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RATE OF NO_X EVOLUTION FROM SODIUM NITRITE/BORIC ACID SOLUTIONS (U)

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APPROVALS

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INTRODUCTION

The Defense Waste Processing Facility (DWPF) utilizes 40% sodium nitrite solution and potentially could utilize 5% boric acid solutions. These solutions are stored under ambient conditions within a common containment system inside the facility. The maximum volume of each chemical in DWPF is 615 gallons of sodium nitrite and 180 gallons of boric acid. Sodium nitrite solutions release NO and NO_2 (NO_x) gas when mixed with acids. The amount of NO_x released if the boric acid and sodium nitrite are mixed was measured to determine if the TEEL-1 limit of 2 ppm will be exceeded in a 49,000 ft^3 volume.

The chemical equations that govern the reaction of boric acid with sodium nitrite are shown below:

$$H_3BO_{3\,(aq)} \rightarrow H^+_{(aq)} + H_2BO_3^-{}_{(aq)}$$

$$H^+_{(aq)} + NO_2^-{}_{(aq)} \rightarrow HNO_{2\,(aq)}$$

$$2HNO_{2\,(aq)} \rightarrow NO_{(g)} + NO_{2\,(g)} + H_2O$$

TASK OBJECTIVE

The objective of the testing was to determine the release rate of NO_x from mixtures of sodium nitrite and boric acid solutions.

TEST METHODS

The tests were conducted with 1 liter of sodium nitrite and 293 ml of boric acid solution (1/2328 scale). The solution was continuously stirred during the experiment to ensure that all gases were removed from the solution as they were generated and that the boric acid and sodium nitrite solutions were in intimate contact. A water jacket was utilized to maintain a constant temperature during the experiment. The NO and NO_2 generated was measured by an Enerac 2000E gas analyzer for one to two hours after the chemicals were mixed. Calculations were then performed to determine the release rate from a mixture of the full-scale volumes and the resulting NOx concentration in a 49,000 cubic feet volume. The experimental apparatus is shown in Appendix A and sample results from the solution makeups are shown in Appendix B.

RESULTS

Two runs (Baseline Run 1 and 2) were conducted to determine the rate of NO_x evolution from a mixture of 1 liter of 40% sodium nitrite and 293 milliliters of 5% boric acid at 25

degrees Celsius. No evolution of NO_x was detected from the sodium nitrite solution until the boric acid was added. Figures C-1 and C-2 of Appendix C show the amount of NO_x emitted during the runs as a function of run time. As shown in the figures, the NO_x evolution rate peaked during the run then reached a steady state value during both runs. NO_2 readings were very similar during both runs, and NO readings were similar if the readings from the first run are adjusted for an offset noted during Run 1. The NOx measured during the run contained approximately equal amounts of NO and NO_2, as predicted by the reaction stoichiometry and the two readings followed similar trends during the tests.

The offset noted during Baseline Run 1was 8 PPM prior to the boric acid addition. After the run, the NO reading remained at 14 PPM after the probe was removed from the vessel. The calibration check also showed a 14 PPM offset from the initial calibration when the instrument was checked after the run. An offset was not noted during Baseline Run 2 before or after the run. The data shown in the tables and figures of this report reflect the experimental result without adjustment for the offsets noted.

The time required for the NO_x emission to peak was significantly different between the two runs. The boric acid solution was warmed in a water bath prior to the second run, resulting in less temperature drop when the boric acid was added. In addition, the time required to completely mix the two chemicals was less for the second run. Two liquid phases were present during both runs after the boric acid addition. The two phases were completely mixed together after 45 minutes during Run 1 and 25 minutes during Run 2. When the solution became homogeneous in appearance, the NO_x emission dropped rapidly from the peak values to the steady state values, as shown in Figures C-1 and C-2. As shown in Table 1, the steady state generation rate would exceed the allowable amounts even without the initial peaks.

