**ANALYSIS OF STAINING OBSERVED ON
STRUCTURES IN THE GEORGETOWN,
SOUTH CAROLINA AREA**

Final Report

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Analysis of Staining Observed on Structures in the Georgetown, South Carolina, Area

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Problem: Beginning around 1970, the Georgetown SC community complained about black dust and red stains collecting on houses, cars, boats, and other structures. The community, through the South Carolina Department of Health and Environmental Control (SCDHEC), seeks to identify the source or cause of the staining and ways to reduce or eliminate it in the future.

Background

Georgetown, SC, is a small historical city situated on Winyah Bay on the SC coast. International Paper (IP) built a Kraft paper mill southwest of and adjacent to the downtown area in the early 1900's. This mill operated with little complaint from the community regarding environmental emissions. Georgetown Steel Corporation (GSC) built a steel mill south of and adjacent to the downtown area in 1969. GSC added a direct reduced iron (DRI) facility to the steel mill site in 1971. The Santee Cooper – Winyah Station (SCWS) is a coal-fired electric generating facility 5-7 miles southwest of Georgetown. An aerial view of the area showing the location of these facilities is shown in Figure 1.

Complaints of black dust and red staining of homes, Figure 2, and other structures in the downtown area began around the time the GSC steel mill site was developed. Complaints about red staining have continued over the years, although there is a perception that conditions that may lead to red staining have improved.

SCDHEC maintains environmental monitoring sites at the Howard High (Adult Center) and Winyah in the downtown area, Figure 2. An estimate of the downtown area most affected by red staining is shown by the map in Figure 3.

Environmental Chemistry

The Georgetown, SC, area is a part of the eastern seaboard that is generally affected by low pH precipitation, often referred to as "acid rain," resulting in part from acidic gases (sulfur dioxide and nitrogen oxides) absorbed by moisture in the atmosphere. Ideally, precipitation pH in an unpolluted environment would be about 5.6 as the result of ambient carbon dioxide dissolved in the moisture.

Precipitation pH over much of the eastern seaboard on an annual average basis is well below the ideal of pH 5.6, e.g., pH values from 3.6 to 5. The precipitation pH in individual storms may be even lower, particularly at the beginning when acid gases are scrubbed from the atmosphere. This may be important to conditions in Georgetown because poorly soluble minerals such as iron oxides are more readily dissolved in lower pH water. Low pH precipitation impacting the surface of buildings and other structures is often defined by atmospheric chemists as wet deposition (of acidic species), Figure 4.

Another component of atmospheric chemistry impacting surfaces is dry deposition (of acidic species), Figure 4. It may also be important to conditions in Georgetown. Dry deposition involves acidic gases depositing directly on surfaces, in dew and other thin layers of water present at high relative humidity, without the aid of bulk water such as precipitation. Instead, dew and surface moisture are sufficient to retain the acidic gases on the surface and create a layer of low pH acidic moisture, which can also dissolve poorly soluble minerals such as iron oxides.

These conditions allow the more soluble components of the mineral to dissolve and wash away in precipitation draining from the surface, i.e., runoff, Figure 4. The poorly soluble minerals carried away in runoff may not be removed entirely from structures. Instead, they may re-precipitate on structures at locations somewhat displaced from their origin. This is most likely to happen when the volumes of moisture in the runoff are small and evaporation and other factors can aid the precipitation. Staining will be apparent if the mineral has color in contrast to that of the underlying surface.

Regional Environmental Chemistry: Spence et al. (*Spence 1992*) reported 1982-1988 annual average environmental measurements for North Carolina (Research Triangle Park, NC, area) in a study of the effect of wet and dry deposition on the atmospheric corrosion of galvanized steel. The precipitation rate was 100.3 cm/y, pH 4.4, and sulfur dioxide gas concentration $6.3 \mu\text{g}/\text{m}^3$. Cramer et al. (*Cramer 1993*; *Cramer 2000*) reported ambient levels of nitric acid gas at background sites on the east coast around $3 \mu\text{g}/\text{m}^3$, with higher levels expected at urban sites.

Georgetown Environmental Chemistry: SCDHEC sulfur dioxide readings in the Georgetown area rarely are above baseline, i.e., $0 \mu\text{g}/\text{m}^3$ (0 ppb). Values of 2.7 to $5.5 \mu\text{g}/\text{m}^3$ (1 to 2 ppb) are occasionally measured in the area of staining, Figure 1. Approximately 7 months of data from Georgetown shows precipitation pH ranging from 4.0 to 5.7.

