
# PURE NATURAL POZZOLAN CEMENT

**Stronger**

**Reduced Cost**

**Reduced Emissions**

**. . . *A Better Alternative***

# HIGH QUALITY NATURAL POZZOLAN
# AVAILABLE FROM
# AZMAR INTERNATIONAL, Inc.

## INTRODUCTION

Mt. Pagan of the Northern Mariana Islands in the western Pacific Ocean, erupted in May 1981. The eruption deposited over 200 million tons of natural pozzolan, which blankets about 5 square miles of the northwestern slope in vast drifts ranging from 30 feet to over 100 feet deep.

**MT. PAGAN VOLCANO**

Random samples were collected throughout the deposit. Numerous test reports have confirmed that the whole deposit is of uniformly high quality, contains no carbon and virtually no sulfur trioxide, and is free from any contamination In the shape of porous rocks, this natural pozzolan can be easily ground into very fine power and can quickly react with lime.

After thorough testing, professor Anders Henrichson of the Technical University of Denmark gave the following recommendation:

> "The material can be characterized by its uniformity. the high reactivity which equals that of OPC, and its contribution to the durability of concrete, particularly that which is exposed to marine conditions of sulfate rich environments."

The high quality natural pozzolan on Pagan Island is an ideal concrete strengthening additive.

## HISTORY OF POZZOLAN

There are 1,282 volcanos in the world considered to have been active in the past ten thousand years. Only 3 volcanoes deposited high quality natural pozzolan.

The first one is Santorini Volcano, Greece, which erupted during 1600 BC ~ 1500 BC. Mt. Vesuvius, Italy, is the second volcano which erupted in AD 79. Pozzolan was names after the town of Pozzoli where it was deposited. The third, Mt Pagan is the only one which has erupted in modern times.

**NATURAL POZZOLAN DEPOSIT AT BASE OF OUTCROPPING ON PAGAN ISLAND**

Scientists have proven that the ancient Greeks began to use natural pozzolan-lirne mixtures to build water storage tanks some time between 700 BC and 600 BC.

This technique was then passed to the Romans about 150 BC.

According to Roman engineer Vitruvius Pollio, who lived in the first century BC:

> "The cements made by the Greeks and the Romans were of superior durability, because neither waves could break, nor water dissolve the concrete."

Many great ancient structures, such as the Colosseum, the Pantheon, the Bath of Caracalla, as well as other structures that are still standing in Italy, Greece, France, Spain and the islands in the Mediterranean Sea, were built with natural pozzolan-lime mixtures. Many of them have lasted two thousand years.

**ROMAN COLOSSEUM**

After the invention of Portland cement, natural pozzolan was used as a concrete strengthening additive to improve characteristics such as durability, compressive strength, chemical resistance. hydration heat, permeability etc..

In Europe and the USA, there have been numerous high rise buildings, highways, dams, bridges, harbors, canals, aqueducts and sewer systems built with natural pozzolan-cement mixtures.

**ROMAN PANTHEON**

Due to the limited and sporadic supply of high quality natural pozzolan. in the last 30 years, the USA and European countries were compelled to lower their quality criteria so that waste materials such as fly ash could be used as a substitute for natural pozzolan.

**FLY ASH vs NATURAL POZZOLAN**

Known to be much inferior to natural pozzolan, fly ash normally contains excess amounts of carbon dioxide and sulfur trioxide, which are trapped inside the spherical envelope while coal powder burns. As the waste of coal-fired power plants, fly ash is inconsistent in chemical composition.

When fly ash cement is hydrated, the envelope covering each fly ash particle prevents or slows down its reaction with calcium hydroxide curing the cementing period. When the envelope breaks in a later stage, destructive DEF (Delayed Ettringite Formation) occurs around the partly reacted fly ash particle.

Fly ash is also known to be inferior to natural pozzolan in the control of alkali-aggregate reaction, because the envelope slows down its reaction with calcium hydroxide which is produced by hydration of Portland cement. The envelope also slows down the reaction of the silicate inside the particle with the alkali in the cement.

