A NEW LOOK TO AN OLD POZZOLAN:
CLINOPTILOLITE – A PROMISING POZZOLAN IN CONCRETE

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ABSTRACT

Clinoptilolite $[(Na_4K_4)(Al_8Si_{40}O_{96}).24H_2O]$, the most common natural zeolite occurring as widespread tuffaceous lacustrine sedimentary deposits in the Western United States was used as a pozzolan at 0 to 40 percent by mass of portland cement replacements in concrete mixtures to investigate the effects of zeolite on fresh and hardened concrete properties, and durability.

Fresh concrete properties, e.g., temperature, air content, yield, unit weight were apparently unaffected by zeolite incorporation. A reduction in bleeding, and an accelerated initial setting at 10 to 30 percent cement replacement levels was noticed by zeolite. The main effect, however, was in noticeable reduction in workability, especially at greater than 10 percent level, which required addition of mid-range and high-range water reducing admixtures in the mixture.

Compared to the control mixtures, zeolite-blended concrete mixtures showed an improvement in compressive strength at 10 percent cement replacement level at 56 days, whereas 20 to 30 percent replacements caused a modest reduction in strength at the same age by approximately 10 percent. Pozzolanic effects of strength improvement are more pronounced at late ages (i.e., beyond 28 days) than at early age. Effects of pozzolanic reactions of clinoptilolite, however, are far more significant in improving concrete durability than compressive strength.

The most significant effects are in reduction in chloride permeability, a significant reduction in expansion due to alkali-aggregate reaction, and an improved resistance to acid and sulfate attacks, all of which are related to the overall densification of the microstructure, alkali-binding capacity of zeolite-blended cement pastes, and pozzolanic consumption of calcium hydroxide component of portland cement hydration in the paste. Drying shrinkage of zeolite-blended concrete mixtures having 10 to 20 percent zeolites are identical, and slightly higher than that of the control mixture. The benefits in durability far outweigh the slow rate of strength development at early age, or a modest strength reduction at 20 to 30 percent levels. The concrete industry should take advantage of this abundant "gold mine" in the Western United States as a promising pozzolan, especially when its importance in concrete durability is undeniable.

NATURAL ZEOLITES – A BRIEF REVIEW

Zeolites (from Greek words ζειυ λιθοσ or 'zein' and 'lithos' meaning "boiling stones") are crystalline, hydrated aluminosilicate minerals of alkali and alkaline earth metal cations, having an open, three-dimensional framework structure (tectosilicate) consisting of: (a) repeated fundamental building units of silicon-oxygen and aluminum-oxygen tetrahedras forming single 4/6-ring, double 4/6-ring, or larger symmetrical polyhedral SiO_4-AlO_4 framework, (b) charge-balancing, exchangeable mono and divalent alkaline and alkaline earth metal cations (Na^+, Ca^{2+}, K^+, Mg^{2+}, Sr^+, Ba^{2+}) present in the interconnected void spaces or spacious channels ("cages") in the framework and in intraframe cavities, and (c) highly variable amounts of water molecules in the cavities that are weakly bonded to anionic framework atoms [1].

Zeolites constitute one of the largest groups of minerals known with more than 50 distinct natural species recognized and more than 100 species having no natural counterparts have been synthesized in the laboratory [1, 2, 3]. Natural zeolites occur in a variety of geologic settings and ages such as deposits formed in [3]: (a) hydrologically closed systems of volcanic materials in saline/alkaline lakes, (b) open systems of fresh water lakes and groundwater; (c) low grade burial metamorphic formations; (d) hydrothermal or hot water activities; (e) deep marine volcanoclastic sediments; and (f) weathered soil from volcanic materials.

Despite their well-known, ubiquitous occurrences as well-formed crystals in vugs, cavities, veins, and crevasses of basic volcanic rocks (basalts and other trap rock formations) and related late-stage hydrothermal environments (the *amygdaloidal zeolites*), and the knowledge of existence of natural zeolites for more than 200 years, it is indeed the discovery of widespread occurrences of zeolites in the late 1950s as major constituents of numerous volcanic tuffs in the ancient saline, alkaline lake deposits (sedimentary and volcanoclastic formations of Tertiary age) of the western United States and in thick marine tuffs of Italy and Japan (the *sedimentary zeolites*), which boost their geological, commercial, agricultural, and industrial importance [2]. More than 1000 occurrences of zeolites have been reported from volcanogenic (tuffaceous) sedimentary rocks of more than 40 countries and zeolites are regarded as among the most common authigenic silicates in sedimentary rocks of diverse age, lithology, and depositional environment [3, 4]. The high purities, fine particle size, flat-laying nature, and large-scale occurrences of authigenic zeolite deposits in lacustrine and marine tuffaceous sediments have attracted considerable commercial importance. Unlike formation of large, beautiful zeolite crystals as cavity-fillings in basalts by hydrothermal alterations, sedimentary zeolites are formed by diagenetic alterations of silicic volcanic tuffs and volcanic glasses with the water trapped during sedimentation in saline/alkaline lakes, and marine environments. Besides lacustrine and marine sedimentary and volcanoclastic environments, large occurrences of microcrystalline zeolites have been reported in hydrothermally altered volcanic tuffs, glasses, and trasses (e.g., in Greece) and in low-grade metamorphic rocks. Contrary to the well-formed large amygdaloidal zeolites, in all other occurrences of commercial importance zeolite grains are usually too fine (micron-sized) to be adequately detected with a petrographic microscope but can be positively identified by using scanning electron microscopy or especially x-ray diffraction. Nearly all the minable zeolite deposits in the world occur as fine-gained zeolitized ash fall tuffs interbedded with marine and lacustrine sediments, zeolitized vitroclastic tuffs in volcanic rocks, and zeolitized vitrophyres and vitroclastic tuffs as a result of hydrothermal alternation.

In the western United States, several hundred known occurrences of natural zeolites are found in sedimentary and volcanoclastic deposits of Tertiary age where resources of clinoptilolite, mordenite, and erionite are extensive, whereas chabazite and phillipsite are more limited [3]. Figure 1 shows locations of minable zeolite deposits in the United States [3]. Extensive deposits

of commercial importance have been discovered in the states of Alabama, Mississippi, Alaska, Arizona, California, Colorado, Idaho, Montana, Nevada, New Mexico, Oregon, South Dakota, Texas, Utah, and Wyoming. Eyde and Holmes [3] provided a detailed list of deposits in the United States. Worldwide, natural zeolites have been commercially produced in 37 countries (with China, Cuba, Japan, Hungary, USA, and Bulgaria being the major producers and smaller tonnages from Australia, Germany, New Zealand, Italy, and South Africa); and located in another 28 countries.

Natural zeolites are used as [1, 3]: (a) excellent ion exchangers in pollution-control processes such as radioactive waste disposal, sewage and agricultural-effluent treatment, water purification, agricultural wastewater treatment, stack-gas cleanup, oil-spill clean up, in the separation of oxygen and nitrogen from air; (b) energy-conservation applications such as coal gasification, natural-gas purification, dehydrated zeolites as desiccants for removal of water from gaseous hydrocarbons and petroleum, solar energy use and heat exchange, petroleum production, as reforming petroleum catalysts; (c) in agricultural applications such as fertilizer extenders and soil conditioners, pesticides, fungicides, herbicides, heavy metal traps, animal nutrition and dietary supplements, excrement treatment, aquacultural uses; (d) in mining and metallurgical applications such as exploration aids, as ion exchangers for concentration of heavy metals from wastewater effluents of mining and metallurgical operations; and (e) in miscellaneous other applications such as: filler in paper industry, odor control, dimension stone in buildings, pozzolans and lightweight aggregates (in calcined and expanded forms) in construction industry, and as effective ion exchanger in some medical and personal care applications.

Of the 50+ known natural zeolite species, only six types, e.g., analcime, chabazite, clinoptilolite, erionite, mordenite, and phillipsite are common in many saline lake deposits, such as the ones widespread in the western United States. In 1933, two U.S. Geological Survey geologists, M. N. Bramlette and E. Posjnak reported several occurrences of clinoptilolite in vitric tuffs in various parts of the western United States. Probably the earliest record of zeolites in sedimentary rocks was published in 1876 by Lew, who described chabazite from a tuff bed in Arizona. Although sedimentary zeolites were identified in saline, alkaline-lake deposits in the western United States in the 1920s, it was not until the late 1950s that such occurrences were found to be commonplace in many tuffaceous lacustrine sediments of this and other countries.

NATURAL ZEOLITES AS POZZOLANS IN CONCRETE

The use of natural zeolites as pozzolanic materials in construction dates back 3000 years, to the Greek and Roman periods when zeolites occurred as altered volcanic ash, tuff, and trass were used with lime in mortars and concretes for construction. The Romans used Neapolitan Yellow Tuff near Pozzuoli, Italy in construction of aqueducts, public buildings, and highways. The lime-zeolite combination showed excellent cementitious property. Natural zeolite tuffs have been used for many years for cement pozzolans in Serbia, Germany, Italy, Bulgaria, China, and Russia [3, 4].

Despite their widespread applications in pollution-control, energy-conservation, agricultural, mining, and metallurgical applications during the last few decades, construction industry appears to be the largest natural zeolite end user. Out of the estimated total worldwide natural zeolite production of 3.6 Mtpy in 2004, construction industry appears to consume about 2.4 Mtpy, where the bulk of the production is in dimension stones used in building construction and lesser amounts in lightweight aggregate concrete and as pozzolans in concrete [4].

Approximately 50,000 tons/year of zeolitic tuff is being used for the production of portland-pozzolan cements in Germany. Italy consumes yearly about 3 million tons and China about 5 million tones of zeolitic tuffs as a component of blended portland cements.   The use of natural zeolite as a pozzolan in the US cement and concrete industry, though not recent, however, is still limited. As early as in 1912, the Monolith Portland Cement Company used zeolitic ash-flow tuffs near Tehachapi, California for use as a pozzolan at 25 percent portland cement replacement level to build the 400-km-long Los Angeles aqueduct.

Despite their inherent crystalline nature, the fine size and higher surface area of the natural sedimentary zeolites and their strong cation-exchange capacity make them a suitable pozzolan in cements; zeolites consume the calcium hydroxide component of portland cement hydration by the base exchange process and form cementitious products. Pozzolanic characteristics of many natural finely crystalline zeolites are easily comparable to or, in some instances, even better than their aluminosilicate "glassy" rivals such as fly ash, or ground granulated blast furnace slag.

CLINOPTILOLITE AS A POZZOLAN IN CONCRETE

The present study provides a comprehensive laboratory investigation of the effects of incorporation of clinoptilolite $[(Na_4K_4)(Al_8Si_{40}O_{96}).24H_2O]$, a common natural sedimentary zeolite in the western United States as a pozzolan at various levels of substitutions of portland cement (from 0 to 40 percent by mass of total cementitious materials) on the properties of fresh and hardened concrete and on concrete durability (e.g., alkali-aggregate reaction, drying shrinkage, chloride permeability, and resistance to acid and sulfate attacks).

Clinoptilolite used in this study came from a tuffaceous lacustrine deposit, Bear River Zeolite (BRZ), located 10 km from Preston, Idaho and owned by the Bear River Zeolite Company (Figure 1). A wholly owned subsidiary of U. S. Antimony Corporation, the company produces clinoptilolite from a green zeolitized tuff in the Eocene Salt Lake Formation that crops out over a large area in southeastern Idaho. The deposit occurs in very fine crystalline form and has been supplied for this study in its natural state after mining as "fugitive dust" from crushing with no calcining or other processing operations.

Table 1 provides specifications of Bear River Zeolite as published in their website (www.bearriverzeolite.com). Table 2 provides detailed chemical compositions and physical properties of clinoptilolite used in this study and a comparison of these properties with an ASTM C 618 Type N natural pozzolan. Figures 2 and 3 show the clinoptilolite deposits from BRZ, the zeolite mine, and the mining process. Based on chemical and physical testing, *clinoptilolite conforms to the chemical and physical requirements of ASTM C 618 for a Type N pozzolan.* The deposit contains 70.3 percent SiO_2, 12.5 percent Al_2O_3, 3.4 percent Fe_2O_3, 3.0 percent CaO, 5.5 percent K_2O, 3.6 percent Na_2O_{eq}, 4.6 percent loss on ignition, and 0.02 percent SO_3. Figure 4 shows optical and scanning electron micrographs of clinoptilolite powders with typical equant, lath, or blade shaped angular grains of clinoptilolite and energy-dispersive x-ray elemental analysis showing the characteristic composition of silica, alumina, sodium, potassium, iron, calcium, and oxygen. Figure 5 shows x-ray diffraction pattern of the sample confirming its clinoptilolite mineralogy. Figure 6 shows particle-size distribution of clinoptilolite (measured by using a Malvern Mastersizer LASER diffractor) having a mean particle size of 12.27μm. The mineral is pale green in color with a density at 20ºC of 2.19 g/cc; received as very fine powder with a Blaine fineness of 1107 m^2/kg (portland cements used in the study have Blaine Finenesses of 377 to 403 m^2/kg); the Mohs hardness is 4; and percent retained on 325 sieve is 26.94 percent. Clinoptilolite has a typical oxide formula of $(Na_2, K_2)O.Al_2O_3.10SiO_2.8H_2O$ and a typical unit cell contents of $Na_6[(AlO_2)_6(SiO_2)_{30}].24H_2O$ [Ca, K, Mg ions are also present; Na, K » Ca; Si/Al

ratio varies from 4.25 to 5.25]. It belongs to a monoclinic symmetry with a space group of I 2/m; unit cell constants are: a=7.41A, b=17.89A, c=15.85A, and β=91º21´. The term 'clinoptilolite' means 'oblique feather stone' in Greek, indicating its monoclinic symmetry. Although occurring in all common crystal habits of natural zeolites such as tabular, blade or lath-shaped, rod-shaped, acicular, fibrous, equant or blocky, clinoptilolite grains in this study are mostly angular, blade or lath-shaped in the secondary electron images, some of which are miniature versions of the megascopic forms of their monoclinic calcium cousin, heulandite [$Ca_4(Al_8Si_{28}O_{72}).24H_2O$] found in many basalt cavities.

MATERIALS AND MIXTURE PROPORTIONS

Crushed limestone coarse aggregate having a nominal maximum size of 12.5 mm (#67 limestone), natural siliceous-calcareous sand fine aggregate having a nominal maximum size of 9.4 mm., portland cement, and zeolite were used as the basic solid ingredients in all concrete mixtures. Aggregates, cement, and zeolite were in conformance to ASTM C 33, ASTM C 150 Type I, and ASTM C 618 Class N specifications, respectively. Six different non-air-entrained concrete mixtures were prepared incorporating 0, 10, 20, 30, and 40 percent zeolite by mass of total cementitious materials (portland cement plus zeolite), and three additional air-entrained mixtures were prepared by using 0, 10, and 30 percent zeolite replacements by mass of total cementitious materials. All mixtures were prepared by using a fixed total cementitious materials content of 356 kg/yd^3, a water-cementitious materials ratio (*w/cm*) of 0.38, similar aggregate-to-cementitious materials mass ratio of 5.1 - 5.5, mid-range water reducer (Polyheed 997) of 3.33 l/yd^3, and progressively increasing amounts of high-range water reducer (Rheobuild 1000) from 2 to 8 l/yd^3 for non-air-entrained mixtures having 0 to 40 percent zeolite replacements, and 1.32 to 6.85 l/yd^3 for air-entrained mixtures having 0 to 30 percent zeolite replacements. Incorporation of zeolite makes concrete sticky and unworkable due to a loss of mix water to zeolite (due to its very high surface area and open crystal structure), which required addition of high range water reducer to maintain the optimum slump at a given *w/cm*. Tap water was used in all mixtures. An air-entraining chemical (MB-VR) at dosages of 0.19 to 0.58 l/yd^3 was used in the air entraining mixtures. Table 3 provides the details of concrete materials and mixture proportions.

TESTING STRATEGY

The following ASTM and other standard methods were used in the investigation of the effects of zeolite incorporation on concrete properties and durability:

(a) Sampling and Concrete Mixture Proportions – Casting of 100 × 200 mm size concrete cylinders (ASTM C 192)
(b) Fresh Properties – Concrete Temperature (ASTM C 1064), Slump (ASTM C 143), Air Content (ASTM C 231), Unit Weight and Yield (ASTM C 138), Initial Time of Set (ASTM C 403), and Bleeding (ASTM C 232 Method A).
(c) Hardened Properties – Compressive Strength (ASTM C 39).
(d) Durability – Drying Shrinkage (ASTM C 311), Rapid Chloride Permeability (ASTM C 1202), Alkali-Silica Reactivity (ASTM C 311), and acid/sulfate resistance (ASTM C 1012).
(e) Length change measurements for drying shrinkage and ASR tests – ASTM C 157.
(f) Mechanical mixing of mortars for drying shrinkage, ASR, and sulfate/acid resistant tests – ASTM C 305.
(g) Microstructure – Microstructure of hardened zeolite paste, mortar, and concrete by Petrography (ASTM C 856) and Scanning Electron Microscopy (SEM); and degree of Pozzolanic Reaction by SEM, DSC, TGA, and XRD.

