Chapter NR 446

CONTROL OF MERCURY EMISSIONS

NR 446.01 Applicability; purpose NR 446.02 Definitions NR 446.03 Mercury emission limits NR 446.04 Stack sampling NR 446.05 Emission monitoring

NR 446.01 Applicability; purpose. (1) APPLICABILITY. This chapter applies to all air contaminant sources which may emit mercury and to their owners and operators.

(2) PURPOSE This chapter is adopted under ss. 144.31, 144.375 and 144.38, Stats., to establish emission limitations, stack sampling procedures and emission monitoring requirements for mercury emissions from air contaminant sources in order to protect air quality.

History: Cr. Register, September, 1986, No. 369, eff. 10-1-86; am. (1), Register, May, 1992, No. 437, eff. 6-1-92

NR 446.02 Definitions. The definitions contained in chs. NR 400 and 445 apply to the terms used in this chapter. In addition, the following definitions apply to the terms used in this chapter:

- (1) "Cell room" means a structure housing one or more mercury chlor-alkali cells.
- (2) "Condenser stack gases" mean the gaseous effluent evolved from the stack of processes utilizing heat to extract mercury metal from mercury ore.
- (3) "Denuder" means a horizontal or vertical container which is part of a mercury chlor-alkali cell and in which water and alkali metal amalgam are converted to alkali metal hydroxide, mercury, and hydrogen gas in a short-circuited, electrolytic reaction.
- (4) "End box" means one or more containers located on one or both ends of a mercury chlor-alkali electrolyzer which serves as a connection between the electrolyzer and denuder for rich and stripped amalgam.
- (5) "End box ventilation system" means a ventilation system which collects mercury emissions from the end boxes, the mercury pump sumps, and their water collection systems.
- (6) "Hydrogen gas stream" means a hydrogen stream formed in the chlor-alkali cell denuder.
- (7) "Mercury chlor-alkali cell" means a device which is basically composed of an electrolyzer section and a denuder or decomposer section and utilizes mercury to produce chlorine gas, hydrogen gas, and alkali metal hydroxide.
- (8) "Mercury chlor-alkali electrolyzer" means an electrolytic device which is part of a mercury chlor-alkali cell and utilizes a flowing mercury cathode to produce chlorine gas and alkali metal amalgam.
- (9) "Mercury ore" means a mineral mined specifically for its mercury content.

- (10) "Mercury ore processing facility" means a facility processing mercury ore to obtain mercury.
- (10m) "Method X", where "X" is a number or a number followed by a letter, means the specified method contained in Appendix B of 40 CFR part 61, incorporated by reference in s. NR 484.04.
- (11) "Sludge" means sludge produced by a treatment plant that processes municipal or industrial wastewater.
- (12) "Sludge dryer" means a device used to reduce the moisture content of sludge by heating to temperatures above 65°C (ca. 150°F) directly with combustion gases.

History: Renum from NR 154.01, Register, September, 1986, No. 369, eff. 10-1-86; am. (intro.) and (2), cr. (10m), Register, May, 1994, No. 461, eff. 6-1-94; am. (10m), Register, December, 1995, No. 480, eff. 1-1-96.

NR 446.03 Mercury emission limits. No person may cause, allow or permit emissions of mercury:

- (1) In such quantity and duration as to cause the ambient air concentration to exceed 1 μg/m³, averaged over a 30-day period.
- (2) In quantities greater than 2,300 grams per 24-hour period from mercury cell chlor-alkali plants, or mercury ore processing facilities.
- (3) In quantities greater than 3,200 grams of mercury per 24-hour period from sludge incineration plants, sludge drying plants, or a combination of these that process wastewater treatment plant sludges.

History: Renum. from NR 154.19 (3) (a), Register, September, 1986, No. 369, eff. 10-1-86; am. (intro.), Register, May, 1992, No. 437, eff. 6-1-92; am. (2), Register, May, 1994, No. 461, eff. 6-1-94

- NR 446.04 Stack sampling. (1) MERCURY ORE PROCESSING FACILITIES. (a) Unless a waiver of emission testing is requested and obtained from the department, each owner or operator of a facility processing mercury ore on which construction or modification commenced after February 1, 1984 shall test emissions from the source in accordance with Method 101 within 90 days after startup.
- (b) The department shall be notified at least 30 days prior to a stack or performance test to afford it the opportunity to have a representative present to witness the testing procedures. The notice shall include a test plan in accordance with s. NR 439.07.
- (c) Samples shall be taken over such a period as is necessary to accurately determine the maximum emissions which will occur in a 24-hour period. No changes in the operation may be made which would potentially increase emissions above that determined by the most recent source test until the new emission level has been

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estimated by calculation and the results reported to the department.