Natural pozzolan is formed when silica rich magma meets with a large quantity of under

ground water in the volcano conduit. Under high pressure and high temperature, water in steam form dissolves into the magma mixing with the dissolved carbon dioxide and sulfur gases. When this magma reaches the earth's surface, it blows off the top of the volcano cone. Because the pressure is suddenly reduced, all the gases inside the magma are released and the magma, blown up like pop-corns, falls to ground then cools into small porous rocks.

After being ground into a find powder natural pozzolan can quickly react with calcium hydroxide to can trap the alkali inside the cement paste. Thus, it helps to form a denser paste with virtually no alkali aggregate reaction.

**GRANULATED BLAST FURNACE SLAG vs NATURAL POZZOLAN**

Good quality granulated blast furnace slag is a good cementitious material. But, in order to produce good quality slag, steel plants must sacrifice the quality and some quantity of their steel products. Therefore, good-quality slag is very difficult to find.

Uniformity is another problem. The mixture of the left over from burning the iron ore, lime stone, and coal, can vary from ton to ton in chemical composition.

Water cooling may help to purify the slag, but still, there are certain quantities of gases such as carbon dioxide, carbon monoxide and sulfur gases trapped in the slag.

Slag cement is well known for its slowness in developing its compressive strength. Adding expensive silica fume can accelerate the development, but the result is still not very satisfactory.

Containing 30% to 40% silicate and about the same amount of calcium oxide, slag is far inferior to natural pozzolan in reactivity with the calcium hydroxide produced by cement hydration.

The natural pozzolan on Pagan Island is unique in its uniformity and high reactivity.

**BENEFITS AND ADVANTAGES**
**OF THE NATURAL POZZOLAN ON PAGAN ISLAND**

Substituting 30% Portland cement with the Azmar natural pozzolan will accomplish the following:

1. Lithification
2. Autogenous healing
3. Fatigue properties
4. Reduces permeability and voids
5. Reduces expansion and heat of hydration
6. Reduces creep and cracks
7. Reduces micro-cracking
8. Increases compressive strength
9. Increases resistance to chloride
10. Increases resistance to sulfate attack
11. Reduces alkali-aggregate reaction
12. Impedes carbonation

13. Reduces freeze-thaw damage
14. Protects steel reinforcement from corrosion
15. Increases abrasion resistance
16. Lowers water requirement with high fluidity, self-leveling and self-compression
17. Improves durability
18. Reduces costs of production and construction
19. Increases production capacity and reduces energy requirements and costs
20. Reduces carbon dioxide emissions
21. Unifies quality

**1. Lithification**

Once a natural pozzolan-lime mixture is hydrated, pozzolanic reaction begins and will continue many years. Eventually, the mass will reach a complete lithification, forming a rocky mass similar to plagioclase with some content of magnetite.

The compressive strength and flexural strength will continue to increase for a long time This unique characteristic is one of the main reasons why many great ancient structures have lasted for over two thousand years.

**2. Autogenous Healing**

Another unique characteristic of Azmar's natural pozzolan is its inherent ability to heal or reduce cement cracks within the concrete by means of its continuation of pozzolanic reaction with the calcium hydroxide freed from the hydration of Portland cement. This autogenous healing mechanism mends the structures by filling up most of the gaps inside the hardened concrete matrix.

**3. Fatigue Properties**

All engineering materials are subject to potential failure caused by progressive fracture under action of repeated loadings. The stress level (the ration of applied stress to the modulus of rupture) gradually decreases.

The flexural strength of Azmar's natural pozzolan-Portland cement mixture, like the compression strength, increases with time. Its autogenous healing mechanism also helps to mend the fractures and recover the stress level.

**4. Reduced Permeability and Voids**

The leaching of water-soluble calcium hydroxide produced by the hydration of Portland cement can be a significant contributor to the formation of voids. Also, the amount of "water of convenience" used to make the concrete workable during the placing process, creates permeable voids in the hardened mass.

