Identifying Alkali-Silica Reaction in Cementitious Materials Using Volatilomics

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Abstract. For millennia, the medical field has utilized the sense of smell for qualitative assessment of health, but recent research shows we can tap into volatile organic compounds (VOCs), which create the odors that we perceive, for quantitative detection and analysis. In this paper, volatile organic compounds produced by the microbes in aged concrete, actively undergoing deterioration due to alkali-silica reaction were analyzed. Volatile organic compounds metabolites, an oft unused resource of chemical information that are produced by concrete-associated microbial communities, were used to detect, and characterize concrete deterioration. In this talk, preliminary results of volatile detection on long-term samples (e.g., ~7 years) will be provided. Scanning electron microscopy with energy disperse x-ray analysis was used to confirm deterioration mechanisms identified using volatilomics. Volatiles were analyzed using direct thermal extraction (DTE) and comprehensive two-dimensional gas chromatography - time-of-flight mass spectrometry (GC×GC–TOFMS).

Identifying VOC biomarkers of concrete health will lay the groundwork for the development of sensors that can provide early deterioration warning, enabling more effective remediation/repair strategies. Microbes may also be sensitive to environmental stress (e.g., climate change), and a sensor based on microbial volatile organic compounds could be used to monitor infrastructure health and provide data to detect environmental stressors relevant to other fields.

Keywords: *alkali-silica reaction, volatilomics, gas chromatography, time-of-flight mass spectrometry, scanning electron microscopy*

1 Introduction

Olfaction is one of our most poignant senses, yet we do not use it to diagnose materials degradation in civil engineering infrastructure. For *millennia* the medical field has utilized the sense of smell for qualitative assessment of health, but recent research shows we can tap into volatile organic compounds (VOCs), an oft unused resource of chemical information, for quantitative detection and analysis [1]. In this paper we utilize the VOCs produced by microorganisms that reside on and inside aging concrete [1, 2] to diagnose concrete deterioration in a similar way to how VOCs from breath, skin, urine, blood, and feces are being used to diagnose a wide range of infectious and non-infectious human and animal diseases.[3] Concrete can undergo deterioration resulting in damage that manifests itself in the form of cracking, staining and/or spalling and ultimately a loss of integrity. To determine the source of cracking, both destructive and non-destructive evaluation methods have been employed for decades. Early concrete deterioration detection is critical, as a correct diagnosis and prognosis can lead to decisions that retain the intended service-life. However, an incorrect diagnosis, where the root cause(s) of the deterioration are not identified could significantly reduce the service-life of the structure or lead to life-safety consequences. Further, calcium silicate cement (**CSC**), is the most ubiquitous binding material (>95%) in concrete world-wide. CSC accounts for ~8% of the world's anthropogenic CO_{2eq}. This is because CSC concrete is the most used construction material in the world; more than twice as much is used as all other building materials combined. [4, 5] Increasing concrete service life through early diagnosis of deterioration is a must to reduce anthropogenic CO_{2eq} emissions by not producing new concrete in excess. What if we could harness one of our most powerful senses for early detection and diagnosis of concrete deterioration?

1.1 Traditional concrete forensic method limitations.

Current concrete forensic methods have several limitations: 1) they are time intensive, 2) rely heavily on invasive destructive methods, 3) give us only one snapshot in time, 4) a high number of samples is typically needed for statistical relevance, and 5) discerning the most significant form of deterioration when multiple mechanisms are in play is very difficult. Non-destructive evaluation has gained significant traction in the past two decades but many of these methods only discern the presence or absence of damage. Perhaps most concerning with all these methods is that at the point we visually observe distress, the extent of damage may be significant, and we may have missed an opportunity to intervene early enough when significant remaining service-life could be achieved. Ultimately pivoting to the area of biomarkers for disease diagnosis will allows us to elegantly obtain a volatile fingerprint for concrete that adds information about what is happening inside, analogous to the way your fitness tracker monitors your blood oxygen level or your heartbeat.