The amount of NO_x emitted during the test was calculated from the measured NO and NO_2 readings and the air purge rate (~510 ml/min) from the vessel. The amount of NO_x was then scaled up to full scale by multiplying the test result by the 2328 scaling factor. This amount was compared to the amount of NO_x allowed in DWPF by converting the 2 PPM limit in 49,000 ft^3 to an amount of NO_x allowed (2780 ml), as shown in Table 1 and Figures C-3 and C-4.

Table 1. NOx Generation Rates

Run Number	Generation after 1 Hour	Steady State Generation Rate	Full-Scale Generation after 1 Hour	Full-Scale Steady State Generation Rate	Full-Scale NO_x Limit	Time to Reach NO_x Limit
	ml of NO_x	ml/hour	ml of NO_x	ml/hour	ml	minutes
Baseline Run 1	3.5	2.6	8200	6100	2780	21
Baseline Run 2	2.4	1.9	5700	4400	2780	21

Two factors could influence the results. First, carbon dioxide absorbed by the boric acid solution could have led to higher initial concentrations of hydronium ion than would normally be present in boric acid solution by the formation of carbonic acid. This factor could partially explain the peaks at the beginning of each run. However, carbonic acid would be present in solutions made-up at DWPF, therefore the impact of the carbonic acid should not be subtracted from the test results. The second factor identified was the presence of the Inconel thermocouple in the solution during the run. Metal can catalyze the decomposition of nitrous acid and lead to higher results. Just as the carbonic acid would be present in DWPF, the impact of metal contact will be present in DWPF and should not be subtracted from the test results.

Temperature was not intentionally varied during the test, but a 2° C dip in temperature occurred during the first run at a run time of 65 minutes. A four PPM dip in NO_x emission was noted at the same time and the readings returned to the previous values when the temperature returned to normal. This dip indicates that temperature likely plays a significant role in the generation rate of NO_x; however, sufficient tests were not conducted to confirm or evaluate the impact of temperature. Ambient temperatures in DWPF could be higher than the test temperature (25° C), therefore the potential exists for higher emission rates than noted during the tests.