Azmar's natural pozzolan can react quickly with calcium hydroxide and form additional C-S-H. Thus, it not only prevents the water soluble compound from migration out of the concrete, but also makes the cement paste denser, with no voids.

In addition, natural pozzolan can increase the fluidity of concrete without "water of

convenience". Therefore, the volume of capillary pores created by water can be minimized.

**5. Reduces Expansion and Heat of Hydration**

Experiments show that replacing 30% Portland cement with natural pozzolan can reduce the expansion and heat of hydration to as low as 40%. Possibly, it is because there is no heat produced when natural pozzolan reacts with calcium hydroxide and that the free calcium oxide in the cement can hydrate with natural pozzolan to form C-S-H.

Azmar's natural pozzolan decreases the heat generated by cement hydration and delays the onset of peak temperature. The graphic pattern of natural pozzolan-Portland cement mixture is extended longer and lower to form a much more moderate curve than the heat of hydration curve of Portland cement itself.

**6. Reduces Creep and Cracks**

While concrete is hardening, the " water of convenience " dries away. Then, the surface of the hardening mass begins to shrink as the temperature goes down from outside. That causes the formation of creep and cracks.

Azmar's natural pozzolan moderates the expansion and shrinkage of concrete. It also helps to lower the water content of the fresh Concrete. Therefore, the creep and cracks can be significantly reduced without the process of water cooling.

**7. Reduces Micro-Cracking**

The expansion and shrinkage mentioned above also create microcracks inside the hardened C-S-H paste and in-between the aggregate and C-S-H paste. These microcracks significantly contribute to concrete permeability as well as other concrete defects.

Azmar's natural pozzolan-Portland cement mixture expands shrinks so moderately that there is micro-cracking inside the C-S-H paste. In addition, the aggregate keeps close contact with C-S-H paste after drying.

**8. Increases Compressive Strength**

The pozzolanic reaction between natural pozzolan and calcium hydroxide happens after the lime and C2S in the cement begin to hydrate. At the early stage of curing, 30% natural pozzolan substituting Portland cement mixture slightly lower than reference OPC in regard lo compressive strength.

As time goes by, natural pozzolan keeps on reacting with the calcium hydroxide produced by cement hydration and increasing the compressive strength by producing additional C-S-H.

After 21 curing days, 30% natural pozzolan 70% Portland cement mixture begins to exceed reference OPC in compressive strength

After 28 days, it exceeds reference OPC by about 15%. Pozzolanic reaction keeps on until there is no free calcium hydroxide available in the mass and the compressive strength exceeds reference OPC by 30% to 40%.

**9. Increases Resistance to Chloride Attack**

Concrete deterioration caused by the penetration of chloride occurs quickly when chloride ions react with calcium hydroxide to form strongly expanding hydrated calcium oxychloride.

The expansion of hydrated calcium oxychloride enlarges the micro-cracks and increases the permeability that causes quicker chloride penetration and more damage from freezing and thawing action.

The 30% natural pozzolan added into cement can react with almost all the free calcium hydroxide and form a much denser paste. Thus, the penetration of chloride can be minimized and the penetrated chloride ions cannot find calcium hydroxide with which to react.

To be durable, concrete structures that are exposed to marine conditions must use natural pozzolan as a strengthening additive.

**10. Increased Resistance to Sulfate Attack**

There are three chemical reactions involved in sulfate attack on concrete:

- Combination of free calcium hydroxide and sulfate to form gypsum (CaSO4-2H20)
- Combination of gypsum and calcium aluminate hydrate (C-A-H) to form ettringite ($C3A\text{-}3CaS0_4\text{-}3H_2O$)
- Combination of gypsum and calcium carbonate with C-S-H to form thaumasite ($CaCO_3\text{-}CaSiO_3\text{-}CaSO_4\text{-}15H_2O$).

