

STATE OF MONTANA AIR QUALITY CONTROL IMPLEMENTATION PLAN	Subject: Yellowstone County Air Pollution Control Program
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BEFORE THE BOARD OF ENVIRONMENTAL REVIEW
OF THE STATE OF MONTANA

In the Matter of the Application of
the Department of Environmental
Quality for Revision of the Montana
State Air Quality Control Implementation
Plan relating to Control of Sulfur Dioxide
Emissions in the Billings/Laurel Area,
Affecting the Following Industries:
Cenex, Inc. (Laurel); Conoco, Inc.; Exxon
Company, USA; Montana Power Company
(J.E Corette and F. Bird Plants); Montana
Sulphur & Chemical Company; and
Yellowstone Energy Limited Partnership.

**STIPULATION OF
DEPARTMENT
AND EXXON
MOBIL
CORPORATION**

The Department of Environmental Quality ("Department"), and Exxon Mobil Corporation ("Exxon") formerly Exxon Company, U.S.A, hereby stipulate to the following paragraphs 1 through 13, including the attachment, in regard to the above-captioned matter and present the same for consideration and adoption by the Board of Environmental Review ("Board").

1. On June 9, 1998, the Department and Exxon executed a document entitled "Stipulation of Department and Exxon," which included an Exhibit A and Attachments 1 and 2 (collectively "1998 Exxon Stipulation"). The 1998 Exxon Stipulation contained the sulfur dioxide control plan for Exxon, as part of the state's efforts to revise the State Implementation Plan for the control of sulfur dioxide (SO₂) emissions in the Billings/Laurel area ("Billings/Laurel SIP").

2. On March 4, 1993, the United States Environmental Protection Agency (EPA) notified the Governor of Montana that it had determined that the existing implementation plan for the control of SO₂ emissions in the Billings/Laurel area was substantially inadequate to attain and maintain the SO₂ National Ambient Air Quality Standards ("NAAQS"). The letter further called for a revision to the implementation plan for the Billings/Laurel area, to assure attainment and maintenance of the SO₂ NAAQS.

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3. The express purpose of the 1998 Exxon Stipulation was to "establish an emission control strategy for Exxon which, together with similar control strategies for the other Billings/Laurel industries, will assure attainment and maintenance" of the primary and secondary NAAQS for SO₂. (1998 Exxon Stipulation, para. 9). As part of the 1998 Exxon Stipulation, Exhibit A contained emission limitations and other conditions, including but not limited to: methods for determining compliance with emission limitations, requirements by which such emission limitations are made quantifiable and enforceable by the Department, and facility modification requirements. Attachment 1 addressed performance specifications for stack flow rate monitors, and Attachment 2 addressed analytical methods for analyzing sour water stripper overheads for hydrogen sulfide, and precision and accuracy methods for the sour water stripper flow meter. The 1998 Exxon Stipulation was approved and made enforceable by Board Order, dated June 12, 1998. On July 29, 1998, the 1998 Exxon Stipulation was submitted to EPA as a revision to the existing Billings/Laurel SIP, in response to the March 1993 SIP Call.

4. In letters to the Department dated January 15 and March 2, 1999, EPA identified several concerns with the 1998 Exxon Stipulation. (Letters from Richard Long, to Mark Simonich, dated 1/15/99 and 3/2/99). Among the concerns noted by EPA were the following: there was not a method to monitor compliance by the Coker CO Boiler with the applicable emission limitations; and there were several questions regarding the methodology proposed in Attachment 2, relating to the analytical method for analyzing sour water stripper overheads for hydrogen sulfide. In a letter dated March 24, 1999, Governor Marc Racicot committed the Department to revise the Billings/Laurel SIP to address these concerns.

5. The purpose of this Stipulation is to revise Exhibit A and Attachment 2 of the 1998 Exxon Stipulation, as necessary to fulfill the Department's commitment to EPA to address the issues described above in paragraph 4. Unless expressly stated otherwise, this document does not in any way supercede or alter the provisions of the 1998 Exxon Stipulation, and except as expressly revised by this document, the 1998 Exxon Stipulation, including Exhibit A and Attachments 1 and 2, remain in full force and effect, as part of the Department's control plan for SO₂ emissions in the Billings/Laurel area.

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6. The parties agree that Exhibit A to the 1998 Exxon Stipulation is revised as follows:

Section 2(A)(11)(d) was stricken by the parties from the 1998 Exxon Stipulation. The following language is now added as Section 2(A)(11)(d):

"For Coker CO Boiler:

- (i) Coker fresh feed rate shall be expressed in barrels per day (barrels/day); and
- (ii) the Hourly SO₂ Emission Rate shall be calculated using the following equation:

$$E_C = 0.0817 * Q_H + 213.02$$

Where:

E_C = Hourly SO₂ Emission Rate from firing Coker Unit flue gases in the Coker CO Boiler in pounds per hour and rounded to the nearest tenth of a pound; and

Q_H = Coker fresh feed rate in barrels/day."