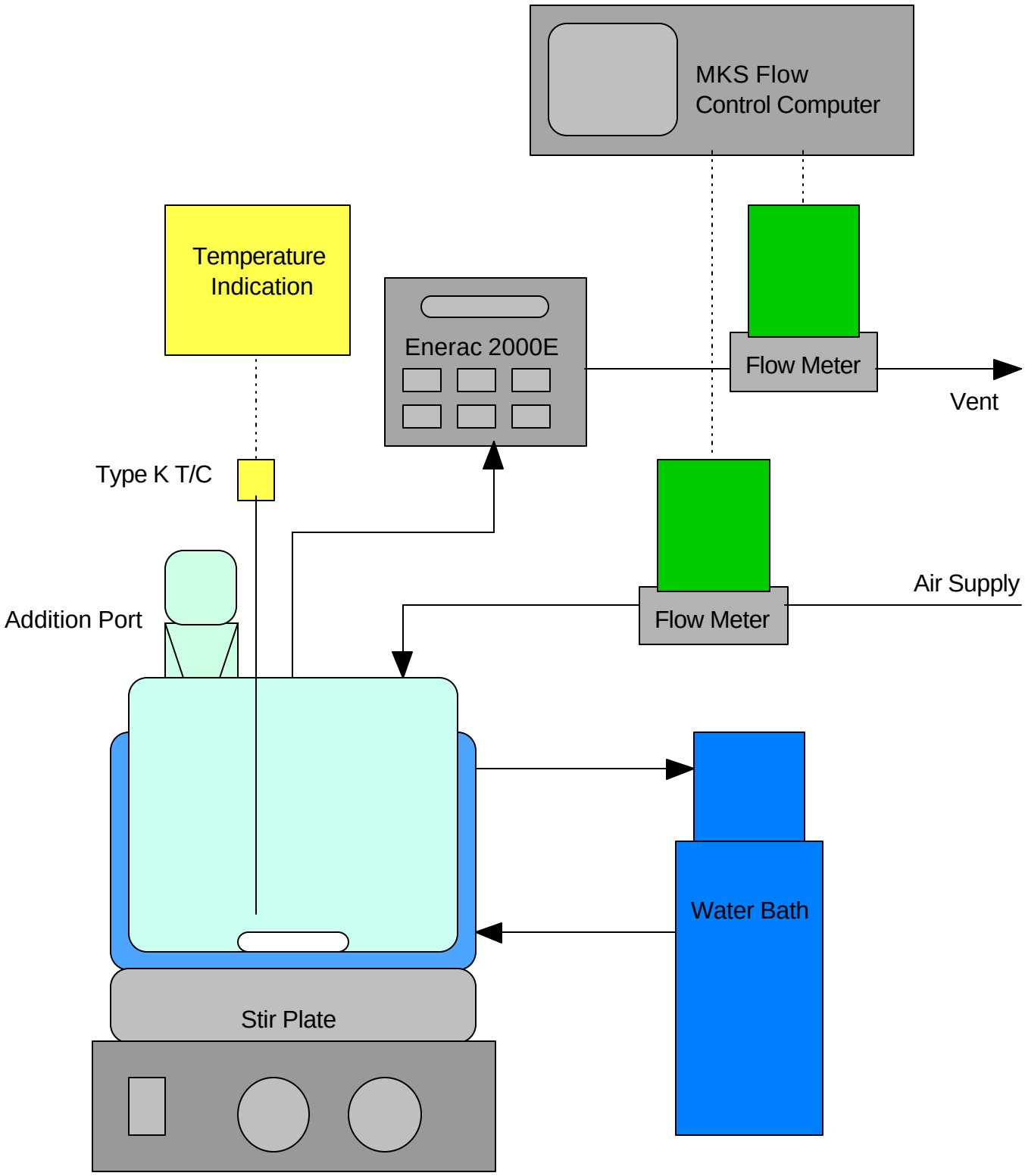
CONCLUSIONS

The NO_x TEEL-1 limit of 2 PPM could be exceeded after twenty-one minutes in a 49,000 ft^3 volume if 180 gallons of 5% boric acid is mixed with 615 gallons of 40% sodium nitrite solutions.

REFERENCES

1. Technical Task Request # HLW/DWPF/TTR-01-0023, Rate of NOx Gas Evolution with Sodium Nitrite and Boric Acid Solutions, June 27, 2001.
2. Task Technical and QA Plan # WSRC-RP-2001-00752, Rate of NOx Gas Evolution with Sodium Nitrite and Boric Acid Solutions, July 19, 2001.
3. M. E. Stone, Baseline Run Plan for Sodium Nitrite and Boric Acid Mixing Tests (U), SRT-GDP-2001-00074, July 7, 2001.
4. Operation of Enerac 2000E NOx Analyzer, L27 – Procedure 2.04, June 9, 1998.
5. Boric Acid / Sodium Nitrite Test Laboratory Notebook, WSRC-NB-2001-00134.

APPENDIX A. EXPERIMENTAL APPARATUS



APPENDIX B. SAMPLE RESULTS FROM SOLUTION MAKEUPS

Solution	Sodium Concentration	Boron Concentration	Calculated Concentration	Density	Wt% Solids	pH
	mg/L	mg/L	wt %	g/l	wt %	
Sodium Nitrite	168,000	-	38.8	1.299	39.8	8.58
Boric Acid	-	9020	5.09	1.014	-	3.76

