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Subject: Background Information for Revised AP-42 Section 11.14, Frit Manufacturing Review and Update Remaining Sections of Chapter 8 (Mineral Products Industry) of AP-42
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From: Richard Marinshaw

To: Ron Myers
EPA/EMAD/EFIG (MD-14)
U. S. Environmental Protection Agency
Research Triangle Park, N.C. 27711

I. INTRODUCTION

This memorandum presents the background information that was used to develop the revised AP-42 Section 11.14 on frit manufacturing. A process description is presented first, followed by a discussion of emissions and controls. Following these sections, a description of the references that were used to develop the draft section is presented. A review of the information contained in the background file for the section is then presented, followed by a discussion of the results of the data analysis and a summary of changes made to the AP-42 section. Finally, the reference list is provided. The AP-42 section is provided as an attachment.

II. PROCESS DESCRIPTION[1-6]

Frit is a homogenous melted mixture of inorganic substances that is used in enameling iron and steel and in glazing porcelain and pottery. Frit renders soluble and hazardous compounds inert by combining them with silica and other oxides. Frit also is used in bonding grinding wheels, to lower vitrification temperatures, and as a lubricant in steel casting and metal extrusion. The Standard Industrial Classification (SIC) code for frit manufacturing is 2899, chemicals and chemical preparations, not elsewhere classified. The six digit Source Classification Code (SCC) for frit manufacturing is 3-05-013.

Frit is prepared by fusing a variety of minerals in a furnace and then rapidly quenching the molten material. Table 1 lists the raw materials used in a typical charge to a continuous frit smelting furnace at one frit manufacturing facility. The constituents of the feed material depend on whether the frit is to be used as a ground coat or as a cover coat. For cover coats, the primary constituents of the raw material charge include silica, fluorspar, soda ash, borax, feldspar, zircon, aluminum oxide, lithium carbonate, magnesium carbonate, and titanium oxide. The constituents of the charge for a ground coat include the same compounds plus smaller amounts of metal oxides such as cobalt oxide, nickel oxide, copper oxide, and manganese oxide.

TABLE 1. COMPOSITION OF CHARGE TO A FRIT CONTINUOUS SMELTING FURNACE[a]

Raw material	Range for porcelain enamel coating, lb/hr	Range for mold powder for steel, lb/hr
Silica	416-687.5	300-470
Fluorspar	None	300-390
Soda ash	0-208	230-550
Sodium nitrate	0-21	None
Calcium carbonate	0-4.2	80-30
Magnesium carbonate	0-21	None
Potassium carbonate	0-83	50-550
Potassium nitrate	0-33	None
Sodium silicofluoride	0-208	None
Potassium silicofluoride	41-208	None
Titanium oxide	92-333	None
Zircon	0-167	None
Borax	208-500	None
Aluminum hydrate	0-13.5	None
Lithium carbonate	0-37.5	0-160
Sodium phosphate	0-100	None
Potassium phosphate	0-25	None
Strontium carbonate	0-42	None
Boric acid	0-83	None
Feldspar	0-625	None
Total charge	1,900-2,100	1,500-1,700

[a]Reference 4.

To begin the process, raw materials are shipped to the manufacturing facility by truck or rail and stored in bins. Next, the raw materials are carefully weighed in the correct proportions. The raw batch then is dry mixed and transferred to a hopper prior to being fed into the smelting furnace. Although pot furnaces, hearth furnaces, and rotary furnaces have been used to produce frit in batch operations, most frit is now produced in continuous smelting furnaces. Depending on the application, frit smelting furnaces operate at temperatures of 930° to 1480°C (1700° to 2700°F). If a continuous furnace is used, the mixed charge is fed by screw conveyor directly into the furnace. Continuous furnaces operate at temperatures of 1090° to 1430°C (2000° to 2600°F). When smelting is complete, the molten material is passed between water-cooled metal rollers that limit the thickness of the material before it is quenched with a water spray that shatters the material into small glass particles called frit.

After quenching, the frit is milled by either wet or dry grinding. If the frit is dry-milled, it may be dried prior to grinding. Frit produced in continuous furnaces generally can be ground without drying. Continuous furnace frit also is sometimes packaged for shipping without further processing. Wet milling of frit is no longer common. However, if the frit is wet-milled, it can be charged directly to the grinding mill without drying. Rotary dryers are the device most commonly used for drying frit. Drying tables and stationary dryers also have been used. The frit is finely ground in a ball mill, into which clays and other electrolytes may be added, and then the product is screened and stored. The frit product then is transported to on-site ceramic manufacturing processes or prepared for shipping. In recent years, the electrostatic deposition spray method has been become the preferred method of applying frit glaze to surfaces. Frit that is to be applied in that manner is mixed with an organic silicon encapsulating agent rather than with clay and electrolytes during the grinding step. Figure 1 presents a process flow diagram for frit manufacturing.