Figure 5 shows the annual wind rosette for 2001. Seasonal wind rosettes for 2001 show that winds during spring tended to come from the west and west southwest, while in the late fall and early winter they also tended to come from the north east. With these exceptions, winds tended to come equally from the remaining directions of the rosette. This would suggest a bulls-eye pattern for staining factors if: (1) they originate at a point source, (2) are dispersed by winds, and (3) are subject to gravitational settling (mineral particulates) rather than broader regional distribution as with gases. The bulls-eye might

be distorted somewhat to the east, to the east northeast, and to the southwest by the prevailing winds if, in fact, this level of detail can be discerned from the ground.

SCDHEC Monitoring for Staining

SCDHEC maintains the two monitoring sites shown in Figure 1 in the Georgetown area, Howard High and Winyah. Another site is maintained at Parklane in Columbia, SC, as a background site since it is well beyond the influence of the Georgetown environment. However, it should be noted that the authors do not think the Parklane site qualifies as a background site for staining since it is located within 200 m of a railroad track and there is the possibility iron minerals can be deposited on sample surfaces as the result of rail traffic.

The Alabama Department of Environmental Management (ADEM) maintains a monitoring site at Mobile, AL, i.e., the CC Williams Treatment Center, similar to the SCDHEC sites, to examine staining caused by the adjacent McDuffie Island DRI facility.

Samples analyzed: Selected samples were analyzed from the above sites. These included the following.

High-vol filter samples. These particulate samples were all from the Howard High site. A series of samples collected over the period 1971 to 2000 were analyzed by energy dispersive X-ray fluorescence (XRF) to determine elemental composition and by X-ray diffraction (XRD) to determine mineral composition. The samples were collected by SCDHEC on glass fiber filters.

DRI powder samples. These were obtained from GSC. They were examined by energy dispersive X-ray fluorescence to determine their elemental composition and determine whether their was sufficient information to use composition to “fingerprint” iron and iron oxide particulate samples.

Vinyl siding samples. These were from the Bi-State Study and from Four Week Exposures. The samples were cut from commercial white vinyl siding and exposed horizontally for varying times at the test sites. They were examined by energy dispersive X-ray fluorescence to determine elemental composition of material deposited on the siding surface and by X-ray photoelectron spectroscopy (XPS) (a more surface sensitive technique) to also determine the elemental composition of the material deposited on the siding surface.

Analytical Results

Hi-vol filter samples: The use of glass fiber filters made XRF and XRD more difficult because the background signal was large compared to the peaks that were analyzed. The XRF sample spectra were corrected by subtracting the spectra for blank filters from the original spectra for the filter samples. This procedure helped to emphasize peaks related

to the particulate material collected on the filters. In addition, iron-based minerals almost always yield weak XRD patterns because of interaction of the element Fe with the Cu X-ray tube characteristic radiation by absorbing the radiation rather than reflecting it. As a result the detectability of the iron-based minerals is an order in magnitude less than for most of the other phases identified in the samples.

XRF results. These are shown in Table 1 where the sample and filter numbers are identified along with the collection date and the size of the particulate sample collected on the filter. The analyses of the filter samples are given in weight percent. Owing to the nature of the analytical technique employed (standardless energy dispersive x-ray fluorescence), and the fact that the background peaks from the filter material itself were quite large, the results should not be regarded as quantitative. Rather, they provide a semi-quantitative picture of the relative amounts of the various elements present on the filter. Note also that the elements are reported as oxide compounds, an assumption inherent in the XRF technique and method of data reduction. The elements may actually be present in other forms. Reporting the elemental content of samples as oxides is a common analytical convention. However, we should be clear that the reporting of Cl_2O is actually a way of indicating the **chloride ion** content of the filter samples.

Table 1. X-ray fluorescence analysis of Howard High Hi-vol filter samples

Sample #	Filter #	Filter sample collection date	Total filter sample collected, mg	Filter sample analysis, weight pct				
				SO_3	Fe_2O_3	BaO	CaO	Cl_2O
N/A	6473	10/26/71	120	71.8	8.6	10.6		
N/A	1056859	10/15/75	252	81.1	3.8	2.2	12.4	
6891	138768	10/18/80	148	36.9	30.6		19.6	11.9
4828	2291061	10/14/82	62	88.1	11.3			
44213	4194589	10/15/84	166	48.1	4.2		40.5	6.9
65784	3122056	10/17/86	136	67.1	6.8		24.9	
86467	8039409	10/18/88	223	37.8	6.3		47.3	6.7
17018	81544	10/15/91	156	54.2	15.8		10.7	11.5
936188	8238093	10/16/93	52	29.6	38.4		16.5	12.0
956432	5049291	10/24/95	88	28.1	16.0		8.7	14.3
974852	6760743	10/13/97	89	28.4	39.1	14.3		15.6
996288	6008120	10/15/99	66	34.2	14.5	30.2		21.1
7102	21230	10/15/00	70	62.5	11.2	23.3		
7524	21233	11/2/00	136	53.7	17.1	18.0	9.6	

