Key Excerpts *from a Commissioned* Research and Development *Report on a Unique* Ultrafine Cementitious *Developed by* Grout

Sandia National Laboratories for the U.S. Department of Energy, the optimization and physical parameter determinations for this unique, ultrafine, pozzolan-charged cementitous grout was done by Atomic Energy Canada's Whiteshell Laboratories.

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The US Grout Story

The U.S. Department of Energy had a problem. Under the New Mexican desert, 2,154 feet down, located in a salt bed approximately 2,000 feet thick, the DOE had carved out a multi-chambered repository designed as a final resting place for transuranic waste generated by the nation's nuclear energy activities—the Waste Isolation Pilot Plant (WIPP).

The weight of the overlying rock subjected the underground storage chamber openings to closure force. This force, equal in all directions, is roughly one pound per square inch per foot of depth. Stress redistribution around the openings resulted in the microfracturing of the salt, extending into the enclosing salt as much as a meter and a half. This microfractured rock salt, called the "Disturbed Rock Zone," would allow brine and radionuclides to bypass any seal placed in the tunnels.

An ultrafine cementitious grout was required to effectively seal these extremely small fractures (often as small as 6 microns). Why cementitious? A cement-based grout was needed "because of the long half-lives of many of the radionuclides of concern, the seal material [grout] must perform acceptably for thousands of years."† As for the need for ultrafine: to enter such tiny fractures, the grout particles had to be even smaller than the fracture width.

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† quoted from page 78 of AECL's Whiteshell Laboratories resesarch findings

Commercially available microfine grouts were analyzed by Sandia National Laboratories (the scientific advisor for the Waste Isolation Pilot Plant) and found to be unsuitable. Sandia then proceeded to develop a new grout which, after extensive laboratory development and testing, was successfully applied underground at the WIPP repository. The permeability of the DRZ was lowered as much as 1,000 times, and the grout was been approved for use at the WIPP.

The keys to the successful development of the needed grout were these:

• technology to effectively process the grout particles to a consistent ultrafine size,

• achieving critical rheology characteristics in the grout paste by adding pumice to the mix design,

• amplifying the life-span and inherent performance benefits of cementitious grouts with the pozzolanic reaction ignited by the pumice—engineered benefits that include improved resistance to chemical attack as the result of decreasing alkalinity and controlling the amount of readily soluble residual lime (Ca(OH)2), improved resistance to thermal cracking (because of lower heat of hydration), and enhancement of strength and decreased permeability because of pore refinement.

Sandia National Laboratories obtained two patents on this grout and transferred the process, under license, to US Grout, LLC, to make the novel ultrafine pozzolanic grout available worldwide.

From that breakthrough beginning, US Grout has formulated additional ultrafine and microfine cementitious grouts to meet a variety of grouting needs—from flexible "squeeze" cements to rehab oil and gas wells to a customizable VX type for use in permeating a variety of soil types. ■

The following excerpts are from the Atomic Energy of Canada Limited Whiteshell Laboratories "Final Report on the Optimization and Determination of the Physical Parameters of Ultrafine Cementitious Grouts for the Sandia National Laboratories."

" The major objective of the laboratory tests undertaken...and discussed in this report was to optimize the quantities (weight percentage) of grout components: cement, pumice, superplasticizer and W/CM ratio to produce an ultrafine grout paste with two hours injectability subsequent to mixing...the selection criteria also included good rheological properties (i.e., stable unset grout paste, low viscosity), low hydraulic conductivity and good mechanical properties.

Tests were also carried out to determine the particle size distribution, viscosity, setting time and bleed properties of the optimized ultrafine cement-based grout pastes manufactured from a dry pulverized grout mix with very fine particle size distribution (90% sub 6µm)." *—from page 79, Atomic Energy of Canada Limited (AECL) Whiteshell Laboratories Report*

RHEOLOGY

" Cement grouts are injected into the rock as a freshly mixed fluid, after which they harden into a rock-like mass. The rheological properties [fluidity] of the freshly mixed grout control the workability of the grout, determine the depth to which the grout will penetrate and seal the rock, the final hardened condition of the grout and, to some extent, the longevity of the materials." *—page 7*

" Early stage rheological properties are an important aspect of formulation because the final properties of a grout can be influenced if the grout workability is inconsistent with its emplacement method. Excessive bleeding and segregation may result, altering the chemistry, integrity and long term stability of the grout. Factors influencing rheology include the initial W/CM ratios and composition and particle size distribution of the cementitious materials. Superplasticizer is also added to the mix to increase the desired flow and to set retardation properties." *—page 23*

" The results show that the main factor affecting the rheological behavior of the mixtures, the fluidity of the paste, was water content. However, as noted above, significant increase in water content can produce grout pastes that may bleed and segregate, and hardened grout paste with high porosity, high permeability and low compressive strength." *—page 23*

PUMICE POZZOLAN

" Previous work indicated that, in most explored cases, increasing the amount of pozzolanic material in the mixes improved the pulverization and rheological characteristics of the cement pastes. The observed effect was attributed to the decrease in the amount of cement and therefore to the decrease in the extent and rate of hydration reactions."
—pages 9-10

