BEAR RIVER ZEOLITE BRZ™
IN POZZOLAN

Cement Plant
By Rjcastillo

INTRODUCTION

A pozzolan is a “siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties” (ASTM).[4]

In “Portland-pozzolan” cement, 10 to 30% of the cement can be replaced by zeolite which is a natural pozzolan.

BENEFITS

INCREASED COMPRESSIVE STRENGTH
- Due to the porous crystalline structure and high surface area of the zeolite, the hydrated phases of lime pozzolan are enhanced and this increases the compressive strength.

REPLACEMENT FOR CLINKER
- Up to 7% BRZ™ can be used to replace clinker in the manufacture of Portland cement without disclosure of the producer.

REPLACEMENT FOR FLY ASH
- Twenty-three micron BRZ™ can be used to replace fly ash to avoid the heavy metals in fly ash.

REDUCTION IN CHLORIDE PERMEABILITY
- This reduces the corrosive effect of chlorination on rebar, mesh, well casing and other iron products.

DECREASES ALKALI-SILICA EXPANSION
- BRZ™ allows the use of clinkers with more than 0.60% Na_2O. (Limit of ASTM description). The zeolite isolates the excess sodium in its crystal lattice. Alkali-silica reaction (ASR) from reactive aggregates causes buckling in concrete highways, bridge collapse, and other problems.

DRIES AND SOLIDIFIES DRILL CUTTINGS
- BRZ™ adsorbs hydrocarbons and holds them. This can be mixed with lime or other activators to form pozzolanic cement

REDUCTION IN WORKABILITY
- The reduction in workability required mid-range and high range water reducers to control slump.

RESISTS SULFATE AND ACID ATTACKS

HELPS RESIST UNDERWATER CORROSION ESPECIALLY IN SALT WATER
- BRZ™ exhibits good chemical resistance.

POWER SAVINGS
- The production of 1 kg of clinker requires 900 Kcal of energy. Ten tons of BRZ™ used as a natural pozzolan to replace Portland cement saves about 1 ton of fuel.

CERTIFIED AS TYPE N (NATURAL) POZZOLAN
- ASTM C 618-03. Colorado Testing Laboratory.

LIGHT WEIGHT CEMENT
- BRZ™ can be heat treated to form lightweight cement. When heated it loses water. When mixed into a cement mixture it rehydrates and releases air. The “foam” or “air entrainment” increases strength and decreases weight
- BRZ™ can be used to replace fumed silica in light weight cement. The density of the concrete can be adjusted by adding a dry-blend 23 micron BRZ product. The product can be used to make cinder block and other light weight building materials.

LIGHT WEIGHT AGGREGATE
- BRZ™ expands into a lightweight aggregate at temperatures between 1200° and 1400° C. Its density is about 0.8 g/cc, and it has a porosity of up to 65%. Light-weight aggregate is commonly used in Japan.