- (d) All samples shall be analyzed, and mercury emissions shall be determined within 30 days after the source test. Each determination shall be reported to the department by registered letter dispatched before the close of the next business day following the determination.
- (e) Records of emission test results and other data needed to determine total emissions shall be retained at the source and made available for inspection by a department representative for a minimum of 2 years.
- (2) MERCURY CHLOR-ALKALI PLANTS HYDROGEN AND END BOX VENTILATION GAS STREAMS. (a) Unless a waiver of emission testing is requested and obtained from the department, each owner or operator of a mercury chlor-alkali cell on which construction or modification commenced after February 1, 1984 shall test emissions from hydrogen streams in accordance with Method 102 and from end-box gas streams in accordance with Method 101 within 90 days after startup.
- (b) The department shall be notified at least 30 days in advance of stack or performance tests to afford it the opportunity to have a representative present to witness the testing procedures. The notice shall include a test plan in accordance with s. NR 439.07.
- (c) Samples shall be taken over such a period as is necessary to accurately determine the maximum emissions which will occur in a 24-hour period. No changes in the operation may be made which would potentially increase emissions above that determined by the most recent source test until the new emission level has been estimated by calculation and the results reported to the department.
- (d) All samples shall be analyzed, and mercury emissions shall be determined within 30 days after the source test. All determinations shall be reported to the department by registered letter dispatched before the close of the next business day following the determination.
- (e) Records of emissions test results and other data needed to determine total emissions shall be retained at the source and made available for inspection by a department representative for a minimum of 2 years.
- (3) MERCURY CHLOR-ALKALI PLANTS CELL ROOM VENTILATION SYSTEM. (a) Stationary sources using mercury chlor-alkali cells may test cell room emissions in accordance with par. (b), or demonstrate compliance with par. (d) and assume ventilation emissions of 1,300 grams per day of mercury.
- (b) Unless a waiver of emission testing is requested and obtained from the department, each owner or operator of a new or modified chlor-alkali plant shall pass all cell room air in forced gas streams through stacks suitable for testing and shall test emissions from the cell room in accordance with Method 101 within 90 days after startup.
- (c) The department shall be notified at least 30 days in advance of stack or performance tests to afford it the opportunity to have a representative present to witness the testing procedures. The notice shall provide a test plan in accordance with s. NR 439.07.

(d) An owner or operator may carry out U.S. environmental protection agency approved design, maintenance and housekeeping practices.

Note: A list of approved practices is provided in appendix A of "Review of National Emission Standards for Mercury," EPA-450/3-84-014a, December 1984. Copies are available from EPA's Central Docket Section, Docket item number A-84-41, III-B-1.

- (4) SLUDGE INCINERATION AND DRYING PLANTS (a) Unless a waiver of emission testing is requested and obtained from the department, each owner or operator of sludge incineration plants and drying plants on which construction or modification commenced after February 1, 1984 shall test emissions from the source within 90 days of startup. The tests shall be conducted in accordance with Method 101A, using the procedures in par. (f).
- (b) The department shall be notified at least 30 days in advance of stack or performance tests to afford it the opportunity to have a representative present to witness the testing procedures. The notice shall include a test plan in accordance with s. NR 439.07.
- (c) Samples shall be taken over such a period as is necessary to determine accurately the maximum emissions which will occur in a 24-hour period. No changes may be made in the operation which would potentially increase emissions above the level determined by the most recent stack tests until the new emission level has been estimated by calculation and the results reported to the department.
- (d) All samples shall be analyzed, and mercury emissions shall be determined within 30 days after the stack test. All determinations shall be reported to the department by registered letter dispatched before the close of the next business day following the determination.
- (e) Records of emission test results and other data needed to determine total emissions shall be retained at the source and shall be made available for inspection by a department representative for a minimum of 2 years.
- (f) If an owner or operator uses Method 105, the following procedures shall be adhered to:
- 1. The sludge shall be sampled after dewatering and before incineration or drying, at a location that provides a representative sample of the sludge that is charged to the incinerator or dryer. Eight consecutive grab samples shall be obtained at intervals of between 45 and 60 minutes and thoroughly mixed into one sample. Each of the 8 grab samples shall have a volume of at least 200 milliliters but not more than 400 milliliters. A total of 3 composite samples shall be obtained within an operating period of 24 hours. When the 24-hour operating period is not continuous, the total sampling period may not exceed 72 hours after the first grab sample is obtained. Samples may not be exposed to any condition that may result in mercury contamination or loss.
- 2. The maximum 24-hour period sludge incineration or drying rate shall be determined by use of a flow rate measurement device that can measure the mass rate of sludge charged to the incinerator or dryer with an accuracy of plus or minus 5% over its operating range. Other methods of measuring sludge mass charging rates may be used if they have received prior approval by the department.

