Chapter NR 234

INTERIM EFFLUENT LIMITATIONS FOR THE FERTILIZER INDUSTRY WISCONSIN POLLUTANT DISCHARGE ELIMINATION SYSTEM

Note: Pursuant to Chapter 74, Laws of 1973, in sections 147.04 (3) and (5) and under the procedure of section 227.027, Wis. Stats., the department of natural resources has promulgated interim effluent limitations which become effective February 1, 1974 and will remain in effect for a period of one year. These interim effluent limitations will be periodically replaced by permanent effluent limitations.

NR 234.01 Purpose. The purpose of this chapter is to establish interim effluent limitations for discharges from industrial point sources identified herein as authorized by section 147.04 (5), Wis. Stats.

History: Emerg. cr. eff. 2–1–74.

NR 234.02 Applicability. These limitations apply to Standard Industrial Classification (SIC) Code 2871.

(1) Subcategories included.

(a) Sulfur burning, sulfuric acid plants
(b) Phosphoric acid
(c) Normal superphosphate
(d) Triple superphosphate
(e) Mono-Ammonium phosphate
(f) Di-Ammonium phosphate
(g) N–P–K fertilizers
(h) Ammonia production-centrifugal and reciprocal compressors
(i) Ammonium sulfate
(j) Urea
(k) Nitric acid
(l) Ammonium nitrate

(2) Operations excluded. Other SIC codes are addressed only to a limited extent. Ammonia, ammonium nitrate, ammonium sulfate, and all of the acids (sulfuric phosphoric, and nitric) are also listed under SIC code 2819. Urea is also listed under SIC code 2818. Phosphoric rock mining and potash mining are also listed in SIC code 1474.

(3) Other Limitations. Other interim effluent limitations in chapter NR 217, Wis. Adm. Code, are applicable to discharges from facilities which belong in the classifications of this section but are excluded from, or not specifically included in, its provisions.

History: Emerg. cr. eff. 2–1–74.

NR 234.03 Application of interim limitations. (1) The interim limitations should be used only for primary producers and should not be used for formulators. Capacity of facilities should equal or exceed:

Ammonia	100,000 tons/yr
Prilled ammonium nitrate	100,000 tons/yr
Synthetic ammonium sulfate	100,000 tons/yr
Synthetic diammonium phosphate	100,000 tons/yr
Prilled diammonium phosphate	50,000 tons/yr

History: Emerg. cr. eff. 2–1–74.

NR 234.04 Characteristics of process waste effluents. Fertilizer industry process wastes contain fluoride, phosphorus, suspended solids, oil (primarily from compressor and pumping operations), and nitrogen from ammonia and nitrates. Utility blowdown wastes include alkalinity, suspended solids, phosphorus, zinc, chromium, and free chlorine. Parameters like iron, vanadium, nickel, and cobalt are introduced in water treatment chemicals, catalysts, and from equipment corrosion products (stainless steel and stabilizers). Phosphate rock and raw sulfur sometimes contain significant quantities of selenium arsenic, cadmium and natural uranium. If any of these parameters are present specific limitations may be necessary.

History: Emerg. cr. eff. 2–1–74.

NR 234.05 Description of abatement models. The following paragraphs describe in general terms the type of treatment facilities considered to be best practicable treatment technology for the purpose of establishing the interim effluent limitations of this chapter. This description is included to illustrate the type of treatment required. Other treatment technology may be acceptable.

(1) Phosphate Fertilizer Industry—Phosphorus, fluoride and Suspended Solids—Conventional treatment for waste from the phosphate fertilizer industry is to route the waste flows to an impoundment area and then through a two-stage double liming process. The first stage neutralizes the highly acidic water to a 3–4 pH level and precipitates out some of the fluoride and phosphorus in the wastewater. The second stage further neutralizes the stream to a 6–7 pH level. Some heavy metals precipitate out from this process, but further treatment may be necessary to reach established effluent limitation levels.

(2) Heavy Metals—If the heavy metals content in the effluent from the double liming process does not meet limitation levels additional treatment will be necessary. The location of the precipitation–sedimentation system used to remove the heavy metals will depend on the waste stream being treated and the design situation. It may be integrated with the double liming process or follow directly behind it. The procedure is basically the adjustment of pH, usually with lime, to achieve an alkaline condition, followed by precipitation of the hydroxide. Coagulating aids are often required to achieve the levels of precipitation necessary. Variations include reduction or oxidation and removal of interfering constituents prior to precipitation.