These results show high levels of sulfur compounds in the particulate samples over the entire monitoring period. This sulfur is related to long-distance transport of sulfur compounds such as aerosols of ammonium sulfate, and long-distance transport and local point sources of sulfur dioxide and other sulfur compounds such as gypsum. Their presence suggests favorable conditions probably exist in the Georgetown area for

reaction of acidic sulfur gases with basic mineral oxides to form neutral salts such as sulfates and sulfides.

The results also show iron and iron compounds are present in the particulate sample over the entire monitoring period. Other minerals are present in the particulate samples on a less regular basis, including calcium minerals and chlorides such as marine salt.

XRD results. XRD identified quartz, gypsum, calcite, and salt (NaCl) as primary phases on a regular basis. These would all appear to be of local origin, related to local industry and the coastal location of Georgetown. The quartz is an indicator of dust or dirt collected in the filter sample. On one occasion magnetite (Fe₃O₄) was also identified in a significant amount. General absence of iron-base minerals in the XRD analyses is related to the high background from the glass fiber filter material and the reduced sensitivity (or detectability) of iron-base minerals by XRD.

DRI powder samples: The MIDREX DRI process involves the following reactions:

where the iron oxide is Fe₂O₃ and Fe₃O₄. For reactions 1 and 2 to produce a product with high iron content, the ore must be finely powdered and the DRI iron product will also be finely powdered, as was observed in the samples available. This would suggest particle size distribution both in the ore and the DRI product should be considered in evaluating the potential for the fines to be dispersed into the local environment. SCDHEC has observed rust spots on vinyl plates exposed to the Georgetown environment ranging in size from 4.4 to 300 µm in size.

The results of XRF analysis of the powder are shown in Table 2. There is nothing in these results that would suggest DRI powder analysis could be used to fingerprint and

Table 2. X-ray fluorescence analysis of DRI powder samples

Element	Concentration in sample, weight pct.	
	GSC DRI 01-26-82	GSC DRI 01-26-84
Fe	87.3	91.1
Al	3.3	2.8
Si	6.1	3.3
Ca	2.8	2.3
Mn	0.4	0.4
Cu	0.1	0.1

identify particulates collected in the local environment.

The results show a reasonably well reduced ore containing roughly 10 percent other metallic elements that, except for the copper, would not be unexpected in High-Vol

particulate samples. Copper was one of the minor elements found by XRF in the High-Vol particulate samples. However, copper was not present in every sample from the Howard High site. Copper would have to be present in samples from the Howard High and Winyah sites, Figures 1 and 2, while absent from a background site to begin to establish a link between particulate samples and the DRI facility.

Vinyl siding samples: Red stains were observed on each of the samples recovered from the Howard High, Winyah, and Mobile sites. No staining was observed on the blank or the sample recovered from the Parklane background site.

XRF results. The XRF results are given in Table 3 for samples from the Bi-State Study and the Four Week Exposures. Qualitative results are given, with a ranking of very strong, strong, moderate, weak, trace or none given based on the strength of the characteristic X-ray peak relative to different samples and relative to the iron peak. The Cl and Ti peaks are related, at least in part, to the vinyl substrate surface. Chloride is an integral part of the PVC siding material. It could also be present as salt deposited on the siding as marine salts. The titanium is probably a component of the pigment. The calcium peak may be associated with soiling (from dirt or dust) of the vinyl sample surface.

Table 3. X-ray fluorescence analysis of vinyl panels from the Bi-State Study and the Four Week Exposures.

