Pumice Pozzolan: Summary *of* Phase Two Research on Hess Pozz

Quantifying the Effectiveness of Pumice-Blended Cement on Mitigating the Alkali-Silica Reaction[1]

by the Concrete and Materials Research and Evaluation Laboratory, Department of Civil and Environmental Engineering, University of Utah.

IN 2012, Hess Pumice contracted with the University of Utah to conduct a series of tests using two grades of carefully refined pumice to determine and quantify its effectiveness as a concrete pozzolan. This quantitative analysis was initiated for several reasons:

1) The on-going shortcomings of fly ash as a consistent and effective pozzolan (in terms of color, preferred-type availability, contaminant levels, and performance);

2) The desire for hard numbers on the pozzolanic performance of the Hess pumice deposit in particular, and a definitive confirmation in general of the old-world Roman practice of using pumice as an incredibly effective concrete pozzolan;

3) The green building industries' need for a clean, natural SCM that improves the performance, strength, and effective lifespan of concrete and does so while replacing a portion of the needed Portland cement—produced via a very energy-extensive process—thus bringing this critical and extensively-used building material inline with responsible green building goals.

4) As an expansion on the pozzolanic component of a research and development effort by the U.S. Department of Energy (Sandia National Laboratories) and Atomic Energy of Canada (Whiteshell Laboratories) that developed a cementitious grout with the requisite strength, density and durability to seal the microfractures deep underground in the saltrock surrounding the confinement chambers of the DOE's Waste Isolation Pilot Plant in New Mexico. This ultrafine, highly effective cement-based grout specified the use of pumice from Hess Pumice Product's deposit in Southeast Idaho as the performance-critical pozzolanic component.[2]

That University of Utah research yielded the expected results in terms of Hess pumice as a highly effective concrete pozzolan, but it also produced some unexpected data: in the presence of reactive aggregate, Hess Pozz absolutely flatlined the alkali-silica reaction. Not unexpected in that pumice (like most pozzolans) had an attenuating effect on ASR, but rather unexpected in terms of just how effective it was in mitigating, even eliminating the alkali-silica reaction.

This impressive level of ASR mitigation launched, at the University's request, a phase two follow-up study that focused specifically on the use of Hess Pozz as a specialty mitigation agent to combat the plague of ASR. The data from that completed study provided the validation to market a specific ASR mitigation product: ASR Miti•Gator™

1 • Research was conducted by **Uma Ramasamy** in partial fulfillment of the requirements for a doctorate degree.

2 • This patented grout is produced commercially by US Grout and available through and supported by Avanti International

HESS POZZ GRADES

Hess StandardPozz DS-325 (**ASR Miti•Gator**™)

PARTICLE SIZE SPECIFICATION

Dx	Micron Size
D50	14 - 16

Hess UltraPozz NCS-3

PARTICLE SIZE SPECIFICATION

Dx	Micron Size
D50	2 - 4

CHEMICAL COMPOSITION

Common Name: **Pumice**
Chemical Name: Amorphous Aluminum Silicate
Silicon Dioxide - 87.4%
Aluminum Oxide - 10.52%
Ferric Oxide - 0.194%
Ferrous Oxide - 0.174%
Sodium - 0.128%
Potassium - 0.099%
Calcium - 0.090%
Titanium Dioxide - 0.0074%
Sulfate - 0.0043%
Magnesium Oxide - 0.126%
Water - 1.11%

"There have been few publications documenting the usage of pumice as a SCM in concrete. Furthermore, there have been no publications prior to this research about the usage of pumice to specifically arrest ASR expansion."

—Uma Ramasamy

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PREVIOUS RESEARCH using pumice as a supplementary cementitious material (SCM) was found to exhibit good resistance to ASR expansion, sulfate attack, and chloride intrusion—and to be uniquely more effective than other durability test responses. Further experimental investigation of pumice as a SCM was conducted in this study to understand the potential ASR resistance for different reactive aggregates.