(3) Arsenic—The stream can be treated by adjusting the pH to around 10, adding coagulating aids, and allowing settling, followed by filtration if necessary.

(4) Ammonia Nitrogen—Treatment methods include biological denitrification, air stripping, and steam stripping. Steam stripping appears to be the most dependable. If it becomes economically desirable to recover ammonia or if an air pollution problem exists for a certain site location, then the overhead from the stripping tower can be recovered through the application of reflux, compression, and purification.

(5) Nitrate Nitrogen—Good housekeeping and inplant controls are required in order to meet limitations. Off gas from the neutralizer can be vented directly to the atmosphere. In situations where this will not be allowed, the off gas must be condensed and the condensate treated to remove ammonia and ammonium nitrate, and recycled back to the neutralizer, or concentrated and used directly as product. For plants where the effluent does not meet limitations and recycling and inplant modifications have been applied, additional waste treatment will be required. One treatment system being used involves ion exchange. The essential steps are filtering through anthracite coal to remove particulate matter and contacting wastewater with strong acid cation exchange resin that removes the ammonium cation contaminant. A dual effect evaporator system may also be used for treating waste liquors containing ammonium nitrate. (These wastes include condensed neutralizer off gas, leaks, spills, etc). The liquor is concentrated to 60–80% depending on the point of usage in the plant. The only waste discharge is steam from the evaporators.

(6) Organic Nitrogen—The major source of organic nitrogen in waste effluent is the production of urea. Urea production can be broken down into three categories of plants: once-through, partial recycle, and total recycle of unreacted ammonia and carbon dioxide. With once-through and partial recycle systems, there is no process effluent other than leaks and spills. Total recycle plants have a considerable amount of effluent containing significant amounts of urea and ammonia. One waste removal system uses urea hydrolysis and steam stripping to give an effluent of 75 pounds ammonia nitrogen and 85 pounds organic nitrogen per 1000 tons of urea production (total recycle plants). The limitations allow for fluctuations in the system.

(7) Oil and Grease—Where oil and grease in the waste effluent are a problem, a properly operated API-designed oil separator or the use of air flotation and skimming can reduce the oil in the effluent to meet the limitation levels.

History: Emerg. cr. eff. 2–1–74.

234.06 Table of interim effluent limitations (In Pounds per 1000 Tons of Product).

Subcategory	TSS[1]	Iron	Oil	Ammonia Nitrogen	Other	
(1) Sulfuric Acid Sulfur Burning	25.0	1.0			Arsenic	0.25
					Selenium	0.5
					Vanadium	1.0
(2) Phosphoric Acid	625.0	25.0			Cadmium	5.0
					Fluorine	125.0
					Phosphorus	125.0
					Heavy metals[2]	25.0
(3) Normal and Triple Superphosphate	208.0	8.3			Cadmium	1.7
Mono-and Di-Ammonium Phosphate N–P–K					Fluorine	41.5
					Phosphorus	41.5
					Heavy metals[2]	8.3
(4) Ammonia Production Centrifugal and Reciprocal Compressors	130.0	5.3	52.0	52.0	Nickel	2.6
(5) Ammonium Sulfate	50.0	2.0		19.8	Nickel	1.0
(6) Urea[3]	80.0	3.2	32.0		Cobalt	1.6
					Nickel	1.6
					Organic Nitrogen	32.0
						100.00
(7) Nitric Acid	72.0	2.9	28.0	28.0	Cobalt	1.4
					Nickel	1.4
					Nitrate Nitrogen	28.0
(8) Ammonium Nitrate	62.5	2.5	25.0	25.0	Nickel	1.3
					Nitrate Nitrogen	25.0

NOTES:
[1]TSS means total suspended solids.
[2]Heavy metals means the combination of U, Nat, Va.
[3]The 32 pound limits apply to once-through and partial recycle urea plants and the 100 pound limits to total recycle plants as described in NR 234.05 (6).

History: Emerg. cr. eff. 2–1–74.