



University Transportation Research Center - Region 2

Final Report



Nitrogen Dioxide Sequestration Using Demolished Concrete and its Potential Application in Transportation Infrastructure Development

Performing Organization: Stony Brook University, SUNY



April 2016



University Transportation Research Center - Region 2

The Region 2 University Transportation Research Center (UTRC) is one of ten original University Transportation Centers established in 1987 by the U.S. Congress. These Centers were established with the recognition that transportation plays a key role in the nation's economy and the quality of life of its citizens. University faculty members provide a critical link in resolving our national and regional transportation problems while training the professionals who address our transportation systems and their customers on a daily basis.

The UTRC was established in order to support research, education and the transfer of technology in the field of transportation. The theme of the Center is "Planning and Managing Regional Transportation Systems in a Changing World." Presently, under the direction of Dr. Camille Kamga, the UTRC represents USDOT Region II, including New York, New Jersey, Puerto Rico and the U.S. Virgin Islands. Functioning as a consortium of twelve major Universities throughout the region, UTRC is located at the CUNY Institute for Transportation Systems at The City College of New York, the lead institution of the consortium. The Center, through its consortium, an Agency-Industry Council and its Director and Staff, supports research, education, and technology transfer under its theme. UTRC's three main goals are:

Research

The research program objectives are (1) to develop a theme based transportation research program that is responsive to the needs of regional transportation organizations and stakeholders, and (2) to conduct that program in cooperation with the partners. The program includes both studies that are identified with research partners of projects targeted to the theme, and targeted, short-term projects. The program develops competitive proposals, which are evaluated to insure the most responsive UTRC team conducts the work. The research program is responsive to the UTRC theme: "Planning and Managing Regional Transportation Systems in a Changing World." The complex transportation system of transit and infrastructure, and the rapidly changing environment impacts the nation's largest city and metropolitan area. The New York/New Jersey Metropolitan has over 19 million people, 600,000 businesses and 9 million workers. The Region's intermodal and multimodal systems must serve all customers and stakeholders within the region and globally. Under the current grant, the new research projects and the ongoing research projects concentrate the program efforts on the categories of Transportation Systems Performance and Information Infrastructure to provide needed services to the New Jersey Department of Transportation, New York City Department of Transportation, New York Metropolitan Transportation Council, New York State Department of Transportation, and the New York State Energy and Research Development Authority and others, all while enhancing the center's theme.

Education and Workforce Development

The modern professional must combine the technical skills of engineering and planning with knowledge of economics, environmental science, management, finance, and law as well as negotiation skills, psychology and sociology. And, she/he must be computer literate, wired to the web, and knowledgeable about advances in information technology. UTRC's education and training efforts provide a multidisciplinary program of course work and experiential learning to train students and provide advanced training or retraining of practitioners to plan and manage regional transportation systems. UTRC must meet the need to educate the undergraduate and graduate student with a foundation of transportation fundamentals that allows for solving complex problems in a world much more dynamic than even a decade ago. Simultaneously, the demand for continuing education is growing – either because of professional license requirements or because the workplace demands it – and provides the opportunity to combine State of Practice education with tailored ways of delivering content.

Technology Transfer

UTRC's Technology Transfer Program goes beyond what might be considered "traditional" technology transfer activities. Its main objectives are (1) to increase the awareness and level of information concerning transportation issues facing Region 2; (2) to improve the knowledge base and approach to problem solving of the region's transportation workforce, from those operating the systems to those at the most senior level of managing the system; and by doing so, to improve the overall professional capability of the transportation workforce; (3) to stimulate discussion and debate concerning the integration of new technologies into our culture, our work and our transportation systems; (4) to provide the more traditional but extremely important job of disseminating research and project reports, studies, analysis and use of tools to the education, research and practicing community both nationally and internationally; and (5) to provide unbiased information and testimony to decision-makers concerning regional transportation issues consistent with the UTRC theme.