III. EMISSIONS AND CONTROLS[1,7-10]

Significant emissions of particulate matter (PM) and PM less than 10 micrometers (PM-10) in the form of dust and fumes are created by the frit smelting operation. These emissions consist primarily of condensed metallic oxide fumes that have volatilized from the molten charge. The emissions also contain mineral dust and sometimes hydrogen fluoride. Emissions from furnaces also include products of combustion, such as carbon monoxide (CO), carbon dioxide (CO_2), and nitrogen oxides (NO_x). Sulfur oxides (SO_x) also may be emitted, but generally are absorbed by the molten material and form an immiscible sulphate that is eliminated in the quenching operation. Particulate matter also is emitted from drying, grinding, and materials handling and transfer operations.

Emissions from the furnace can be minimized by careful control of the rate and duration of raw material heating to prevent volatilization of the more fusible charge materials. Emissions from rotary furnaces also can be reduced with careful control of the rotation speed to prevent excessive dust carry over. Venturi scrubbers and fabric filters are the devices most commonly used to control emissions from frit smelting furnaces, and fabric filters are commonly used to control emissions from the grinding operation. No information is available on the type of emission controls used on quenching, drying, and materials handling and transfer operations.

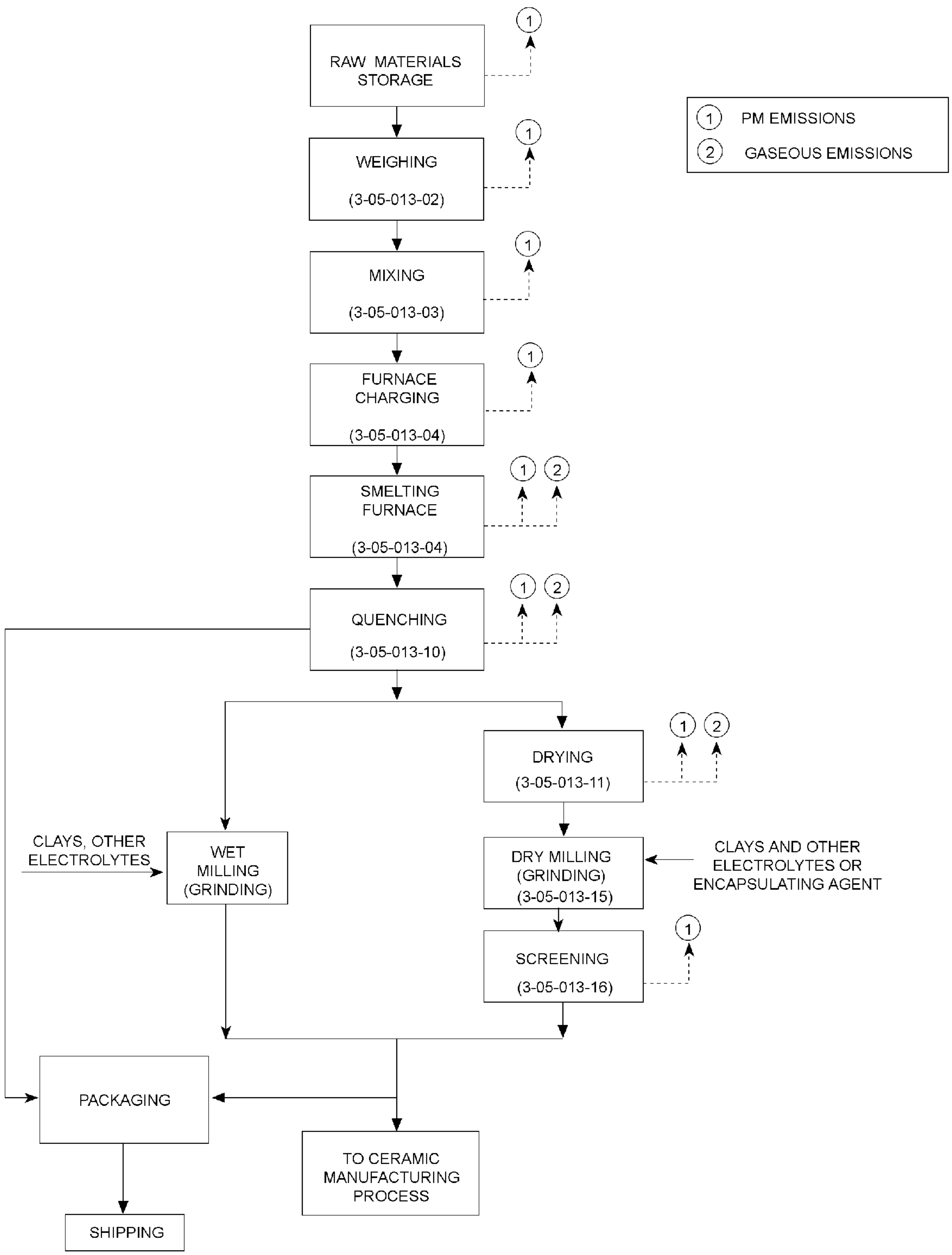

Figure 1. Process flow diagram for frit manufacturing.
(Source Classification Code in parentheses)

IV. DESCRIPTION OF REFERENCES

This section describes the primary references (References 1, and 7 to 10) that present data on emissions from frit manufacturing that were used to develop the revised AP-42 section. References 2 through 6 did not include emission data but were used to prepare the process description for the revised AP-42 section.

A. Reference 1

This document is the main reference for the current AP-42 section and is discussed in Section V, Review of Background File, of this memorandum.

