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Mr. Karl Everett O-N Minerals (Chemstone) Operations 1696 Oranda Road Strasburg, Virginia 22657

Re: Information regarding particle size distributions and condensable PM speciation Air Control Techniques, P.C. file 1215

Dear Karl,

Air Control Techniques, P.C. has evaluated the technical procedures prepared by Mr. Don Sheperd of the National Park Service ("NPS") to estimate the particulate matter size and speciation characteristics of emissions from the Calcimatic and Rotary Kilns at the Strasburg, Virginia plant. These particulate matter characteristics calculated based on the data used by NPS are to be part of the input data set to a CALPUFF model to evaluate the visibility impact of the emissions in Class 1 areas. Based on our evaluation of the available data, Air Control Techniques, P.C. has recommended two changes in the NPS calculation approach. These changes are necessary, among other reasons, to ensure that the emission calculations are not biased by the well recognized flaws in the condensable particulate matter test method that were in use in the early 1970s when all of the data cited in AP42 Section 11.17 applicable to condensable particulate matter emissions were obtained.

I believe that the revised NPS emission estimation procedures are more accurate and representative of actual emissions from lime kilns. Accordingly, this revised NPS calculation approach should be supplied to Virginia Department of Environmental Quality ("DEQ") for use in the CALPUFF modeling to be conducted by DEQ.

An electronic copy of the revised NPS spreadsheets for rotary lime kilns equipped with fabric filters and calcimatic lime kilns equipped with venturi scrubbers is attached to this letter. Changes to the NPS spreadsheet are clearly marked to indicate the improvements to the emission calculation approach.

1. Background

Air Control Techniques, P.C. agrees with Mr. Sheperd that there are very little data available to evaluate the particulate matter emission characteristics from lime kilns. Essentially all of the condensable particulate matter information available was obtained prior to 1977 using sampling and analytical procedures that (1) were never developed or intended for use on sources with sulfur dioxide, (2) were rejected by the newly formed U.S. Environmental Protection Agency in 1971 for inclusion in the Group 1 Standards or Performance for New Sources ("NSPS"), and (3) were not included in Method 202, the method developed in 1991 for condensable particulate matter.

NPS has based condensable particulate estimation procedures on U.S. EPA AP42, Section 11.17, References 8, 20, 21, 22, 23, 33, and 34 (listed in footnotes "m" and "x" in Table 11.17-2). All seven of these references involve tests conducted between 1974 and 1977.

Air Control Techniques, P.C. has reviewed the emission test reports that were cited as the sources of the test data and identified major technical flaws in the test data and in the emission factors compiled based on the test data. This letter provides (1) a summary of the flaws with the AP42 emission factors cited, (2) a summary of the biases associated with condensable particulate matter testing in sulfur dioxide-containing gas streams, and (3) a recommended modified NPS calculation procedures based on other, more reliable and more direct AP42 emissions data. At the conclusion of this letter, I have also discussed the limited information concerning the size distributions of filterable particulate matter emissions from lime kilns.

2. Technical Deficiencies of AP42 Section 11.17 Condensable PM Emission Factors

2.1 Condensable PM Emissions Data, References 8, 20, 21, 22, 23, and 33

These references were cited by EPA in Section 11.17 as the support for the condensable particulate matter emission factor of 0.38 pounds per ton of lime. A technical review of these references demonstrates that there is no adequate support for this emission factor.

Reference 8 did not concern a lime kiln. Instead, these tests concerned a set of baghouses serving raw material screens and crushers at a stone crushing plant. In the Background Support Document for AP42 Section 11.17 EPA states the following regarding the condensable particulate matter data:

"Although back half PM catches are reported in the results, these processes operate at ambient temperature and should not emit condensable PM. Therefore, it is assumed that the back half catches are the result of an anomaly in the sampling and analytical procedures used. The test report does not include adequate information to determine the origin of this apparent anomaly." EPA, 11.17 Background Support Document Section 4.2.1.2

This report should not have been included in AP42 Section 11.17. Furthermore, the condensable particulate matter data are clearly in error because it is not possible to have condensable particulate matter at ambient temperature.