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16. Abstract Achieving environmental sustainability of the US transportation infrastructure via more environmentally sound construction is not a trivial task. Our proposal, which addresses this critical area, is aiming at transforming concrete, the material of choice for many transportation projects, into less environmentally harmful and better performing component of the US infrastructure. This will be extremely relevant to construction of pavements, bridges, tunnels, airports, marine installations and other transportation projects. Simultaneously, our project will address one of the most pressing public health issues, such as NO ₂ emissions from cement kilns, by developing new applications of crushed concrete aggregates (CCA), which are already contributing to resource conservation and elimination of solid waste disposal issues. NO ₂ emissions can cause various environmental and health problems. They contribute to the formation of acid rain, atmospheric particles, and various other toxic substances resulting in health problems, visibility reduction, eutrophication and global warming. One of the most prevalent problems with NO ₂ emissions is the formation of ground level ozone, which is produced by NO _x (NO+NO ₂) reacting with volatile organic compounds (VOCs) and CO in the presences of sunlight. Ground level ozone can damage lung tissue and reduce lung function. It is a significant problem nationwide as millions of Americans live in areas that do not meet the health standards for ozone. Among many sources of NO _x emissions cement kilns are very significant contributors. They emit over 219,000 tons/year of NO _x , which amounts to approximately 20% of all industrial emissions. High temperatures reached in cement kilns are favorable for NO _x emissions and cannot be avoided. <i>We propose an innovative approach of utilizing a waste concrete material which, based on our preliminary studies, can offer a new way of removing NO₂ from flue-gas in a cheap and sustainable way. After all, more than 140 million tons of crushed concrete aggregate are produced in the US with 41 states utilizing it for transportation infrastructure applications. This can be potentially a viable way to offset emissions from cement manufacturing factories (as well as other industrial installations) thereby minimizing their environmental impacts. Moreover, this project will explore the new paradigm of employing waste material and turning it into a useful product. The NO₂ sequestered demolished concrete (NSDC) can be potentially recycled in new concrete either as a set accelerating admixture or as a corrosion inhibitor. The use of recycled concrete as aggregates for new concrete by itself is a big leap towards better sustainability, given that it conserves valuable natural resources and reduces landfill waste. The synergic effect of capturing NO_x and using the NSDC as a corrosion inhibitor will further increase the positive impact on the environment and the longevity of the new reinforced concrete structures.</i>					
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1. Executive Summary

Our research suggests that one of the more innovative uses of concrete is to use it as an adsorbent for NO_x gases to reduce pollution generated by cement production. This will help in sustainable reuse of concrete that is generally disposed in landfills. This work is focused on understanding the feasibility of such an undertaking and clarifying the reaction mechanisms involved.

It is known that NO_x and SO_x emissions are both present at the cement kilns. Therefore, it is important to study interactions of SO_x with concrete surfaces, which occur alongside with NO_x adsorption. For this purpose, we prepared several concrete samples with different base constituents and exposed them to SO_2 under controlled conditions. These samples were studied by XRD, DRIFTS and XANES. Our results indicate that sulfate and sulfite species are formed upon exposure to SO_2 , suggesting that both NO_2 and SO_2 might compete for the same adsorption sites.

Importantly, SO_x adsorption occurs much faster than NO_x adsorption, with sulfur species being observed as early as 1 hour of exposure. Our results suggest that waste concrete can be used as an efficient adsorbent for several components of flue gases emitted from cement kilns. Similar approach can be also used more distributed transportation related emissions. The data also suggest that this new approach in emission's mitigation might be more efficient for SO_x removal as compared to that for NO_x removal.

2. Background

Concrete is one of the most widely used construction materials around the world. Last year alone the total concrete consumption was over 100 million tons for the U.S. which is 5 times the consumption of steel by weight. However, with the widespread use of concrete the cement industry has become one of two largest producers of carbon dioxide (CO₂), creating up to 7% of worldwide man-made emissions of this gas, of which 50% is from the chemical process and 40% from burning fuel [1] making it, potentially, the largest anthropogenic source of air pollution. Further, cement manufacturing produces a number of other harmful emissions. The typical gaseous emissions to air from cement production, apart from CO₂, include NO_x, SO_x, CO, H₂S, and VOCs, dioxins, furans and particulate matters [1, 2]. These major pollutants can be classified in two categories- gaseous and particulates. Fuel combustion process is the source of gaseous emissions which include oxides of nitrogen, oxides of sulfur, oxides of carbon and volatile organic compounds and hydrogen sulfide. Of these, the most significant environmental health and safety concern is NO_x and SO_x emission [3]. Cement kilns emit over 219,000 tons/year of NO_x, which amounts to approximately 20% of all industrial emissions [4, 5]. These emissions are a significant problem nationwide as millions of Americans live in areas that do not meet the health standards for ozone [6].

3. Objectives

The primary objective of this research is to gain substantial understanding of NO_x removal using concrete aggregate. NO_x emissions are a major health concern across the world with a large part of the world's population living in harmful conditions. The environmental and human effects of NO_x range from health problems, visibility

reduction, eutrophication and global warming. Furthermore, cement production itself is a major contributor to these emissions. A creative idea of using crushed demolished concrete as adsorbent to decrease such harmful emissions at the source would be an extremely sustainable solution.

However, a review of the literature regarding NO_x removal using adsorbents shows that in most realistic situations the emissions are not homogenous and contain a number of other pollutants such as Mercury, SO_x and H_2S along with NO_x . An analysis of the flue gas concentrations reported in these papers showed that high concentrations SO_x and NO_x present after removal of heavy metals and mercury. In depth analysis of the literature surrounding the simultaneous removal of SO_x and NO_x is provided in the next section. Thus for us to have a clear understanding of removing NO_2 from cement kilns we first need to know how NO_x and SO_x adsorption using crushed concrete function individually. This will allow us to optimize the conditions in which we can have maximum adsorption of NO_x . The objectives of this research overall remain the same but the direction of the experiments as described in the proposal differ from the work detailed in this report as our analysis of existing literature shows. The criterion of success, therefore, is to obtain a better understanding of the mechanics behind adsorption of SO_x on crushed concrete.