B. Reference 7

This test report includes measurements of filterable PM and carbon dioxide (CO_2) emissions from a frit furnace at a frit manufacturing plant conducted in 1987. The measurements were made at the outlet of a venturi scrubber with a pressure drop of 10.9 kilopascals (kPa) (44 inches of water column [in. w.c.]) located downstream of the furnace. The test was sponsored by the plant for compliance purposes. Filterable PM emissions were measured using EPA Method 5, and CO_2 emissions were quantified by Fyrite.

A rating of A was assigned to the test data for filterable PM, and a rating of C was assigned to the test data for CO_2. The report included adequate detail, the PM test methodology was sound, and no problems were reported during the valid test runs. The CO_2 data were downrated to C due to the relative inaccuracy of the Fyrite method for measuring CO_2 concentrations. The emission data for this test are summarized in Table 2.

C. Reference 8

This test report includes measurements conducted in 1989 of filterable PM and carbon dioxide (CO_2) emissions from a frit furnace at a frit manufacturing plant. The plant is the same as was tested in the test described in Reference 7, but the test was conducted on a different frit furnace. The measurements were made at the outlet of a venturi scrubber with a pressure drop of 10.2 kPa (41 in. w.c.) located downstream of the furnace. The test was sponsored by the plant for compliance purposes. Filterable PM emissions were measured using EPA Method 5, and CO_2 emissions were quantified by Fyrite.

A rating of A was assigned to the test data for filterable PM, and a rating of C was assigned to the test data for CO_2. The report included adequate detail, the PM test methodology was sound, and no problems were reported during the valid test runs. The CO_2 data were downrated to C due to the relative inaccuracy of the Fyrite method for measuring CO_2 concentrations. The emission data for this test are summarized in Table 2.

TABLE 2. SUMMARY OF EMISSION DATA FROM FRIT FURNACE TEST REPORTS[a]