APPENDIX C. CHARTS FROM MIXING TESTS

Figure C-1. Measured NO_x Concentrations from Baseline Run 1

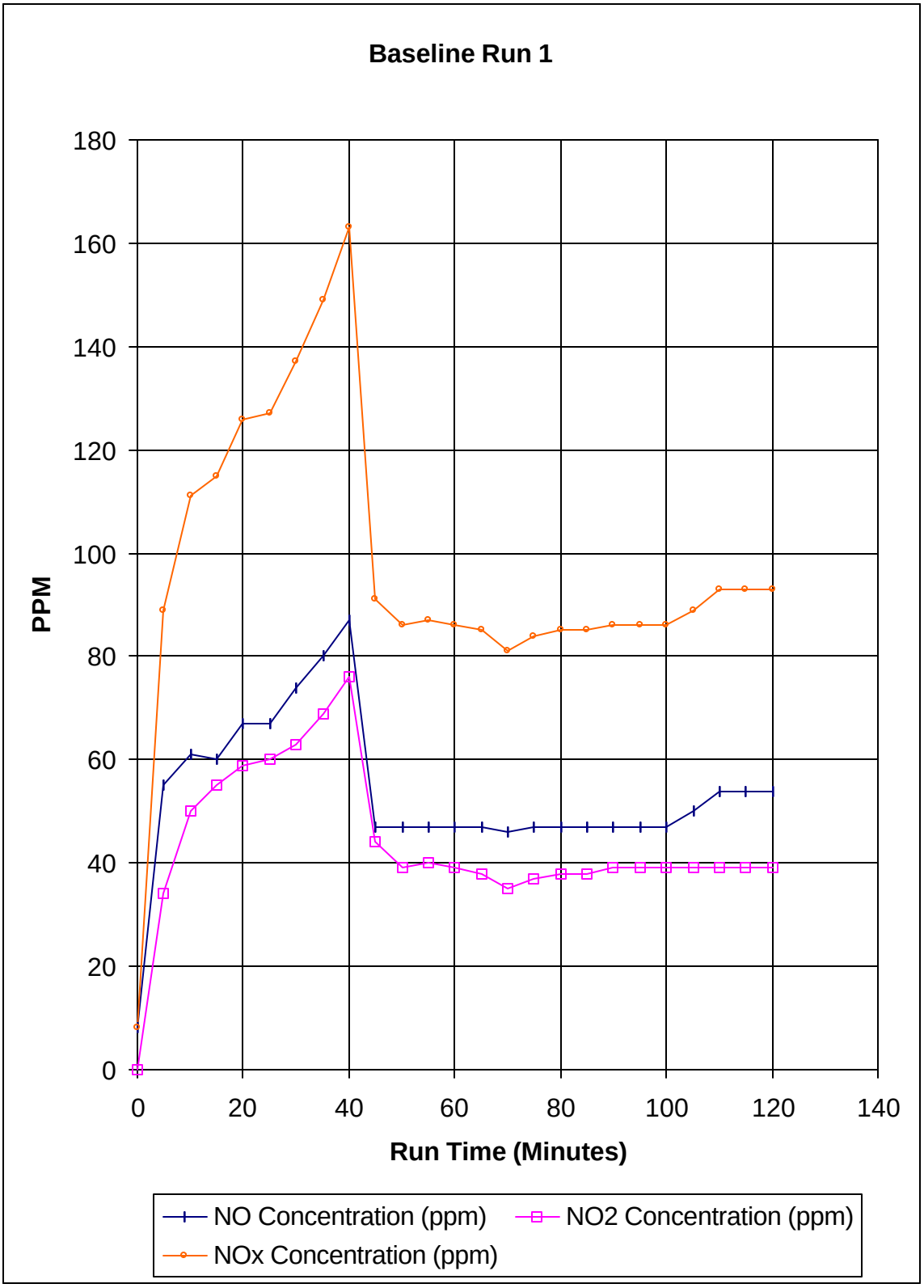