Section 3 is revised to add the following introductory text after the section title "Emissions Limitations and Facility Modifications," and before the Section 3(A) text:

"Exxon may be subject to (hourly, daily, and annual) SO₂ emission limits in an air quality permit that are more restrictive than those presented here. In those instances where permit emission limits are more stringent, Exxon shall comply with those permit limitations."

Section 3(A) is revised to read:

"The following emission limitations shall apply whenever the Yellowstone Energy Limited Partnership facility is receiving Exxon Coker unit flue gas or whenever the Exxon Coker unit is not operating:"

Section 3(A)(1) is revised to read:

"Refinery Fuel Gas Combustion from the following units: Coker CO Boiler, FCC CO Boiler, F-2 Crude/Vacuum Heater, F-3 unit, F-3X unit, F-5 unit, F-700 unit, F-201 unit, F-202 unit, F-402 unit, F-551 unit, F-651 unit, and standby boiler house (B-8 boiler);

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- a. Combined Three Hour Emissions of SO₂ from the Refinery Fuel Gas Combustion Units shall not exceed 92.4 pounds per three hour period; and
- b. Combined Daily Emissions of SO₂ from the Refinery Fuel Gas Combustion Units shall not exceed 739.2 pounds per Calendar Day."

Section 3(B) is revised to read:

"The following emission limitations shall apply whenever the Yellowstone Energy Limited Partnership facility is not receiving Exxon Coker unit flue gas and the Exxon Coker unit is operating:"

Section 3(B)(1) is revised to read:

"Coker CO Boiler stack (includes process exhaust gases and F-202 heater fuel gas firing emissions);

- a. Three Hour Emissions of SO₂ from the Coker CO Boiler stack shall not exceed 2,142.9 pounds per 3-hour period; and
- b. Daily Emissions of SO₂ from the Coker CO Boiler stack shall not exceed 17,143.1 pounds per Calendar Day."

Section 3(E)(3) is revised to read:

"Exxon shall not restore the fuel oil guns to the F-2 Crude/Vacuum Heater, F-3 and F-5 units. This is consistent with Section 3(F)(3) of Exhibit A of the Stipulation between the Department and Exxon dated January 28, 1997, and adopted by the Board through Board Order dated February 7, 1997."

Section 4(C) was stricken by the parties from the 1998 Exxon Stipulation. The following language is now added as Section 4(C):

"Unless a CEMS, or CEMS-Equivalent Alternative Monitoring Plan approved by the Department and EPA, is required for compliance as specified in Section 6(B)(4), compliance with the emission limitations contained in Section 3(B)(1) shall be determined in accordance with the equation in Section 2(A)(11)(d). Whenever Coker Unit flue gases are being burned in the Coker CO Boiler, Exxon shall obtain hourly readings from the Coker unit fresh feed rate meter beginning with the first Clock Hour that Coker unit flue gas is burned in the Coker CO Boiler. Exxon shall record those readings in units of barrels per day (barrels/day) and maintain a log of the hourly readings.

In order to assure the continued reliability of the equation prescribed by Section 2(A)(11)(d) and used to calculate Hourly SO₂ Emission Rates from the Coker CO Boiler, Exxon shall sample the Coker unit reactor feed stream and analyze each of the required samples for sulfur content using ASTM Method 1552-83 or an equivalent method approved by the Department and EPA. The equation prescribed by Section 2(A)(11)(d)

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shall be considered reliable for predicting SO₂ emissions from the Coker CO Boiler when reactor feed sulfur content is determined to be less than or equal to 5.11 percent by weight. Exxon shall conduct the required sampling in accordance with the following schedule and procedure.

Exxon shall collect one sample of Coker unit reactor feed for each Calendar quarter during any part of which Coker unit flue gases are burned in the Coker CO Boiler. Exxon shall collect the required quarterly sample within four hours of the time the Coker unit flue gas stream is first routed to the Coker CO Boiler during each Calendar quarter. Exxon shall analyze that sample for sulfur content as soon as possible but no later than 5 business days from the time the sample was collected. Exxon is not required to collect a reactor feed sample for any Calendar quarter during which no Coker unit flue gas is burned in the Coker CO Boiler.

If the results of the required sampling and analysis indicate that the sulfur content of the reactor feed is in excess of 5.11 percent by weight, Exxon shall notify the Department of those results by the next business day following its receipt of the results. Exxon shall then work with the Department and, as appropriate, EPA to determine what additional actions, if any, may be necessary to provide assurance that the Coker CO boiler emissions remain within the limitations set forth in Section 3."