Type of control	Pollutant	No. of test runs	Data rating	Emission factor range, kg/Mg (lb/ton)	Average emission factor, kg/Mg (lb/ton)	Ref. No.
Venturi scrubber	Filterable PM	3	A	0.8-1.1 (1.6-2.2)	0.95 (1.9)	7
Venturi scrubber	Carbon dioxide	3	C	140-150 (280-290)	150 (290)	7
Venturi scrubber	Filterable PM	3	A	0.65-0.70 (1.3-1.4)	0.65 (1.3)	8
Venturi scrubber	Carbon dioxide	3	C	1,100-1,300 (2,200-2,500)	1,200 (2,400)	8
Venturi scrubber	Filterable PM	3	A	1.3-1.5 (2.5-3.0)	1.4 (2.7)	9
Venturi scrubber	Carbon dioxide	3	C	650-950 (1,300-1,900)	750 (1,500)	9
Fabric filter	Filterable PM	2	C	0.010 - 0.010 (0.020 - 0.020)	0.010 (0.020)	10
Fabric filter	Barium	2	C	1.2×10^{-5} - 1.7×10^{-5} (2.3×10^{-5} - 3.2×10^{-5})	1.4×10^{-5} (2.8×10^{-5})	10
Fabric filter	Chromium	2	C	6.2×10^{-6} - 7.7×10^{-6} (1.2×10^{-5} - 1.6×10^{-5})	6.9×10^{-6} (1.4×10^{-5})	10
Fabric filter	Cobalt	2	D	1.4×10^{-6} - 2.8×10^{-6} (2.7×10^{-6} - 5.8×10^{-6})	2.1×10^{-6} (4.3×10^{-6})	10
Fabric filter	Copper	2	C	5.7×10^{-6} - 1.3×10^{-5} (1.1×10^{-5} - 2.7×10^{-5})	9.4×10^{-6} (1.9×10^{-5})	10
Fabric filter	Lead	2	C	4.5×10^{-6} - 5.0×10^{-6} (9.0×10^{-6} - 1.0×10^{-5})	4.8×10^{-6} (9.6×10^{-6})	10
Fabric filter	Manganese	2	C	5.7×10^{-6} - 8.7×10^{-6} (1.1×10^{-5} - 1.7×10^{-5})	7.2×10^{-6} (1.4×10^{-5})	10
Fabric filter	Nickel	2	D	4.5×10^{-6} - 1.2×10^{-5} (9.0×10^{-6} - 2.3×10^{-5})	8.3×10^{-6} (1.6×10^{-5})	10
Fabric filter	Zinc	2	D	2.3×10^{-5} - 1.0×10^{-4} (4.5×10^{-5} -2.0×10^{-4})	6.3×10^{-5} (1.2×10^{-4})	10
Fabric filter	Total fluorides	2	C	0.40 - 0.47 (0.82 - 0.93)	0.43 (0.88)	10
None	NO_x	4	B	7.8 - 8.8 (16 - 18)	8.2 (16)	10
None	CO_2	4	A	220 - 320 (430 - 620)	260 (520)	10

[a]Emission factors in units of raw material feed.

D. Reference 9

This test report includes measurements of filterable PM and carbon dioxide (CO_2) emissions from the same frit furnace that was tested in the test documented in Reference 8. The test was conducted in 1991. The measurements were made at the outlet of a venturi scrubber with a pressure drop of 9.7 kPa (39 in. w.c.) located downstream of the furnace. The test was sponsored by the plant for compliance purposes. Filterable PM emissions were measured using EPA Method 5, and CO_2 emissions were quantified by Fyrite.

A rating of A was assigned to the test data for filterable PM, and a rating of C was assigned to the test data for CO_2. The report included adequate detail, the PM test methodology was sound, and no problems were reported during the valid test runs. The CO_2 data were downrated to C due to the relative inaccuracy of the Fyrite method for measuring CO_2 concentrations. The emission data for this test are summarized in Table 2.

E. Reference 10

This report documents measurements of emissions of filterable PM, eight metals, total fluorides, and NO_x from six frit smelters. The test was conducted in 1994 to demonstrate compliance with State regulations. The facility operates eight continuous and three rotary frit smelting furnaces, all of which are ducted to the same fabric filter. The smelting furnaces are operated at a temperature of 1480°C (2700°F). During the test, only six of the furnaces were operating.

Filterable PM emissions were measured using Method 5, Method 0029 was used to quantify metals emissions, and total fluoride emissions were quantified using Method 13B. Two test runs of the PM, metals, and fluorides sampling trains were conducted, and both runs were anisokinetic (85 percent for the PM/metals train, and 71 to 72 percent for the fluorides train). In addition, for three of the metals the mass collected during one of the two runs was below the detection limit.

Four NO_x emissions test runs also were performed using Method 7A. In addition, the concentrations of CO_2 in the exhaust stream were measured using Method 3A (Orsat) during four test runs.

Emission factors were developed for controlled emissions of filterable PM, total fluorides, and eight metals. For the metal runs for which the mass collected was below detection limit, a value of one-half the detection limit was used in the emission factor calculations. The factors for filterable PM, fluorides, barium, chromium, copper, lead, and manganese are rated C because only two runs were conducted and both were anisokinetic. The factors for cobalt, nickel, and zinc were downrated to D because only one of the two runs was above detection limit.

Emission factors also were developed for uncontrolled emissions of NO_x, and CO_2. The process rates for Runs 3 and 4 of the NO_x sampling train were not reported. Therefore, the average of the process rates for the previous runs was used in the emission factor calculation, and that factor is rated B. The factor for CO_2 emissions was assigned a rating of A.