For each mixture: (a) six 100 × 200 mm size cylinders were prepared for compressive strength testing at 3, 7, 28, and 56 days (two cylinders for 28 and 56 day tests); (b) one additional 100 × 200 mm cylinder was prepared for 91-day compressive strength for each of the three air entrained mixtures; (c) four additional cylinders from each mixture were prepared for rapid chloride permeability, petrography, and scanning electron microscopy. All cylinders were cured in lime-saturated water until the time of testing.

For chloride permeability, multiple 50-mm thick cylindrical sections were saw-cut from the middle of the cylinders. The end saw-cut surfaces were lapped to smooth surface, cleaned, and then tested by following the procedures of ASTM C 1202.

For drying shrinkage tests according to ASTM C 311, three 25 × 25 × 285-mm long mortar bars were prepared from each mortar mixture. Four different mixtures were prepared by mixing portland cement, zeolite (at 0, 10, 20, and 30 percent by mass of total cementitious materials), sand, water, (w/cm = 0.47), and Rheobuild high-range water reducer. A total of twelve bars (three bars per mixture for a total of four mixtures) were cured in lime-saturated water for 7 days and thereafter air-cured until the length change measurements at 7, 14, 44, and 66 days by following the procedures described in ASTM C 157 and C 311. Table 5 provides the details of materials and mixture proportions used in drying shrinkage test.

For the alkali-silica aggregate reaction test according to ASTM C 311, a low alkali-portland cement was used with borosilicate glass and water plus high-range water reducer (w/cm = 0.48) for a control mixture; and a high-alkali portland cement with borosilicate glass plus zeolite plus water plus high-range water reducer were used (w/cm = 0.48) for two zeolite mixtures with 10 and 30 percent zeolite by mass of total cementitious materials. Three mortar bars were prepared for each of the three mixtures, cured, and kept above water in a sealed container until the length change measurements at 1, 14, 40, and 92 days by following the procedures described in ASTM C 157 and C 311. Table 6 provides the details of materials and mixture proportions.

The acid and sulfate resistance of clinoptilolite are being tested according to ASTM C 1012 by preparing several 25 × 25 × 285-mm mortar bars (3 bars per sample) having portland cement, siliceous sand, and clinoptilolite at 0, 10, and 30 percent levels of the total mass of cementitious materials, total water-cementitious materials ratio of 0.48 by mass, total cementitious materials to sand ratio of 1 : $2^3/4$ by mass. The samples are mixed, prepared, and tested by following the procedures of C 305, C 490, and C 1012. The samples were kept in molds for 24 hours, followed by saturated lime water at 23 ± 2°C for 48 hours, initial length measurements were taken after curing in lime water, and then in sulfate and acidic solutions (presently exposed to 1 percent HCl and 50 g/L Na_2SO_4 solutions). The conditions of the bars were visually examined and length change measurements were taken at regular intervals of 1 week.

For pozzolanic reaction tests, four neat pastes were prepared by thorough hand-mixing of 100 grams of portland cement and 0, 10, 20, and 30 percent zeolite addition by mass and water at total water-cementitious materials ratios of 0.47. After 24 hour curing in 50-mm size plastic molds, the hardened pastes were de-molded and cured in a lime-saturated water for 91 days. After curing the pastes were pulverized to fine powder and analyzed for calcium hydroxide contents in the pastes by thermal analysis (TGA and DSC) and x-ray diffraction (XRD). Table 7 provides the results of calcium hydroxide contents from TGA, DSC, and XRD in hardened pastes.

For microstructural investigation of the nature of pozzolanic reaction of zeolite, two additional neat pastes were prepared by hand mixing zeolite and water at a water-to-zeolite mass ratio of

0.75 in one paste and zeolite, hydrated lime, and water at water-to-solid (zeolite plus lime) mass ratio of 0.75 in the second paste. In both pastes, four drops of concentrated Rheobuild 1000 were added during mixing to plastisize the paste for thorough mixing. The pastes were cured in sealed plastic containers. The purpose of this test is to determine the nature of the pozzolanic reaction products in the zeolite-lime paste and the change in the composition of clinoptilolite by pozzolanic reactions.

INSTRUMENTATION

A digital length comparator was used for length change measurements of mortar bars in the drying shrinkage and alkali-silica reaction tests. A Nikon Labophot 2 POL and an Olympus BX petrographic microscope both equipped with transmitted/reflected/fluorescent-light capabilities were used for optical microscopical examinations of zeolite powder, paste, and concrete. A Camscan Series II SEM equipped with SE-BSE-EDS detectors, 4Pi image acquisition and analytical hardware and software, and a 20kv acceleration voltage were used for scanning electron microscopy and elemental analysis of zeolite power, paste, mortar, and concrete. A Siemens D 5000 x-ray diffractometer (having θ-2θ geometry) was used for XRD analyses of zeolite powder and pastes; by using a copper Kα radiation having (at 40KV and 20mA); the samples were scanned between 4 and 64 degrees two-theta at a scan rate of two degrees per minute.   Chemical analysis of zeolite powder was done by atomic absorption and x-ray fluorescence methods.   Mettler Toledo TGA-DSC instruments were used for thermal analysis of zeolite pastes, where the 60 milligrams of pulverized hardened pastes were heated at 30 to 600ºC for DSC and 30 to 1000ºC for TGA at a heating rate of 10ºC/min, in a nitrogen atmosphere, at a flow rate of 75 microliters per minute. Chloride permeability of sectioned hardened concrete cylinders were measured by using "Proove it", manufactured by Germann Instruments (sample diameters were 102 mm, voltage used was 60, and testing time was 6 hours). Particle-size distribution of zeolite was measured by using a Malvern Mastersizer LASER diffractor.

FRESH CONCRETE PROPERTIES

Table 3 provides properties of fresh concrete mixtures with and without zeolite-blended portland cements. Incorporation of zeolite in concrete does not show any noticeable effect on concrete temperature, even at the highest level (40 percent) of cement substitution.   The concrete temperatures of the control and zeolite-containing mixtures are all around 20°C.

Air contents, yield, and unit weights of concrete mixtures are also unaffected by zeolite incorporation. In air-entrained mixtures, zeolite incorporation and additions of mid and high-range water reducers do not affect the plastic air contents.

The significant effect of zeolite, however, is found in clear reduction in workability, which required addition of a mid-range water reducer and progressively increasing amounts of high-range water reducer, as mentioned before, with increasing amount of zeolite in the mixture. By appropriate dosages of the high-range water reducer, slump of all mixtures were kept within 88 to 100 mm.

The initial setting time shows a reduction in non-air-entrained mixtures from 0 up to 30 percent zeolite replacement, after which at 40 percent level the settling time shows a significant increase from that in the control mixture (see Table 3). For air-entrained mixtures, the initial setting time shows a reduction from 10 to 30 percent zeolite replacement levels. Similar accelerated setting is reported for chabazite [$(Na_2, Ca)_6(Al_{12}Si_{24}O_{72}).40H_2O$] incorporation in pure C_3S early-age hydration studies, due to accelerated hydration of C_3S by chabazite; another species, mordenite,

however is reported to retard C_3S hydration; and both species are reported to retard pure C_3A hydration. Due to the strong ion exchange capacity of zeolites, alkali-calcium exchange reactions between clinoptilolite and pore solution in concrete are judged to have an influence on the rate of hydration of calcium silicates and aluminates.

Compared to the control mixture, all non-air-entrained as well as air-entrained mixtures with zeolite showed negligible bleeding.

HARDENED CONCRETE PROPERTIES

Compressive Strength – Table 4 and Figure 7 provide results of compressive strength tests and rate of strength development in different concrete mixtures. For both air-entrained and non-air-entrained mixtures, zeolite incorporation at 10 percent level showed 3 and 7-day compressive strengths comparable to (or slightly less than that of) the control mixtures but higher-than-control strength at 28 and 56 days. Therefore, at 10 percent cement replacement level zeolite incorporation showed a clear strength benefit compared to the control mixture. Compressive strengths at 28 days are as high as 66 MPa and 63.8 MPa for the non-air-entrained and air-entrained mixtures, respectively (all at total *w/cm* of ~ 0.40).

At higher levels of zeolite incorporations (e.g., from 20 to 40 percent), however, compressive strengths show a modest reduction (within 10 percent) from the control mixture at 28 and 56 days but slowed down the strength gain at early ages. For example, the 3-day strength of a mixture containing 40 percent zeolite is 22.5MPa, which is only 50 percent of the control mixture strength of 47.4 MPa. Such lower-than-control strengths of zeolite mixtures at early age (prior to 28 days) but strengths comparable to or higher than the control mixture at late ages (after 28 days) are typical in many other pozzolans as well (e.g., Class F fly ash).

Other studies on compressive strengths of zeolite-blended portland cement concretes showed strength-benefit, comparable-strength, and modest reductions compared to the strength of control mixtures. Such variations in strength results are due to the differences in chemical composition, fineness, reactivity, and percent zeolite levels in the blended cements. Mordenite incorporation is reported to produce a higher compressive strength in concrete than clinoptilolite; the latter in a different study is reported to show similar compressive strengths at 7+ days to that of a control at 15 and 25 percent mass replacements at a *w/cm* of 0.25, whereas a modest strength reduction compared to that of a control at a *w/cm* of 0.30 (Luke [5]). Chabazite and phillipsite additions up to 40 percent mass are reported to show improved strength development and higher reactivity than a pozzolanic glass.

In summary, based on the present study and others, depending on the type, fineness, reactivity, and the amount in the blended cement, zeolite incorporation may show a modest strength benefit or a reduction compared to that in a non-zeolite control. Irrespective of comparative strengths with a control, however, the absolute levels of compressive strengths obtained even at higher cement replacement levels is encouraging for its use in structural concretes.

DURABILITY

Rapid Chloride Permeability – Perhaps one of the most important effects of clinoptilolite in concrete durability is the significant reduction in chloride permeability of concrete as evidenced by reduction in coulomb values of zeolite mixtures compared to that of the control in rapid chloride permeability test (ASTM C 1202). Table 5 and Figure 8 provide results of rapid chloride permeability of zeolite mixtures. Compared to the control, incorporation of 40 percent zeolite

show almost 40 percent reduction in coulomb values in as early as 3 days (this early age effect, however, is more pronounced in non-air-entrained mixtures than in air-entrained ones). At 28 days and beyond, both air-entrained and non-air-entrained mixtures show significant coulomb reductions with increasing zeolite contents in mixtures. Coulomb values decrease both with increasing zeolite replacement in mixtures at a particular age, and with increasing age of a mixture – sometimes increasing zeolite replacements at a particular age in mixtures caused more reduction in coulomb than that achieved by ages of individual mixtures.

Drying Shrinkage – Drying shrinkage of zeolite-blended concrete mixtures are usually higher than that of the control, and shrinkage values at a particular age increases with increasing zeolite percent but rates of increase of shrinkage with age for all mixtures are identical to that of the control. The 7-day drying shrinkage in mixtures having 10, 20, and 30 percent zeolite were 577, 583, and 733 microstrain, respectively, compared to 537 microstrain in control concrete. The maximum shrinkage results at 66 days are 960 microstrain for the control mixture and 1023, 1007, and 1140 microstrain for mixtures containing 10, 20, and 30 percent zeolite, respectively. The shrinkage graphs (see Table 6 and Figure 9) at 10 and 20 percent cement replacement levels are identical and slightly higher than the control during the duration of the test. The higher shrinkage values of zeolite mixtures are partly responsible for the increased water content in the mixture from the water from high-range water reducers (whose amount increases with increasing zeolite content), and partly from absorption of part of the mix water by the zeolite particles having high surface area and an open ("caged") crystal structure. Therefore, in field concrete, excessive addition of water to improve the workability of zeolite mixture (without adding a high-range water reducer) can introduce high drying shrinkage of concrete.

Alkali-Aggregate Reaction – Incorporation of clinoptilolite shows a clear and significant reduction in mortar bar expansions due to ASR in the ASTM C 311 test. Table 7 and Figure 10 provide results of ASR expansion tests. Mixture incorporating 30 percent zeolite, highly reactive borosilicate glass, and a high-alkali portland cement shows no expansion at all for 92 days. Compared to the control, a 10 percent cement replacement by zeolite shows a significant reduction in expansion. Clearly, use of clinoptilolite as a pozzolan is an effective means of mitigating or eliminating expansions due to ASR. The crystalline nature and high specific surface area of zeolite make it more effective to attack by alkaline solutions, which, in turn, promote a more rapid development of an abundant low basic, amorphous hydrated calcium aluminosilicate hydrate phase. The hydrated zeolite paste thus formed incorporates a significant amount of alkalis that would otherwise be available for reaction with reactive aggregates. Other studies on zeolite incorporation also showed its effectiveness in minimizing alkali-aggregate expansion (Sersale and Frigione [6], Feng et al. [7]).

Acid and Sulfate Resistance – Mortars made using zeolite-blended portland cements are reported to show significant improvements in resistance to acidic and sulfate solutions compared to that of the straight portland cement mortars. Factors responsible for such improved acid and sulfate resistance of zeolite-cement mortars are: (a) a reduction in calcium hydroxide component of portland cement hydration by pozzolanic reactions, which would otherwise be leached away by the acid or participate in chemical sulfate attack, (b) overall densification of the microstructure by pozzolanic reactions creating a fine pore structure (having significantly higher micropore volume, decreased pore median radius, and increased total porosity than portland cement mortar), which improves resistance to ingress of acidic/sulfate solutions, (c) a reduction in sulfate and aluminate levels of blended cements compared to that in portland cement, and (d) high resistance of zeolite itself to acidic solutions and its effective neutralization ability compared to that of portland cement. Previous studies by Janotka et al. [8] on acid and sulfate resistance of mortars made using straight portland cement and blended cement having 65 weight percent portland cement and 35

weight percent natural zeolite (having 68 percent clinoptilolite) and kept for 1 to 2 years in 0.5 and 1.0 percent HCl solution, 5 percent Na_2SO_4 solution, and in reference water showed improved resistance of zeolite-cement mortar to acid/sulfate attacks (and decreased weight loss of zeolite-blended mortars in sulfate/acidic solutions) compared to that of straight portland cement mortar; zeolite-cement mortar showed late strength comparable to that of portland cement mortar.

Inspired by the above study, acid and sulfate resistance of present clinoptilolite are being tested according to ASTM C 1012. The testing protocol is given in the previous section on the testing strategy. So far, the results are in line with the previous study, i.e., compared to the normal portland cement mortar, zeolite cement mortars clearly have a better resistance to the ingress of both acidic and sulfate solutions.

POZZOLANIC REACTION OF ZEOLITE IN CEMENT PASTE AND MICROSTRUCTURE OF ZEOLITE-BLENDED PORTLAND CEMENT PASTE

Pozzolanic Reaction – The pozzolanic reaction of clinoptilolite is detected by two series of tests. In the first series, reduction in calcium hydroxide component of portland cement hydration in the neat zeolite-blended cement pastes are measured at varying levels of zeolite additions. Pastes having water-cementitious materials mass ratios of 0.47 and 0, 10, 20, and 30 percent *additions* of clinoptilolite by mass of portland cement were prepared (without reducing the portland cement content in the zeolite-blended pastes) and cured in lime-saturated water for 91 days. After curing, pastes were pulverized to fine powder and tested for the amount of calcium hydroxide by thermal analysis (DSC, TGA) and XRD. Results show a clear decrease in calcium hydroxide contents in zeolite-cement pastes and greater reduction of calcium hydroxide in pastes having higher amounts of zeolite incorporations, indicating a higher degree of pozzolanic reaction (Table 8 and Figure 11).

In the second series of tests, lime-zeolite pastes having 1:1 by mass mixtures of hydrated lime and zeolite and water-to-lime plus zeolite mass ratio of 0.75 are prepared, cured in lime-saturated water for two weeks, and then the lime content in the neat paste was compared with a dry powder of thoroughly mixed zeolite and hydrated lime having a 1:1 mass ratio. Results (Figures 12 through 14) show a decreased lime content in the paste compared to that in the dry mixed powder due to the pozzolanic consumption of lime by zeolite. X-ray diffraction patterns of dry mix and paste (Figure 12) show a clear reduction in portlandite [$Ca(OH)_2$] content in the paste compared to that in the dry mix. Figures 13 and 14 are the results of optical and scanning electron micrography and x-ray elemental analyses showing the residual zeolite grains, clumps of lime, and calcium aluminosilicate composition of the lime-zeolite paste.

