

ALKALINE HYDROLYSIS – A DESTRUCTIVE MECHANISM FOR REFRACTORY CONCRETE – WHAT IS IT? – WHY DOES IT OCCURRENT? HOW CAN IT BE SOLVED ?

ALKALINE HYDROLYSIS IN REFRACTORY AND INSULATING CONCRETES

Mechanisms, causes, diagnosis and solutions

1. INTRODUCTION

Refractory and insulating concretes, widely used in industrial furnaces, petrochemical plants, and steel mills, are subjected to highly aggressive environments: high temperatures, humidity, alkaline vapors, and chemically active atmospheres.

One of the most critical—and often underestimated—deterioration mechanisms is **alkali hydrolysis**, a chemical phenomenon that leads to loss of mechanical properties, cracking, and structural degradation. The first visible symptom is usually the **detachment of powdery material from the surface**, easily removable by hand.

In many cases, this process occurs in combination with, or similarly to, **the alkali-silica reaction (ASR)**, which is extensively studied in conventional concretes. It is essential that the installed concrete meets all of these conditions for this chemical process to occur:

- ❖ **High alkali content in the concrete mix** (primarily sodium and potassium). This is more common in lightweight insulating concretes.
- ❖ **Inadequate curing (setting) of the material**, resulting in a higher water retention rate and preventing the curing process from occurring.
- ❖ **High ambient temperatures**, typical of summer, exceeding 30°C. This accelerates the reaction.
- ❖ **High porosity in the material**. This allows oxygen to diffuse from the surface into the interior of the mass. This can occur due to the addition of too much water or because it is a lightweight porous (insulating) concrete. Therefore, this phenomenon is more likely in insulating concretes than in dense ones.
- ❖ **High percentage of liquid water and water chemically bound to the cement**. Insulating concretes often have very high percentages (from 30% to over 100%).
- ❖ **Failure to perform convective drying within a reasonable timeframe** (within 30-60 days of pouring). This gives the retained water time to begin searching for alkalis and trigger the chemical reaction characteristic of hydrolysis.



2. DESCRIPTION OF THE PHENOMENON

Alkaline hydrolysis can be defined as:

The chemical decomposition of cement or aggregate phases by the action of highly alkaline solutions (NaOH, KOH) in the presence of water.

In refractory concretes, it occurs mainly in:

Calcium aluminate cements (CAC)

Systems containing **reactive silica**

Environments with **alkaline vapors or infiltration of alkaline liquids**

In general terms, the phenomenon involves:

1. **Dissolution** of sensitive components (silica or hydrated phases)
2. **Formation of gels** or unstable phases
3. **Expansion, cracking, or loss of cohesion** (the material pulverizes, from the surface inward)

3. CHEMICAL MECHANISM

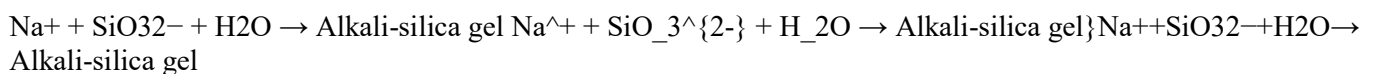
3.1 Fundamental reactions

In systems with reactive silica:

- Silica dissolution:



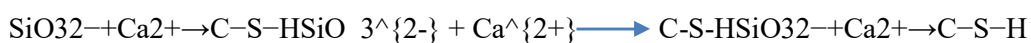
- Alkali gel formation:



This gel absorbs water and expands, generating internal stresses and causing the hydraulic bond to break down, resulting in dust on the surface and a progressive loss of strength towards the interior of the coating thickness.

3.2 Interaction with calcium

Subsequently:

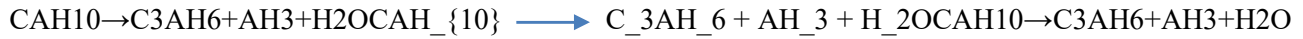


The gel can be partially transformed, but it remains **volumetrically unstable**.