Reference 20 concerned a coal-fired rotary kiln and a hydrator. The specific procedures used to measure condensable particulate matter are not discussed. However, the method appears to be similar to the method published in 1967 to measure condensable particulate matter from Federal facility waste incinerators. The condensable particulate matter data are highly suspect in that the "back half" catch weights during the tests of the hydrator averaged 35 milligrams while the "back half" catch weights for the kiln average only 27.3 milligrams per run. There is no obvious source of condensable particulate matter from a lime hydrator. Accordingly, all of the condensable data reported in Reference 20 appears to be based on test method error.

References 21, 22, and 23 concern filterable and condensable particulate matter tests at an unnamed set of lime plants. It is inappropriate to base emission factors based on "anonymous"

sources that are not described in sufficient detail. In all three cases, the test reports clearly indicate that the testing contractors used silicone grease to seal the glass joints of the impingers. The dissolution of even a small fraction of the silicone grease can significantly bias the condensable particulate matter test results. Accordingly, the use of silicone grease in sampling trains used for condensable particulate matter testing has been strongly discouraged for many years. These test reports do not provide valid condensable particulate matter data and should not be used as a basis for a condensable particulate matter emission factor.

Reference 33 concerns filterable and condensable particulate matter tests at a rotary lime kiln. The EPA testing contractor tested only two of the four stacks and assumed that emissions in the other two stacks were similar. This report does not provide sufficient detail to determine the condensable particulate matter testing and analytical procedures used. The condensable particulate matter emission rates (0.069 lb/ton) are well below the 0.38 pounds per ton emission factor listed in EPA AP42 Section 11.17.

In addition to the very significant problems discussed above, all of the references cited in AP42 Section 11.17 that provide condensable particulate matter data appear to be based on a 1967 U.S. Public Health Service procedure for evaluating condensable particulate matter emissions from waste incinerators at federal facilities. Due to the inherently low sulfur dioxide concentrations in incinerator effluent gas streams, this method did not need to be designed to address the chemical reactions of sulfur dioxide that absorbs in the impinger solutions.

In combustion gas streams having moderate-to-high sulfur dioxide levels, dissolution of sulfur dioxide is favored by (1) the undiluted, high concentrations of sulfur dioxide in the sample gas streams that maximizes mass transfer driving force, (2) the very cold impinger solutions that maximizes absorption, and (3) the extremely efficient gas-liquid contact in the impingers. These conditions are not representative of the mass transfer conditions that exist in plumes or in the ambient air. Once in solution in the sampling train impingers, the dissolved sulfur dioxide gas reacts rapidly to form sulfate compounds that were inadvertently counted as condensable particulate matter. These condensable particulate matter test method errors are discussed in more detail in a subsequent section of this letter.

For these reasons, the late 1970s based emission factor of 0.38 pounds condensable particulate matter (100% sulfate material) used in the NPS calculation spreadsheet is not technically valid or supported by the data cited in AP42. This emission factor appears to be substantially biased by (1) the probable use of silicone grease in the sampling trains involved in most of the tests and (2) the well recognized conversion of gaseous sulfur dioxide to sulfate condensable particulate matter in the impinger solutions of the sampling trains.

2.2 Organic/Inorganic Condensable PM, Reference 34

The ratio between organic and total condensable particulate matter used in the NPS spreadsheet were based entirely on AP42 Section 11.17 Reference 34. This reference was subject to some of the issues discussed above. However, there are some additional problems relating specifically to this ratio derived by NPS based on this one reference.

A summary of the raw test data relevant to condensable particulate matter emissions is provided in Table 1. The condensable particulate matter data shown in this Table were re-calculated by

Air Control Techniques, P.C. based on the raw test data provided in the test report. These data clearly demonstrate that (1) the organic fraction of the total condensable particulate matter were less than the value stated in AP42 and (2) the test conditions described in Reference 34 were extremely non-representative of lime kilns.