1.2 Cementitious Materials

It is well known that microbiomes are significantly affected by the pH of their surroundings, and therefore the pH of concrete will influence its microbial community and the VOCs that can be detected. CSC concrete has a pH between 12.5-13.5 [6, 7]. Once alkali-silical reaction (ASR) is initiated the pH of concrete undergoing ASR will be lower than the pH of concrete that is not [8]. The amount of reduction in pH due to ongoing ASR depends on factors such as the aggregate reactivity, efficiency of prevention measures used, and the extent of ASR. The initiation or progression of ASR also depends on the pore solution pH. The hydroxyl concentration of pore solution below which ASR does not progress is called threshold alkalinity for ASR, corresponding to a pH from 13.40 to 13.60 depending on the aggregate type in the concrete mixture [9-11].

Biomarkers are measurable substances produced by organisms (e.g., genes (DNA), gene transcripts (RNA), proteins, metabolites) whose presence is indicative of the organisms' health, disease, or environment. Though most biomarker work revolves around biotic systems, particularly humans, animals, or plants, the resident and transient organisms that inhabit abiotic and built environments are a rich source of potential biomarkers. Diverse communities of microbes have been detected in harsh natural and anthropogenically altered concrete-analogue environments with pH > 12 [12]. Maresca et al. utilized 16S rRNA gene sequencing to identify bacteria in CSC concrete that was exposed outdoors for two years and found several genera of bacteria associated with the ASR system compared to concrete treated with supplementary cementitious materials (SCMs) to prevent ASR [2, 13]. Interestingly, no overlap with microbial communities affiliated with microbially induced corrosion (MIC) were observed. Though the sample sizes in these pilot studies were small, they demonstrated a potential link between concrete deterioration mechanism and the microorganisms that are present. However, identifying the microbes that are present in concrete by genome sequencing required destructive sampling methods, thus limiting applicability for routine monitoring.

2 Research Methods

In this paper we provide preliminary results of our investigations into the use of VOCs to diagnose premature concrete deterioration with a focus on alkali-silica reaction. The results presented herein were obtained by taking concrete cores from outdoor exposure blocks that were aged for ~7.5 years in Corvallis, Oregon. Two exposure blocks were chosen for this preliminary investigation. The blocks were originally cast from the same mixture used for ASTM C1293 testing as outlined in Li et al. [14]. The cementitious materials content was 420 kg/m^3 and the mixture was boosted to 1.25% Na_2O_{eq}. Blocks were placed outdoors at an exposure site in Corvallis, Oregon in late 2015. One block was a control mixture and used a very highly reactive (ASTM C1778 classification) fine aggregate that is volcanic in nature and from the Bend, Oregon area (BN) [15]. The second block utilized this same reactive fine aggregate, however, 50% of it by volume was replaced with an expanded clay fine lightweight aggregate. Further details of the mixture designs and materials specifics are found in a publication by Li et al. [14]. The mixture proportions follow that of ASTM C1293 using 420 kg/m3 of cement, a w/cm of 0.42, and a coarse aggregate volume fraction of 0.70. In this case the cement was a high alkali cement (0.90 +/- 0.10 Na_2O_{eq}) boosted to 1.25 Na_2O_{eq} using 1 N NaOH included in the mixing water.

2.1 Expansion Measurements

Expansion measurements of the concrete blocks were taken using a mechanical comparator with digital strain gage. Readings were taken in English units to the nearest 0.00005 in. and converted to percent (%) relative to the initial measurement.

2.2 Concrete Coring and Sample Sectioning

Cores measuring just under 50 mm × varying length (target of 200 mm) were obtained using a commercially available coring rig. The cutting media was water. After coring the samples were removed by hand (nitrile gloves used) and the cores were wrapped in commercially available aluminum foil to limit exposure to VOCs. The cores were then placed in a commercially available freezer (-20°C) without auto defrost feature until, and between further sampling steps.

Cores were cut using a rotary saw with water as the cutting media into 19 mm sections, starting from the surface up to an initial depth of 75 mm. The cut samples and the remaining core section (retained for future analysis) were stored using the previously outlined aluminum foil/freezing procedure. To prepare for both scanning electron microscopy (SEM) and VOCs analysis, smaller samples were cut in half using a hammer and chisel. This was done to limit further contact with water as a cutting agent. The samples used for VOCs analysis were prepared by use of a mortar and pestle that was cleaned after every use. Samples were crushed until there was an even mixture of fine and coarse particles with the maximum coarse particle size approximately 6 mm in diameter. The crushed concrete was collected in separate glass vials which were then wrapped in aluminum foil and stored in the same commercial freezer as the core and cut sections. Crushed samples were shipped in an insulated container with cold packs using next day air to Arizona State University for VOCs analysis via direct thermal extraction – comprehensive two-dimensional gas chromatography – time-of-flight mass spectrometry (DTE–GC×GC–TOFMS) analysis.