3.3 In calcium aluminate (CAC) cements

In refractories:

Hydrolysis of aluminates:



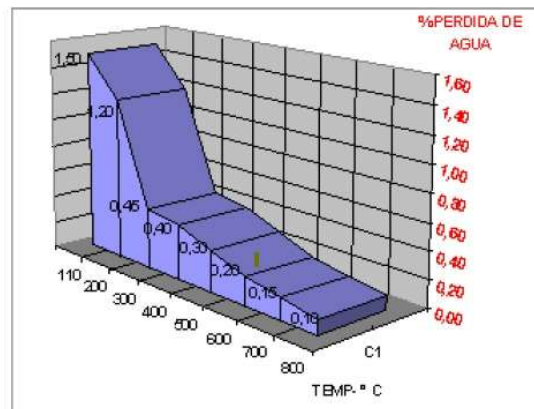
This implies:

- Loss of strength
- Increased porosity
- Structural instability

3.4 Necessary conditions

Three factors are essential:

1. **High alkalinity** (pH > 12)
2. **Presence of reactive phases** (amorphous silica or aluminates)
3. **Available moisture** (Nonexistent or deficient drying)



4. CAUSES OF ALKALINE HYDROLYSIS

4.1 Internal Factors

- Use of aggregates in concrete with **reactive silica**
- Cements with high **Na₂O** and **K₂O** content
- Microstructure with high porosity (typical in very lightweight insulation, or cast with too much water)
- Presence of unstable hydrated phases

4.2 External Factors

- Water or steam **infiltration**
 - Exposure to alkaline **salts (Na, K)**
 - Thermal cycles with condensation
 - Industrial atmospheres (furnaces, petrochemical plants)
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4.3 Operational Factors

- Poor or incomplete curing.
 - Inadequate drying before commissioning. **Convective drying** is essential here.
 - Designs with cold zones (condensation)
 - Frequent shutdowns with moisture ingress
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5. CONSEQUENCES IN REFRACTORY AND INSULATING CONCRETES

5.1 At the microstructural level

- Dissolution of cementing phases
 - Formation of expansive gels
 - Increased porosity
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5.2 At a macroscopic level

- Map-type cracking
- Internal volumetric expansion, progressive loss of strength.
- Scaling and exfoliation. Loose material is visible on the surface.
- Loss of cohesion

The expanding gel can generate stresses exceeding the tensile strength of the material, causing widespread cracking.

5.3 Impact on properties

- Decreased mechanical strength
 - Reduction in elastic modulus
 - Increased permeability
 - Loss of insulating capacity
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6. DIFFERENCES BETWEEN REFRACTORIES AND INSULATING

Characteristic	Dense Refractories	Insulating
Porosity	Low	High
Sensibility	Medium	High
Damage Rate	Slow	Fast
Type of failure	Structural Cracking	Disintegration

Insulating castables are more vulnerable due to their **high water absorption**.

7. DIAGNOSIS OF THE PROBLEM

7.1 Visual Inspection

Typical indicators:

- Irregular pattern cracking (“map cracking”)
- Exudation of gel or whitish material
- Localized swelling
- Surface disintegration (dust).Indicadores típicos:

7.2 Laboratory tests

- X-ray diffraction (XRD)
- Scanning electron microscopy (SEM)
- Chemical analysis of gels
- Measurement of expansion

7.3 Indirect indicators

- Increased internal humidity
- Loss of strength without obvious thermal cause
- Premature failures in cold areas

7.4 Differential diagnosis

It must be distinguished from:

- Thermal shock
 - Acid chemical corrosion
 - Mechanical erosion
 - Carbonation
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8. PREVENTIVE MEASURES

8.1 Material selection

- Non-reactive aggregates. Select materials with low alkali content or designed to prevent alkali hydrolysis. [See special products for protection against alkali hydrolysis.](#)
 - Convective drying.
 - Use retarder membranes on the surface. [See protective membranes.](#)
 - Low-alkali cements. Like the aggregates, they should have lower alkali content.
 - Use microsilica or inert admixtures.
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8.2 Material Design