✓ Section 6(B)(7) is revised to read:

"Exxon shall operate and maintain a continuous flow rate meter to determine the fresh feed rate to the Coker Unit."

✓ Section 7(B)(1)(d) is revised to read:

"Hourly SO₂ Emission Rates in pounds per Clock Hour from the F-2 Crude/Vacuum Heater stack (when sour water stripper overheads are being burned in the F-1 Crude Furnace), FCC CO Boiler stack, refinery fuel gas system, and Coker CO Boiler stack (when YELP is not receiving Coker unit flue gas and the Coker Unit is operating);"

✓ Section 7(B)(1) is revised to add paragraph (i) which reads:

"the Hourly Average fresh feed rate to the Coker Unit."

✓ Section 7(C)(1)(b) is revised to read:

"Three Hour Emissions of SO₂ in pounds per three hour period from the F-2 Crude/Vacuum Heater stack (when sour water stripper overheads are being burned in the F-1 Crude Furnace), FCC CO Boiler stack, Coker CO Boiler stack (when YELP is not receiving Coker unit flue gas and the Coker Unit is operating), and combined Three Hour Emissions from the fuel gas combustion units (listed in Section 3 (A)(1) and (B)(2), as appropriate)."

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Section 7(C)(1)(d) is revised to read:

"Daily Emissions of SO₂ in pounds per Calendar Day from the F-2 Crude/Vacuum Heater stack (when sour water stripper overheads are being incinerated in the F-1 Crude Furnace), FCC CO Boiler stack, Coker CO Boiler stack (when YELP is not receiving Coker unit flue gas and the Coker Unit is operating), and combined Daily Emissions from the fuel gas combustion units [listed in Section 3 (A)(1) and (B)(2), as appropriate]."

Section 7(C)(1)(f) is revised to read:

"the Operating hours during the calendar quarter for the sources or units associated with the F-2 Crude/Vacuum stack or the flare (when sour water stripper overheads are being burned in the F-1 Crude Furnace or the flare), FCC CO Boiler stack, Coker CO Boiler stack (when YELP is not receiving Coker unit flue gas and the Coker Unit is operating), and refinery fuel gas system;"

Section 7(C)(1) is revised to add paragraph (l) which reads:

"the results of the sampling of Coker ^{reactor} ~~fresh~~ feed and analyses for sulfur content required by Section 4(C)."

7. The parties agree that Method #6A of Attachment 2 to the 1998 Exxon Stipulation, entitled "Analytical Method for Analyzing the Sour Water Stripper Overheads (SWSOH) for Hydrogen Sulfide (H₂S)," is superceded in its entirety, and is replaced by the updated Method #6A-1, entitled "Analytical Method for Analyzing the Sour Water Stripper Feed for Hydrogen Sulfide (H₂S) (October 1999)." The updated Method #6A-1 is the attachment to this Stipulation.

8. This Stipulation, including the attachment ("Stipulation"), shall become effective immediately upon the issuance of an order by the Board in this proceeding.

9. It is the intent of the parties that this Stipulation, after adoption and incorporation by Board Order, shall be submitted to the EPA for review and approval as revisions to the Exxon control strategy for the attainment and maintenance of the primary and secondary SO₂ NAAQS in the Billings/Laurel area, as part of the State Implementation Plan. The revised requirements in this Stipulation shall supersede any less stringent corresponding conditions pertaining to SO₂ sources in any existing permit currently issued to Exxon.

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10. The 1998 Exxon Stipulation, as revised by this Stipulation, is intended to assure attainment and maintenance of the primary and secondary NAAQS for SO₂, but is not intended to address attainment or maintenance of the Montana Ambient Air Quality Standards.

11. This Stipulation may be subject to modification as provided in paragraphs 18 and 19 of the 1998 Exxon Stipulation.

12. Exxon does not waive and expressly reserves its right to contest any Board order or federal action which, without the written consent of Exxon, modifies this Stipulation.

13. Accordingly, the parties agree that the Board shall issue an order adopting the terms of this Stipulation. Upon adoption in a Board Order, this Stipulation shall be enforceable by the Department.

Exxon Mobil Corporation, formerly
Exxon Company, U.S.A.

Montana Department of
Environmental Quality

By ^{DMC} Atwood R. Lopez

By Mark A. Simonich
Mark Simonich
Director

Date ^{2/8/00} 2/8/00

Date 2/14/00

Approved as to form:

Approved as to form:

By Sumi J. Ph...
Attorney

By IN 072, R. B. C.
Attorney

Date 2/04/00

Date 2/14/00

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METHOD #6A-1

**ANALYTICAL METHOD FOR ANALYZING THE SOUR WATER STRIPPER FEED FOR
HYDROGEN SULFIDE (H₂S)
(October 1999)**

1.0 SCOPE AND APPLICATION

This method is applicable to the measurement of total and dissolved sulfides in sour water produced by the refinery. Acid insoluble sulfides are not measured by the use of this test. (Copper sulfide is the only common sulfide in this class).