V. REVIEW OF BACKGROUND FILE

The current version of AP-42 Section 8.12 is based on two references. The first reference is an earlier version of AP-42 and could not be located. The second AP-42 reference, which is referred to as Reference 1 in this memorandum, is an excerpt from the May 1973 edition of Air Pollution Engineering Manual, otherwise known as AP-40. It appears that the previous AP-42 section on frit manufacturing was based primarily on AP-40.

Reference 1 includes the results from 23 emission tests conducted on rotary frit smelters. Sixteen of the tests documented measurements of uncontrolled emissions of dust and fumes from six frit smelters, and three of the tests documented measurements of controlled dust and fume emissions from three smelters. Although the test methods are not specified, it is assumed that these emissions represent filterable PM emissions (front half of a Method 5 sampling train). Emissions from the latter three tests were controlled with venturi scrubbers, all of which operated with a pressure drop of 5.2 kPa (21 in. w.c.). This reference also includes the results of six measurements of CO emissions from two frit smelters, six measurements of uncontrolled fluoride emissions from four frit smelters, and three measurements of controlled fluoride emissions from three frit smelters. The results of these tests are summarized in Table 3.

Emission data from secondary references, such as Reference 1, generally are not used to develop emission factors for AP-42. In addition, because the tests documented in this reference predate EPA reference test methods, it is likely that the data are suspect. However, due to the lack of other test data, the uncontrolled PM and CO emission factors developed from Reference 1 have been included in the revised AP-42 section. These emission factors should be useful for order of magnitude estimates and are assigned a rating of E. The fluoride emission factors are not presented in the AP-42 section because higher quality data were obtained for fluorides.

VI. RESULTS OF DATA ANALYSIS

Candidate emission factors were developed for venturi scrubber-controlled filterable PM emissions using data from References 7, 8, and 9. The data from References 7 and 9 were combined because the tests were performed on the same furnace, and the combined data were averaged with the data from Reference 8 to determine candidate emission factors for frit furnaces controlled by venturi scrubbers. The filterable PM emission factors were assigned a D rating because they were developed from emission data from two units at a single plant. Reference 10 was used to develop a candidate emission factor for fabric filter-controlled filterable PM emissions from frit smelting furnaces. This factor is rated E because it is based on C-rated data. Reference 10 also was used to develop candidate emission factors for fabric filter-controlled emissions of fluorides, barium, cobalt, chromium, copper, lead, manganese, nickel, and zinc from frit furnaces. These factors, all of which are based on C- or D-rated data, are rated E.

A candidate emission factor for NO_x emissions from frit furnaces was developed from Reference 10. This factor is assigned a rating of E because it is based on a single B-rated data set.

TABLE 3. SUMMARY OF TEST DATA ON FRIT SMELTERS FROM AP-40[a]

Source	Type of control	Pollutant	Test No.	Emission rate, lb/hr	Process rate, ton/hr	Emission factor	
						kg/Mg	lb/ton
Rotary smelter	None	Dust & fume	1	1.41	0.0870	8.10	16.2
		Dust & fume	2	5.11	0.0870	29.4	58.7
		Dust & fume	3	5.32	0.0870	30.6	61.1
		Dust & fume	4	1.25	0.146	4.28	8.56
		Dust & fume	5	1.79	0.146	6.13	12.3
		Dust & fume	6	1.57	0.146	5.38	10.8
		Dust & fume	7	2.70	0.236	5.72	11.4
		Dust & fume	8	2.20	0.236	4.66	9.32
		Dust & fume	9	3.30	0.236	6.99	14.0
		Dust & fume	14	2.71	0.429	3.16	6.32
		Dust & fume	15	2.34	0.429	2.73	5.46
		Dust & fume	16	4.15	0.445	4.66	9.33
		Dust & fume	17	3.82	0.445	4.29	8.58
		Dust & fume	18	8.37	0.680	6.15	12.3
		Dust & fume	19	8.60	0.680	6.32	12.6
		Dust & fume	20	1.78	0.680	1.31	2.62
		Average				8.12	16.2
	Venturi scrubber	Dust & fume	18	2.72	0.680	2.00	4.00
		Dust & fume	19	2.85	0.680	2.10	4.19
		Dust & fume	20	1.35	0.680	0.993	1.99
		Average				1.70	3.39
	None	CO	1	0.121	0.0870	0.695	1.39
		CO	2	0.0670	0.0870	0.385	0.770
		CO	3	0.142	0.0870	0.815	1.63
		CO	7	1.95	0.236	4.13	8.26
		CO	8	1.98	0.236	4.19	8.37
		CO	9	1.97	0.236	4.17	8.33
		Average				2.40	4.79
		Fluorides	10	0.73	0.0870	4.20	8.39
		Fluorides	11	0.48	0.0870	2.76	5.52
		Fluorides	12	1.68	0.0810	10.4	20.7
		Fluorides	13	0.50	0.0810	3.09	6.17
		Fluorides	21	3.38	0.680	2.49	4.97
		Fluorides	22	5.03	0.680	3.70	7.40
		Fluorides	23	0.48	0.680	0.353	0.706
		Average				3.85	7.70
	Venturi scrubber	Fluorides	21	0.22	0.680	0.162	0.324
		Fluorides	22	0.29	0.680	0.213	0.426
		Fluorides	23	0.26	0.680	0.191	0.382
		Average				0.189	0.377