Microstructure – Incorporation of zeolite causes the following important microstructural modifications, which are responsible for the overall improved durability of concrete: (a) a decrease in calcium hydroxide component of portland cement hydration in the paste by the pozzolanic reaction, (b) densification of the cement paste microstructure by combined pore-size and grain-size refinements, which cause an increased volume of very fine pores at the expense of the large pores, and (c) improvement of aggregate-paste interfacial zone by a combination of filler effects and pozzolanic reaction effects. Natural zeolite can be utilized not only as a pozzolan but also as a microfiller in the concrete for the overall densification of microstructure.

Extensive petrographic examinations and scanning electron microscopical examinations of zeolite-blended neat cement paste, mortar, and concrete were carried out to determine the overall improvement in microstructure by zeolite. The study shows a clear densification of the bulk microstructure of concrete by pozzolanic consumption of the calcium hydroxide component of

portland cement hydration. Figures 15 through 18 show optical and scanning electron micrographs and x-ray elemental analyses of hardened zeolite-blended cement pastes prepared in this study. Compared to the portland cement paste where Ca/Si is > 1, the zeolite-blended portland cement paste has Ca/Si ratios < 1 (Figures 17 and 18). The zeolite-blended cement paste shows an overall high levels of alkalis (K > Na) due to contribution of alkalis from zeolite itself and the alkali-binding capacity of zeolite-cement paste, which are not so evident in the straight portland cement paste. The enriched alkali levels in the paste, however, did not contribute to any deleterious alkali-silica reaction. Zeolite incorporation showed a significant reduction in the potential for ASR expansion in our test where the paste contained highly reactive borosilicate glass as aggregates. It is indeed this alkali-binding capacity of the zeolite-cement paste along with the overall densification of microstructure, which have contributed to this reduction in alkali-aggregate expansions. Figure 19 shows microstructures of portland cement and zeolite-blended portland cement mortars in secondary electron and backscatter electron images where the former contain a very thin layer of calcium hydroxide hydration products along the aggregate-paste interfaces, which are not so common or absent in the zeolite-blended cement mortars.

Residual zeolite grains in the paste can be detected by using a petrographic microscope. Due to the fine grain-size (~10 - 15 microns), however, ultra-thin sections (~15 microns) or ultra-thin oil immersion mounts and high magnifications of 1000X are required for positive identification. Compared to the residual portland cement particles, clinoptilolite grains in paste thin section show angular shape, colorless, finer size (most grains are less than 10 microns), lower (negative) relief, lower refractive index (RI < 1.54, ~1.50), and weak (to zero) birefringence to near-isotropic character. The hydration rims around the residual portland cement particles in zeolite-blended cement paste are somewhat thinner than that in the straight portland cement paste. Compared to optical microscopy, however, scanning electron microscopy is more useful for zeolite detection, where it shows its characteristic alkali aluminosilicate composition.

CONCLUSIONS

The following conclusions can be drawn from this study:

(1) Clinoptilolite used in this study confirms to the ASTM C 618 specifications for a Type N pozzolan.

(2) Incorporation of clinoptilolite in concrete mixtures up to 40 percent by mass of the total cementitious component show a significant reduction in workability of the fresh mixture (due to the high surface area of zeolite) requiring addition of both mid-range and high-range water reducers. Except for this effect on workability, a somewhat reduced bleeding, and accelerated setting from 0 to 30 percent levels of zeolite incorporation are also noticed; temperature, unit weight, yield, air content, or other properties of fresh concrete remained unaffected.

(3) Based on the present study, therefore, zeolite incorporation does require addition of a mid-range and preferably high-range water-reducing admixture to maintain the desired workability.

(4) Compared to the control mixtures, zeolite-blended mixtures (*w/cm* ~ 0.40) show an improvement in compressive strength of concrete at 10 percent cement replacement level at 56 days, whereas 20 to 30 percent replacements have caused a modest reduction in strength at the same age by approximately 10 percent. Overall, the strength results of zeolite-blended cement mixtures up to 10 to 20 percent portland cement replacement levels are comparable to or modestly lower than that of the control mixtures.

(5) The significant improvements of concrete properties, however, are not in compressive strength but in durability. Zeolite incorporation showed a marked decrease in chloride permeability of concrete, a similar significant decrease in expansion due to alkali-silica reaction, and an improvement in acid and sulfate resistance. Drying shrinkage of zeolite mixtures at 10 and 20 percent portland cement replacement levels are similar, and at slightly higher level than that of the control mixture during the length of the test (up to 66 days).

(6) All these durability-enhancement properties are directly related to the overall improvement in the cement paste, mortar, or concrete microstructure by zeolite incorporation, and its excellent pozzolanic properties. Durability improvements are related to the densification of microstructure by increased volume of fine pores at the expense of the larger ones, densification of aggregate-paste interfaces, alkali-binding capacity of paste, reduction in amount of calcium hydroxide component of portland cement hydration, reduced sulfate and aluminate levels in zeolite-blended cement than in straight portland cement, etc.

Based on the present study concrete mixtures incorporating approximately 15 to 20 percent clinoptilolite as portland cement replacement (and with added water-reducers for improved workability) are judged to show improved durability in terms of increased resistance to ingress of chloride/sulfate/acidic solutions and ASR expansions, a comparable or slightly reduced compressive strength compared to that of control mixture, and therefore, a good potential for use as a pozzolan in the construction of durable concretes. The benefits of zeolite incorporation on concrete durability, however, can be fully appreciated as long as the mixture maintains a desired workability during placement and is being designed, placed, finished, and cured properly.

Due to wide compositional variability of natural zeolites (even in the same geological occurrence), however, caution is needed to extend the observed effects of clinoptilolite in concrete for the other zeolite group of minerals. Previous works on other zeolites (e.g., mordenite, chabazite) show their contrasting effects on rate of hydration of calcium silicates and aluminates in cement and hence the setting behavior. The rate of development of compressive strength also depends on the type, composition, grain size, and the added amount of zeolite. Such variations, therefore, indicate the need for extensive research of the effects of other zeolites on concrete. Most studies, however, do indicate a clear benefit of zeolite addition in improving the durability of concrete such as suppression of extension due to alkali-silica reaction, improved sulfate resistance, improved impermeability – all of which are related to the overall densification of zeolite-cement paste and concrete. Hopefully, this present comprehensive study should steer interests among the industry professionals to utilize this large natural resource along the Western United States and around the world for greater utilization in building durable concrete structures.

ACKNOWLEDGMENTS

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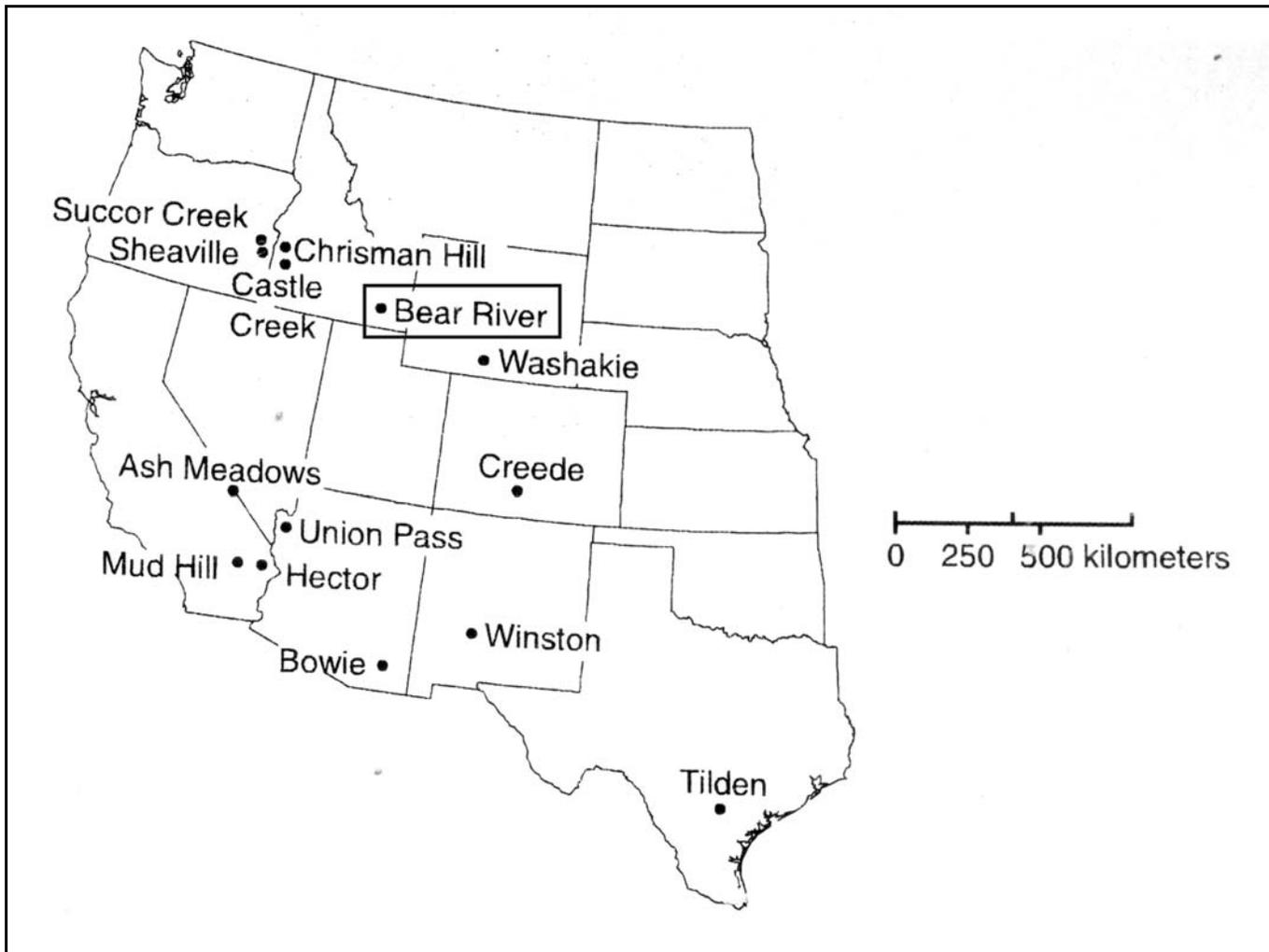
Figure 1: The locations of productive zeolite deposits in the United States, including
the Bear River Zeolite deposit from where the samples for this study came
(adapted from Eyde and Holmes 2006).

Figure 2: Large crystals of clinoptilolite as cavity filling (amygdule) in basalt (left photo) versus ultra-fine powdered form of clinoptilolite from widespread tuffaceous lacustrine deposits in the western USA [middle and right photos showing clinoptilolite deposits from the Bear River Zeolite (BRZ) mine in Preston, Idaho, the location of the sample for the present study]. Unlike the museum quality hydrothermal (amygdaloidal) form, the sedimentary (diagenetic) form has commercial and industrial importance and pozzolanic properties in concrete.