To clean the implements such as the mortar, pestle, chisel, and file used to crush the samples, Alconox powdered cleaner was applied on the mortar and pestle with ~100 mL of tap water. The pestle was rubbed against the mortar until almost all fine concrete dust was removed. Then, Liquinox liquid detergent was applied and again the pestle was rubbed against the mortar until all visual evidence of concrete dust was gone from both. Lastly, the mortar and pestle were rinsed with 18 MΩ-cm DI water to remove all cleaning solutions.

2.3 Scanning Electron Microscopy

The opposite half of each remaining core slice sent for VOCs analysis were prepared and analyzed using scanning electron microscopy (SEM). SEM preparation was performed following the approach outlined in [14]. This involved epoxy mounting the specimens and polishing in successive steps from 9 to 1 micron diamond spray suspensions using a non-water-based lubricant. The total polishing time was approximately 4.5-6 hours depending on the sample. The surface was gold sputter coated prior to SEM analysis. An FEI Quanta 600F SEM was used to locate qualitative evidence of ASR in prepared samples. Backscatter electron image analysis at 15-30 kV was done on all prepared samples.

2.4 DTE–GC×GC–TOFMS

Samples were analyzed via direct thermal extraction (DTE; Gerstel MPS Robotic Maestro Software version 1.5.3.2., Linthicum Heights, MD) coupled with comprehensive two-dimensional gas chromatography–time-of-flight mass spectrometry (GC×GC–TOFMS; LECO Pegasus 4D and Agilent 7890 GC, ChromaTOF software version 4.71, LECO Corporation, St. Joseph, MI). Each DTE microvial was filled approximately one quarter full of fine aggregate for each sample (BN control surface: 0 to 19 mm depth; BN control interior: 38 to 57 mm). The microvials were dry purged under helium at 2 mL/min for 2 min at 25°C, desorbed at 220°C for 3 min, then transferred to the cooled injection system with a transfer line temperature of 250°C, and cryofocused onto a glass-wool packed unbaffled liner at -20°C. VOCs were injected into the GC×GC at 250°C for 3 min, without split. Additional gas chromatography, mass spectrometry, and data processing parameters by Ebadzadsahrai et al. were followed, with a modification to the modulator offset (+15°C) from the primary oven [16].

3 Results and Discussion

Figure 1 shows the expansion of the BN control and BN with 50% replacement by expanded fine lightweight aggregate (clay).

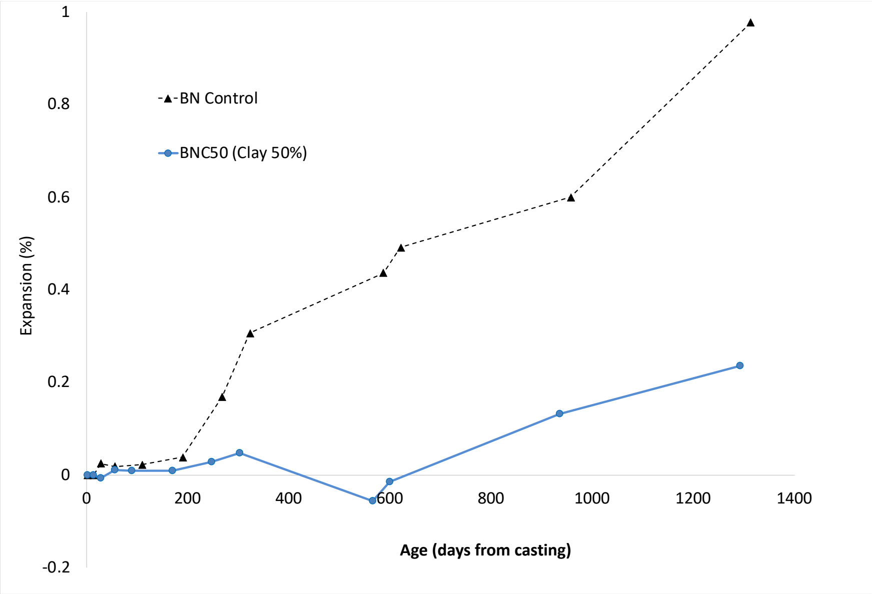

Figure 1. Expansion after seven years of exposure for the BN fine aggregate and BN fine aggregate replaced by 50% fine lightweight aggregate (clay)

This plot shows that the BN control was just below 1.0% expansion after seven years of exposure. The same mixture with 50% replacement of the fine aggregate (reactive component) showed a reduced level of expansion at around 0.2% compared to the control at the same age.