4. Introduction and Summary of Literature Review

As mentioned earlier, NO_x and SO_x are commonly observed together in practical conditions such as cement kiln flue gas emissions, power plant discharge, etc. [7, 8]. In order to understand how NO_x adsorption on concrete occurs in the presence of both gases, we need to first know how each of them interacts individually. While there have been studies in the combined adsorption of NO_x and SO_x on Ca based sorbents, these results from these studies have been mostly inconclusive [9-12]. Some researchers have reported that the presence of NO_2 in the flue gas could improve the SO_2 removal capacity of Ca-based sorbents. On the other hand, the effect of SO_2 on NO_2 removal was also studied by some researchers. It was found that slightly higher NO_x removal occurred in both spray drier and baghouse system with the increase of SO_2 concentration [13]. Further, it was also pointed out that the presence of SO_2 in the flue gas could enhance NO_2 removal by Ca-based absorbent at the bag-filter conditions [14]. Lastly, many of the reported experimental data was done under dry or semi dry conditions, and there has been very little research conducted under humid ambient temperature conditions. Thus to gain better insight of NO_2 and SO_2 removal by concrete this subject was investigated further.

5. Summary of Work Performed

Over the course of this research, interactions of SO_2 with concrete using experimental methods like DRIFTS, and XANES were studied. The prepared samples were also characterized using XRD to understand the initial conditions of the concrete sample. Different concrete samples were prepared to study the effects of concrete composition, including proportion of such on components as cement, water, fine and

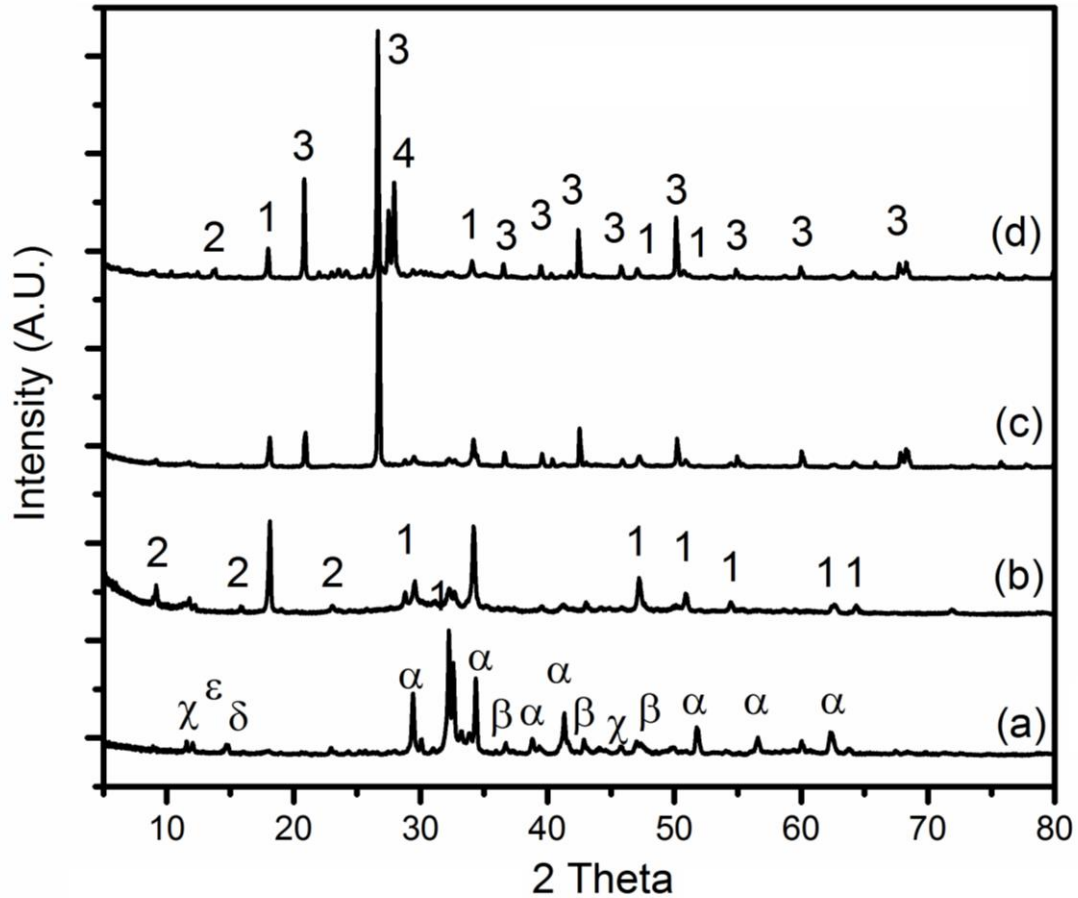
coarse aggregates; on SO₂ adsorption. In order to understand the effect of each component in concrete the samples prepared for these experiments consisted of a) cement and water (C+W) b) cement, water and fine aggregates (C+W+F) and c) cement, water, fine aggregates and coarse aggregates (C+W+F+Cr).