It was essential to investigate why this particular pumice (from the Hess Pumice deposit) was effective in mitigating ASR expansion, and especially effective compared to other durability mechanisms.

The four factors which influence ASR in a concrete structure are alkali content, moisture, siliceous aggregate, and free calcium hydroxide (CH). If the system is starved from any of these influencing factors, it is possible to mitigate ASR. Previous research by others has confirmed that the alkali-silica-gel formation occurs only in the presence of calcium hydroxide.

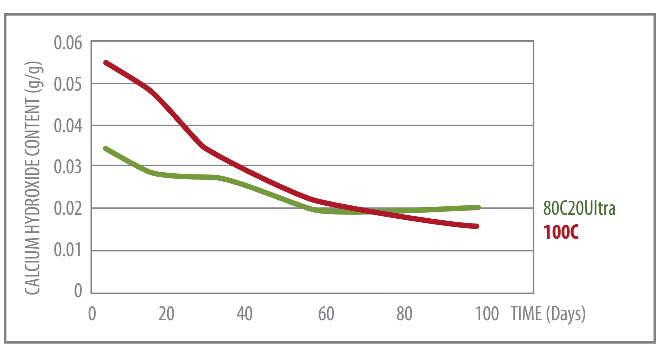
This research quantified the amount of CH and determined its importance in ASR expansion, especially in an aggressive environment (1 N NaOH solution and 80 °C).

CALCIUM HYDROXIDE CONTENT OF ASR SPECIMENS

Calcium hydroxide (CH) content of mortar specimens in an aggressive ASR environment (80 °C and 1 N NaOH) across time from **XRD analysis**. The CH content decreased across time in 100C by participating in ASR and 85C15U by participating in pozzolanic reaction and ASR. The reduction rate of CH content was higher at initial age because of higher availability of CH in the mixture, while at later ages, the ASR expansion rate was reduced due to lower CH production rate from the remaining hydration reaction.

SPECIMEN AGE	100%CEMENT		85%C15%ULTRA	
DAYS	QUARTZ%	$Ca(OH)_2$	QUARTZ%	$Ca(OH)_2$
7	75.8	24.2	88.5	11.5
14	83.1	16.9	87.6	12.4
28	87.4	12.6	89.1	10.9
56	92.4	7.6	91.2	8.8
93	96.8	3.2	92.9	7.1

Average CH content determined from **TGA analysis** of mortar specimens in an alkali-silica reaction (ASR) environment (80°C and 1 N NaOH) across time. The 15% cement replaced specimens (85C15U) showed less CH content compared to 100C (100% cement) at initial age. The CH content decreased across time in 100C by participating in ASR and 85C15U by participating in pozzolanic reaction and ASR.



Stomping ASR by Reducing Calcium Hydroxide

As substantial ASR mitigation was witnessed when pumice was utilized as a SCM, the scope of this research was to quantify the amount of CH in mix designs containing pumice as a pozzolan, as well as determine the CH content in relation to the amount of expansion. Thermo-gravimetric analysis (TGA) and X-ray diffraction (XRD) were used to quantify the relative amount of CH across time. CH content decreased across time for both the 100% cement and pumice blended cement specimens in the ASR environment—consumed by the alkali-silica reaction (100% cement) and the pozzolanic reaction (pumice-blended cement), respectively. The samples with pumice replacement of cement had lower CH content compared to those with 0% pumice as confirmed quantitatively by TGA and indicated by XRD.

These analyses demonstrate how the amount of pumice replacement of cement correlates to the rate of CH reduction and a subsequent reduction in ASR expansion.

Mitigating ASR Using Pumice-Blended Cement

Alkali-silica reaction (ASR) has been recognized as a potential distress in concrete structures since the late 1930s.