Figure 3: The Bear River Zeolite Plant in Preston, Idaho (a wholly owned subsidiary of United States Antimony Corporation) from which the clinoptilolite sample was received for this study. Top left = Mine; Top right = Processing Plant; Bottom Left = Mining operations. Bottom right = Crusher. The photos are from www.bearriverzeolite.com.
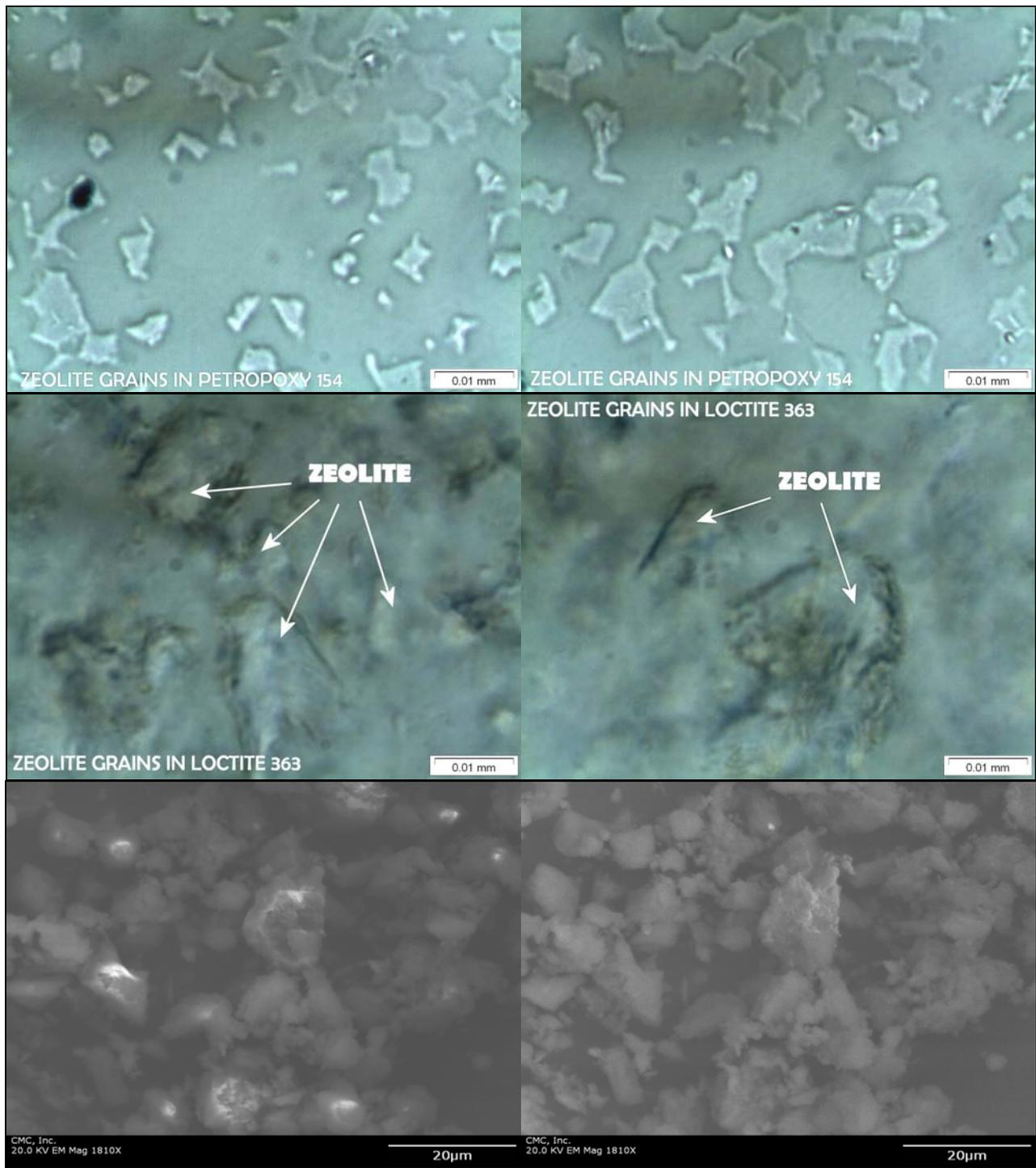
Figure 4a: Photomicrographs of zeolite powder: (a) Top photo = A few grains sprayed on a glass slide and mounted on an epoxy (Petropoxy 154, RI = 1.54); (b) Middle Photo = Grains mounted on Loctite 363; (c) Bottom Photo = Grains mounted on a carbon tape. The top and middle photos are taken by using a petrographic microscope at a magnification of 1000X where most grains are less than 10 microns in size. The bottom photos are secondary electron image (left photo) and backscatter electron image (right photo) of grains taken by using a scanning electron microscope. Both optical micrographs and scanning electron micrographs show the angular shape and very fine size of zeolite grains.
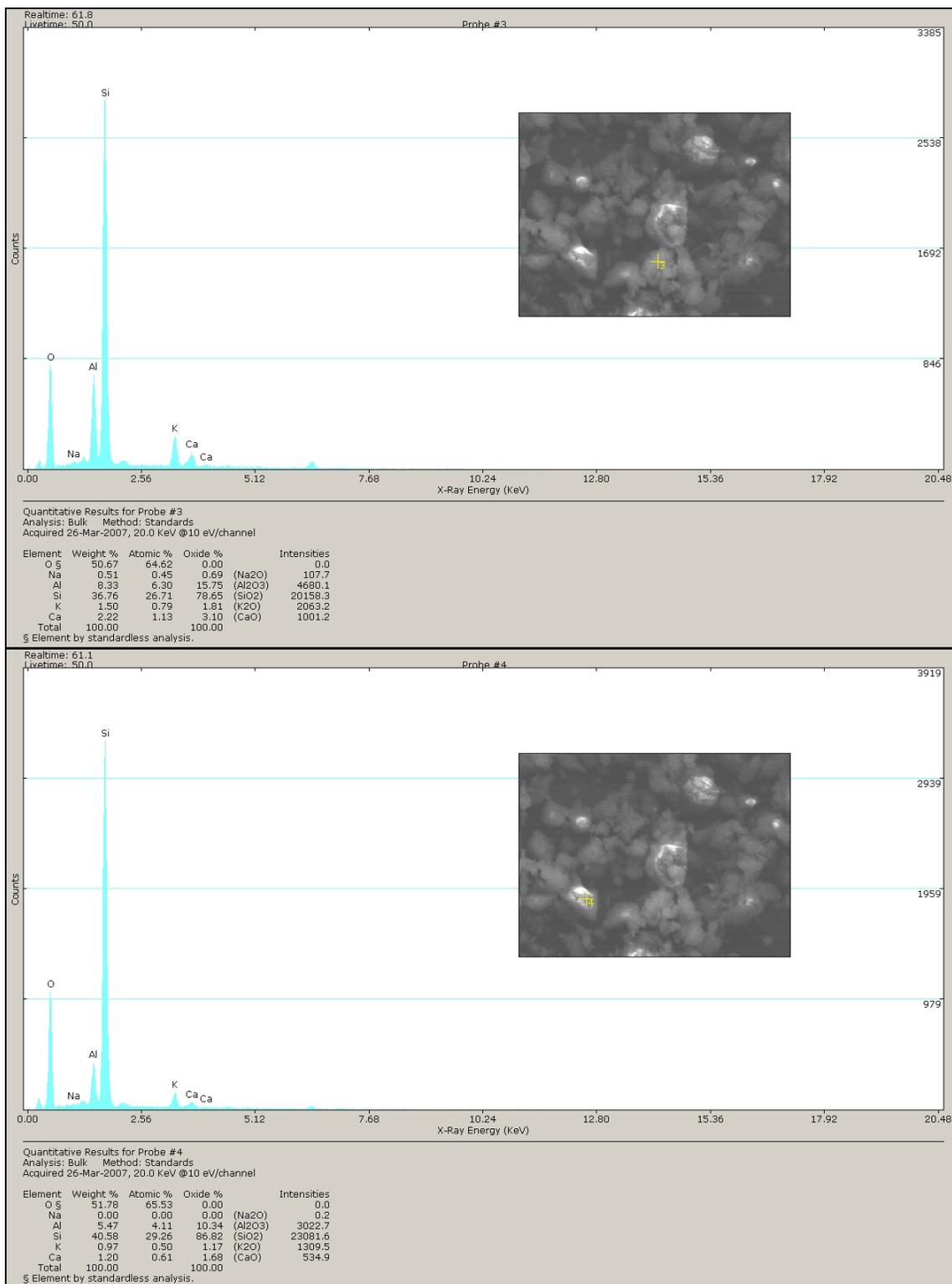
Figure 4b: X-ray elemental spectra of zeolite grains taken from an energy-dispersive x-ray spectrometer in a scanning electron microscope showing the presence of major amounts of silica (Si), moderate amounts of alumina (Al), minor amounts of alkali (Na, K) and calcium (Ca), and trace amounts of iron (Fe) and magnesium (Mg). All grains are more or less homogeneous in composition. The inset photos are secondary electron images of the grains indicating the ones being analyzed.
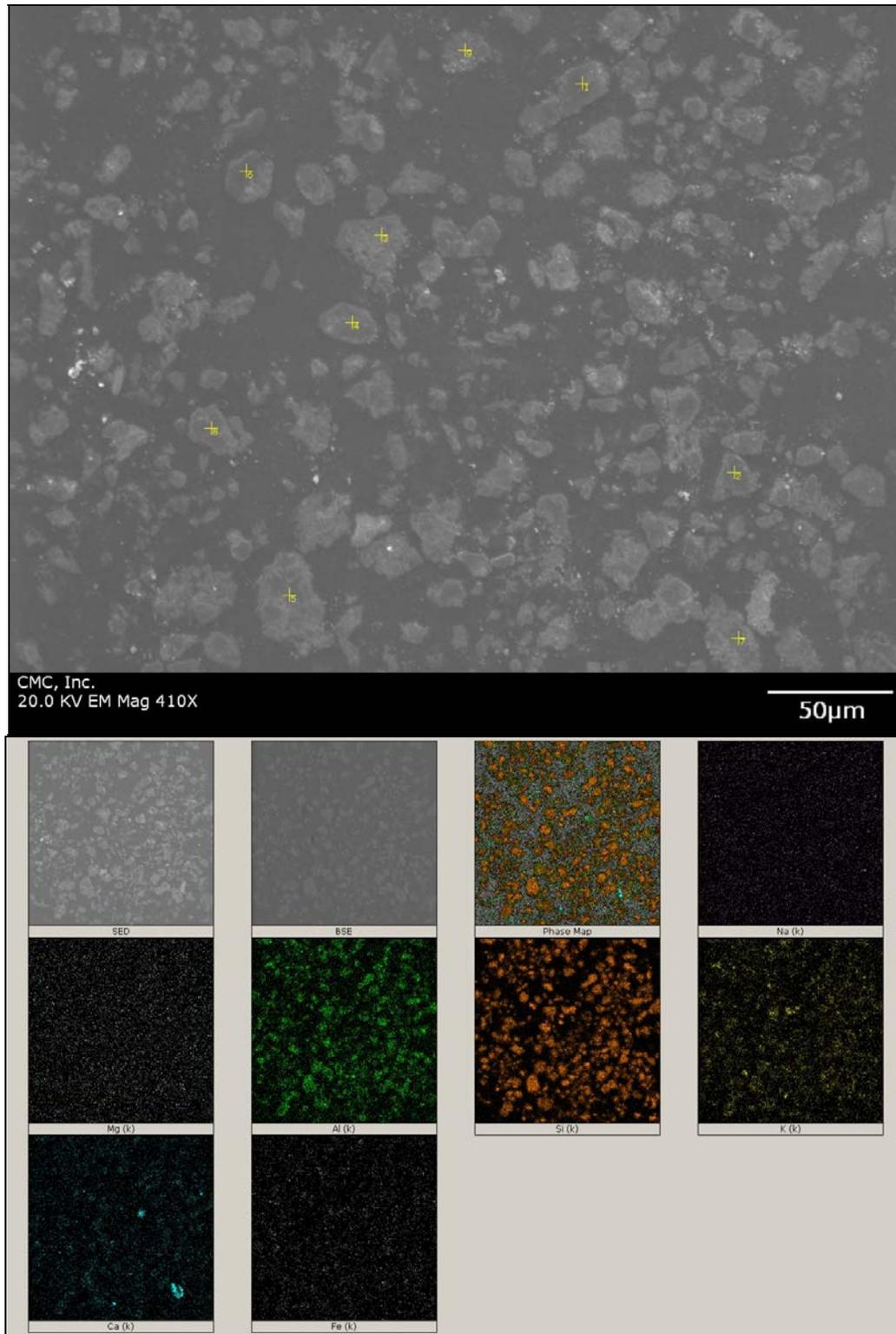
Figure 4c: Top Photo = Secondary electron image of zeolite grains mounted on a glass slide with Petropoxy 154. The grains with plus (+) marks are individually analyzed (analyses of two such grains are given in the next Figure). Bottom Photo = X-ray elemental map of the grains in the top photo showing the abundance of silicon (Si) and alumina (Al) highlighted by these elements' maps at the locations of the grains.

Quantitative Results for Probe #2
Analysis: Bulk   Method: Standards
Acquired 27-Mar-2007, 20.0 KeV @10 eV/channel

Element	Weight %	Atomic %	Oxide %		Intensities
O §	48.47	63.46	0.00		0.0
Na §	0.13	0.12	0.18	(Na2O)	76.9
Mg §	0.19	0.17	0.32	(MgO)	195.3
Al §	6.72	5.22	12.70	(Al2O3)	8715.7
Si §	34.65	25.84	74.12	(SiO2)	51880.5
K §	5.59	2.99	6.73	(K2O)	3717.6
Ca §	4.15	2.17	5.81	(CaO)	3104.9
Fe §	0.10	0.04	0.14	(Fe2O3)	36.2
Total	100.00		100.00		

§ Element by standardless analysis.

Quantitative Results for Probe #9
Analysis: Bulk   Method: Standards
Acquired 27-Mar-2007, 20.0 KeV @10 eV/channel

Element	Weight %	Atomic %	Oxide %		Intensities
O §	49.33	64.49	0.00		0.0
Na §	0.10	0.09	0.14	(Na2O)	37.6
Mg §	0.11	0.09	0.18	(MgO)	71.5
Al §	2.57	1.99	4.85	(Al2O3)	2186.1
Si §	38.54	28.70	82.46	(SiO2)	40195.2
K §	3.99	2.13	4.81	(K2O)	1704.9
Ca §	3.33	1.74	4.66	(CaO)	1622.2
Fe §	2.03	0.76	2.90	(Fe2O3)	483.4
Total	100.00		100.00		

§ Element by standardless analysis.

Figure 4d: X-ray elemental spectra of two zeolite grains from Figure 4c showing the presence of major amounts of silica (Si), moderate amounts of alumina (Al), minor amounts of alkali (Na, K) and calcium (Ca), and trace amounts of iron (Fe) and magnesium (Mg). All grains are more or less homogeneous in composition. The inset photos are secondary electron images of the grains indicating the ones being analyzed.
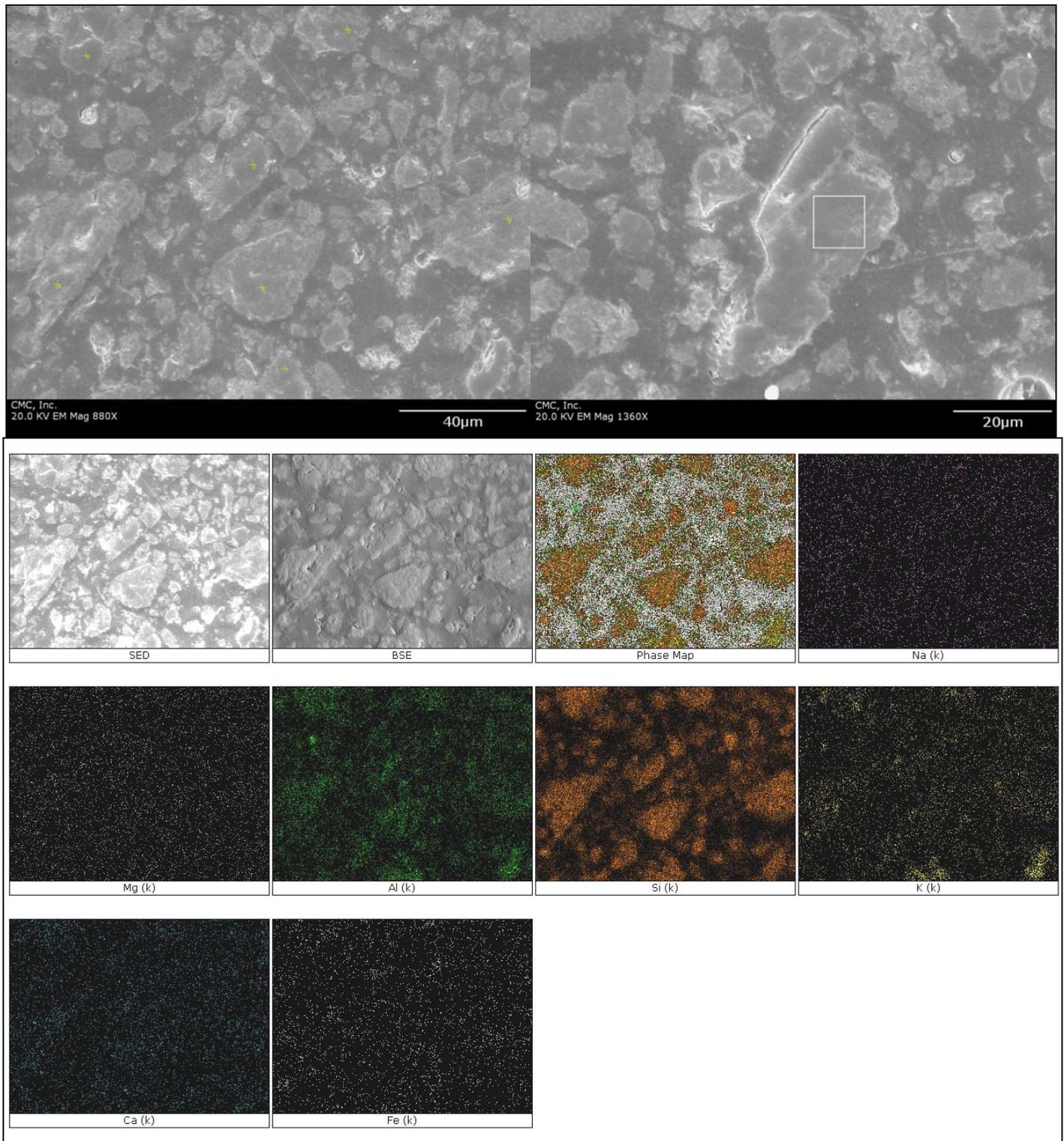
Figure 4e: Top Photo = Secondary electron images of zeolite grains mixed with an epoxy in a viscous consistency, encapsulated in a mold, cured, sectioned, and polished. The boxed area in the top right photo in one grain is analyzed (results are shown in the bottom photo of Figure 4f). Bottom Photo = X-ray elemental map of the grains in the top photo showing the abundance of silicon (Si) and alumina (Al) highlighted by these elements' maps at the locations of the grains.

Realtime: 65.5
Livetime: 50.0
Probe #1

Quantitative Results for Probe #1
Analysis: Bulk   Method: Standards
Acquired 26-Mar-2007, 20.0 KeV @10 eV/channel

Element	Weight %	Atomic %	Oxide %		Intensities
O §	49.49	64.27	0.00		0.0
Na §	0.11	0.10	0.14	(Na2O)	14.8
Mg §	0.13	0.11	0.21	(MgO)	30.1
Al §	4.77	3.67	9.01	(Al2O3)	1456.7
Si §	37.43	27.69	80.09	(SiO2)	13181.4
K §	3.92	2.08	4.72	(K2O)	572.7
Ca §	3.67	1.90	5.14	(CaO)	611.1
Fe §	0.48	0.18	0.69	(Fe2O3)	39.3
Total	100.00		100.00		

§ Element by standardless analysis.

Realtime: 65.4
Livetime: 50.0
Spectrum2

Quantitative Results for Spectrum2
Analysis: Bulk   Method: Standards
Acquired 26-Mar-2007, 20.0 KeV @10 eV/channel

Element	Weight %	Atomic %	Oxide %		Intensities
O §	49.78	64.44	0.00		0.0
Na §	0.04	0.03	0.05	(Na2O)	5.1
Mg §	0.02	0.02	0.04	(MgO)	5.5
Al §	2.86	2.20	5.41	(Al2O3)	866.0
Si §	39.94	29.45	85.45	(SiO2)	14358.6
K §	6.41	3.39	7.72	(K2O)	904.8
Ca §	0.78	0.40	1.09	(CaO)	123.3
Fe §	0.17	0.06	0.24	(Fe2O3)	13.6
Total	100.00		100.00		

§ Element by standardless analysis.

Figure 4f: X-ray elemental spectra of one zeolite grain from the top left photo of Figure 4e showing the presence of major amounts of silica (Si), moderate amounts of alumina (Al), minor amounts of alkali (Na, K) and calcium (Ca), and trace amounts of iron (Fe) and magnesium (Mg). All grains are more or less homogeneous in composition. The bottom spectrum is the result of analysis of the boxed area in a grain in the top right photo in Figure 4e.