Table 1. AP42 Section 11.17 Reference 34 Raw Data								
Parameter	Stack 1	Stack 2	Stack 3	Stack 4	Stack 5	Stack 6		
Total Condensable PM Catch, milligrams	162.3	202.8	235.4	156	164.2	240.4		
Volume metered, DSCF	181.6	162.7	163.91	161.0	161.5	155.3		
Stack Flow Rate, DSC per hour	1,427,802	1,344,402	1,389,731	1,274,832	1,492,680	1,389,359		
Stack Flow Rate, DSCFM	23,797	22,407	23,168	21,247	24,878	23,155		
Stack Gas Oxygen, % volume	19.5	19.5	16.5	16.5	16.5	16.5		
Stack Gas Carbon Dioxide, % volume	6.8	6.8	7.0	7.0	7.0	7.0		
Stack Gas Moisture, % volume	6.5	4.8	6.3	7.5	7.4	6.3		
SO2 Concentration, ppm	80.9	77.4	106	90.7	100	94.8		
Total Condensable PM, lb/ton lime	0.893	1.173	1.368	0.847	1.051	1.490		
Condensable Organic PM Fraction	0.026	0.017	0.014	0.028	0.037	0.022		
Condensable Inorganic PM Fraction	0.974	0.983	0.986	0.972	0.963	0.978		

When the condensable particulate matter emissions calculated from the raw test data are summed for all six compartments, the total emission rate is equivalent to 1.14 pounds per ton of lime produced. This is similar to the 1.15 pounds per ton of lime emission factor value shown in AP42, Section 11.17, Table 11.17-2.

The organic condensable emission factor of 0.15 pounds per ton of lime produced listed in Table 11.17-2 is <u>not</u> consistent with the test data provided in Reference 34. As indicated in Table 1 of this letter, the organic fraction of the condensable material averaged 2.4% for the tests. This is well below the 12% value implied by the AP42 emission factors and used in the NPS calculations.

A review of the Background Support Document with respect to the Reference 34 test data indicates that there is no basis for the value listed in AP42. The organic fraction of condensable particulate matter measured in this test program was 2.4%.

There are a number of other deficiencies in the test program that affect the accuracy and representativeness of the Reference 34 test results. Only one test run was conducted on each of the stacks rather than the set of three runs on each stack required by Method 5. The filter temperatures were often outside of the required range of 248±25°F. The measured oxygen concentrations were in the unusual range of 16.5% to 19.5%. The use of a thirteen-foot stainless steel probe provided a reactive surface for catalytic reactions that could have contributed to the formation of artifact inorganic condensable particulate matter. Also, there are no indications that leak checks were conducted at the conclusion of the test runs. These data do not meet basic quality assurance standards.

2.3 Summary, AP42 Condensable Particulate Matter References

All of the references cited in AP42 with respect to condensable particulate matter are subject to significant error due to major flaws with the condensable particulate matter test method discussed in more detail in Section 3 of this letter. These out-of-date and highly inaccurate emission factors should not be used in any emission calculations.

3. Sulfur Dioxide Related Biases in the Measurement of Condensable Particulate Matter

3.1 Development of Condensable Particulate Matter Test Methods

The U.S. Public Health Service procedures published in 1967 for the measurement of condensable particulate matter were rejected by the EPA standards development division and the testing community in 1971 due to well recognized problems with the dissolution and chemical reaction of gases in the cold impinger solutions. Due to these problems, condensable particulate matter testing was not included in the various NSPS standards, including the one applicable to lime kilns. However, some EPA sponsored tests continued to be conducted using this old method without the benefit of any substantial research effort to minimize the severe biases to higher-than-true emissions. In 1991, EPA developed Method 202 based, in part, on this old method. Extraction procedures were improved, and an option was provided for post-test purging the impinger solutions with clean nitrogen in order to minimize the well recognized bias to substantially higher-than-true sulfate emissions. Furthermore, by 1991 impinger designs had advanced to include O-ring seals to replace silicone grease seals and "screw-top" seals.

Despite EPA's best intentions in 1991, the revised method for measuring condensable particulate matter emissions continues to be plagued by bias problems. These include a bias to higher-thantrue sulfate (inorganic) concentrations due to (1) incomplete sulfur dioxide purging of the impingers, (2) sulfur dioxide oxidation in the impingers during the test run, and (3) continued sulfur dioxide oxidation to sulfates in the time period following the run and before purging. These problems are discussed in detail in the two attached papers prepared by Air Control Techniques, P.C., one prepared for the National Lime Association, and one presented recently at a 2005 Air & Waste Management Association meeting.