Materials and Methods

Concrete samples were prepared for all experiments according to ASTM specifications (ASTM C150 and C192). All the cement samples were prepared with deionized water according to manufacturer specifications and poured into polycarbonate sample trays. The samples were allowed to cure at 20 °C in 50% RH for 28 days to attain strength. To produce the powder fractions concrete slabs were pulverized and passed through a set of standard sieves. SO₂ in N₂ gas mixture (10 ppm initial concentration) obtained from Praxair Gases was used for the all experiments described in this report.

XRD Analysis

X-Ray Diffraction analysis of the cement constituents as well as 3 cement samples of different composition was conducted in order to evaluate phases formed during hydration and subsequent hardening. The dried samples from the surface layers were ground by micro mill grinder (Scienceware Ltd) to a fine powder (< 63 μm. The powder was packed into a sample holder for examination in a Philips 1710 X-ray diffractometer using monochromatic CuKα radiation operating at a voltage of 50 kV and current of 30 mA. A scanning speed of 2°2θ/min and a step size of 0.01° were used to examine the samples in the range of 5–80°2θ.



- 1) Portlandite (98-020-2228) 2) Ettringite (98-015-5395)
 3) Quartz (98-009-0145) 4) Undefined
 α) Alite (98-016-2744) β) Belite (98-008-1096)
 χ) Ferrite (98-009-8827) δ) Aluminate (98-000-1841)
 ε) Gypsum (98-008-6316)

Figure 1: XRD spectra of Cement and 3 concrete samples showing different phases. The spectra correspond to the samples as follows (a) cement, (b) C+W, (c) C+W+F and (d) C+W+F+Cr; where C is cement, W is water, F is fine aggregate and Cr is coarse aggregate

The Figure 1a showing XRD patterns of cement clinker demonstrate that it is comprised of four major phases: alite, belite, aluminate and ferrite. Cement also contains minor contributions of gypsum and few other calcium sulfates. Once the

cement is hydrated, it forms the C-S-H gel constituting up to 50 to 60% of the overall volume of concrete sample

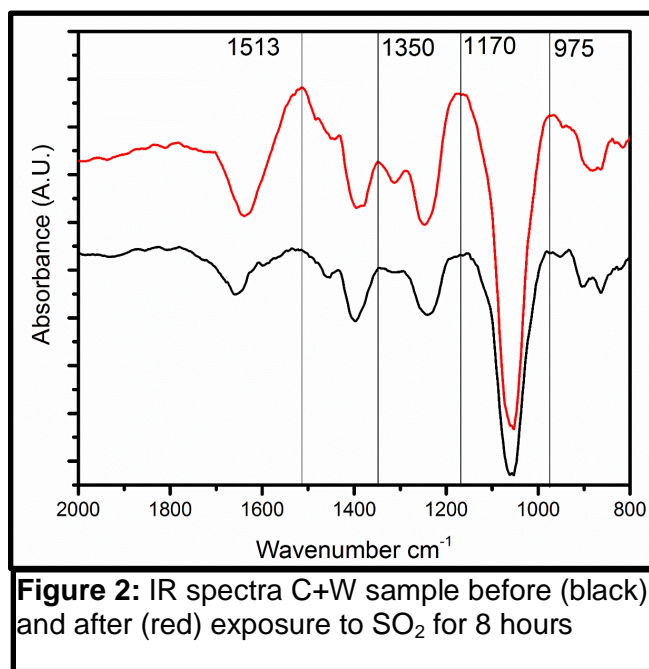
However, the C-S-H phase is very difficult to measure directly due to its amorphous nature and its indeterminate composition. The identification of cement phases present in concrete has additional challenges given poorly crystalline nature of calcium silicate hydrates, which manifest in weak diffraction peaks. These peaks also tend to suffer from interference from very pronounced diffraction peaks originating from such constituents as calcium hydroxide (or from contributions from other minerals).

As only cement and water were used to prepare the first sample show in Figure 1 b, we observe that it mainly constitutes of portlandite and ettringite phases. With further addition of fine aggregates, primarily sand, to the C+W+F and C+W+F+Cr samples we notice the strong diffraction peak at around 27° signifying the quartz phase (Figure 1c, d). Many of the other features in these two spectra are unfortunately overwhelmed by quartz phase contribution, resulting in loss of valuable information. Finally, in the Figure 1d though most phases have been identified there are a few undefined phases which could be attributed to the coarse aggregates present in this sample. These coarse aggregates have an extremely heterogeneous chemistry comprising of a number of minerals and are difficult to accurately identify.

