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“MULTI-POLLUTANT EMISSIONS CONTROL & STRATEGIES”

**COAL-FIRED POWER PLANT MERCURY CONTROL BY
INJECTING SODIUM TETRASULFIDE**

By

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I. ABSTRACT

Babcock Power has undertaken a program to test the effectiveness of sodium tetrasulfide (Na_2S_4) to control mercury emissions from coal combustion. Sodium tetrasulfide has been shown in other applications to remove both the elemental and ionic forms of gaseous mercury to form solid mercury (II) sulfide, HgS . Mercury sulfide is an insoluble, thermally stable solid. Thus, the process effectively immobilizes the mercury by chemical binding. Mercury sulfide is then removed from flue gas by a particulate removal device such as a baghouse or ESP.

Tests were conducted at Southern Research Institute's Combustion Research Facility, firing an Eastern bituminous coal and a Powder River Basin coal. Sodium tetrasulfide was injected as an aqueous solution upstream of a baghouse, at rates up to 100 mg Na_2S_4 /dscm flue gas (0.7 or 1 g Na_2S_4 /kg coal for PRB or bituminous coal, respectively). While firing bituminous coal and injecting sorbent at 100 mg/dscm, the mercury concentration at the baghouse outlet was reduced about 90% compared to the inlet concentration without sorbent injection.

With the PRB coal, mercury was reduced by 90% at the baghouse outlet at a sorbent injection rate of 50 mg/dscm. Injection at 100 mg/dscm gave 98% mercury reduction at the baghouse outlet with the PRB coal.

II. INTRODUCTION

Coal-fired power plants in the United States may have to reduce their mercury emissions by up to 90% by 2007–2009. EPA has formulated a goal to reduce mercury emissions from coal-fired power plants 50 to 70% by 2005 and 90% by 2010. Senator Jeffords has proposed a 90% reduction in Hg emissions by 2007. President Bush's Clear Skies proposal has two steps in Hg reduction, 45% by 2008 and 67% by 2018. Proposed regulations could affect up to 1,100 utility boilers. Regardless of the details of future legislation, a major challenge in controlling mercury emissions from coal-fired boilers is the high degrees of Hg capture required in combination with the very low mercury concentration in typical boiler flue gas.

Mercury may be removed from flue gas to a greater or lesser extent by devices such as electrostatic precipitators, baghouses, SCRs, and SO₂ scrubbers used to control other emissions. The efficiency of such co-beneficial collection depends on the specific equipment and operating parameters, as well as on the chemical form of mercury in the flue gas, which in turn is influenced by fuel composition and combustion parameters.

Sorbents and reagents have been commercially proven in waste-to-energy plants to augment the removal of mercury. These include activated carbon, lignite coke, sulfur containing chemicals, or combinations of these compounds. Experience controlling mercury emissions has been gained in more than 60 US and 120 international waste-to-energy plants. These commercial plants burn municipal or industrial waste or sewage sludge. In waste-to-energy plants, the ratio of Cl to Hg is relatively high, and the ratio of ionic Hg to elemental Hg in the flue gas is also high.

In coal-fired plants, the ratio of Cl to Hg is lower, and the fraction of elemental mercury is higher. The removal of elemental Hg is generally more difficult to accomplish than removal of ionic Hg. For example, 85-95% of ionic mercury may be removed in a wet flue gas desulfurization system, with no significant removal of elemental mercury. In addition, while total emissions of mercury from coal-fired plants are significant, the concentration of mercury in power plant flue gas is much lower than in waste-to-energy plants. As determined in the EPA measurement program, nearly 90% of all coals contain less than 100 mg/kg mercury, and 80% of boiler exit flue gas mercury concentrations are less than 10 µg/dscm. This presents a daunting challenge for meeting the high removal requirements in proposed legislation for coal fired power plants.

Differences in coal type and pollution control devices make it necessary to develop customized solutions for each utility/plant. There can be no uniform mercury control method for all plant configurations, coal types, and existing flue gas controls used for other pollutants. In addition, the complicated chemistry and multiple mechanisms governing mercury speciation in coal-fired boilers makes it necessary to investigate Hg emission control technologies at conditions relevant to full-scale units

There are significant data related to mercury emissions from coal-fired plants. Of primary concern are the emission data related to Powder River Basin (PRB) and lignite coals. Approximately 36% of the coal burned in the US is PRB coal. More of the mercury is emitted in elemental form with PRB compared to bituminous coal, due, at least in part, to its low chlorine content. Therefore, mercury removal in conventional pollution control devices is significantly less in plants firing PRB coal than in plants firing bituminous coal.

Estimates of mercury emissions from coal-fired utility boilers in the United States vary from 45 to 57 tons per year. Since there are approximately 1,140 utility coal-fired boilers operating, this means that the “average” plant emits about 80 pounds per year. While the individual plant emission rates are low, coal-fired boilers in the aggregate are the largest source of man-made mercury emissions in the US. In comparison, Municipal Waste Combustors (MWCs) were previously the second largest source, emitting approximately 34 tons annually. However, the MWC emissions have been reduced more than ten fold to less than 2 tons per year.