2.0 SUMMARY OF METHOD

Excess iodine is added to a sample which has been treated with zinc acetate to produce zinc sulfide. The iodine oxidizes the sulfide to sulfur under acidic conditions. The excess iodine is back titrated with sodium thiosulfate.

3.0 COMMENTS

Reduced sulfur compounds, such as sulfite, thiosulfate and hydrosulfite, which decompose in acid may yield erratic results. Also, volatile iodine-consuming substances such as mercaptans will give high results.

The sample source is hot and under pressure.

The volumes of preservative and the normality of the reagents have been modified from the referenced methods. The modifications are to make the method appropriate for the expected high concentrations of sulfide in the samples. The method calculations are also modified to correct for the sample dilution from the preservative.

4.0 APPARATUS

- 4.1 Ordinary laboratory glassware.
- 4.2 130 ml HDPE bottles. These bottles are pre-charged with preservative. For the sour water stripper feed inlet the bottle contains 5 ml of zinc acetate and 10 ml of sodium hydroxide.

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5.0 REAGENTS

- 5.1 Hydrochloric acid, HCl, 6 N
- 5.2 Standard iodine solution, 0.1000 N: Dissolved 20 to 25 g KI in a little water in a liter volumetric and add 12.8 g iodine. Allow to dissolve. Dilute to 1 liter and standardize against 0.1000 N sodium thiosulfate using a starch indicator.
- 5.3 Sodium thiosulfate 0.1000N: Dissolve 24.82 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in water. Add 1 ml of chloroform and dilute to 1000 ml.
- 5.4 Starch indicator: Dissolved 10 g soluble starch and 10 mg Hg_2I in hot water and dilute to 4 liters.
- 5.5 Standardize the sodium thiosulfate against KIO_3 . Adjust the concentration to 0.1000 N. Use this sodium thiosulfate to standardize the iodine solution.
- 5.6 Zinc acetate solution, 2N: Dissolve 220 g $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ in water and dilute to one liter.
- 5.7 Sodium hydroxide, 6N: Dissolve 240 grams of sodium hydroxide in 800 ml of water, Dilute to one liter. Caution: much heat will be liberated.

6.0 SAMPLING

- 6.1 The sample bottles (4.2) are pre-charged with zinc acetate and sodium hydroxide preservative and labeled. The sample bottle sample contains 5 ml of preservative and 10 of sodium hydroxide.
- 6.2 The sample is obtained by carefully filling the appropriate bottle. Fill the bottle slowly to prevent the sample from splashing the preservative out or overflowing the bottle. The bottle should be completely filled with no headspace air. If necessary, the sides of the bottle can be squeezed while screwing on the lid to exclude the remaining air.
- 6.3 Experience shows that the pH of these samples, taken and preserved as described, are above 9. No further pH adjustment is required.

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7.0 PROCEDURE

- 7.1 Shake the container to suspend all solids and remove the sample. Measure the volume of sample. This is used to correct the results for the dilution due to the preservative. Check the pH of the sample using pH test paper to confirm that it is 9 or higher.
- 7.2 Place 20 ml of standard iodine solution (5.2) into a 500 ml iodine titration flask.
- 7.3 Add 15 ml of 6N HCl (5.1).
- 7.4 Thoroughly mix the sample and quickly take a 25 ml aliquot and place it in the flask.
- 7.5 If the iodine color disappears, add more iodine until the color remains. Record the total number of milliliters of standard iodine used steps 7.2 and 7.5.
- 7.6 Titrate with the reducing solution (0.1 N sodium thiosulfate) to a pale straw color. Add the starch indicator and titrate until the blue color disappears. Record the volume used.

8.0 CALCULATIONS

8.1 Sulfide as H₂S, mg/l = $\frac{(A - B) \times 17.01 \times 1000}{\text{sample aliquot, ml} \times K}$

Where: A = Volume of Iodine, ml * Normality of Iodine

B = Volume of Thiosulfate, ml * Normality of Thiosulfate

K = $\frac{\text{ml of sample} - \text{ml of preservative}}{\text{ml of sample}}$

This is a correction for the preservative volume. The volume of sample is the total volume in the sample container including the preservative. The volume of preservative is the volume added to the container before the sample was obtained.

9.0 REFERENCES

- 9.1 Standard Methods for the Examination of Water and Wastewater, 19th Edition, p 4-127, Method 4500-S₂ F, (1995)
EPA Method 376.1

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