DRIFTS Experiments

Figure 2 shows the DRIFTS spectra of the C+W (cement + water) samples before and after exposure to SO_x for 8 hours. The initial and the final spectra are compared so as to determine the change of surface composition due to SO_2 uptake on the concrete sample in the presence of moisture. IR peaks at 1513, 1425, 1350, 1285, 1150, and 975 cm^{-1} were affected by SO_x exposure, with intensity of the peaks increasing over time. The prominent peak detected at 1170 cm^{-1} in the final spectra shows the highest change in its intensity as compared to

other peaks. According to several studies [15, 16], this band could be assigned to the SO_4^{2-} (sulfate) species. A comparison with the NIST database for calcium sulfate spectra shows the presence of a double peak in this region. Further, the minor peak at 975 cm^{-1} can be ascribed to the SO_3^{2-} (sulfite) species. This is confirmed by both literature data [15, 16]



and NIST spectra for calcium sulfite, which is believed to be the product of SO_2 reacting with the portlandite component in concrete. Another interesting observation is the evolution of the double peak 1500 cm^{-1} . The peak sharpens and intensifies after SO_2 exposure. While it resembles the characteristic peak attributed to sulfite species, albeit slightly blue shifted, unambiguous assignment of this peak to these species is probably

premature. Lastly the broad band at $1400\text{-}1200\text{ cm}^{-1}$ as seen in Figure 2 resolve into two distinct peaks after exposure to SO_2 at 1350 and 1285 cm^{-1} .

Figure 3 represents the IR spectra of the C+W+F (Cement + Water + Fine Aggregate) sample. It is evident that these spectra are more complex than the previous sample. However, many of the characteristic peaks seen earlier are observed here as well. As discussed previously, the peaks at 1165 and 975 cm^{-1}

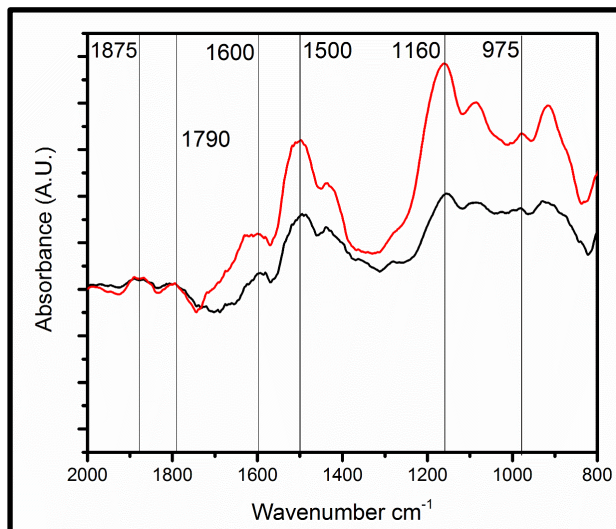


Figure 3: IR spectra C+W+F sample before (black) and after (red) exposure to SO_2 for 8 hours

showing marked changes in intensity can be assigned to sulfate and sulfite species respectively. Moreover, similarly to Figure 2, 1500 cm^{-1} is present as well. Both the intensity and the blue shift seem to again suggest the presence of sulfite species. Finally, three minor peaks at 1875 , 1790 and 1600 can be correlated to addition of fine aggregates and to either formation of intermediate phases or the adsorption of water (O-H bending).

Figure 4 shows the IR spectra of the C+W+F+Cr sample analyzed using the DRIFTS cell. This sample shows similar

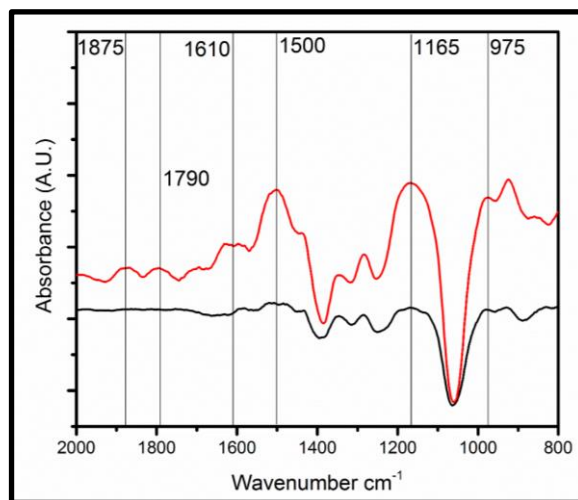
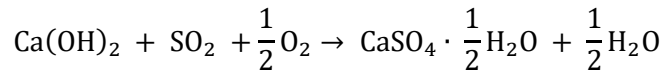
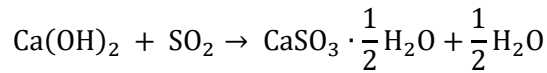


Figure 4: IR spectra C+W+F+Cr sample before (black) and after (red) exposure to SO_2 for 8 hours

features as described in the prior section. Peaks at 1160 and 975 cm^{-1} along the broad band at 1500 cm^{-1} are all present. The increase in the intensity of the sulfite peak at 975 cm^{-1} , however seems to have smaller intensity than that shown in Figure 2 and 3. The two peaks amid 1400-1200 cm^{-1} are also visible although both of them seem to be present even before exposure to SO_2 . This could suggest that the increase in peak intensity might be more due to bonded water molecules rather than to SO_2 adsorption and subsequent reaction.