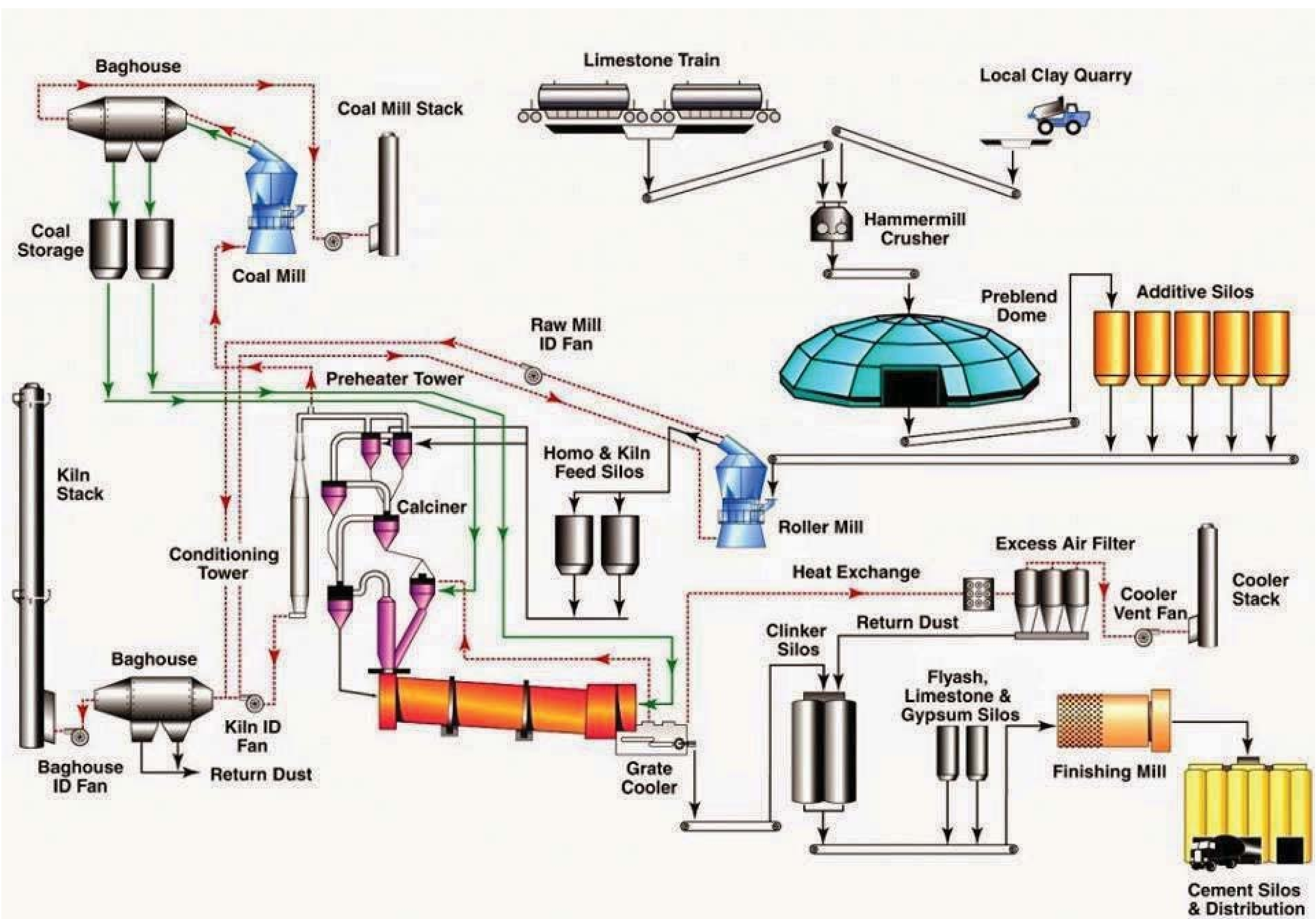
BEAR RIVER ZEOLITE, PO Box 643, 47 Cox Gulch Road, Thompson Falls, MT 59873
406-827-3523 • FAX: 406-827-3543 • www.bearriverzeolite.com • tfl3543@blackfoot.net

APPLICATION METHODS OF BRZ™ AS POZZOLAN

METHOD 1: 20-25 micron BRZ™ can be added to the cement at the batch plant as a dry blend.

METHOD 2: BRZ™ can be added at the cement plant after the kiln as minus 6 inch rock directly to the inter-grind circuit. The advantage is that it does not go through the kiln that requires massive amounts of fuel and does not generate carbon dioxide.

FLOWSHEET: TYPICAL CEMENT PLANT



Flowchart of Cement Industry (Dry Process)

CEMENT COMPOSITION[1]

Modern cements are often Portland cement or Portland cement blends, but other cements are used in industry.

Cement Components[2]

Comparison of Chemical and Physical Characteristics[a]

Content (%)	Portland Cement	Siliceous (ASTM C618 Class F) Fly Ash	Calcareous (ASTM C618 Class F) Fly Ash	Slag Cement	Silica Fume
SiO_2	21.9	52	35	35	85-97
Al_2O_3	6.9	23	18	12	
Fe_2O_3	3	11	6	1	
CaO	63	5	21	40	<1
MgO	2.5				
SO_3	1.7				
Property					
Specific surface[b] (m^2/kg)	370	420	420	400	15,000-30,000
Specific gravity	3.15	2.38	2.65	2.94	2.22
General use in concrete	Primary binder	Cement replacement	Cement replacement	Cement replacement	Property enhancer

[a] Values shown are approximate: those of a specific material may vary.
[b] Specific surface measurements for silica fume by nitrogen adsorption (BET) method, others by air permeability method (Blaine)