Figure C-2. Measured NO_x Concentrations from Baseline Run 2

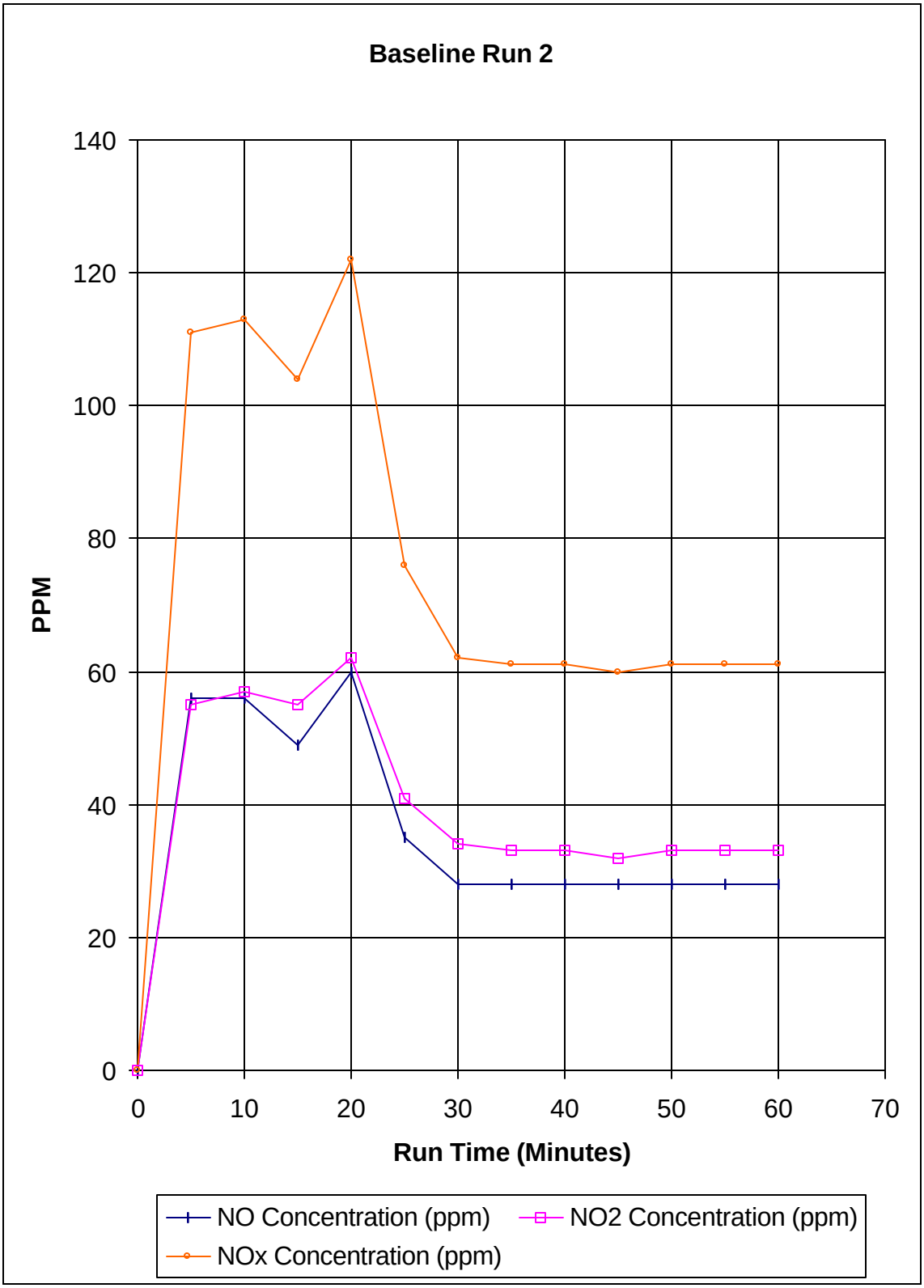