Site	Sample number	Date exposed	Days exposed	Relative concentration			
				Fe	Cl	Ti	Ca
Parklane	007825		61	trace	moderate	weak	trace
“	011452	2-2-01	30	none	weak	trace	trace
“	012185	3-2-01	28	none	moderate	weak	trace
Howard High	011549	2-2-01	30	moderate	strong	weak	trace
“	012202	3-2-01	28	weak	weak	trace	trace
Winyah	008085		66	strong	trace	trace	trace
“	011538	2-2-01	30	moderate	trace	trace	trace
“	012195	3-2-01	28	weak	trace	trace	trace
Mobile	008604		63	very strong	trace	weak	trace
“	011785	2-2-01	30	weak	strong	weak	trace
“	012623	3-2-01	28	trace	moderate	weak	trace

The results show that only a trace of iron was observed at the Parklane background site (noting the authors objection to this as a background site) in the 61 day exposure and no iron observed in shorter exposures. They show trace to very strong peaks for samples recovered from the sites neighboring the GSC facility. By comparison with the Parklane results, this would suggest that the observed iron is not a constituent of iron rich dusts or particulates. Rather, it is characteristic of the sample site proximity to the steel facility and, in the case of the Mobile site, to the DRI facility.

XPS results. The XPS results are given in Table 4. Considerable information is contained in this table related to possible compounds present on the vinyl sample surface. But the key fact is that no iron was observed on the blank surface nor the sample recovered from the Parklane background site. In contrast to this, iron was present on the surface of each of the samples recovered from sites near steel making facilities. The sample from Mobile was analyzed “as-received” and then wiped to removed particulates from the stained surface. While there is evidence that some material was removed from the surface, there was still substantial iron retained on the surface in the red stains remaining on the sample.

**X-ray photoelectron spectroscopy analysis of vinyl panels from the
Bi-State study plus a Howard High panel.¹**

XPS peak	B.E. eV	Vinyl panel surface analysis, atomic pct.					
		Blank	Parklane (007825)	Howard High (011549)	Winyah (008085)	Mobile as-received (008604)	Mobile wiped (008604)
Fe 2p1	711.6			0.8	2.9	3.3	2.5
Cl 2p	200.0	6.7	6.4	3.4	3.4	1.6	6.8
Cl 2p	201.7	2.2	3.0	0.5		0.5	1.9
O 1s	532.0	12.7	24.9	34.4	40.4	42.5	33.3
C 1s	284.8	65.4	30.5	43.4	37.8	29.3	30.6
C 1s	286.6	7.2	25.6	2.7		14.6	13.5
C 1s	288.5	2.5	1.7	2.7	4.9		4.4
S 2p	168.4			1.4		0.7	
N 1s	400.3					4.6	1.6
P 2p	134.2					3.0	1.8
Si 2p	102.6	1.8	5.5	8.8	6.2		2.0
Al 2p	74.5		2.4		3.6		1.5
Ca 2p	347.8	0.8		0.8	0.5		
Ca 2p	351.7	0.5		0.5	0.3		
Na 2p3	1071.9			0.5			

¹ panel numbers are given in parentheses.

As a point of information, XPS is a technique that is sensitive to approximately the top 4 to 8 layers of atoms on the sample surface. Since all surfaces are covered with adsorbed molecules from the environment, such as hydrocarbons, water, and carbon dioxide, the signals from the elements carbon and oxygen predominate in the XPS spectra (hydrogen is not detectable by XPS), and the reported values for carbon and oxygen are high. If the adsorbed molecules were absent, the values for the element iron, as well as the other elements would be much higher than reported in Table 4.

The absence of iron from the Parklane site sample agrees with the X-ray fluorescence results and indicates that iron in the stain is not originating in the general environment but has a specific source. The absence of Ti from all samples indicates the XPS results are

based only on material deposited on the sample and do not include components of the PVC siding material.

The staining mechanism

The mechanism for staining as seen in Georgetown is a complicated one involving not only iron-rich particulates but chemicals such as moisture and acidic gases that can react with and modify the particulates.

Where do the iron-rich particulates come from? There is no direct evidence that iron-rich particulates staining surrounding homes and structures originate at the GSC facility in Georgetown, or at the DRI facility in Mobile. No fingerprint or tag was evident in the analysis of the DRI powders or the rust stained vinyl surfaces that traces these particulates from their source to their destination.

However, analysis of the stained vinyl samples indicates the staining is due to the presence of iron minerals on the sample surface. Furthermore, results from the background site suggest these iron minerals do not originate in dusts from the local soils or general environment. The ground survey of the area most heavily affected by staining centers around the GSC facility, Figure 3, as it should if iron-rich particulates from the facility, such as fines from the DRI plant or another part of the facility, were dispersed into neighboring areas. Calculations based on particulate size and density can be used to model the gravitational settling rate for these particulates and, combined with local meteorological data such as the wind rosettes in Figure 5, estimate the area that would be impacted by the particulates. This was not done here as it is outside the scope of this report. However, it is reasonable to assume that larger sized particulates from the GSC facility would settle in its immediate vicinity.