3.2 Summary of Sulfate-Related Bias to Higher-than-True Emissions

To evaluate the remaining bias problems of the Method 202 sampling train (and the earlier versions of this sampling technique), Air Control Techniques, P.C. installed a set of continuous emission monitors on a Method 202 sampling train to monitor performance during a test run. As illustrated in Figure 1, a large quantity of sulfur dioxide was absorbed in the impinger solutions during the first fifteen minutes of the test run. Absorption stopped only after the solutions reached saturation predicted by Henry's Law.



Figure 1. Laboratory Monitoring of SO₂ Absorption in Method 202 Test Run Impingers (SO₂ inlet concentration of approximately 180 ppm during the entire run)

The dissolved sulfur dioxide remains in solution during the test run and reacts with dissolved oxygen or other oxidants (i.e. ozone, nitrogen dioxide) to form sulfates. Sulfates formed due to the reaction of dissolved sulfur dioxide are counted as inorganic condensable particulate matter. However, these sulfates exist only because of the residence time in the impingers and the conditions created that are conducive to aqueous phase oxidation. These artificially formed sulfates are not representative of the emissions to the atmosphere of the source tested.

The extent of sulfur dioxide gas captured in the Method 202 impinger solutions has been calculated based on the minimum absorption rates predicted by Henry's Law. The extent of sulfate formation from the dissolved sulfur dioxide has been calculated using a first order reaction rate of 4% per hour. This reaction rate is consistent with the sulfur dioxide conversion rates observed in atmospheric air mass and urban plume reaction rate studies. Based on this very basic technical approach, it is apparent that very high artificial levels of sulfates are formed in the Method 202 impingers even when purging is conducted shortly after the test run and efficiencies in the 80% to 95% range.

Air Control Techniques, P.C. has applied this sulfate bias measured during laboratory (ultraclean sample gas stream, no true condensable particulate matter) tests to calculate the inorganic condensable particulate matter emissions reported in the AP42 Section 11.17 references. The bias measured in the laboratory calculations (0.016 grains/DSCF, no purging included) was similar to the "condensable particulate matter" concentrations observed in most of the tests cited in AP42 Section 11.17.

The laboratory data demonstrate that the large fraction of the inorganic condensable particulate matter measured in the AP42 Section 11.17 references is due simply to the dissolution of sulfur dioxide and the subsequent oxidation of sulfur dioxide to sulfates due to the favorable reaction conditions in the impingers. None of the AP42 cited tests included purging to minimize the bias.

Furthermore, none of the AP42 cited tests were conducted using procedures that were developed for sulfur dioxide containing gas streams.

4. Recommended Alternative Procedure for Estimating Condensable Particulate Matter Emissions

The test procedures that are available for measuring condensable particulate matter are severely flawed and should not be used in CALPUFF modeling programs. As an alternative procedure, Air Control Techniques, P.C. recommends that emission factors that relate directly to the various types of condensable particulate matter be used. This approach is consistent with the NPS recommendation that, "Primary sulfates should be estimated separately...."

Inorganic condensable particulate matter emissions from lime kilns are the combined result of (1) sulfuric acid and (2) nitric acid. The organic condensable particulate matter is composed of moderate-to-high molecular weight organic compounds.

In the case of lime kilns, essentially all of the vapor phase organics in the gas stream are due to volatilization of naturally occurring organic compounds in the limestone feed. Most of the organic material released from limestone is low molecular weight compounds that do not condense under atmosphere conditions. Accordingly, the true condensable organic vapor levels in lime kilns are very small. This is confirmed by lime kiln dust analyses which indicate that filterable carbonaceous material is approximately 1% by weight of the dust. Until more definitive data are available, Air Control Techniques, P.C. recommends that lime plants be modeled based on the 2.4% of total condensable particulate matter measured in the Reference 34, AP42 Section 11.17 tests.