Figure C-3. Scaled NO_x Generation Amount in Baseline Run 1

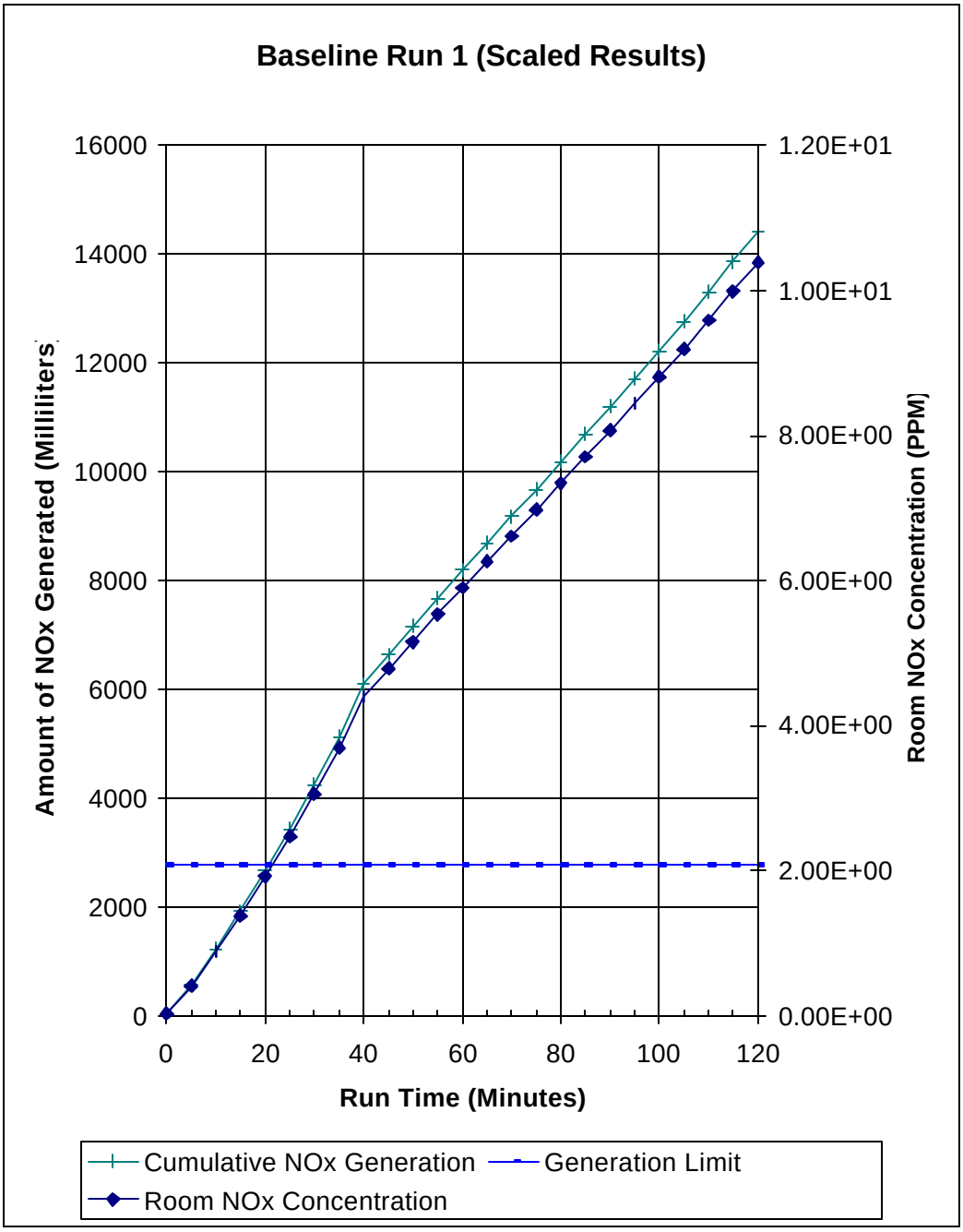
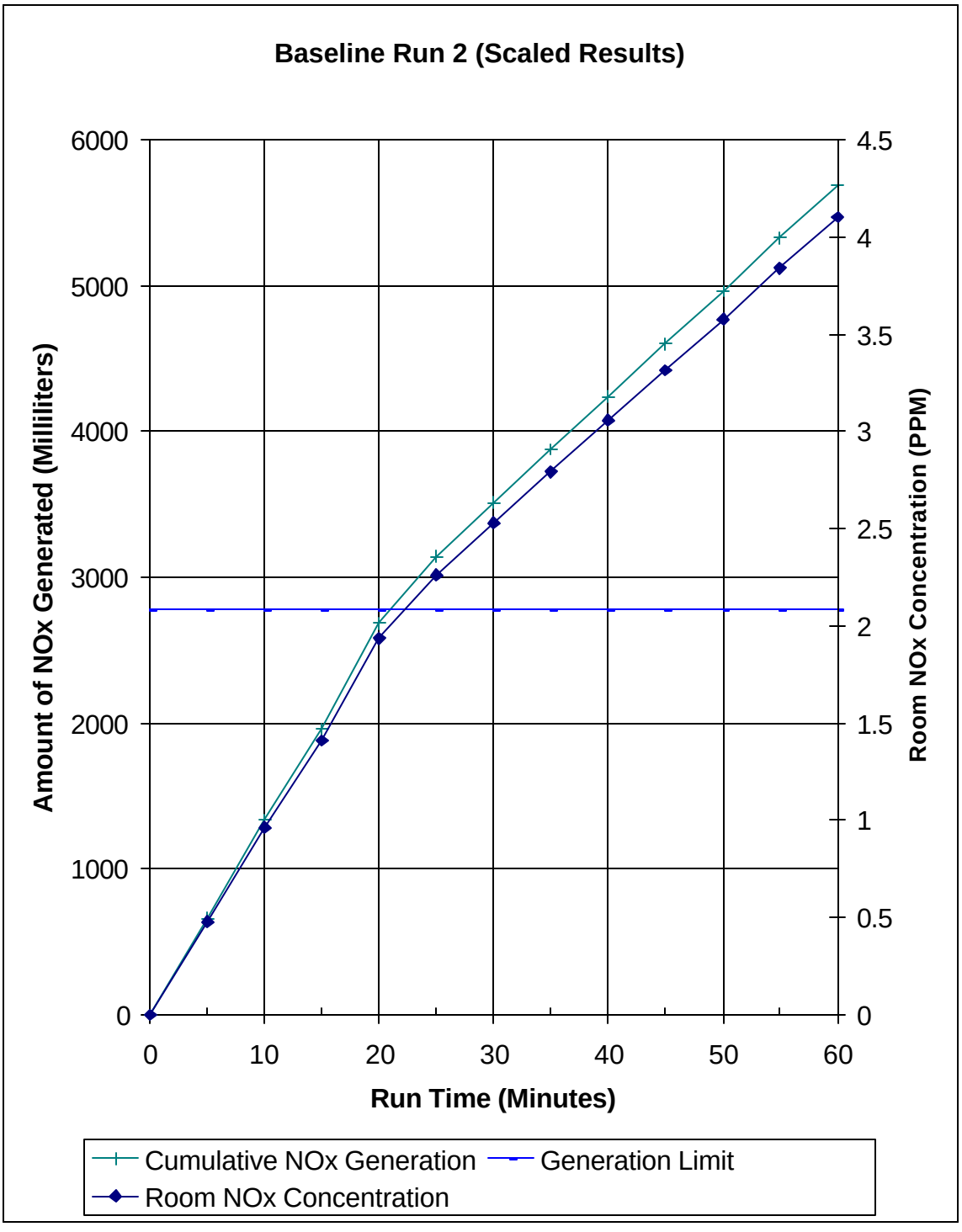


Figure C-4. Scaled NO_x Generation Amount in Baseline Run 2



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