All these reactions result in an expansion and disruption of concrete, and thaumasite in particular is accompanied by a very severe damaging effect which is able to transform hardened concrete into a pulpy mess.

Pagan's natural pozzolan contains virtually no sulfate in itself and can quickly react with free calcium hydroxide to form additional C-S-H which makes the paste much denser. Therefore, it eliminates the formation of gypsum, ettringite and thaumasite.

Experiments demonstrate that with only 20% Azmar natural pozzolan substituting for cement can reduce sulfate expansion by 80%.

**11. Reduces Alkali-Aggregate Reaction**

Expansion due to alkali-aggregate reaction can be a serious problem with OPC. This undesirable expansion causes micro-cracks between and hardened cement paste.

Experiments show that substituting only 25% of Azmar natural pozzolan for OPC can reduce alkali-silica expansion by 70%.

(A) The alkalies in Azmar’s natural pozzolan are fixed in the glass phase
(B) During cement hydration, natural pozzolan reacts with the freed calcium hydroxide and maintains the PH level in the paste.
(C) By trapping the alkalics inside the paste in the form of alkali-silica gel, the silica in nature pozzolan renders the alkalies in the Portland cement unavailable for

reaction with aggregate.

**12. Impedes Carbonation**

Carbonation of cement/concrete is a multi factor phenomenon, which despite being abundantly researched, still remains to be fully understood.

The following chemical equations prove that alkali functions as a catalyst in the deterioration cement/concrete:

(1) $CO_2 + 2NaOH \quad Na2CO_3 + H_2O$

(2) $3Na_2CO_3 + 3CaO\text{-}2SiO_2\text{-}4H_2O \quad 3CaCO_3 + 2SiO_2 + 6NaOH + H_20$

Part of the sodium hydroxide reacts with silica to form water soluble alkali-silica gel and the remainder can react with carbon dioxide again.

Numerous still standing ancient building clearly demonstrate that natural pozzolan can impede cement carbonation.

Adding 30% Azmar natural pozzolan into Portland cement enhances its resistance to carbonation.

- The concrete made from this mixture has virtually no micro-cracking to allow diffusion of carbon dioxide
- Its paste has very low permeability
- It traps all the alkali in cement to form alkali-silica gel scattering within the glassy matrix, so it prevents the alkali to act as a catalyst in cement carbonation.

**13. Reduces Freeze-Thaw Damage**

Adding Azmar's natural pozzolan to Portland cement assists the concrete in resisting freeze/thaw damage by minimizing the permeability, voids, cracks induced by chemical expansion and attack. The paste made from Azmar's natural pozzolan-Portland cement mixture is so dense and closely cohered with aggregate that moisture only minimally penetrates its matrix.

**14. Protects Steel Reinforcement From Corrosion**

The above discussions demonstrate that concrete made from a mixture of 30% Azmar natural pozzolan and 70% Portland cement protect steel reinforcement in an alkaline environment that is so densely sealed no liquids and gases can penetrate to cause corrosion of the steel.

**15. Increases Abrasion Resistance**

Azmar's natural pozzolan increases the compressive strength of concrete and makes the concrete matrix denser and stronger. It also prevents the formation of pulpy, crispy or water soluble materials created by chemical attack. Therefore, it helps the concrete to durably resist abrasion.

**16. Lowers Water Requirement With High Fluidity, Self-Leveling and Compression**

In normal operations, the bulk volume of concrete in the constructions are placed and compacted by use of high frequency poke vibrators. The rapid vibration induces segregation phenomena in all orders of magnitude in the fresh concrete e.g., stone segregation, internal bleeding giving bonding failures in homogeneous cement paste and airvoid systems.

A 30% Azmar natural pozzolan : 70% Portland cement mixture can achieve high concrete fluidity with low w/c ratio. Thus, the resulting concrete can be self-leveled and self-compressed without the use of a vibrator.