Figure 5: X-ray diffraction pattern of zeolite used in this study showing its clinoptilolite mineralogy.
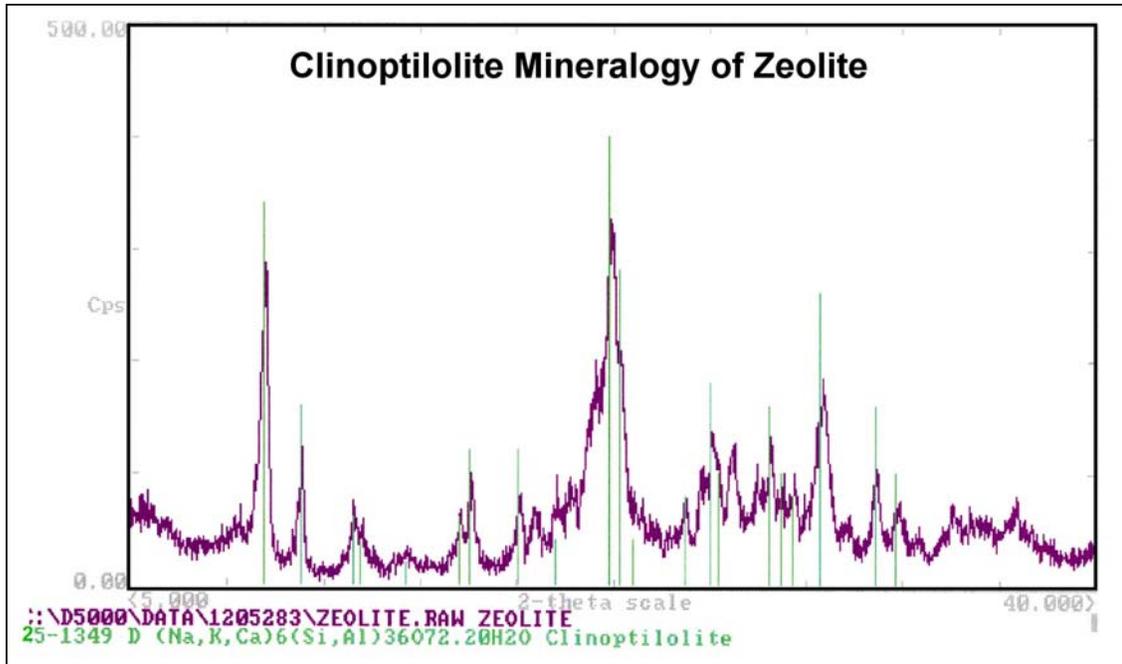
Figure 6: Particle size distribution of clinoptilolite measured by using a Malvern Mastersizer LASER diffractor, giving a mean particle size of 12.27μm.
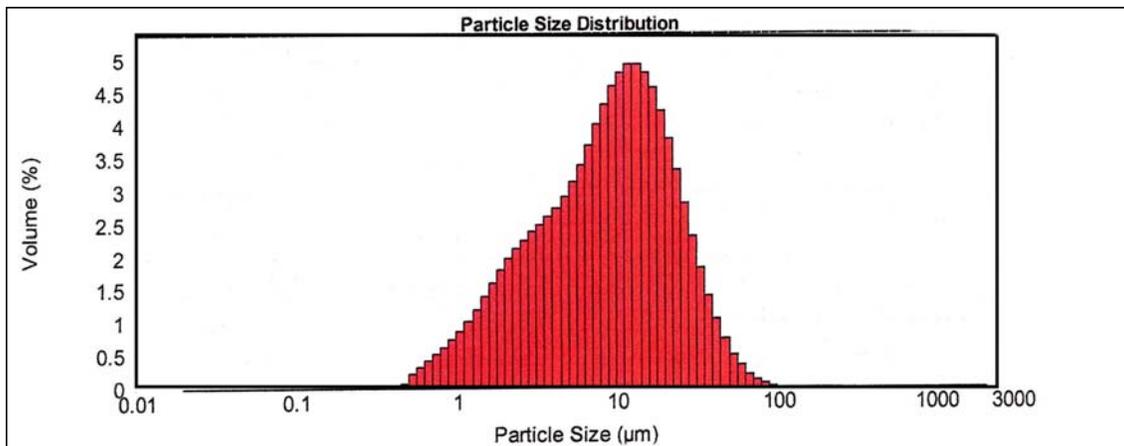
Table 1: Specifications of Bear River Zeolite [From the website of Bear River Zeolite, www.bearriverzeolite.com]

| GENERAL: |
| --- |
| Mineral Component: 85% Clinoptilolite, rest opaline silica
Cation Exchange Capacity: 1.5 to 1.8 meq/gram (as ammonium, -N)
Maximum Water Retention: >55 WT %
Overall Surface Area: 24.9 square meters/gram
Bulk Density (Weight): Approx. 55 - 60 pounds per cubic foot
Hardness: Mohs No. 4
Color: Pale green
Sizes: 3/8" x ¼". 4 x 8, 4 x 14, 14 x 40, 40 x 100, -100, -40 mesh
Transportation: Truck or Rail
Reserve: Approximately 200,000,000 tons |
| **CHEMICAL COMPOSITION:** |
| Cations:
Potassium: 3.47%; Calcium: 1.60%; Sodium: <0.5%

Other   Elements:
Cu = 25 ppm; Zn = 35 ppm; Rb = 120 ppm; Fe = 1.3%; Zr = 480 ppm; Y = 55 ppm; Nb = 40 ppm; Sr = 560 ppm; Nd = 45 ppm; La = 55 ppm; Ba = 1200 ppm; Ce = 130ppm; Pb = <30ppm

Rock Analytical Data:
 SiO_2 = 67.4%; Al_2O_3 = 10.6%; Fe_2O_3 = 1.7%; MgO = 0.45%; CaO = 2.23%; Na_2O = 0.59%; K_2O = 4.19%; TiO_2 = 0.27%; P_2O_5 = 0.10%; MnO = <0.01%; LOI @925C = 11.4% |
| **CERTIFICATION:** |
| U.S. Food and Drug Administration (FDA) Registration 17000178052
Canadian Animal Feed registration No. 990643
Swimming Pools & Spas-ANSI/NSF standard 50 (ZeoSand),
Drinking Water Treatment-ANSI/NSF standard 60 (ChemSorb® Sorbent Powder),
Drinking Water-ANSI/NSF standard 61 (ChemSorb® Filter Granules)
GRAS (generally regarded as safe) under 21 CFR Part 182.2729, 40 CFR Part 180.1001

General Physical Attributes: Non-dusting, resistant to attrition, non-clouding in liquids
(due to absence of clays), good permeability, relatively high density, high water retention.

Applications: Fertilizer and soil amendments; water and other liquid purification and clarification; odor abatement; oxygen production and gas separations; ion exchange; absorption and adsorption; nitrogen (ammonia/ammonium) abatement; hydrocarbon abatement; abatement of certain toxic waste and acid wastes; fillers; desiccants; construction materials; aquaculture water treatment; radioactive waste management; animal feed additive supplements; catalysts substrates; wastewater treatment;
oil spill sorbent; biological and animal waste management; and many others. |

Table 2: Chemical, Mineralogical, and Physical Properties of Ultrafine Zeolite used in this study, along with ASTM C 618 requirements for natural pozzolan (i.e., Type N) and ASTM C 150 Type I portland cements used in this study.

Properties	Zeolite (Clinoptilolite) used in this study	ASTM C 618 Type N Pozzolan	Portland Cements		
			Essroc Low-alkali	Cemex Low-alkali	Cemex High-Alkali
Silicon Dioxide (SiO₂)	70.32	-	20.3	19.8	20.6
Aluminum Oxide (Al₂O₃)	12.55	-	5.3	5.0	5.1
Ferric Oxide (Fe₂O₃)	3.38	-	3.3	3.8	2.7
SiO₂ + Al₂O₃ + Fe₂O₃	86.25	70 (min)	-	-	-
Sulfur Trioxide (SO₃)	0.02	4 (max)	2.7	3.2	3.3
Calcium Oxide (CaO)	3.05	-	63.6	63.4	63.8
Magnesium Oxide (MgO)	0.48	-	1.1	2.5	1.0
Sodium Oxide (Na₂O)	0.03	-	-	-	-
Potassium Oxide (K₂O)	5.50	-	-	-	-
Equivalent Alkali – Sodium Oxide (Na₂Oeq)	3.65	-	0.59	0.52	0.85
C3S in portland cement	-	-	56	59	55.6
C2S in portland cement	-	-	-	13	17.3
C3A in portland cement	-	-	8.5	7.0	8.9
C4AF in portland cement	-	-	-	12	8.1
L.O.I. (loss of ignition)	4.63	10 (max)	-	-	-
L.O.I. @ 110°C	3.00	3 (max)	-	-	-
L.O.I. @ 110° - 750°C (for cements @ 950°C)	4.63	-	1.4	1.8	1.24
Air Content of Cements	-	-	5.4	8.0	-
Zeolite Mineralogy from XRD (See Graph)	Clinoptilolite	-	-	-	-
Density, g/ml @ 20°C	2.19	-	-	-	-
Blaine Fineness, m²/kg	1107	-	377	384	403
Zeolite Color	Pale Green	-	-	-	-
Mohs Hardness of zeolite	4	-	-	-	-
Percent retained on 325 sieve (45-μm), as received	26.94	34 (max)	-	-	-
Percent retained on 45-μm sieve, after grinding by hand	3.22	-	-	-	-
Autoclave soundness	0.02	+0.8 (max)	-	-	-
Strength Activity Index	See below:	See Below:	-	-	-
- Water (percent of control)	110.0	115 (max)	-	-	-
- 7-day (percent of control)	75.5	75 (min)	-	-	-
- 28-day (percent of control)	111.90	75 (min)	-	-	-
Free Moisture Content	3.0	3 (max)	-	-	-

Note: Essroc portland cement was used in mixtures prepared for determination of fresh concrete properties, compressive strength, chloride permeability, drying shrinkage, and pozzolanic reactions. Cemex low and high alkali-portland cements were used for the alkali-silica reaction test.

Table 3: Mixture Proportions and Fresh Concrete Properties.

Mixtures	Non-air-entrained Mixtures					Air-entrained Mixtures		
Percent Zeolite Replacement	0	10	20	30	40	0	10	30
Mixture Proportions Per Cubic Yard								
Portland Cement, Type I, kg.	356	320	285	249	214	356	320	285
Zeolite Ultrafine, kg.	0	36	71	107	142	0	36	71
Coarse Aggregate, #67 Limestone, kg. (SSD)	1068	1068	1068	1068	1068	1068	1068	1068
Fine Aggregate, Sand, kg. (SSD)	893	879	867	854	842	776	762	737
Aggregate-to-Cementitious Materials Ratio	5.5	5.5	5.4	5.4	5.4	5.2	5.1	5.1
Water, kg.	134	134	134	134	134	134	134	134
MB-VR (A.E.A.), L	-----	-----	-----	-----	-----	0.19	0.27	0.58
Polyheed 997, (MRWR), L	3.33	3.33	3.33	3.33	3.33	3.33	3.33	3.33
Rheobuild 1000 (HRWR), L	2.01	4.03	5.73	8.05	14.6	1.32	2.90	6.85
Mixture Water-Cementitious Ratio (*w/cm*)	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38
Total Water-Cementitious Ratio* - (*w/cm*)	0.39	0.39	0.39	0.40	0.41	0.39	0.39	0.40
Total Batch Weight, kg., ASTM C 192	2457	2446	2437	2426	2422	2340	2328	2308
Fresh Concrete Properties								
Concrete Temp., °C, ASTM C 1064	20.0	21.1	21.1	21.1	19.4	20	20	19.4
Slump, mm, ASTM C 143	100	100	88	94	100	100	94	94
Air Content, %, ASTM C 231	2.9	2.4	2.3	2.2	2.4	5.5	6.5	5.5
Unit Weight, kg/m^3, ASTM C 138	2426	2429	2419	2406	2377	2348	2313	2332
Yield, m^3, ASTM C 138	1.013	1.007	1.007	1.008	1.019	1.00	1.006	0.99
Initial Time of Set, ASTM C 403	7 hr. 45 min.	7 hr. 14 min.	6 hr. 17 min.	5 hr. 50 min.	11 hr. 13 min.	7 hr. 35 min.	7 hr. 42 min.	6 hr. 13 min.
Bleeding, %, ASTM C 232	0.44	0	0	0	0	0	0	0

Note: *Total water-cementitious materials ratio contains water contributed from the Polyheed 997 and Rheobuild 1000 water reducing admixtures. Specific gravities of the materials used are: Limestone coarse aggregate = 2.70, Fine aggregate = 2.61, Portland cement = 3.15, Zeolite = 2.20, City Water = 1.00, Polyheed 997 = 1.28, and Rheobuild 1000 = 1.20.

Table 4: Compressive Strengths (in MPa) of Zeolite Mixtures (ASTM C 39).

Days	Non-air-entrained Mixtures					Air-entrained Mixtures		
Percent Zeolite Replacement	0	10	20	30	40	0	10	30
3-day	47.4	45.5	37.3	26.9	22.5	43.3	37.6	26.9
7-day	57.6	55.9	48.0	37.9	33.2	53.5	46.1	36.8
28-day	63.9	66.0	63.8	60.9	59.4	58.4	63.8	55.6
56-day	73.1	74.8	67.9	64.3	63.0	65.2	67.1	60.3
91-day	-	-	-	-	-	64.8	72.4	67.2

Note: 28, and 56-day results are the average of two 4 × 8 in. cylinders

Figure 7: Compressive strengths of various zeolite mixtures with and without air entrainment
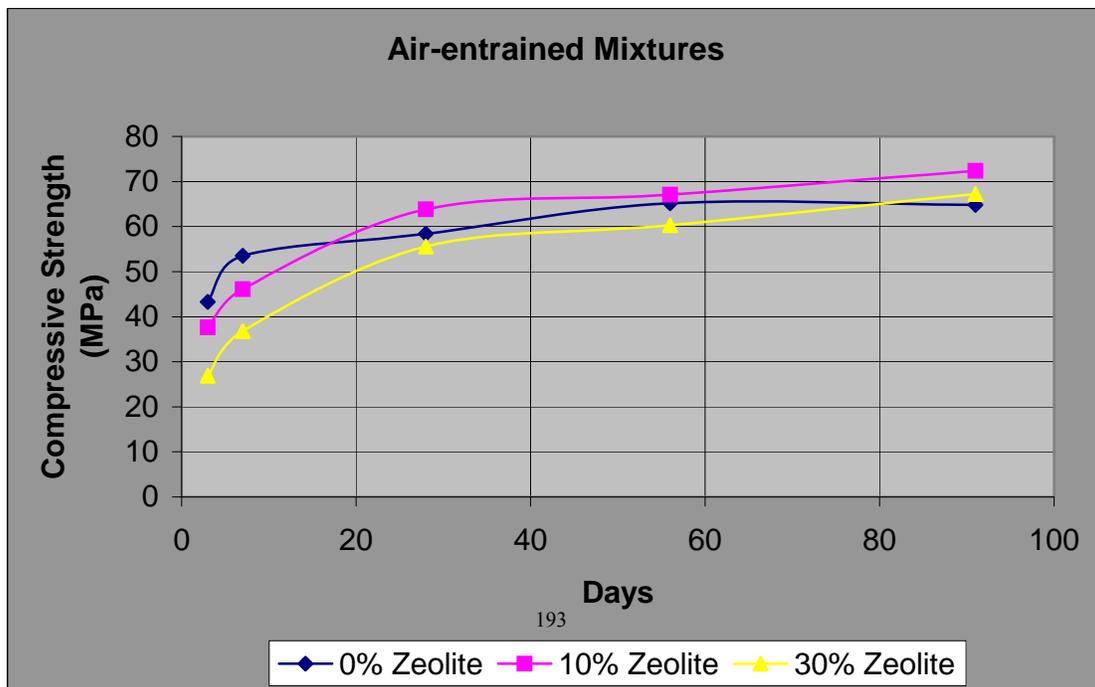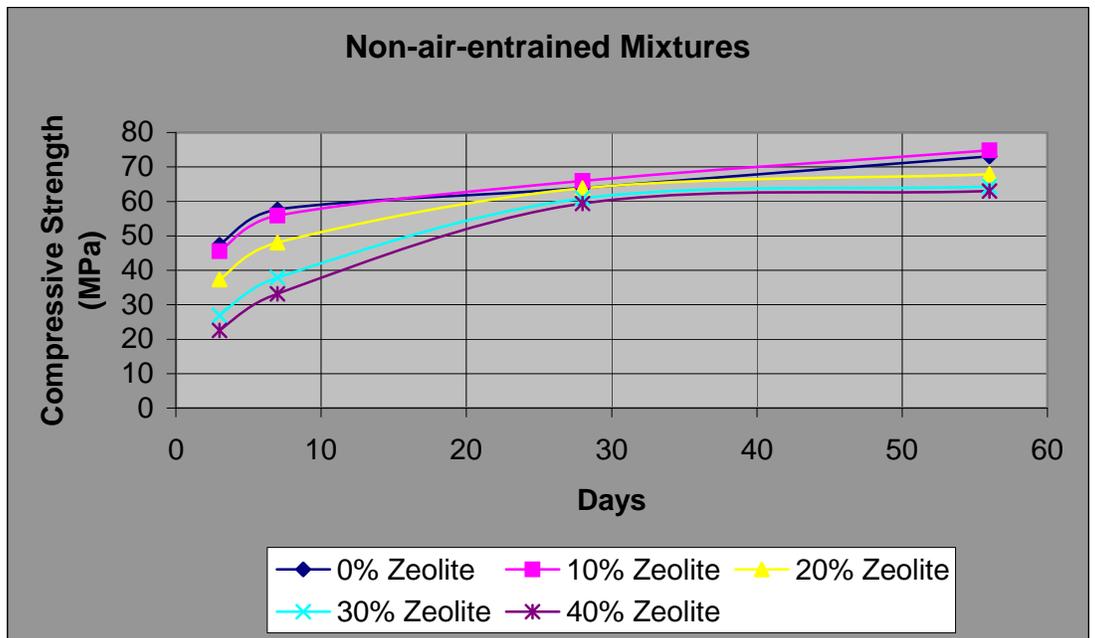
Table 5: Rapid Chloride Permeability Tests of Zeolite Mixtures (ASTM C 1202).