ASR is a chemical reaction in concrete or mortar caused by the presence of certain reactive siliceous minerals in aggregate, hydroxyl ions, and alkalis in hydraulic cement. This reaction leads to an "alkali-silica gel" formation which has the tendency to imbibe water and swell. Under significant moisture conditions, swelling builds up pressure and the expansion causes cracking.

Pozzolans are siliceous and aluminous materials that react with soluble calcium oxides from hydrated cement to form calcium silicate hydrate (C-S-H) amorphous gel structures, as well as other stable silica aluminate compounds. A supplementary cementitious material (SCM) is implemented to replace a portion of Portland cement with a finely ground pozzolan or other hydraulic reacting material to potentially reduce demand and cost associated with Portland cement, while also maintaining or improving the long-term strength, workability, or durability properties. Some naturally occurring and artificially produced materials can demonstrate this pozzolanic reaction and, thus, can be used as a supplementary cementitious material (SCM).

Pozzolans should be either economically viable or provide superior performance enhancements. Currently, the industry utilizes many of the byproducts or waste-based pozzolans due to cost-saving, but with diminishing supply of such materials.

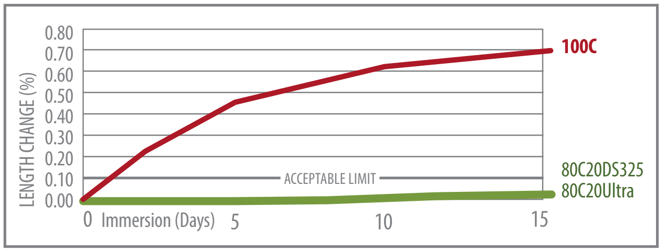
Pumice is a naturally-occurring pozzolan formed from volcanic activity. Pumice has been verified to be pozzolanic and, thus, potentially complementary in its reactions in Portland cement concrete.

Among all the pumice-contributed durability benefits (detailed hereafter), the reduction in ASR expansion was considered significant, especially due to the presence of high amounts of silica and alkalis in the pumice. The scope of this research was to

MITIGATING ALKALI SILICA REACTION

Mortar Mix designs tested according to a modified ASTM C1567 procedure using Type 1 cement and **25% replacement** of fine **Moderately Reactive aggregate** with **ground cullet Glass**. The percent length change for "acceptable expansion" is less than 0.10% at 14 days in an accelerated ASR environment.

MIXTURE MR+G	ASR % LENGTH CHANGE	RATING
100C 25%Glass	0.699	Deleterious Expansion
80C20DS325 25%Glass	0.029	Acceptable Expansion
80C20Ultra 25%Glass	0.017	Acceptable Expansion

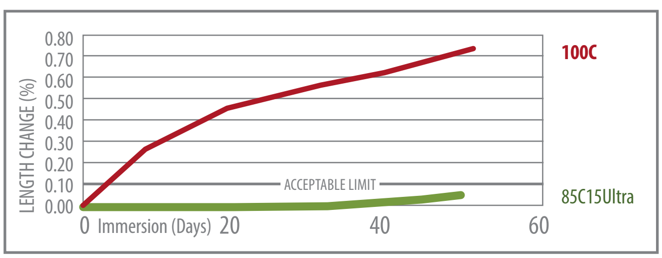


Mortar Mix designs tested according to a modified ASTM C1567 procedure using Type 1 cement and **Highly Reactive aggregate** in an accelerated ASR environment (80° C and 1 N NaOH solution) over 16 days.

MIXTURE HR	ASR % LENGTH CHANGE	RATING
100C	1.041	Deleterious Expansion
80C10Ultra*	0.247	Deleterious Expansion
80C15Ultra*	0.089	Acceptable Expansion

*When it was determined that Ultrafine pumice provided best performance at least replacement percentage, all subsequent tests were run using only Ultrafine pumice.