**17. Improves Durability**

The benefits and characteristics of natural pozzolan mentioned above clearly explain why the ancient structures built by the Greeks and the Romans have survived more than 2000 years of weathering.

**18. Reduces Costs of Production**

At present, Azmar's natural pozzolan is available at a price substantially below that of Portland cement. Additionally, its workability characteristics contribute construction cost reductions including manpower, vibration and water cooling.

**19. increases Production Capacity and Saves Energy**

Cement producers can achieve a 30% increase in production capacity and eliminate some energy inputs by mixing Azmar's natural pozzolan with their Portland cement - without additional any kiln.

**20. Reduces Carbon Dioxide Emissions**

The carbon dioxide emission produced by cement plants is an environmental concern. Because kiln requirements are reduced, adding Pagan's natural pozzolan to substitute for 30% Portland cement reduces $CO_2$ emissions.

**21. Unifies Quality**

Uniformity of cement quality is an important requirement for building large structures. Most available pozzolanic additives cannot meet this criterion.

Research shows the quality of Azmar's natural pozzolan material surpasses criteria of GB/T2 for pozzolanic materials used for cement and exceeds all requirements for a natural pozzolan in accordance with ASTM C618.

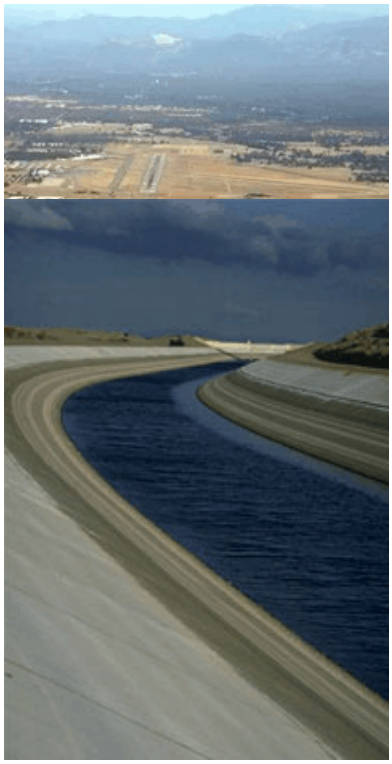
For the construction use as an additive to concrete, conforming to ASTM C-618 in the U.S. and G8/T2846 in China. or use as a major ingredient for producing Portland Pozzolan Cement, conforming to ASTM C-595 98 in the US. and BS6610; 1Qg6 in the U.K.

## Major Pozzolan Concrete Projects

East Bay Municipal Utility District Wastewater Treatment Plant - California
Auburn Dam - California
Palo Verde (Nuclear) Power Generating Plant - Arizona
Sacramento Wastewater Treatment Plant - California
Southern Nevada Water Project - Nevada
Tehama-Colusa Canal - California
George R. Moscone Convention Center - California
Port of Richmond - California
Pacheco Pass Tunnel - California
Idaho Falls Hydro Electric - Idaho
American River Falls Power Plant - Idaho
Coyote Power Generating Plant - North Dakota
San Francisco Wastewater Treatment Plant Project - California
Pioneer Reservoir - California
Chabot Darn - California
Dumbarton Bridge - California
Peace Valley Water Project - California
Pyramid Lake Powerhouse - California
Rock Springs Wyoming Power Plant - Wyoming
Hong Kong Center - California
Graduate Theological Union Building, UC Berkeley - California
Pacific Gas & Electric - California
Helms Creek Powerhouse Pump Station - California
North Point Seawall - California
Bechtel Engineering Center, UC Berkeley - California
Redding Airport Runway - California
Los Angeles Aqueduct (1910-1912) - California
Los Angeles Flood Control District during the 1920's and 1930's
Bonneville Dam (1935) - Oregon
Golden Gate Bridge (1937) - California
Piers of the San Francisco-Oakland Bay Bridge (1935) - California
Friant Dam (1942)

**GOLDEN GATE BRIDGE**

**BONNEVILLE DAM**



**CALIFORNIA AQUEDUCT**

Nearly all of the concrete in the California State Water Project Including the California Aqueduct 1960's and the 1970's.