Portland cement is by far the most common type of cement in general use around the world. This cement is made by heating limestone (calcium carbonate) with other materials (such as clay) to 1450 °C in a kiln, in a process known as calcination, whereby a molecule of carbon dioxide is liberated from the calcium carbonate to form calcium oxide, or quicklime, which then chemically combines with the other materials that have been included in the mix to form calcium silicates and other cementitious compounds. The resulting hard substance, called 'clinker', is then ground with a small amount of gypsum into a powder to make 'ordinary Portland cement', the most commonly used type of cement (often referred to as OPC). Portland cement is a basic ingredient of concrete, mortar and most non-specialty grout. The most common use for Portland cement is in the production of concrete. Concrete is a composite material consisting of aggregate (gravel and sand), cement, and water. As a construction material, concrete can be cast in almost any shape desired, and once hardened, can become a structural (load bearing) element. Portland cement may be gray or white.

CEMENT CHEMISTRY

Non-hydraulic cement, such as slaked lime (calcium hydroxide mixed with water), hardens by carbonation in the presence of carbon dioxide which is naturally present in the air. First calcium oxide (lime) is produced from calcium carbonate (limestone or chalk) by calcination at temperatures above 825 °C (1,517 °F) for about 10 hours at atmospheric pressure:

$$CaCO_3 \rightarrow CaO + CO_2$$

The calcium oxide is then spent (slaked) mixing it with water to make slaked lime (calcium hydroxide):

$$CaO + H_2O \rightarrow Ca(OH)_2$$

Once the excess water is completely evaporated (this process is technically called setting), the carbonation starts:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

This reaction takes a significant amount of time because the partial pressure of carbon dioxide in the air is low. The carbonation reaction requires the dry cement to be exposed to air, and for this reason the slaked lime is a non-hydraulic cement and cannot be used under water. This whole process is called the lime cycle.

Activators for Zeolite Well Cements

Halliburton has several patents covering the use of activators that make a slurry of zeolite, such as clinoptilolite, set in the down hole annulus for oil and gas wells. The compressive strength of the cement is said to vary from 290 – 750 psi at 24 HRs and 160°F depending on the amount of activator used.

The activators listed in the patents are:

Calcium hydroxide	Sodium silicofluoride	Potassium carbonate
Calcium oxide	Magnesium silicofluoride	Sodium hydroxide
Sodium silicate	Zinc silicofluoride	Potassium hydroxide
Sodium fluoride	Sodium carbonate	Sodium sulfate

Examples are given in the patents claiming that a mix of, 10 – 30% lime by weight of zeolite, and 109 – 136% water by weight of zeolite, will give a cement with a compressive strength of 290 – 750 psi in 24HRs @160°F, and they begin to set up in just 4HRs at a compressive strength of 280 – 500 psi depending on the amount of activator added. (Halliburton U.S. Patent Nos. 6,989,057, 6,964,302, 7,285,166)

NOTES

1. "As of 2016 the world's annual production of natural zeolite approximates 3 million tonnes. Major producers in 2010 included China (2 million tonnes), South Korea (210,000 t), Japan (150,000 t), Jordan (140,000 t), Turkey (100,000 t) Slovakia (85,000 t) and the United States (59,000 t)."[6]
2. Some 60-75% of all the zeolite mined is used as a pozzolan.*
3. "The use of natural zeolites dates back more than 3,000 years to the Greek and Roman periods."[3]
4. "This material (BRZ™) achieved an incredible amount of strength from 7 days to 28 days. Combined with a high-range water reducer, it may compete favorably with silica fume and super-fine fly ash."[5]

   Principal Commercial Testing Laboratories Inc.
   A Division of CTL | THOMPSON, INC.
   1971 W. 12th Ave., Denver, CO. 80204
   303-825-0777, fax: 303-825-4252
   https://www.ctlthompson.com/
5. "Fresh concrete properties, e.g. temperature, air content, yield, weight were apparently unaffected by zeolite incorporation."[3]
6. "A reduction in bleedin, and accelerated initial setting at 10 to 30% replacement levels was noticed with zeolite."[3]
7. "The main effect, however, was in noticeable reduction in workability, especially at greater than 10% level, which required additional mid-range and high-range water reducing admixtures in the mixture."[3]
8. "Zeolite-blended concrete mixtures showed an improvement in compressive strength at 10% cement replacement level at 56 days, whereas 20 to 30% replacement caused a modest reduction in strength a the same age by approximately 10%. Effects of pozzolanic reactions of clinoptilolite, however, are far significant in improving durability and compressive strength."[3]

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*Additional information on file at Bear River Zeolite, Co.
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