- Low permeability. Select the most suitable material.
 - Porosity control. Install the product correctly, limiting the water percentage to that indicated in the technical data sheet.
 - Low-hydration systems. Pre-wetting can be performed, followed by a pneumatic spraying process (gunning) to adjust the water percentage and prevent excess.
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8.3 Process control

- **Proper curing.** Water can be added by spraying, or damp blankets or plastic sheeting can be used to retain moisture.
- **Controlled drying before operation.** Convective drying removes all water present in the poured or shotcreted concrete. This includes primary water (excess liquid H₂O) and secondary water (water chemically bound to the cement, which also disintegrates during convective drying).
- **Preventing moisture and air penetration.** There are also [products \(paints or sprays\)](#) that are applied in a thin layer to the surface to prevent the penetration of water or oxygen, which is also necessary to activate hydrolysis. These products are applied as soon as the concrete is installed, aiding in setting and extending the time needed to begin convective drying.



8.4 Operational design

- Minimize condensation areas
 - Control thermal cycles
 - Protection against alkaline vapors
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9. CORRECTIVE MEASURES

Once the process has started, it is difficult to stop it completely.

9.1 Palliative actions

- [Surface sealing \(surface membrane\)](#)
 - Humidity reduction (convective drying)
 - Infiltration control
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9.2 Repair

- Removal of affected areas
 - Replacement with resistant materials
 - Application of protective coatings
 - Controlled curing followed by **convective drying** as soon as possible. **Do not leave the coating undried for too long.**
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9.3 Engineering solutions

- Redesign the lining. Opt for improved thickness configurations.
 - Use of refractories with low chemical reactivity. Opt for higher quality materials.
 - Incorporation of moisture barriers. Specific membranes or coverage with damp blankets..
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10. CONCLUSIONS

Alkaline hydrolysis is a critical degradation mechanism in refractory and insulating concretes, especially in industrial environments with moisture and alkalis.

Its main characteristics:

- It is a progressive internal **chemical process**.
- It causes **expansion, cracking, and loss of strength**.
- It is **difficult to stop once it has started**.
- Its control depends **primarily on prevention**.

In industrial applications, a proper understanding of it allows for:

- Increasing the service life of linings.
- Reducing maintenance costs.
- Preventing catastrophic failures.

11. FINAL RECOMMENDATION (INDUSTRIAL APPROACH)

Para aplicaciones como hornos petroquímicos o agroindustriales:

- Prioritize **low-alkalinity materials**.
- **Design systems with steam control**.
- Implement early **periodic inspections**.
- Incorporate **integrated solutions** (materials + installation + operation).

Summary:

Alkaline hydrolysis is a chemical process that significantly reduces the strength of cast products, especially from the surface inwards. Its main causes are: the types of materials used, improper curing, and the **most significant cause: failure to perform adequate convective drying immediately after the curing process is complete**. Insulating concretes are more susceptible to this phenomenon.

This is where we believe [Soluciones Refractarias SRL](#) comes in, to anticipate, solve, and repair these problems. Our company has all the resources to address these issues:

- ❖ Top-level technical advice.
- ❖ State-of-the-art materials specifically designed for this problem.
- ❖ Liner design and thermal calculations.
- ❖ Installation of the various materials using appropriate procedures.
- ❖ Convective hot air drying.

Our WEB : www.solucionesrefractarias.com.ar

Our Social networks : <https://taplink.cc/solucionesrefractarias>

Consult us at : info@solucionesrefractarias.com.ar

Related Links :

[Installation Service](#)

[Installation Procedures](#)

[Dry-Out Curves](#)

[Convective drying of refractory castables](#)

[Membrane for surface application \(avoid water and air penetration\) .](#)

[Specific products for low alkalinity](#)

[Specific Products for Fast drying.](#)

Note: This report aims to illustrate all aspects and complexities of the topic covered. It should not be taken literally for valuation decisions or absolute final results regarding the scope of the report. For specific calculations or decisions, we recommend consulting specific sources.

Sources: Primarily original research, publicly available information, and specific notes in books.

[All aspects concentrated in one place, our space !!!!](#)