Coulombs	Non-air-entrained Mixtures					Air-entrained Mixtures		
Percent Zeolite Replacement	0	10	20	30	40	0	10	30
3-day	6169	4431	4267	4061	3766	4408	4468	4210
28-day	3793	3073	2405	2112	2116	3646	3318	1191
56-day	3415	2129	1449	1238	1324	3394	2259	1220

Figure 8: Rapid chloride permeability of various zeolite mixtures with and without air entrainment
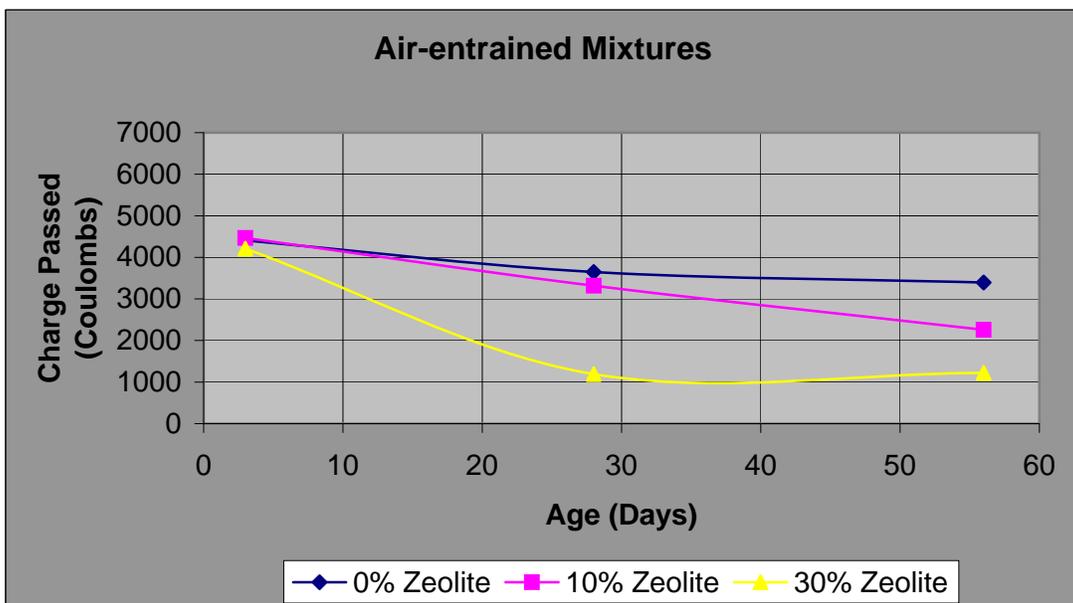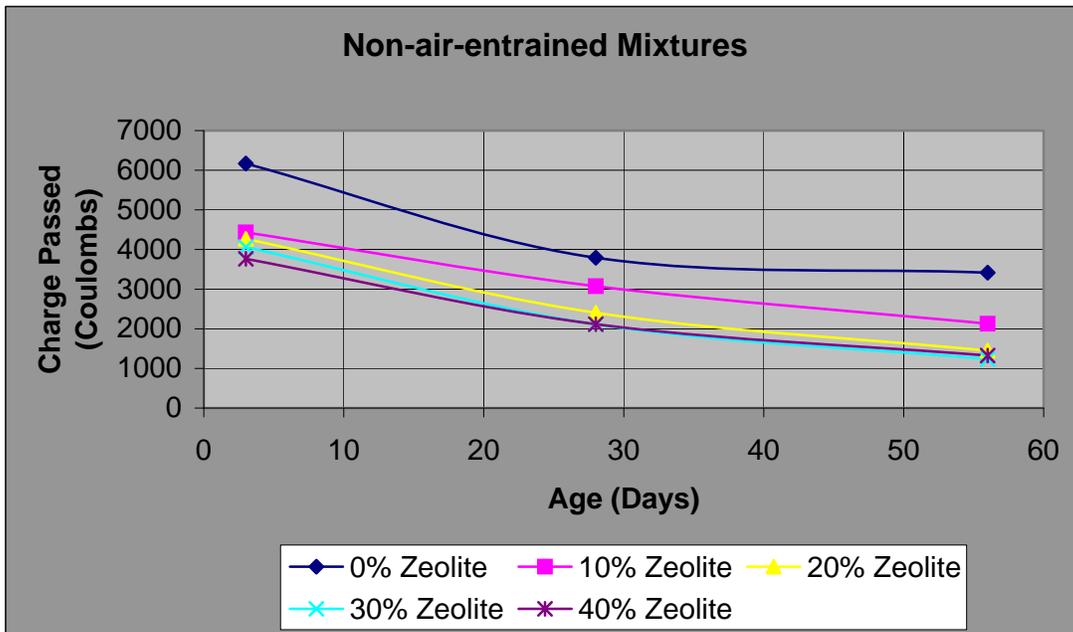
Table 6: Mixture Proportions and Changes in Lengths (measured in microstrain) of Mortar Bars used for Drying Shrinkage Test (ASTM C 311).

Mixture Proportions @ w/cm = 0.47	Portland Cement (gm)	Zeolite (gm)	HRWR (Rheobuild 1000), mL	Sand (gm)	Water (gm)
Control	500	0	2.82	1375	235
10% Zeolite	450	50	5.65	1375	235
20% Zeolite	400	100	8.05	1375	235
30% Zeolite	350	150	11.31	1375	235
Days in air after 7-day lime water curing	Zeolite Replacement (%)				
	0	10	20	30	
7	537	577	583	733	
14	763	847	827	963	
44	843	913	900	1033	
66	960	1023	1007	1140	

Note: Shrinkage results are the average of three mortar bars.

Figure 9: Drying shrinkage tests of zeolite mixtures
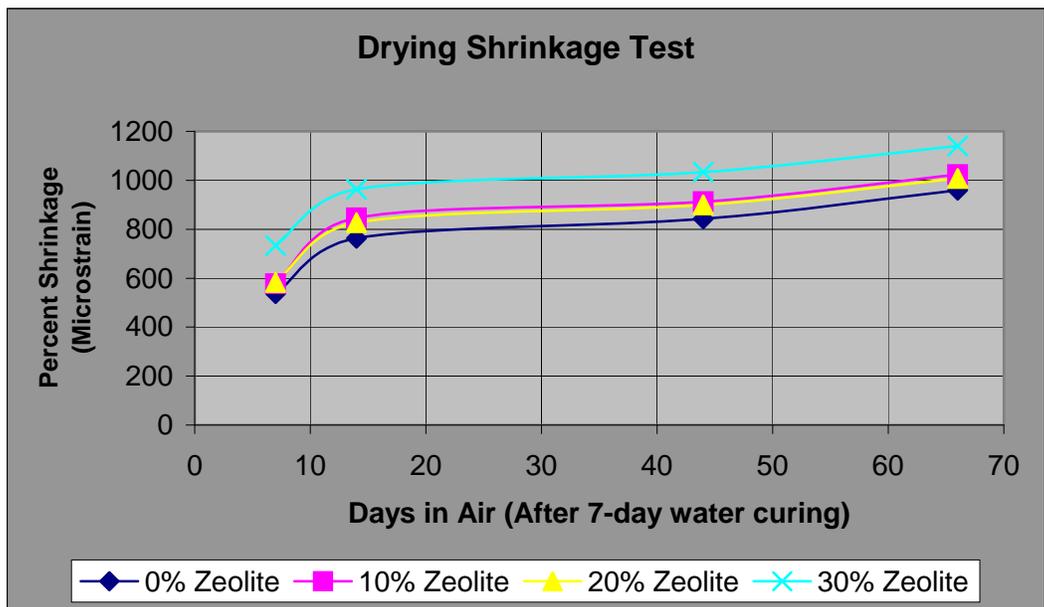
Table 7: Alkali-Silica Reactivity tests of Zeolite Mixtures (ASTM C 311).

| Mixture Proportions @ *w/cm* = 0.48	Portland Cement (gm)	Zeolite (gm)	HRWR (Rheobuild 1000), mL	Borosilicate Glass (gm)	Water (gm)
Control with low alkali cement	400	0	2.25	900	192
10% zeolite with high alkali cement	360	40	4.52	900	192
30% zeolite with high alkali cement	280	120	9.05	900	192
Days Above Water	**Control**	**10% Zeolite**	**30% Zeolite**		
1	0.0010	-0.0030	0.0023		
14	0.0160	0.0063	0.0017		
40	0.0380	0.0170	0.0003		
92	0.1455	0.0813	-0.0010		

Note: A Cemex low-alkali-portland cement was used for the control mixture and a Cemex high-alkali portland cement was used for the mixtures containing zeolite (see Table 1 for cement compositions). The borosilicate glass has the following composition: SiO_2=79.87, Al_2O_3=2.29, Na_2O=4.04, K_2O=0.03, CaO=0.0, MgO=0.03, B_2O3=13.45, Fe_2O_3=0.02, BaO=<0.005. Each result is an average of three mortar bars.

Figure 10: Alkali-Silica Reaction tests of Zeolite Mixtures
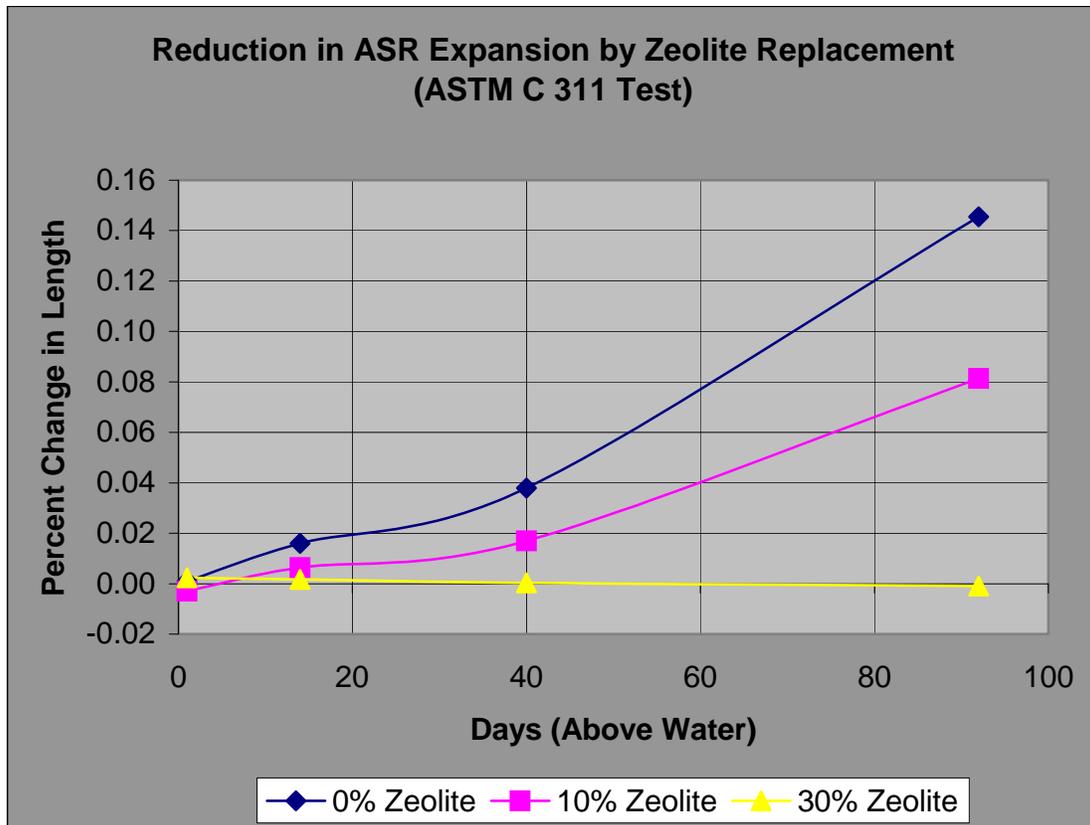
Table 8: Pozzolanic Reaction Tests of Neat Pastes of Zeolite Mixtures.

Neat Paste Mixture Proportions for Pozzolanic Reaction Test, *w/cm* = 0.47	Portland Cement (g)	Zeolite (g)	Water (g)	
Control	100	0	47.0	
+10% Zeolite	100	10	51.7	
+20% Zeolite	100	20	56.4	
+30% Zeolite	100	30	61.1	
XRD, TGA & DSC Results after 91-day lime water curing of neat pastes	Control	10% Zeolite	20% Zeolite	30% Zeolite
% Calcium hydroxide of paste, XRD	15.5	9.0	5.0	4.0
% Calcium hydroxide of paste, TGA	22.2	19.5	14.7	10.8
% Calcium hydroxide of paste, DSC	13.4	10.6	7.1	3.6

Note: TGA method overestimates calcium hydroxide content because some of the hydrate water from calcium silicate hydrate is included in the calcium hydroxide region of mass loss. DSC method provides the most accurate determination of calcium hydroxide.

