enables demoulding in a rational time frame, as A sets twice as fast as B (433min/7.2h) or D (467min/7.8h).
The influence of CAC's on the strength of a refractory product, in this case **Hot Modulus of Rupture** (HMoR) at 1500°C/5h holding time, can also be dramatic. The graph shows 6 different commercially available 70% alumina CAC's. They have been tested in a high purity Tabular/Calcined Alumina vibration LCC.

![Graph showing HMoR values for different CACs](image)

The HMoR value is directly reflecting the purity of the used cement. Impurities forming low melting compounds such as SiO₂, Fe₂O₃, Na₂O have been summed up for each product. Major contributors are SiO₂ and Fe₂O₃, either due to raw material impurities or to milling contamination. A level of 0.5% impurities and less enables superior hot performance. With 1% impurities and higher the HMoR values of the castables are cut by half or more.

Again the importance of purity is shown: in this case for the cement influence on the refractory product hot properties, earlier for the consistency of the CAC product itself.

## 4 Chemical Binders

The term "Chemical Binders" refers to a group of products. The definition for chemical binders is that they are "non-hydraulic, inorganic, and cold setting". The most important product families are:

- Phosphates
- Water Glass (Alkali-Silicates)
- Magnesia Cement (for basic products)
- Silica or Alumina sols.

Let's focus on the first two families, as being the major chemical binders for monolithics.

### 4.1 Phosphates

Family one: Phosphate binders. They can be divided in two subgroups:

I. Phosphoric Acids
II. Aluminium Phosphates
Monolithics bonded with these are called phosphate bonded refractories

4.1.1 Phosphoric Acids

The name “Phosphoric acids” is standing for a group of acids. The principal representative in refractories industry is H₃PO₄ orthophosphoric acid, often simply referred to as phosphoric acid. Orthophosphoric acid is commercially available as a 70-85% aqueous solution, but also in powder form as condensed phosphoric acid (105%). - Phosphoric acid additions are about 2-8%. Usually no extra water is added to the mix.

**Bonding:** H₃PO₄ reacts with metal hydroxides or oxides to form salts which function as a bonding agent. The most common oxides for phosphate bonded refractories are Al(OH)₃ or Al₂O₃. The reaction with Al(OH)₃ is fast proceeding at room temperature. The reaction with alumina is slow at RT, but increasing with rising temperature. The reaction product is Monoaluminumphosphate, short MAP.

\[
\text{Al}_2\text{O}_3 + 3 \text{H}_3\text{PO}_4 \rightarrow 2 \text{Al}(\text{H}_2\text{PO}_4)_3 + 3 \text{H}_2\text{O}
\]

**Heating:** Phosphate bonded materials gain strength when heated to around 100°C, as MAP looses part of its water and hardens. When exposed to moisture its bonding strength drops again and cracks can be formed. It requires temperatures above 350°C to produce nonhygroscopic behaviour. (note: CAC and phosphate binder combined can give a fast setting: CAC hydration gives Al(OH)₃ formation, which is itself again a nucleus for phosphate salt formation.)

MAP undergoes several conversions when heated up. With starting dehydration it shows polykondensation. At 1300-1500°C the decomposition leads to P₂O₅ formation. It can react with other oxides - with alumina it forms AlPO₄. Al₂O₃ is decomposing again at 1600°C: P₂O₅ vaporises, alumina is left as corundum.

Application temperatures of phosphate bonded corundum can be as high as 1700°C and above.

**Silica** enters into no reaction with Phosphoric acid at room temperature, no bonding takes place at elevated temperature SiO₂-P₂O₅ and 2SiO₂-P₂O₅ are formed, with liquid phases at 1100 and 1300°C. Low hot strength is the result.

**MgO** and Mg(OH)₂ rapidly react with phosphoric acid in an exothermic reaction (often added as setting agent), but bonding strength is weak. Furthermore low melting Magnesium Phosphate compounds are formed ([1-3]MgO-P₂O₅) at 1160 - >1380°C, lowering the hot strength.

4.1.1 Aluminium Phosphates

Aluminium Phosphates include many compounds (>50) with complicated chemistry. Of these the most often used refractory binder is Monoaluminum Phosphate Al(H₂PO₄)₃ or MAP for short. It is favoured for its solubility in water, stability, strength etc.

It is manufactured by reacting phosphoric acid with aluminium hydroxide at 100°C−200°C. A concentrated MAP solution can be spray dried to powdery MAP, but the product remains strongly hygroscopic.

The bonding mechanism in a monolithic mixed with MAP & water is similar to phosphoric acid, being slow at RT. Rapid hardening is again promoted by heating up to 100°C.
Again MgO is used as a setting agent, pro and con of using MgO was discussed earlier for phosphoric acid binding.

Also again care has to be taken to heat the product above the point of non-hygroscopic behaviour of >350°C to prevent strength loss and crack formation.

A MAP premixed dry product has a short shelf-life. Due to the strong hygroscopic behaviour ageing is promoted, by picking up moisture from the surrounding aggregates, or through the lining of the packaging material.

4.2 Water Glass

The second family is that of water glasses. Correct generic naming here is Alkali Silicates. Alkali silicates used for refractory binding are Sodium and Potassium Silicates (Na₂O, K₂O)ₙSiO₂·ₘH₂O.

This anhydrides are transparent as glass, and dissolve in water. The aqueous solution is often referred to as water glass. The viscosity of the water glass is depending on the concentration and on the SiO₂/Na₂O molar ratio. The larger, the higher the viscosity, the greater the length of the hydroxy silicate ion. Typically the ratio is 2.5-3.5. A typical chemical composition is H₂O = 59-68%, Na₂O = 7-13%, SiO₂ = 25-33%.

A common way of production is to mix silica sand and sodium bicarbonate and fuse at around 1200°C. The melt is cooled (glass), and dissolved in water.

The bonding mechanism is very complex. The reaction is steered by additions of setting agents such as acids or salts. Generally it is proceeding through decomposition through, gel formation and final condensing.

The hydrolysation is also using CO₂ from the air. Fast setting at the surface can lead to a dense surface film, which at fast heat up prevents water evaporation and leads to explosive spalling. The film formation is stronger with increasing Soda content in the water glass.

When heated up, dewatering is taking place at 100-200°C. Sodium silicates melt as low as 800°C, but can react with surrounding aggregates to higher refractoriness compounds. Soda vapour can form and condense at cooler parts of the furnace.

Water glass is mostly used in Chamotte mixes, the application temperature is limited to 1000°C. Additions of high quality aggregates or fillers (silica, corundum, MgO, Chromite) have proven to increase the refractoriness, but creeping is high due to the melt formation. For to increase refractoriness higher refractoriness binders should be used (CAC, Phosphate).

5 Final Statement:

For the Manufacturing of high quality Monolithics:

Only Careful Selection and Application of the Most Suitable Binder is giving the Best Final Performance to your Refractory Products.
6 Reference list:

- Akira Nishikawa: Technology of Monolithic Refractories. Plibrico Japan Company Ltd., 1984


  -> p. 155-166: M. Murat, El. H. Sadock; "Role of foreign kations in solution in the hydration kinetics of high alumina cement".


- ALCOA brochure: Methods of testing Calcium Aluminate Cement. 1994, reprint 1996.