SEM Images of different magnifications were taken from a BN Control surface (0-19 mm depth) sample. In Figure 2A and B, cracking is seen across the face of the aggregate, along the interfacial transition zone (ITZ) and the paste. ASR reaction product can more clearly be seen filling cracks and subsequently causing expansion and even more cracking. In Figure 2 C and D the BN 50% Clay samples shows that ASR reaction product is found in the pores of the fine lightweight aggregate (FLWA) used in the mixture. There is cracking in the paste between aggregates as well. While 50% of the reactive aggregate (BN) was replaced by FLWA (clay) and this may have contributed to a reduction in expansion, further investigations by Li et al., showed that the incorporation of fine lightweight aggregate also produced a pozzolanic effect creating more C-A-S-H type product while also lowering the pore solution pH. EDS spectra for alkali-silica reaction products and pozzolanic reaction products done on the companion ASTM C 1293 specimens can be found in [14].

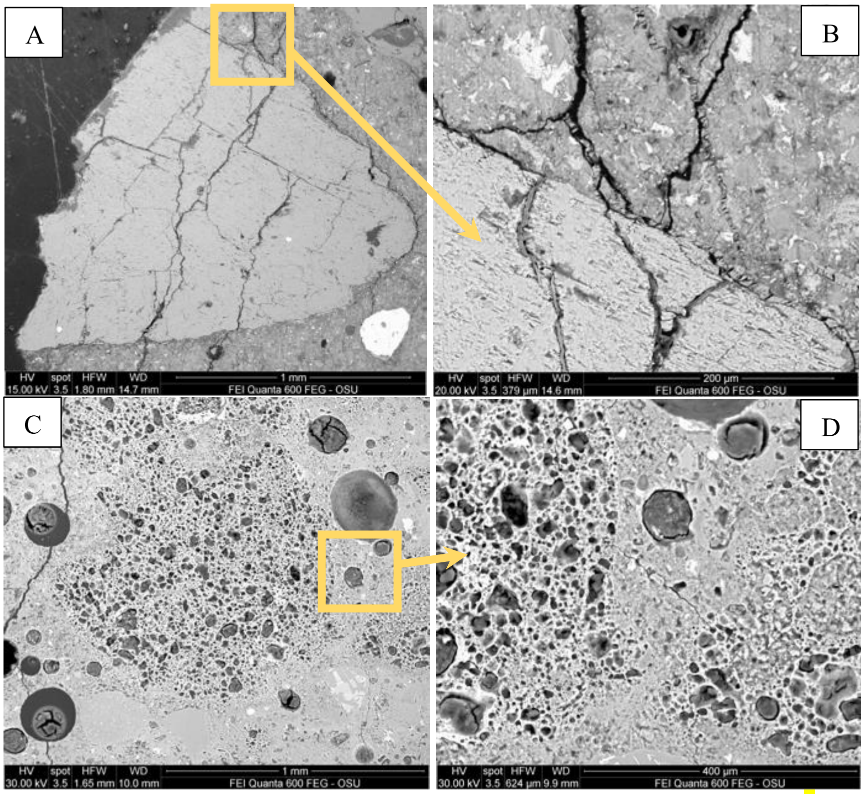

Figure 2. A) Backscattered SEM image of BN control; B) higher magnification of Figure 2A; C) Backscattered SEM image of BN 50% FLWA; D) higher magnification of 2B

Preliminary VOCs analyses were performed on the BN control surface and interior samples using DTE-GC×GC–TOFMS (Fig 2).