# TEST REPORT COMPARISON

**AZMAR PAGAN ISLAND POZZOLAN "N"**
**vs**
**ASTM C618, CLASS N**

Testing conducted by Construction Technologies Laboratories, Inc. of Azmar Pagan Natural Pozzolan are depicted below. The results indicate that following ball milling the product to a Blaine fineness of approximately 8,000 $cm^2/g$, the material exceeds all specifications of ASTM C618 for a natural pozzolan. The sulfate resistance of the material is excellent as indicated by the low expansion values in the ASTM C1012 sulfate resistance test. Utilizing Type II cement as the control, this material should produce the equivalent of a Type V cement.

| Sample ID | Unconfined Comprehensive Strength, PSI | | | |
|---|---|---|---|---|
| Control | 2170 | 3120 | 5970 | 7100 |
| 20% Pagan Pozzolan | 1890 | 2730 | 6410 | 7880 |

| Chemical Analysis | Pagan Pozzolan | ASTM C618, Class N |
|---|---|---|
| Silicon Dioxide, $SiO_2$, % Weight | 51.28 | ----- |
| Aluminum Oxide, $Al_2O_3$, % Weight | 15.41 | ----- |
| Iron Oxide, $Fe_2O_3$, % Weight | 12.97 | ----- |
| $K_2O$ | 0.79 | |
| $TiO_2$ | 0.95 | |
| $P_2O_5$ | 0.14 | |
| $Mn_2O_3$ | 0.21 | |
| SrO | 0.04 | |
| $Cr_2O_3$ | 0.02 | |
| ZnO | 0.02 | |
| Sum of $SiO_2$, $Al_2O_3$, $Fe_2O_3$, % Weight | 79.7 | 70% Minimum |
| Sulfur Trioxide, $SO_3$, % Weight | 0.02 | 4.0% Maximum |
| Moisture Content, % Weight | .10 | 3.0% Maximum |
| Loss on Ignition (950°C)[2] % Weight | -0.09 | 10.0% Maximum |
| Magnesium Oxide, MgO, % Weight | 5.31 | 5.0% Maximum |
| Available Alkalis as $NA_2O$, % Weight | 2.57 | 1.5% Maximum |
| Calcium Oxide, CaO, % Weight | 10.27 | ------ |

| | | |
|---|---|---|
| Alkalis as $Na_2O$ | 3.09 | |

**Theromgravimetric Analysis**
(As Received Basis)

| | | |
|---|---|---|
| Free Moisture (Ambient - 105°C) | 0.10 | |
| L.O.I. (105°C - 750°C) | 0.01 | |
| L.O.I. (750°C - 950°C) | -0.10 | |

**Calculations per ASTM 618C-01**

| | | |
|---|---|---|
| $SiO_2$, $Al_2O_3$, $Fe_2O_3$ | 79.7 | 70% Minimum |
| L.O.I. 750°C basis (dry 105°C basis) | | |

**Physical Analysis**

| | | |
|---|---|---|
| Amount Retained #325 sieve | 32.6 | 34% Maximum |
| Strength Activity Index: | | |
| Portland Cement @ 7 Days | 81 | 75 Minimum |
| Portland Cement @ 28 Days | 87 | 75 Minimum |
| Water Requirement, % of Control | 95 | 115 Minimum |
| Autoclave Expansion, % | 0.02 | 0.8 Maximum |
| Specific Gravity | 2.89 | ----- |
| Increase of Drying Shrinkage, %* | ----- | 0.03 Maximum |

* Optional requirements. This material meets the requirements of ASTM C618 for the parameter tests. Blaine fineness = 7,810 $cm^2g$; or 21,480 $cm^2/cm^3$

These results indicate that mortars containing Azmar Pagan Pozzolan continue to gain strength versus the control at later ages, an excellent indicator of pozzolanic activity.