Concrete Mix designs tested according to a modified ASTM C1293 procedure using Type 1 cement and **Highly Reactive** coarse and fine **aggregate** in an accelerated ASR environment (80° C and 1 N NaOH solution) over 50 days.



check effectiveness of pumice as an SCM in reducing ASR expansion for other various reactive aggregates and to determine an optimal level of replacement of Portland cement in mortar and concrete.

Overall, pumice samples, regardless of the amount of pumice or aggregate type, showed reduced expansion in the accelerated ASR environment compared to 100% cement mixture samples. At 20% pumice replacement of cement, influence of the pumice particle size was negligible and all grades of pumice were equally effective at resisting ASR.

Using more pumice than is required to produce acceptable expansion does not further increase ASR resistance—ideally, the percentage of cement replacement can be chosen based on the reactivity of aggregate.

Other Durability Enhancements

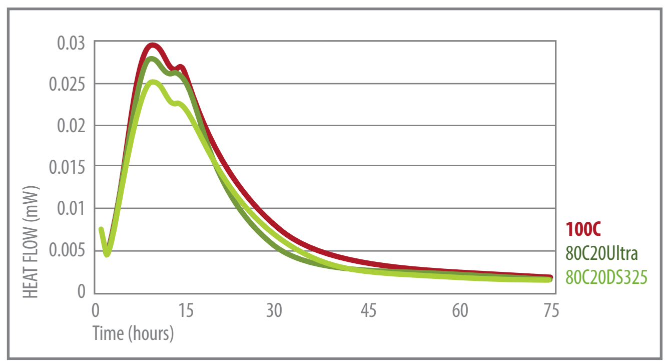
In this research, pumice has been identified as one of the natural pozzolans that can be extensively used as cementitious material to improve overall concrete durability. Concrete containing finely-ground pumice was shown to have improved characteristics in terms of strength, hydration, and durability characteristics such as sulfate resistance and alkali-silica reaction resistance. In addition to improved performance properties, using pumice in concrete can lead to environmental benefits from the reduced demand of cement, and thus, a potential lower carbon footprint.

Hydration Kinetics

Cementitious materials generate heat through exothermic hydration reaction. The exothermic heat produced from mixtures containing pumice was reduced compared to mixtures with 100% cement, which makes it advantageous in mass concrete placements.

HYDRATION KINETICS: PUMICE BLENDED CEMENTS

The kinetics of pozzolanic and cementitious reactions measured with an isothermal heat conduction calorimeter. 100% cement mixture produces more heat as compared to the mixtures containing pumice. As the pozzolanic content increases, the main peak of heat flow decreases.



Strength Development

The compressive strength of concrete is one of the primary considerations in concrete mixture design.

The mixtures containing pumice had lower compressive strengths than the control mixture; however, all mixtures exceeded 28-day 4000 psi (280 kg/cm2) design strength. The minimum strength achieved by all mixture combinations at age 7 days was greater than 3300 psi (230 kg/cm2) and at age 28 days was greater than 4800 psi (340 kg/cm2).

Concrete with slightly slower strength gain qualities is less likely to be subject to early age cracking and has long term strength capability.

By taking into account the expected variation in the strength curve, it can be concluded that the addition of up to 20% pumice does not significantly change the measured strength of the concrete. Comparable strength can be obtained between control and pumice replacement mixture.

COMPRESSIVE STRENGTH (4X8 CYLINDERS)

Following ASTM C39, compressive strength of 4"x8" cylinders were tested. Mixtures containing pumice reached the compressive strength later than control mixture. However, the minimum strength at age 7 days is greater than 4000 psi and at age 28 days is greater than 4800 psi. Mixtures containing Ultrafine pumice reached higher early strength. .