In general, all samples contained peaks at 1160 and 975 cm^{-1} , which can be assigned to sulfate and sulfite groups. The equations 1 and 2 as shown above represent the possible reaction mechanisms for the formation of sulfate and sulfite groups. There are also differences between the samples, such as in the peak at 1600 cm^{-1} range, where the possible bonded water peaks are observed (hydroxyl groups) for both C+W+F and C+W+F+Cr. In addition, there are two undefined peaks at 1875 and 1790 cm^{-1} , which can be attributed to fine aggregates or unknown phases present in the concrete samples as these were only seen in the C+W+F and C+W+F+Cr samples. In contrast, the C+W sample seems to have a strong negative peak in this region. Lastly, the observed peak at 1500 cm^{-1} was not unidentified and not attributed to the surface species it represents.

Time Resolved DRIFTS Experiments

Figure 5 shows the time resolved DRIFTS spectra of the concrete samples exposed to SO_x . A gradual increase in the sulfate (SO_4^{2-}) peaks was observed and shown in Figure 3 (a), (b) and (c). From the Figure 3 it appears that the C+W+F and C+W+F+Cr samples show stronger intensity of sulfate peaks than that for the C+W sample. However, the peak at 1500 cm^{-1} in the C+W samples has contributions from other peaks, resulting in underestimation of SO_x adsorbance on the C+W sample. Lastly, a more prominent presence of sulfite peaks at 965 and 920 cm^{-1} in the C+W and C+W+F samples (Figure 3 a & b) was seen.

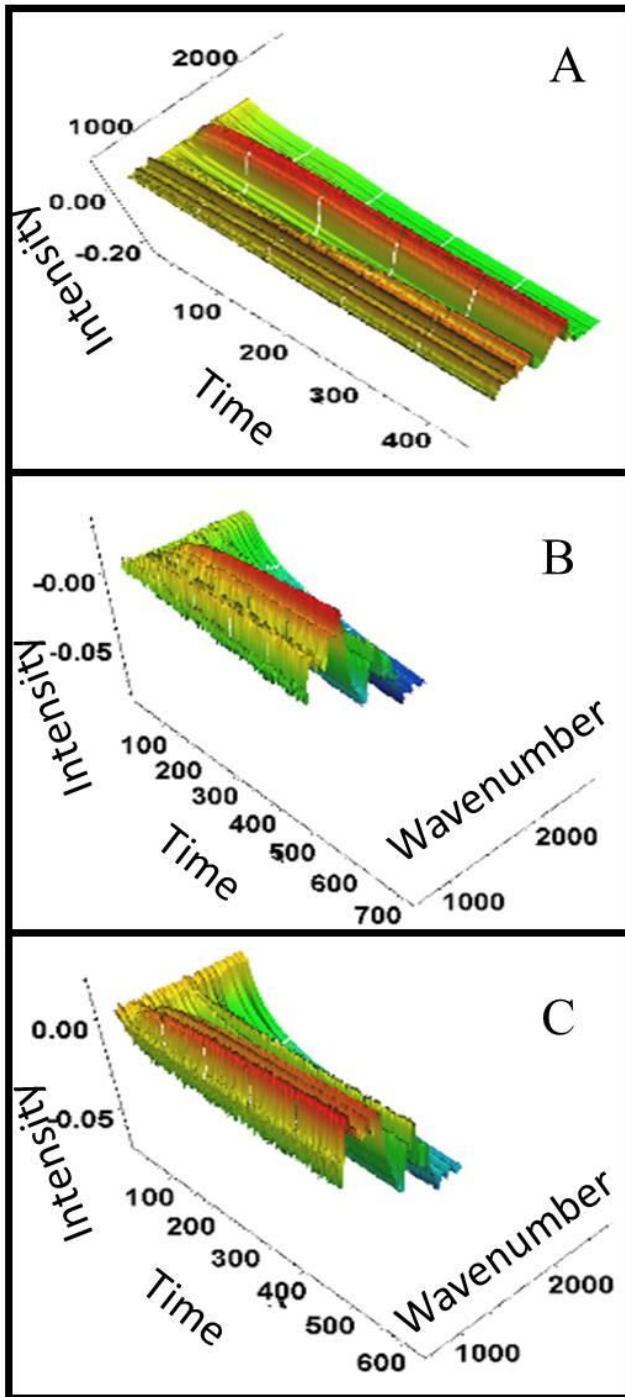


Figure 5: Time resolved IR spectra of concrete after 8 Hrs. of SO_2 exposure showing sulfate and sulfite peaks between 1625 and 1690 cm^{-1} and $\sim 1150\text{ cm}^{-1}$. (A) C+W (B) C+W+F and (C) C+W+F+Cr