The sulfuric acid and nitric acid levels (inorganic condensable particulate matter) are low at lime kilns because conditions for their formation are considerably less favorable than at other types of combustion sources. This is due primarily to the very low oxygen levels maintained in the high temperature combustion zone. Very limited data concerning sulfuric acid emissions are available from lime plants. Chemical Lime Co. has reported sulfuric acid emissions averaging 1.17 ppm (Kiln #1) and 0.72 ppm (Kiln #2) from the Clifton, Texas plant. These emission concentrations are equivalent to emission rates of 0.039 and 0.023 pounds per ton of lime produced. We have not been able to locate nitric acid (nitrate) emission factor data applicable to a lime kiln. However, there is one data point of 0.005 pounds nitric acid per ton of product from the cement industry (AP42 Section 11.06). Lime kilns are similar to cement kilns in that each processes a feed stream that is a minimum of 90% limestone (100% in the case of lime kilns) and operates in a gas-solids counterflow orientation. Both types of sources operate with low kiln oxygen levels and long gas residence times at very high temperatures.

Proposed emission factors for sulfuric acid and nitric acid are summarized in Table 2. These emission factors are based on test procedures for sulfuric acid and nitric acid that are not subject to the silicone grease and sulfur dioxide aqueous phase oxidation related bias problems affecting the condensable particulate matter tests summarized in AP42 Sections 11.17 and 11.06.

Table 2. Proposed Sulfuric Acid (Sulfate) and Nitric Acid (Nitrate) Emission Factors						
for Calculating Inorganic Condensable Particulate Matter Emissions						
Process	Analyte Emission Factor, Lbs/Ton of Lime (or Clinker)		References			
Lime Kiln with Wet Scrubber	Sulfuric Acid (sulfates)	0.039	1997 Test at Kiln #1, Clifton Plant			
Lime Kiln with Wet Scrubber	Sulfuric Acid (sulfates)	0.023	1997 Test at Kiln #2, Clifton Plant			
Sulfuric Acid (sulfates) Average		0.031				
Wet Process Cement Kiln with ESP	Nitric Acid (nitrates)	0.005	AP-42 Section 11.6, Table 11.6-9 (Reference 43)			
Inorganic Condensable PM (sulfates+nitrates)		0.036				

Based on these more directly applicable and representative emission factors, the <u>inorganic</u> condensable particulate matter emissions from a lime kiln would be estimated at 0.036 pounds per ton of lime produced (0.005+0.031 lbs/ton). The <u>organic</u> condensable particulate matter emissions should be estimated as 2.4% of the total condensable particulate matter. This yields an emission factor of 0.037 pounds <u>total</u> condensable particulate matter per ton of lime produced.

At the present time, the 0.037 pounds per ton emission factor is the most accurate and representative predicator of condensable particulate matter emissions from lime kilns. This value has been used in a revised version of the NPS spreadsheet attached to this letter.

5. Size Distributions of Emissions

The data available for estimating the size distributions of filterable particulate matter is as limited as the data concerning condensable particulate matter. A limited review of the particle size data for AP42 Section 11.17 indicates that much of the data were obtained by techniques that are now recognized as inaccurate. However, Air Control Techniques, P.C. agrees with Mr. Sheperd that AP42 Section 11.17-7 may provide the only generic basis available for estimating the fraction of filterable particulate matter in the fine (≤ 2.5 micrometers), coarse (>2.5 and ≤ 10 micrometers), and super-coarse (>10 micrometer) size ranges.

6. Summary

In the attached NPS spreadsheets, I have used the 0.037 pounds condensable particulate matter per ton of lime produced for (1) rotary lime kilns with a fabric filter and (2) calcimatic kilns with a venturi scrubber. I have left all of the other NPS calculations unchanged even though there is

Mr. Karl Everett December 13, 2005

not much technical support for some of the NPS assumptions concerning the composition of filterable and condensable particulate matter (i.e. fine soil content, coarse versus fine size fractions). There simply are no data available with which to proposed alternative emission calculations for some of the speciation estimates. The change to a condensable particulate matter emission factor of 0.037 pounds per ton of lime is needed however, to make the emission estimates consistent with recent information available concerning lime kilns.

I hope that these technical comments are helpful in working with DEQ concerning CALPUFF modeling of lime kiln effluent gas streams.

Regards,

John Ruhas

John Richards, Ph.D., P.E. Air Control Techniques, P.C.