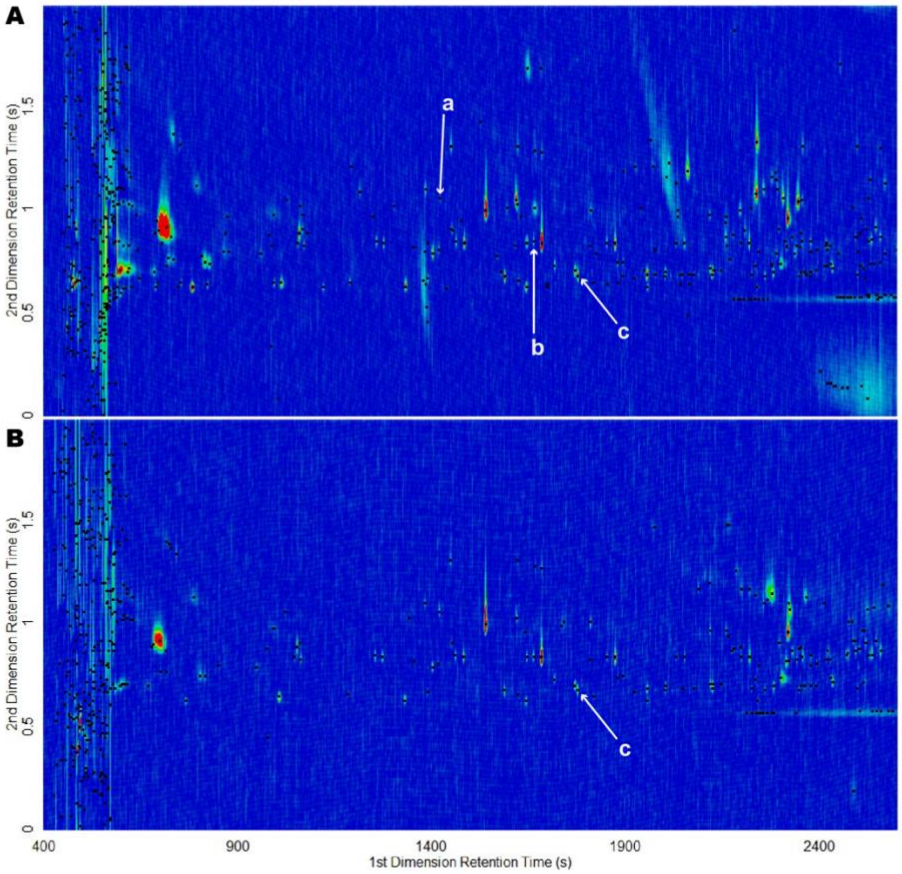

Figure 2. Example GC×GC–TOFMS chromatograms. Peak intensity is expressed using the color scale from light blue (low) to dark red (high). **(A)** BN control surface (0 to 19 mm) sample, highlighting putatively identified microbial metabolites (a) 1-heptanol, (b) 2-nonanone, and (c) dodecane. **(B)** BN control interior (38 to 57 mm) sample, with (c) dodecane labeled.

An estimated 583 and 496 chromatographic features were observed for each sample, respectively. Among these, most putative VOCs were classified as aliphatic alcohols, hydrocarbons, and ketones. Many of the detected VOCs have abiogenic sources, but a subset of these compounds, such as putative VOCs 1-heptanol, 2-nonanone, and dodecane (Fig 2A), are known metabolites of bacteria and fungi [17]. Currently, the DTE method is being optimized for sample-to-sample reproducibility and enhanced signal-to-noise of concrete VOCs, while mitigating the interference of water in the analysis.

3.1 Conclusions

From this work the following conclusions and recommendations for ongoing work include:

- A high level of alkali-silica reactivity was confirmed in one control mixture using a highly reactive fine aggregate by both expansion measurements (near 1.0% at 7 years) and SEM imaging showing cracking through aggregates, cracking in the paste, and the presence of reaction products in the cracks in the aggregate and the paste.
- Less extensive ASR was confirmed in a second mixture that replaced 50% of the reactive aggregate by volume, using an expanded fine lightweight aggregate comprised of clay. This was confirmed expansion measurements (0.20% at 7 years) and SEM imaging that showed very little cracking in the microstructure and aggregates.
- Initial results using DTE-GC×GC–TOFMS demonstrate the feasibility of detecting a broad variety of VOCs in aged concrete. There also appear to be differences between the concrete more severly affected by ASR and the concrete where 50% of the reactive aggregate was replaced by FLWA.
- Further methodology refinement is in process for VOCs analysis to address the high initial signal from water loss in hydrated phases of the microstructure.

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