[a] Reference 1.

For CO_2 emissions from frit smelting furnaces, data were available from four references. The data from References 7, 8, and 9 are rated C, and the data from Reference 10 are rated A. A-rated data generally are not combined with C-rated data. However, in view of the sparsity of data, the results from all tests were combined for the candidate emission factor. Because the data from References 7 and 9 represent the same furnace, those two data sets were first combined; the average factor from those two tests then was combined with the results from the other two tests. Because of the wide range of factors developed from individual tests (150 to 1,200 kg/Mg [290 to 2,400 lb/ton]), this factor is assigned a rating of E.

Candidate emission factors for uncontrolled PM and CO emissions from frit furnaces were developed from Reference 1. As discussed in Section VI above, these emission factors are rated E. In addition, an emission factor for fabric filter-controlled fluoride emissions from frit furnaces was developed from Reference 10. This emission factor is assigned an E rating because it is based on a single test.

Table 4 summarizes the frit manufacturing emission factors that have been incorporated in the revised AP-42 section on frit manufacturing (Section 11.14).

VII. SUMMARY OF CHANGES TO AP-42 SECTION

The section narrative was expanded to include a more detailed process description and description of emissions and controls. In addition, a process flow diagram was added to the section.

The previous AP-42 section on frit manufacturing included C-rated emission factors for uncontrolled emissions of PM and fluorides from frit smelting furnaces. In the revised AP-42 section, these factors were downrated to E (the fluoride emission factors were removed from the section), based on the quality of the data. Furthermore, new emission factors were added for uncontrolled emissions of CO, NO_x, CO_2, and controlled emissions of filterable PM, fluorides, and eight metals from frit smelting furnaces. The revised AP-42 section tables also include SCC's for each emission factor presented.

TABLE 4. SUMMARY OF EMISSION FACTORS FOR FRIT MANUFACTURING[a]

Process	Pollutant	No. of tests	Average emission factor, kg/Mg (lb/ton)	Emission factor rating	Ref. No.
Furnace	Filterable PM	16	8.1 (16)	E	1
Furnace with venturi scrubber	Filterable PM	2	0.90 (1.8)	D	7,8,9
Furnace with fabric filter	Filterable PM	1	0.010 (0.020)	E	10
Furnace	CO	6	2.4 (4.8)	E	1
Furnace with venturi scrubber[b]	CO_2	3	640 (1,300)	E	7,8,9,10
Furnace	Fluorides	7	3.9 (7.7)	NR	1
Furnace	NO_x	1	8.2 (16)	E	10
Furnace with venturi scrubber	Fluorides	3	1.9 (3.8)	NR	1
Furnace with fabric filter	Fluorides	1	0.43 (0.88)	E	10
Furnace with fabric filter	Barium	1	1.4×10^{-5} (2.8×10^{5})	E	10
Furnace with fabric filter	Chromium	1	6.9×10^{-6} (1.4×10^{-5})	E	10
Furnace with fabric filter	Cobalt	1	2.1×10^{-6} (4.3×10^{-6})	E	10
Furnace with fabric filter	Copper	1	9.4×10^{-6} (1.9×10^{-5})	E	10
Furnace with fabric filter	Lead	1	4.8×10^{-6} (9.6×10^{-6})	E	10
Furnace with fabric filter	Manganese	1	7.2×10^{-6} (1.4×10^{-5})	E	10
Furnace with fabric filter	Nickel	1	8.3×10^{-6} (1.6×10^{-5})	E	10
Furnace with fabric filter	Zinc	1	6.3×10^{-5} (1.2×10^{-4})	E	10

[a]Emission factors in units of raw material feed.
[b]Scrubber achieves only incidental control of CO_2 emissions.

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