MIXTURE	STRENGTH: 7 DAYS (PSI)	28 DAYS (PSI)
100C	5636	7400
80C20DS325*	3343	4860
80C20Ultra	4648	7083

*ASR Miti•Gator™

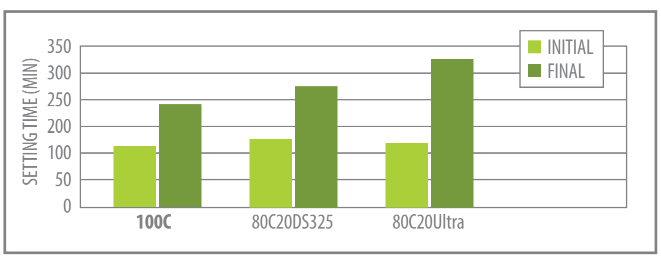
Setting Time and Water Demand

There is an increase in initial and final setting time for the mixtures containing pumice compared to 100% cement (ASTM Type II/V) when tested at a constant flow without admixtures. The increases are well within the limits of ASTM C5957 specification for blended hydraulic cement, which is likely attributed to the increased water demand. Water demand was more for mixtures containing pumice compared to 100% cement. The increase in water demand can be addressed by addition of common water-reducing admixtures.

EFFECT OF PUMICE: SETTING TIME; WATER DEMAND

Setting times were determined by a Vicat Needle test method according to ASTM C19112. Penetration resistance indicates the setting characteristic of cement mixture paste.

MIXTURE	SETTING TIME (min)		WATER USED g (lb)	% INCREASE in WATER
	INITIAL	FINAL		
100C	117	242	173 (0.381)	
80C20DS325	148	271	195 (0.430)	12.7
80C20Ultra	129	323	199 (0.439)	15

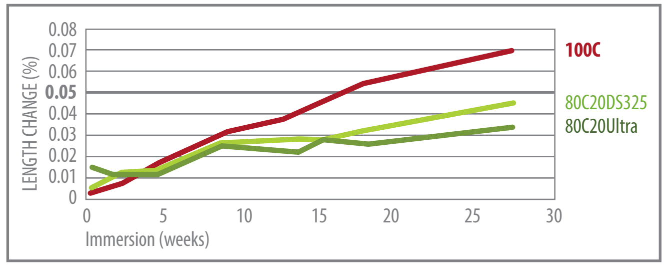


Sulfate Mitigation

Following the procedures of ASTM C101215, five mortar mixture designs were tested for sulfate resistance. The cementitious combinations were the same as used in the compressive strength testing. The specimens were tested through 6 months and the percentage length change of mortar specimens for different mixtures is shown (above right). Test values below 0.05% at 6 months indicate high sulfate resistance and test values below 0.10% at 6 months indicate moderate sulfate resistance. All the pumice-blended mixtures are within the limit of 0.05%, hence qualified to be HS (High Sulfate resistance).

SULFATE MITIGATION

Per ASTM C1012, mortar mixture designs were tested for sulfate resistance through 6 months. Mixtures containing pumice are classified as HS (High Sulfate resistance) as the length change is less than 0.05% after 6 months.



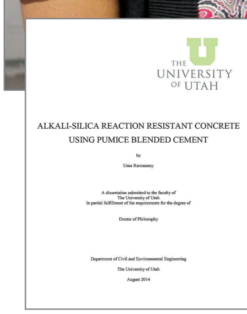
Conclusion

Pumice was shown to be a market- ready SCM for durable and strong concrete.

The results from this research indicate Calcium Hydroxide (CH) content plays a significant role in ASR expansion and pumice helps reduce the CH content in a mixture at an elevated temperature. Hence, if concrete can be designed or altered in a way that has the ability to reduce CH content in the hardened mixture, the structure made with this concrete will have a long-lasting durable service life.

When pumice is used as a supplementary cementitious material, it is possible to produce an enhanced concrete with improved durability properties and the environmental benefits of reduced cement demand. ■

Measuring expansion rates in concrete test samples



THE UNIVERSITY OF UTAH

ALKALI-SILICA REACTION RESISTANT CONCRETE USING PUMICE BLENDED CEMENT

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