What else is needed to cause staining? Iron-rich particulates alone are insufficient to cause staining of the Georgetown homes and structures. If the particulates are DRI, then moisture is required to cause them to rust (an oxidation process) and produce the ferric ions that cause staining. If the particulates are iron oxides, then moisture will dissolve iron-rich phases of the mineral (not an oxidation process unless magnetite is involved) to release the ferric ions that stain a surface.

Figure 6 shows a solubility diagram for ferric oxide, Fe_2O_3 , and ferric hydroxide, $\text{Fe}(\text{OH})_3$, in water as a function of pH (*Bullard 2002*). The data points are the concentration of ferric ion in precipitation collected from rusted mild steel surfaces exposed to atmospheric weathering on the Oregon coast. The curves for the two minerals and the data points suggest the soluble phase released from the surface was ferric hydroxide, a non-protective component of rust and one that is first formed on rusting before weathering produces the less soluble ferric oxide. The figure indicates that the solubility of ferric oxide and hydroxide will increase as the solution pH decreases. The scale of Figure 5 is logarithmic and the solubility may increase by an two orders-of-magnitude as the precipitation pH decreases from 5.6 (the pH in an unpolluted

environment) to pH 4.4 (a value that is found in Georgetown) as a consequence of the effects of acidic gases.

Heavy rains wash a surface and sweep soluble materials from it. On the other hand, light rain, mist, dew, and moisture deposited on surfaces near the dew point from humid air have a longer residence time on the surface. They can dissolve soluble components from iron-rich particulates without sweeping the resulting ferric ion from the surface. Instead the ferric ion may move down a vertical surface, such as the siding on a home or other structure, and then precipitate at a lower location as a consequence of evaporation or an increase in pH caused by basic particulates such as calcium-rich soils or dusts on the surface. This is evident in Figure 2 where the stain forms on the drip line of successively lower siding panels. Here the stain concentrates as repeated iron-rich solutions collect, then dry out, and then weather into less soluble ferric oxide.

The Georgetown area has a source of iron-rich particulates, Georgetown Steel Corporation. There are local sources for acidic gases such as the Kraft paper mill and the coal-fired electric generating facility. The area is affected by regional transport of acidic gases and low-pH precipitation. Each of these is a factor in the staining of the homes and structures in Georgetown.

Which of these factors is necessary for staining to occur? The local sources of acidic gases could be eliminated and staining would continue to occur, only at a slower rate as suggested by the solubility curves in Figure 6. The regional environment could be cleaned up and returned to a pollution-free state with precipitation pH at around 5.6 and staining would continue to occur, only at a slower rate.

Furthermore, the source of iron-rich particulates could be eliminated and staining would continue. The reason: very little ferric ion is needed to stain a surface. In addition, ferric ion is relatively insoluble and not easily washed from a surface once it is in place. Under natural conditions it would take a very long time for the ferric compounds responsible for staining to flush from stained siding.

Of the three contributors to the staining problem (iron-rich particulates, moisture, and acidic gases and precipitation), elimination of the iron-rich particulates is the only one that will eliminate the problem (if the presently stained structures are then properly cleaned or repainted).

Depending on point of view the staining process is complicated or simple. It is complicated because it involves atmospheric chemistry and the complex chemistry of iron compounds. It also **may** involve oxidation processes. It is simple because it can be eliminated in only one way, by the elimination of the iron-rich particulates.

Are there differences between the red stain found at the SCDHEC and ADEM sites? There are no significant differences. The key is significant. There are local and seasonal variations in atmospheric chemistry and meteorology that might affect their chemistry;

but not in a significant way. They are the natural consequence of the interaction of iron-rich particulates and moisture, enhanced possibly by the effects of acidic gases.

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Figure 1. Aerial view of the Georgetown, SC, area showing the location of industrial facilities and SCDHEC monitoring sites.

Figure 2. William Doyle House on Prince Street in Georgetown, SC, showing staining of vinyl siding October 2000.

Figure 3. Map showing Georgetown, SC, area most heavily affected by staining.

Figure 4. Precipitation runoff from a corrosion film (for example, rust on a steel surface) showing contributions from wet and dry deposition, where the metal ion M is Fe.

Figure 5. Wind rosette for Georgetown, SC, for 2001.

Figure 6. Solubility of iron oxides in water at ambient temperature ($\sim 72^\circ \text{F}$), with data points for precipitation draining from mild steel panels collected at two coastal sites in Oregon.