XANES Analysis

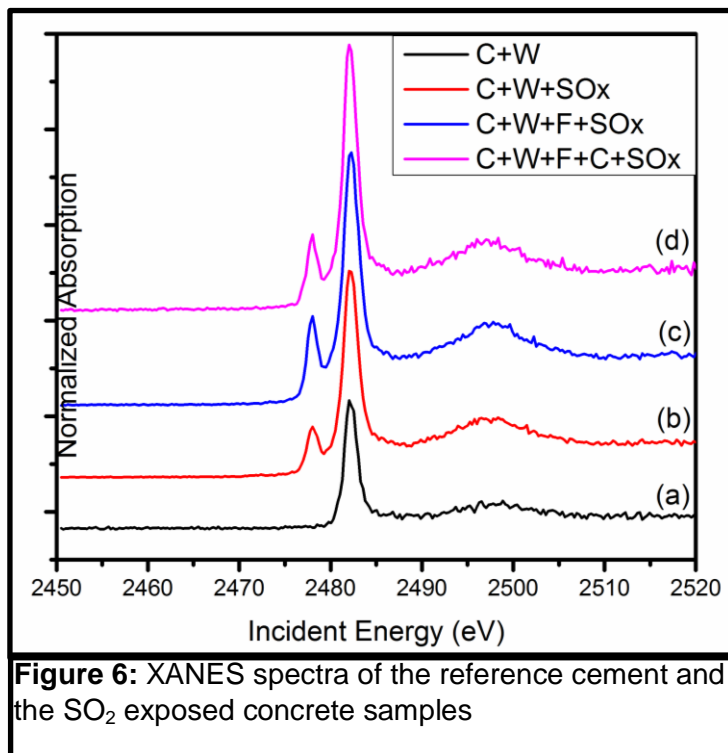
Chemical form and electronic structure of various systems can be determined using the X-ray absorption near edge spectroscopy (XANES). Different materials including asphalt have been analyzed using XANES to study the sulfur speciation [17-20] in these systems. The technique has been recognized as an effective method for characterizing the local environment of sulfur. However, construction materials have not been ordinarily analyzed using the XANES technique owing to their heterogeneous nature [21-23].

Here, the adsorption of SO_x on different concrete samples and its subsequent surface reactions are studied. To corroborate the DRIFTS results of the formation of sulfur species on the surface and to detect changes in the local environment, spatially resolved XANES is utilized. Further, these spectra are compared to the XANES spectrum of unexposed cement and water mixture.

The sulfur K-edge XANES were recorded in the X15B beamline at the National Synchrotron Light Source (NSLS) of Brookhaven National Laboratory. X15B was equipped with a Si(111) monochromator, with an energy resolution of 0.2 eV at the sulfur K-edge. The XANES spectra were acquired in fluorescence mode and the sulfur K-edge fluorescence was isolated from the detector spectrum. The entire sample environment was purged at 1 atm with helium gas. The spectra for both unexposed cement and SO_x exposed concrete samples were collected by scanning incident energy from 2450 to 2526 eV, with a step size of 0.2 eV and an exposing time of 0.1 s for each step. X-ray fluorescence microscopy method was applied for observing heterogeneous

sulfur distribution and selecting several spot positions for XANES measurement. Ten measurements on an identical position were repeated to achieve one averaged XANES spectrum.

The XANES technique has been widely used to characterize sulfur species because it is nondestructive and very sensitive to the electronic structure that allows it to reveal oxidation state and local symmetry of absorbing site [18, 19, 24]. Figure 6 shows the K-edge XANES spectra for the reference concrete and samples exposed to SO_2 for 8 hrs. The XANES spectra



for the concrete samples are dominated by a signal arising from sulfate-type moieties near 2482 eV [25, 26]. This is present in all of the analyzed samples indicating the presence of inherent SO_4^{2-} species in the concrete itself. Further, there is no change in the position of this absorption edge indicating that the oxidation state of elemental sulfur has not changed. However, the increase in the peak intensity on the exposed samples can be interpreted as evidence of formation of surface SO_4^{2-} due to SO_2 adsorption. The appearance of the peak at 2478 eV in the exposed samples can be attributed to the formation of sulfide species SO_3^{2-} [25]. This provides additional support to the observations made earlier in the DRIFTS section.