Figure 11: Pozzolanic Reactions of Zeolite Pastes
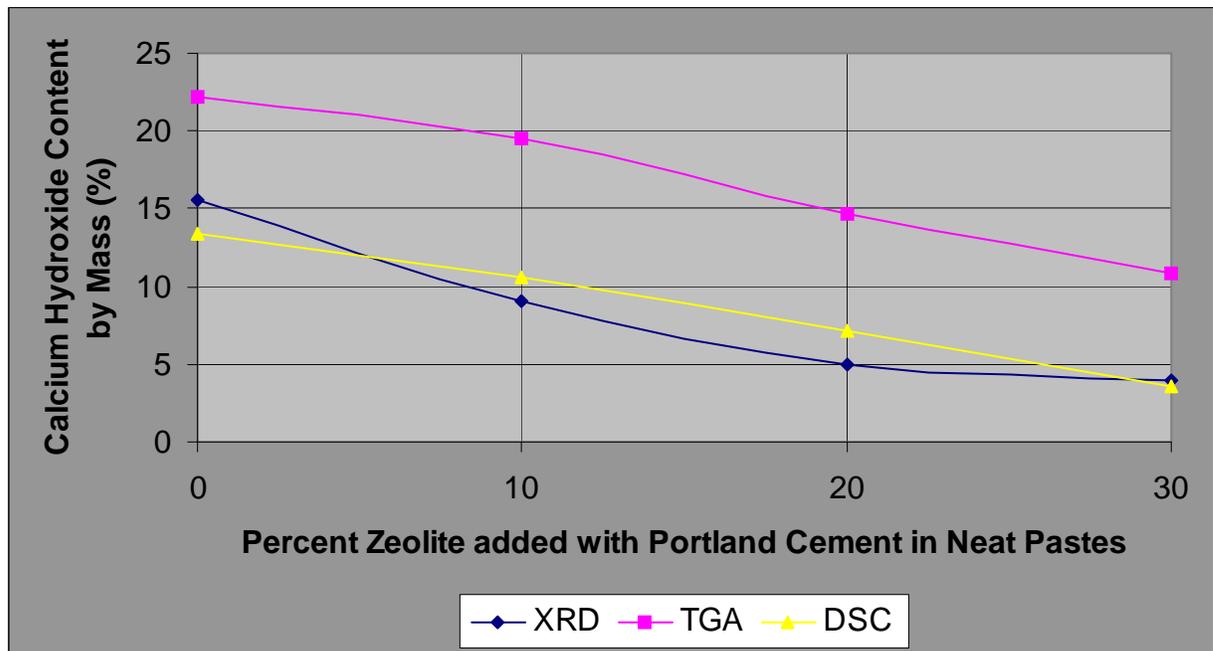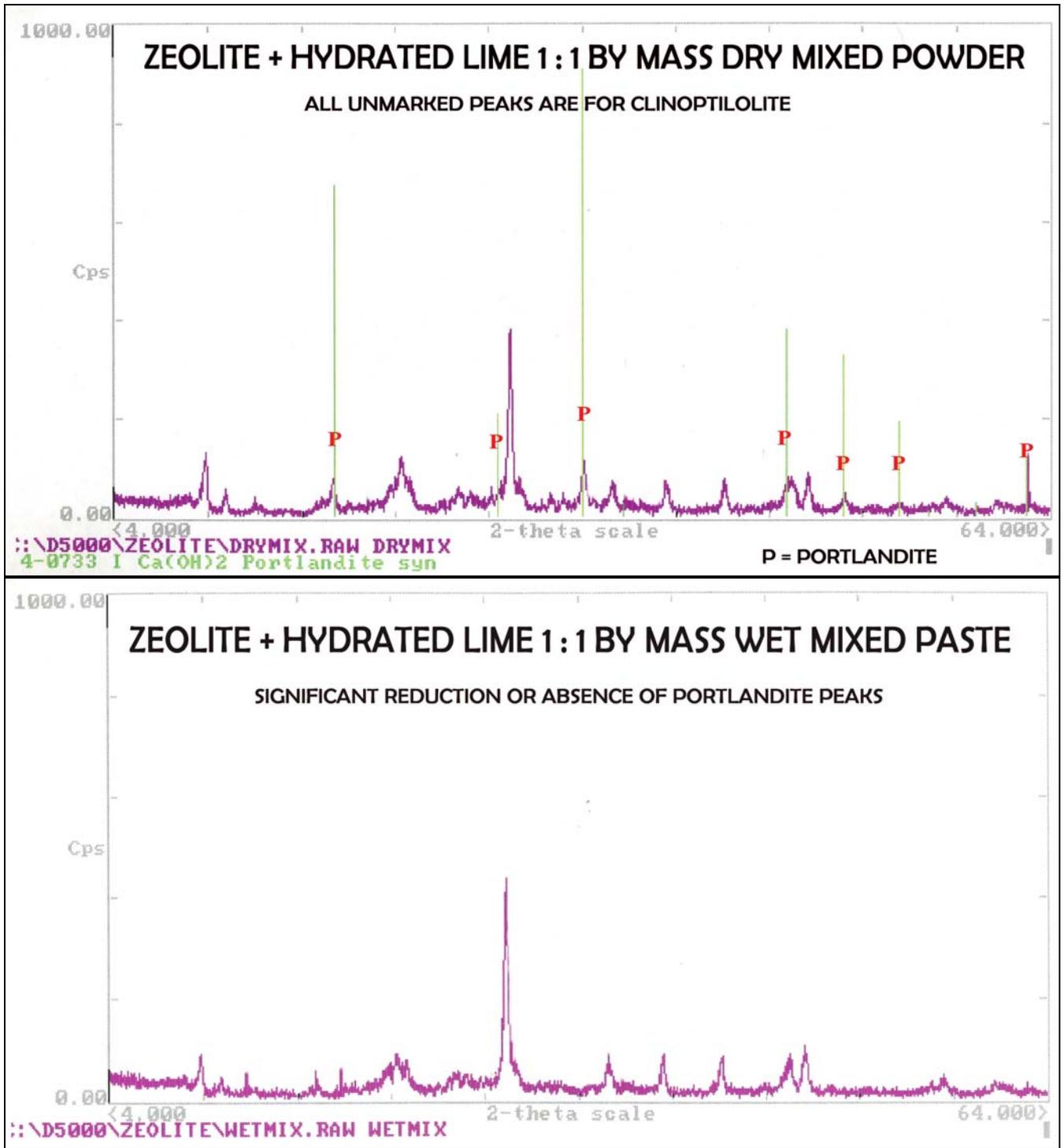
Figure 12 (Lime-Zeolite Mixture): X-ray diffraction patterns of zeolite plus hydrated lime dry-mixed powder (1:1 by mass) at the top and similar lime-zeolite paste (mixed at water-to-zeolite plus lime mass ratio of 0.40) at the bottom showing a significant reduction or absence of portlandite (calcium hydroxide) peaks in the paste, which are present in the dry mixed powder. This indicates the pozzolanic reaction of zeolite in the presence of lime, which reduces the portlandite content in the system and forms calcium aluminosilicate hydrate paste, the composition of which is shown in the next Figures.
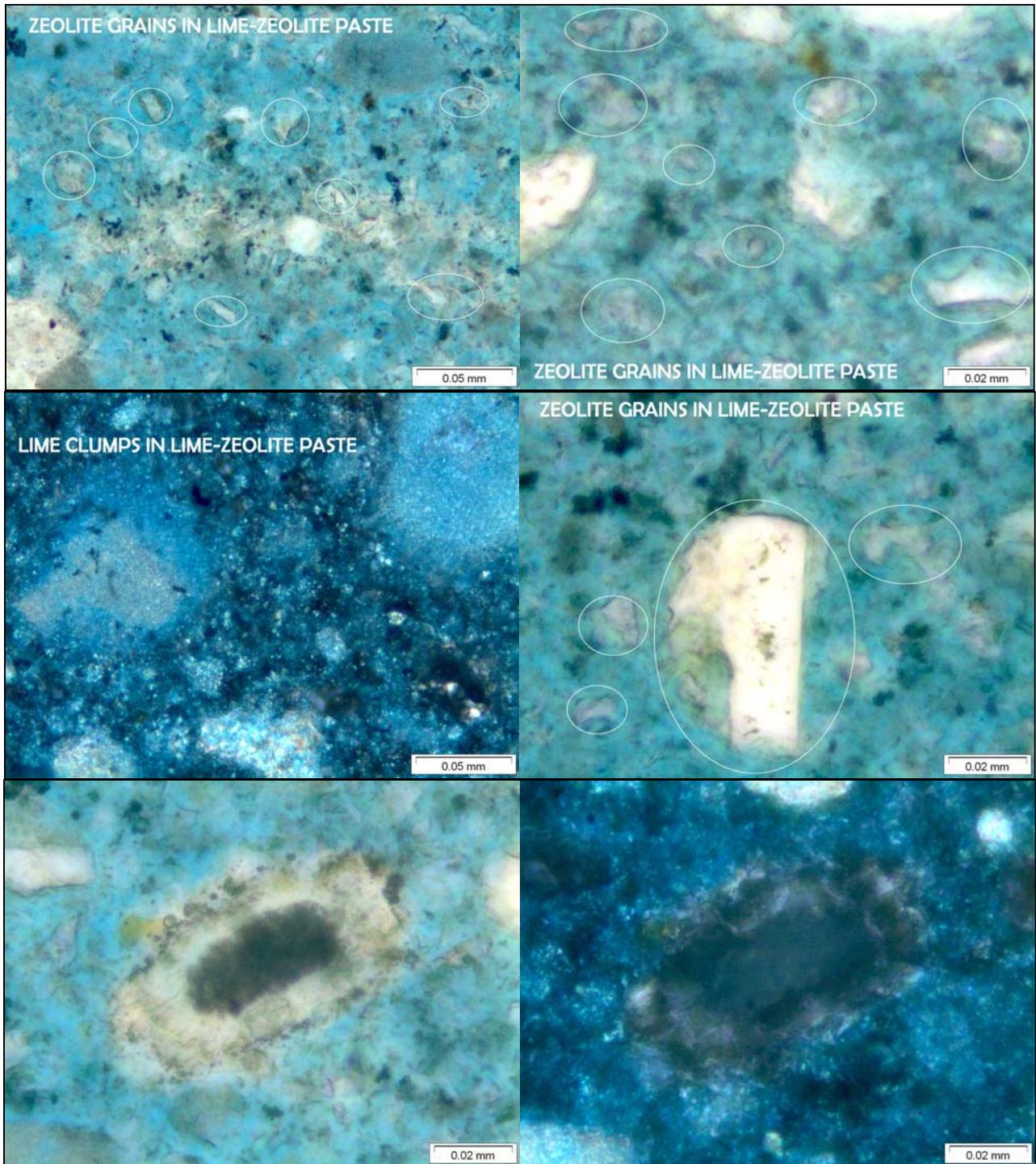
Figure 13a (Lime-Zeolite Paste): Various microstructural features of lime-zeolite paste as revealed in a blue dye mixed epoxy-impregnated thin section observed through a petrographic microscope. The top row photos show several fine zeolite-grains in the paste, a few of which are marked. The middle row photos show lumps of lime and some coarse-grained zeolite grains. The bottom row photos show a "hydration-rim" type microstructure around some zeolite grains in plane and cross polarized lights.
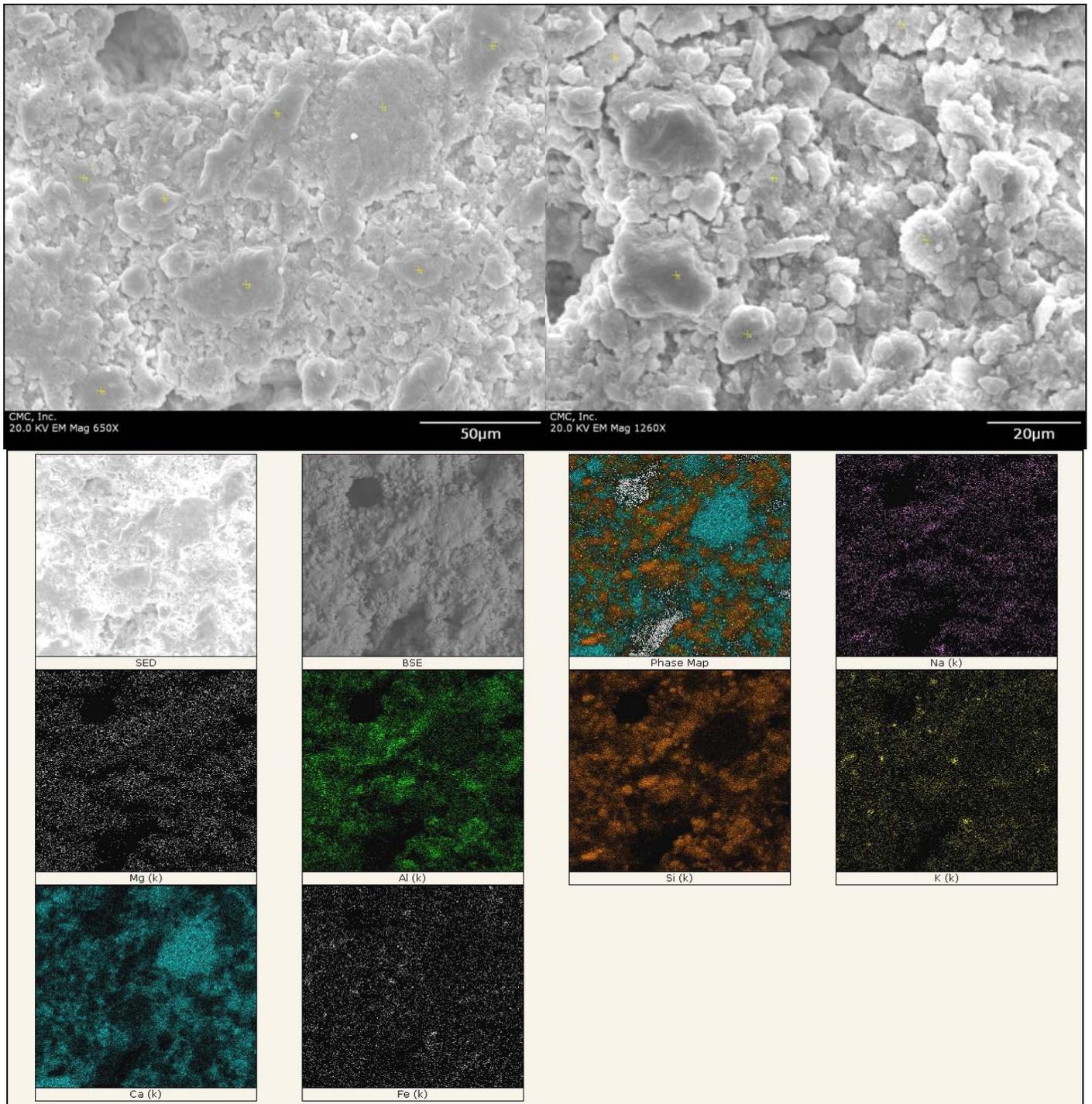
Figure 13b (Lime-Zeolite Paste): Top Photos = Secondary electron images of lime-zeolite mixed paste (mixed in 1: 1 by mass ratio at a water- to-hydrated lime plus zeolite mass ratio of 0.40) showing the pozzolanic characteristics of zeolite and formation of a calcium-silicate-aluminate hydrate paste with a cementitious property. Bottom Photo = X-ray elemental map of the sample (shown in the top left photo) where the calcium and silica/alumina rich areas corresponding to the lumps of hydrated lime and zeolite, respectively, are highlighted.

Quantitative Results for Probe #1
Analysis: Bulk   Method: Standards
Acquired 27-Mar-2007, 20.0 KeV @10 eV/channel

Element	Weight %	Atomic %	Oxide %		Intensities
O §	29.52	50.92	0.00		0.0
Na §	0.00	0.00	0.00	(Na2O)	0.2
Mg §	0.00	0.00	0.00	(MgO)	0.2
Al §	0.00	0.00	0.00	(Al2O3)	0.2
Si §	1.97	1.93	4.21	(SiO2)	560.9
K §	0.36	0.25	0.43	(K2O)	64.8
Ca §	68.03	46.84	95.19	(CaO)	11290.0
Fe §	0.11	0.06	0.16	(Fe2O3)	7.8
Total	100.00		100.00		

§ Element by standardless analysis.

Quantitative Results for Probe #8
Analysis: Bulk   Method: Standards
Acquired 27-Mar-2007, 20.0 KeV @10 eV/channel

Element	Weight %	Atomic %	Oxide %		Intensities
O §	47.46	62.93	0.00		0.0
Na §	0.89	0.82	1.19	(Na2O)	114.2
Mg §	0.32	0.28	0.54	(MgO)	72.4
Al §	5.65	4.44	10.67	(Al2O3)	1649.4
Si §	32.94	24.88	70.48	(SiO2)	11439.0
K §	3.75	2.04	4.52	(K2O)	588.6
Ca §	8.07	4.27	11.29	(CaO)	1425.7
Fe §	0.92	0.35	1.32	(Fe2O3)	78.1
Total	100.00		100.00		

§ Element by standardless analysis.