- 3. The handling, preparation and analysis of sludge samples shall be accomplished in accordance with Method 105.
- 4. The mercury emissions shall be determined by use of the following equation:

$$E_{Hg} = \frac{MQF_{sm(avg)}}{1000}$$

where:

E_{Hg} is the mercury emissions, g/day

M is the mercury concentration of sludge on a dry solids basis, $\mu g/g$

Q is the sludge charging rate, kg/day

 $F_{\text{sm(avg)}}$ is the average weight fraction of solids in the collected sludge after mixing

1000 is the conversion factor, kg µg/g²

- 5. No changes in the operation of a plant may be made after a sludge test has been conducted which would potentially increase emissions above the level determined by the most recent sludge test, until the new emissions level has been estimated by calculation and the results reported to the department.
- 6. All sludge samples shall be analyzed for mercury content within 30 days after the sludge sample is collected. Each determination shall be reported to the department by registered letter dispatched before the close of the next business day following the determination.
- 7. Records of sludge sampling, charging rate determination and other data needed to determine mercury content of wastewater treatment plant sludges shall be retained at the source and made available for inspection by a department representative for a minimum of 2 years.

History: Renum. from NR 154.19 (3) (b), and am., Register, September, 1986, No. 369, eff. 10-1-86; am. (1) (b), (2) (b), (3) (c) and (4) (b), Register, May, 1992, No. 437, eff. 6-1-92; am. (1) (a), (2) (a), (3) (b) and (d) and (4) (a), (f) (intro.), 3. and 4., Register, May, 1994, No. 461, eff. 6-1-94.

- NR 446.05 Monitoring of emissions and operations. (1) All wastewater treatment plant sludge incineration and drying plants for which mercury emissions exceed 1600 grams/day, demonstrated either by stack sampling or sludge sampling according to s. NR 446.04 (4), shall monitor mercury emissions at intervals of at least once per year in accordance with Method 105 or the procedures specified in s. NR 446.04 (4) (f). The results of monitoring shall be reported to the department by registered letter dispatched before the close of the next business day following the monitoring. The results shall be retained at the source and shall be made available for inspection by a department representative for a minimum of 2 years.
- (2) The owner or operator of each mercury cell chloralkali plant hydrogen and end-box ventilation gas streams shall:
- (a) Perform a mercury emission test that demonstrates compliance with the emission limits in s. NR 446.03 (2) (a) on the hydrogen stream by Method 102 and on the end-box stream by Method 101 for the purpose of establishing limits for parameters to be monitored, within one year