6. Conclusions and Recommendations

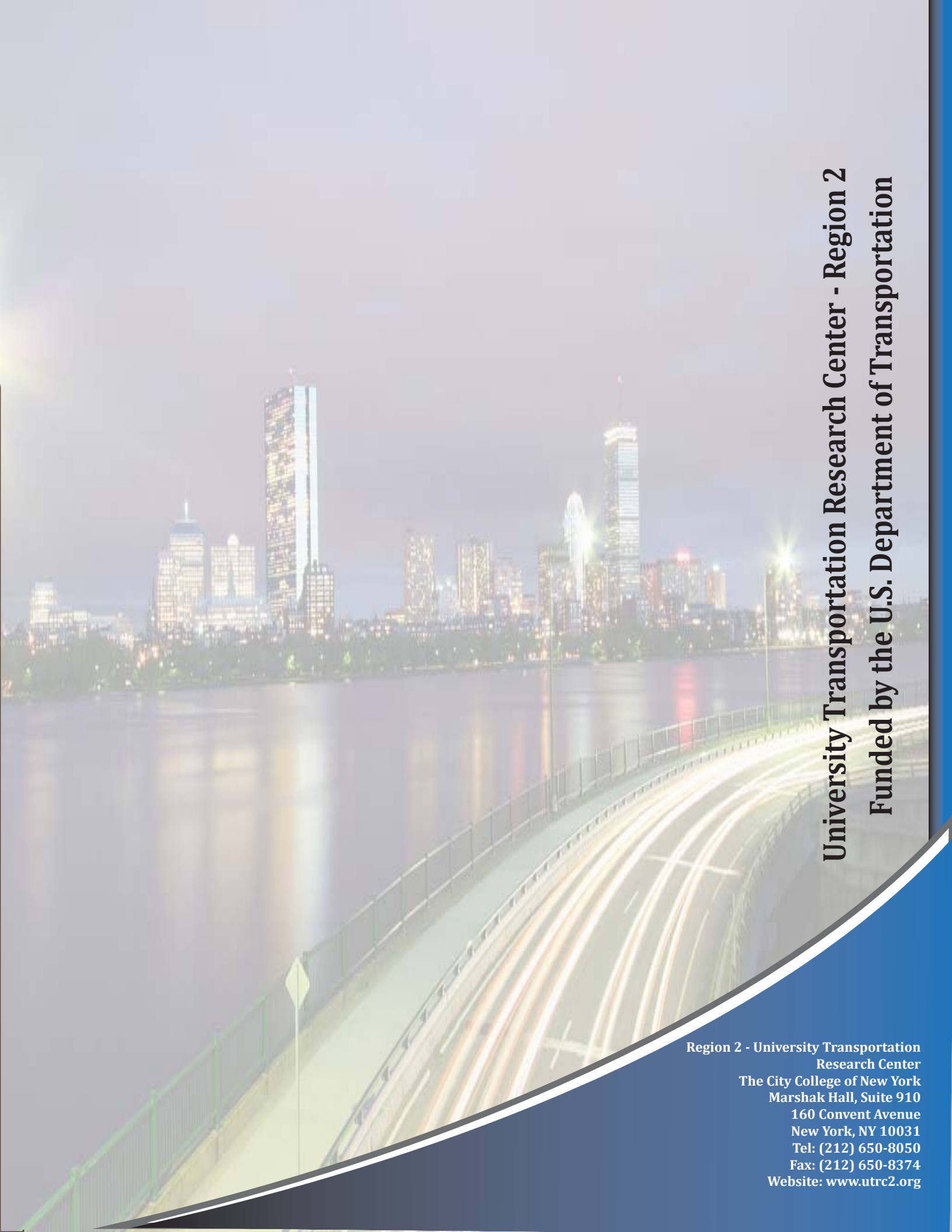
Cement kiln and transportation related emissions contain SO_x and NO_x emission, with both having detrimental effects on health and environment. Our research has demonstrated that using concrete, can remove both NO_x and SO_x emission. It is important to consider the effect of SO_x , as it may compete with NO_x adsorption. The formation of different sulfur species on concrete surfaces was analyzed using several spectroscopic techniques. The data demonstrated that SO_2 adsorbs on the concrete surface and forms sulfate and sulfide. It also indicated that SO_x adsorption occurs at a much faster rate than NO_x . Although our data demonstrate a remarkable potential of waste concrete to be used for environmental mitigation on both kiln and transportation related emissions, a more detailed investigation of combined effects of both pollutants is needed.

7. Implementation and Training

The research results were shared with the listed company (CEMTREX) involved in implementation of air pollution control technologies. One Ph.D. student defended his dissertation focused on waste concrete utilization with help from the UTRC project.

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A long-exposure photograph of a city skyline at night, reflected in a body of water. In the foreground, a bridge or highway is visible with light trails from moving vehicles. The sky is dark, and the city lights are bright and colorful.

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