**Figure 14 (Lime-Zeolite Paste)**: X-ray elemental analyses of lime-zeolite paste showing the areas rich in lumps of lime (top spectrum) and zeolite grains (bottom spectrum) with characteristic calcium-rich and aluminosilicate-rich compositions, respectively. The paste has an overall calcium-alkali-aluminosilicate hydrate composition. The unmarked peaks in all spectra are for the gold coating.
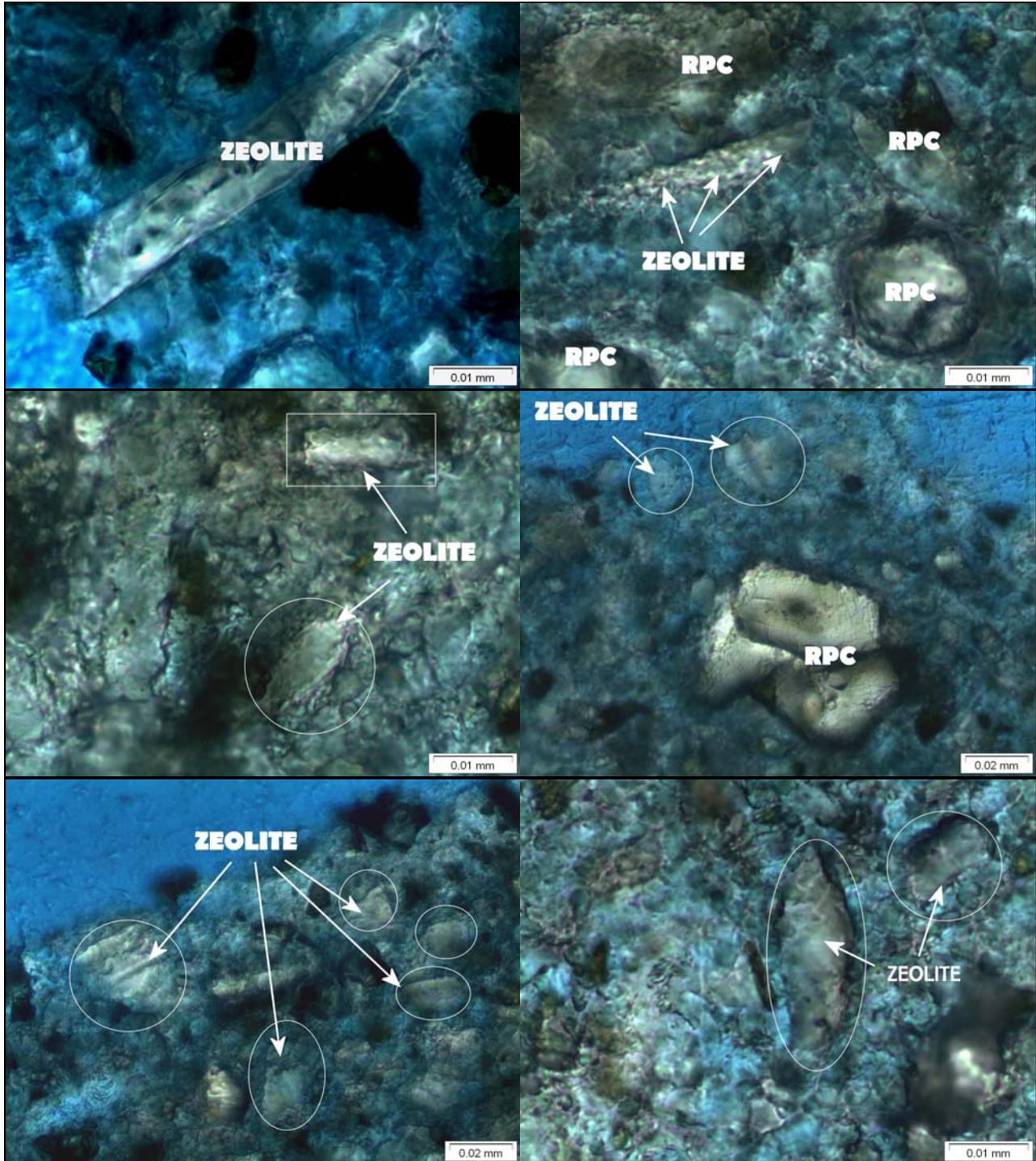
Figure 15 (Zeolite-blended portland cement paste): Photomicrographs of blue-dye mixed epoxy impregnated thin section of zeolite-blended portland cement neat paste (containing 30 percent by mass of zeolite) showing the angular residual zeolite grains in the paste and residual portland cement particles (RPC). The section is approximately 15 microns in thickness; the photos were taken from a Nikon Optiphot 2 POL petrographic microscope at a magnification of 1000X. Zeolite grains are fine, angular, equant, prismatic, or lath-shaped, much finer-sized than RPC.
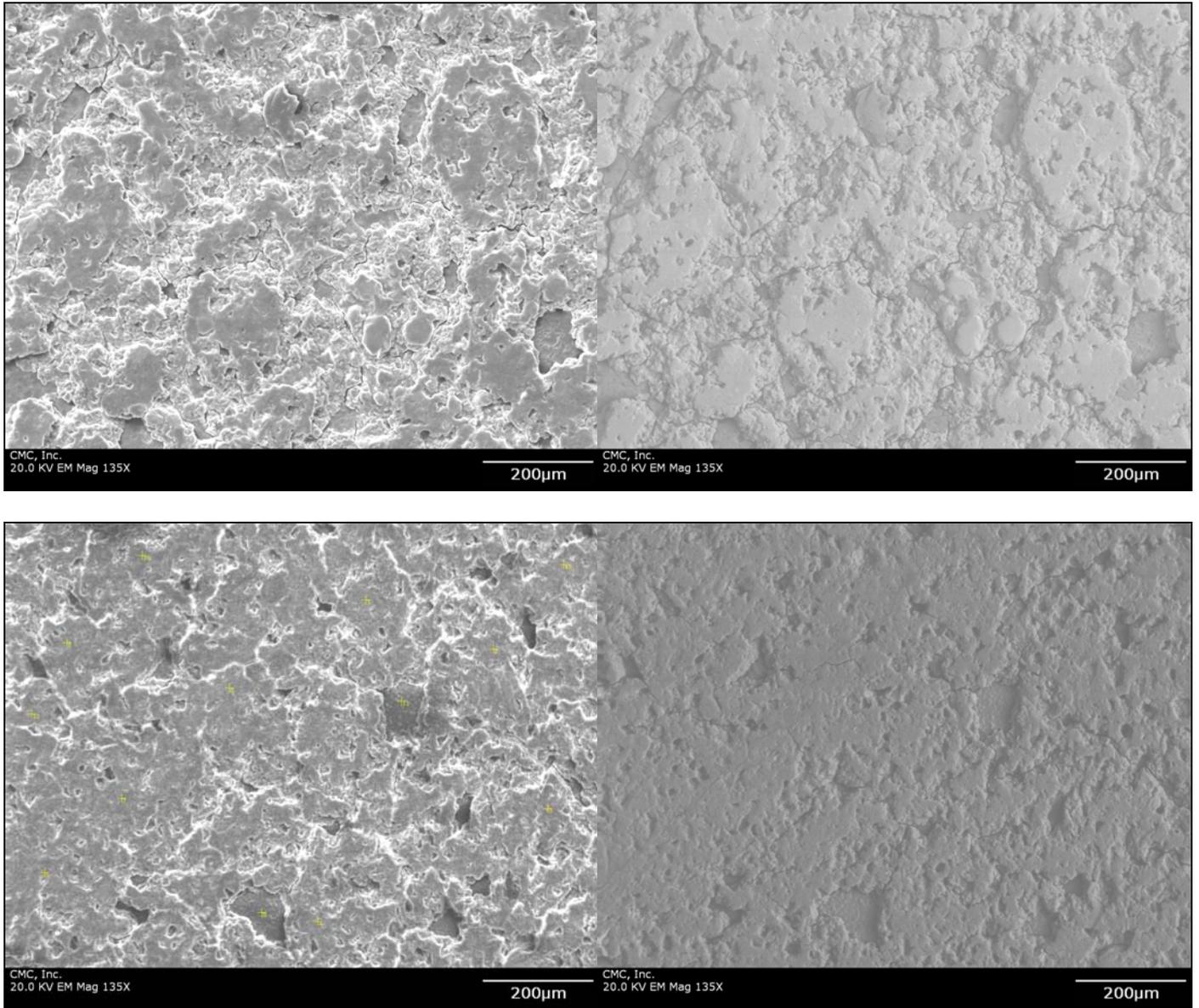
Figure 16 (Portland cement and zeolite-blended portland cement pastes): Secondary electron images (left photos) and backscatter electron images (right photos) of neat pastes containing straight portland cement (top photos) and zeolite-blended portland cement (30 percent zeolite by mass of total cement, bottom photos) showing an overall denser microstructure of the zeolite-blended cement paste in the lower photos. In both top and bottom photos multiple locations were selected for elemental analysis. In the next two figures elemental analyses of two representative locations from each photo are given, which show the overall alkali-enrichment of paste in the zeolite-blended cement (where zeolite contributed the alkalis) compared to the 'normal' alkali levels in portland cement paste (where portland cement contributed the alkalis).
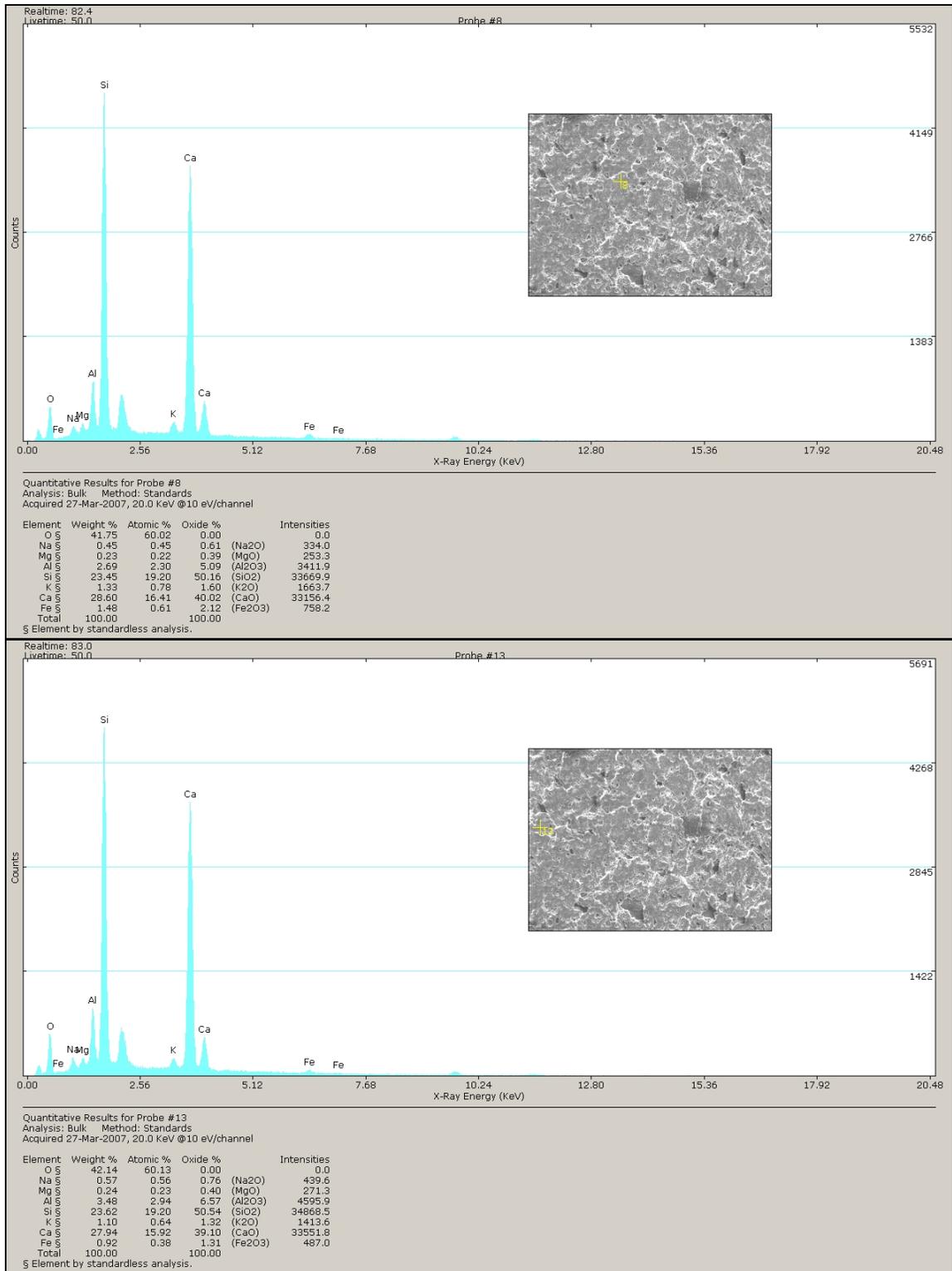
Figure 17 (Zeolite-blended portland cement paste): X-ray elemental analyses of two representative areas of zeolite-blended portland cement pastes showing the calcium-aluminate-silicate-hydrate composition of paste (Ca/Si < 1), and overall higher levels of alkalis in the paste (contributed from zeolites) compared to the alkali levels in straight portland cement paste shown in the next Figure.

Realtime: 86.6
Livetime: 50.0
Probe #8

Quantitative Results for Probe #8
Analysis: Bulk   Method: Standards
Acquired 27-Mar-2007, 20.0 KeV @10 eV/channel

Element	Weight %	Atomic %	Oxide %		Intensities
O §	35.91	56.16	0.00		0.0
Na §	0.16	0.17	0.21	(Na2O)	72.4
Mg §	0.27	0.28	0.46	(MgO)	236.3
Al §	0.90	0.84	1.71	(Al2O3)	1060.1
Si §	13.27	11.82	28.38	(SiO2)	21186.3
K §	0.19	0.12	0.23	(K2O)	168.4
Ca §	48.33	30.17	67.63	(CaO)	42918.1
Fe §	0.97	0.43	1.38	(Fe2O3)	367.0
Total	100.00		100.00		

§ Element by standardless analysis.

Realtime: 88.2
Livetime: 50.0
Probe #11

Quantitative Results for Probe #11
Analysis: Bulk   Method: Standards
Acquired 27-Mar-2007, 20.0 KeV @10 eV/channel

Element	Weight %	Atomic %	Oxide %		Intensities
O §	35.90	56.17	0.00		0.0
Na §	0.11	0.12	0.15	(Na2O)	52.1
Mg §	0.25	0.26	0.42	(MgO)	228.4
Al §	1.50	1.39	2.84	(Al2O3)	1847.0
Si §	12.81	11.41	27.40	(SiO2)	21307.4
K §	0.00	0.00	0.00	(K2O)	0.2
Ca §	48.12	30.05	67.32	(CaO)	45072.4
Fe §	1.31	0.59	1.87	(Fe2O3)	523.8
Total	100.00		100.00		

§ Element by standardless analysis.

Figure 18 (Portland cement paste): X-ray elemental analyses of two representative areas of straight portland cement pastes showing the calcium-aluminate-silicate-hydrate composition of paste (Ca/Si > 1), and overall low levels of alkalis and alumina in the paste (contributed from portland cement) compared to the higher alkali and alumina levels in zeolite-blended cement paste shown in Figure 17.
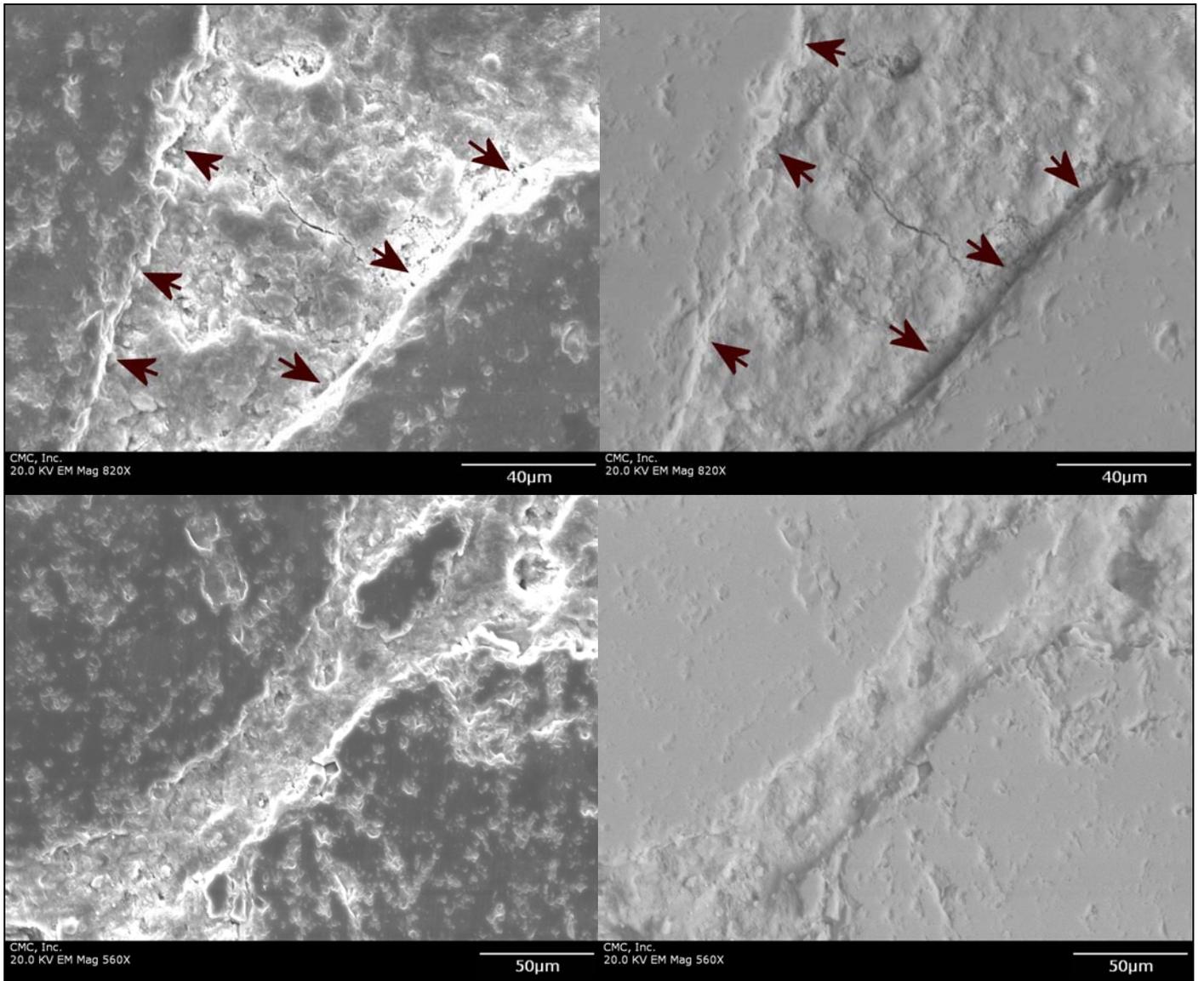
Figure 19 (Portland Cement and Zeolite-blended Cement Mortars): Secondary electron images (left photos) and backscatter electron images (right photos) of portland cement mortar (top photos) and zeolite-blended cement mortar (bottom photo) showing densified aggregate-paste interface and the absence of thin calcium hydroxide hydration rim around the aggregate particles in the zeolite-blended cement mortar. Arrows in the top photo show a very thin layer of calcium hydroxide at isolated locations along the interface, which are not so common or absent in the zeolite-blended cement mortar.