- after June 1, 1994 or within one year of startup for a plant with initial startup after February 1, 1984.
- (b) Monitor and record manually or automatically at least once every 15 minutes during the tests specified in par. (a) all of the following control device parameters, except as provided in par. (c):
 - 1. The exit gas temperature from uncontrolled streams.
- 2. The outlet temperature of the gas stream for the final cooling system when no control devices other than coolers and demisters are used.
- 3. The outlet temperature of the gas stream from the final cooling system when the cooling system is followed by a molecular sieve or carbon adsorber.
- 4. Outlet concentration of available chlorine, pH, liquid flow rate and inlet gas temperature of chlorinated brine scrubbers and hypochlorite scrubbers.
- 5. The liquid flow rate and exit gas temperature for water scrubber.
- The inlet gas temperature of carbon adsorption systems.
- 7. The temperature during the heating phase of the regeneration cycle for carbon adsorbers or molecular sieves.
- (c) Average the parameters recorded in par. (b) over a minimum 6 hour test period. The highest temperature reading that is measured in par (b) 7 is to be identified as the reference temperature for use in par. (f) 2.
- (d) Monitor and record manually or automatically immediately after the completion of the emission tests specified in par. (a) the following:
- 1. The parameters specified in par (b) 1. to 6. at least once per hour.
- 2. The temperature specified in par. (b) 7. during each heating phase of the regeneration cycle.
- (e) Operate, maintain and calibrate monitoring devices according to the manufacturer's instructions. Monitoring devices used in accordance with pars. (b) and (d) shall be certified by their manufacturer to be accurate to within 10%. Records of the certifications and calibrations shall be retained at the chlor-alkali plant and made available for inspection by the department as follows: certification, for as long as the device is used for this purpose; and calibration, for a minimum of 2 years.
 - (f) Notify the department within 10 days when:
- 1. The hourly value of a parameter monitored in accordance with par. (d) 1 exceeds, or, in the case of liquid flow rate and available chlorine, falls below, the value of that same parameter determined in par. (b) for 24 consecutive hours, and
- 2. The maximum hourly value of the temperature measured in accordance with par. (d) 2. is below the reference temperature recorded according to par. (c) for 3 consecutive regeneration cycles.
- (g) Submit semiannual reports to the department indicating the time and date on which the hourly value of each

parameter monitored according to par. (d) 1. and 2 fell outside the value of that same parameter determined under par. (c) and corrective action taken, and the time and date of the corrective action. Parameter excursions shall be considered unacceptable operation and maintenance of the emission control system. In addition, while compliance with the emission limits is determined primarily by conducting a performance test according to the procedures in s. NR 446.04 (2), reports of parameter excursions may be used as evidence in judging the duration of a violation that is determined by a performance test.

- (h) Submit semiannual reports required in par. (g) to the department on September 15 and March 15 of each year. The first semiannual report is to be submitted following the first full 6 month reporting period. The semiannual reports due on September 15 and March 15 shall include all excursions monitored during the 6 calendar months previous to the report date.
- (3) The owner or operator may develop and submit for the department's approval a plant-specific monitoring plan as an alternative to the monitoring, recordkeeping and reporting requirements of sub. (2) (a) to (g). Approval of an alternative plan shall ensure compliance with the emission limits of s. NR 446.03 (1), and proper operation and maintenance of emissions control systems. Any site-specific monitoring plan shall, at a minimum, include all of the following:
- (a) Identification of the critical parameter or parameters for the hydrogen stream and for the end-box ventilation stream that are to be monitored and an explanation of why the critical parameters selected are the best indicators of proper control system performance and of mercury emission rates.
- (b) Identification of the maximum or minimum value of each parameter that is not to be exceeded. The levels shall

- be directly correlated to the results of a performance test, conducted no more than 180 days prior to submittal of the plan, when the facility was in compliance with the emission limits of s. NR 446.03 (1).
- (c) Designation of the frequency for recording the parameter measurements, with justification if the frequency is less than hourly. A longer recording frequency shall be justified on the basis of the amount of time that could elapse during periods of process or control system upsets before the emission limits would be exceeded, and consideration is to be given to the time that would be necessary to repair the failure.
- (d) Designation of the immediate actions to be taken in the event of an excursion beyond the value of the parameter established in par. (b).
- (e) Provisions for reporting, semiannually, parameter excursions and the corrective actions taken, and provisions for reporting within 10 days any significant excursion.
- (f) Identification of the accuracy of the monitoring devices or of the readings obtained.
- (g) Recordkeeping requirements for certifications and calibrations.

Note: The owner or operator of a mercury cell chlor-alkali plant, cell room ventilation system determining cell room emissions, shall maintain records of any leak or spill of mercury. The records shall indicate the amount, location, time and date when the leak or spill occurred, identify the cause of the leak or spill, state the immediate steps taken to minimize mercury emissions and steps taken to prevent future occurrences and provide the time and date on which corrective steps were taken. The results of monitoring shall be recorded, retained at the source and made available for inspection by the administrator for a minimum of 2 years.

History: Renum. from NR 154.19 (3) (c), and am., Register, September, 1986, No. 369, eff. 10-1-86; renum. 446.05 to be (1), cr. (2) and (3), Register, May, 1994, No. 461, eff. 6-1-94.