" Pumice was used as the pozzolanic material. A series of engineering benefits is derived from the use of pozzolanic materials, including improved resistance to chemical attack, as the result of decreasing alkalinity, and controlling the amount of readily soluble residual lime ($Ca(OH)_2$), improved resistance to thermal cracking (because of lower heat of hydration) and enhancement of strength and decreased permeability because of pore refinement." *—page 12*

" The reaction of pozzolan with the lime already existing in cement or liberated during the hydration process modifies some properties of the cement and the resulting grout. Such an effect depends on the amount of pozzolan added as well as on the properties of the cement and the 'activity' of the pozzolan added." *—page 26*

" The results indicated that, in most cases, increasing the amount of pumice in the mixes improved the rheological characteristics of the grout pastes.... According to the results, up to 40 wt% of pumice (pozzolan) could be added to obtain an acceptable 28-day compressive strength. The compressive strength ranged between 32 MPa and 51.3 MPa. The addition of finer pumice to the mixes generally increased the 28-day strength." *—page 26*

" The pumice material used in this study was provided by Hess Pumice Products, Malad, Idaho." *—page 12*

" The lowering of the W/CM ratio also increases strength. However, at any given W/CM ratio, pumice addition increases strength. The contribution of the pumice to the strength of grout is not linear. The increase in pumice content does not necessarily lead to proportional effect on the grout strength."
—page 33

" In general, pozzolanic materials increase the strength of the cement materials at both early and late ages. At an early age, the gain is strength is attributed to an acceleration of the cement hydration, but at later ages, the gain in strength is mostly the result of the pozzolanic reaction." *—page 33*

LONGEVITY

" The main purpose of cement-based grout materials is to seal fractures in rock for perhaps tens of thousands of years." *—page 21*

" …it is known that the use of high water content in cement-based materials will tend to minimize density and increase porosity of the hardened materials. Both factors not only govern the permeability and diffusion, but also the mechanical properties and the durability of cement-based grouts. Permeability and diffusion of ionic species in cementitious grouts are important keys in the long-term performance of grouts." *—page 10*

EFFECTIVENESS

"Practical demonstration of the suitability of this grout to seal an anhydrite layer had been carried out by Sandia National Labratories at the WIPP Repository. Using conventional grouting practice, the transmissivity of the rock mass was successfully reduced. The grout met all of its performance criteria during the tests. Microscopic examination of grouted rock samples revealed that the grout conformed totally to the irregular fracture morphology in the [rock] and that the grout penetrated fissures in the [rock] with apertures smaller than 8 µm. The cement paste was stable, and did not separate into liquid and solid phases, and maintained good workability for more than 3 hours after mixing. The grout remained largely homogeneous during and after the injection into the rock." *—pages 10-11*

"Microscopic examination of specimens sliced from sand columns grouted with [test specimen] grout mixes after curing for 28 days confirmed the ability of the selected grouts to penetrate openings between sand grains with a wide range of apertures.... Difficulties were encountered during the measurements of the very fine openings between the sand grains. In most cases it was difficult to distinguish the boundaries between the grout and sand grains. Microscopic examination of grouted specimens revealed that the sand grains were totally incorporated in the grout mass. The examination also showed that the grout totally conformed to the irregularities of the sand grains. No dislocation of sand grains during cutting of the specimens was observed, suggesting that a good bond was established between grout and sand grains. *[For example, Figure 13 on page 53 is captioned thusly]:* Typical Microstructure of Grouted Sand in Column #4 (Sand Grains 0.212/0.106 mm) after Injection with [test specimen] Grout. Grout penetrated gaps with apertures between 8µm and 80 µm." *—page 46 and Figure 13 on page 53*

"The results from pore structure characterization using Mercury Intrusion Porosimetry (MIP) indicate differences in the total pore volume and pore sized distribution. [The permeability of grout is associated with the microstructure.] The increase in the pumice content as well as the use of materials with a very fine particle size distribution resulted in the development of microstructure with a lower, less connected pore volume. The results from the pore structure characterization indicate changes occurred in the structure of the grout containing pumice during the permeability test [showing] a decrease in the total volume and shift of pore radii toward smaller values. The effects are considered to be mostly caused by the continued hydration reaction as well as the continuation of the pozzolanic reactions and, therefore, progressing densification of the microstructure on the grout when in contact with water. The absence of pores with diameters larger than 1 µm may explain the low hydraulic conductivity of [the test] mixtures." *—page 65; 70*

"The hydraulic conductivity of grout is a factor which is dependent on porosity and is frequently used as a measure of performance. The lower the conductivity, the better the sealing performance of the grout. Water permeability measurements indicated the superior performance of the newly developed ultrafine high-performance grouts. In all cases, the hydraulic conductivity was low and decreased with permeating time. Continued reduction of permeability with time is, however, typical of the grout mixes containing pozzolans." *—page 80*

"The properties of a material are recognized to originate from its internal microstructure, and these properties can be modified by making suitable changes in the structure of the material. The low hydraulic conductivity (<10-14 m/s) and good mechanical strength of the developed grouts can be related to the grout's dense microstructure and lack of pores with diameters larger than 0.1 µm." *—page 77*