Mercury Speciation – Elemental vs. Ionic Forms

Mercury compounds are not stable at high temperatures. Mercury is primarily in the elemental form in the gaseous state in the combustion chamber, independent of the coal composition. There is minimal retention of mercury in the slag due to its high vapor pressure. It is much less than 5% of the total mercury input as shown in various investigations. .

As the flue gas temperature decreases in the convective passes of the boiler, the elemental mercury reacts with other flue gas components. Mercury (II) chloride (HgCl_2) is generally accepted to be the dominant oxidized species. Even for low-chlorine coal, chlorine is available far in excess of the total mercury.

Equilibrium calculations (Brown et al, Gale) indicate complete reaction to mercury (II) chloride below 400-500°C, depending on coal type. Mercury (II) oxide, HgO , appears between 400 and 1000°C, but contributes a minor fraction of total mercury when chlorine is present.

However, oxidation appears to be limited kinetically, since a complete transformation of the Hg^0 into HgCl_2 does not occur. The extent of oxidation observed is extremely variable, but it is consistently much less than 100%. Various studies (Brown, et al) showed 70-88% oxidation of mercury at the control device inlet for bituminous coal, and 15-50% oxidation for PRB. Recent studies (Gale, et al, Niksa and Fujiwara) have identified unburned carbon (UBC) as a catalyst for mercury oxidation by chlorine. PRB coals generally yield lower UBC than bituminous coals, and this may be an important factor in the generally lower extent of mercury oxidation observed with PRB coal.

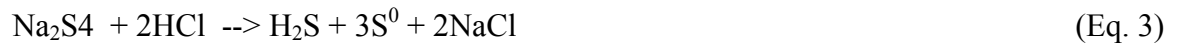
III. THE Na₂S₄ PROCESS FOR MERCURY CONTROL

Sodium tetrasulfide, Na₂S₄, has been used as a sorbent to remove mercury from flue gas in a number of waste-to-energy plants (Schuettenhelm et al, Licata et al, Rosenthal et al). The sorbent converts vapor phase mercury to solid mercuric sulfide, HgS. As the naturally occurring mineral form of mercury, red, or alpha-mercuric sulfide is known as cinnabar. The beta, or black form of H₂S is known as metacinnabar. Mercuric sulfide is a solid at temperatures below about 1,080°F, and is insoluble except under extreme conditions. By converting vapor-phase mercury to an insoluble solid, it may be removed in a baghouse or electrostatic precipitator typically found in a coal-fired power plant. Table 1 compares selected properties of mercury sulfide with elemental mercury and related compounds.

Sodium tetrasulfide can react with both oxidized and elemental mercury in accordance with the following simplified reactions (Licata, Schuettenhelm, &Kline):



At practical injection rates, and typical flue gas mercury concentrations, the mol ratio of sodium tetrasulfide to mercury is very high. The elemental sulfur available from reaction (1) to participate in reaction (2) is limited to the same order of concentration as mercury. Decomposition of Na₂S₄ by an acid such as HCl can provide excess elemental sulfur to augment the reaction with elemental mercury. It can also generate an alternate form of ionic sulfur, H₂S, for reaction with oxidized mercury as shown in the following reactions:



In the absence of HCl, carbon dioxide may act as an acid for decomposition:



Therefore, it is possible to eliminate both the elemental and ionic forms of mercury in the flue gas.

In the process, it is sufficient to inject an aqueous Na₂S₄ solution into the flue gas duct. Such a system can be easily retrofitted to an existing flue gas cleaning plant.

PILOT PLANT TEST PROGRAM

Babcock Power Inc. conducted tests of sodium tetrasulfide injection for removal of mercury from coal-combustion flue gas at the Southern Research Institute (SRI) in April 2003. Babcock Power Environmental Inc. (BPEI) provided the technical lead for this technology, as well as the labor and equipment required for injection of the sorbent. BPEI's interests and expertise in the process stem from development for waste-to-energy applications. Southern Company and SRI co-sponsored the tests, which were conducted under SRI's US Department of Energy-funded program "Mercury Control with Calcium Based Sorbents and Oxidizing Agents (DE-PS26-02NT41183). PPG Industries contributed the sodium tetrasulfide for the tests, as well as consultation on sulfide chemistry.

The tests were performed in SRI's 1 MW_{th} Combustion Research Facility (CRF). The CRF includes vertical radiant furnace, up-fired with a swirl-stabilized burner. Cross-flow, air-cooled tubular heat exchangers simulate the time-temperature profile typical of utility boilers. Coal is pulverized using a bowl mill and fired from storage. There is independent control of primary and secondary air rates and preheat temperatures.

Table 2 shows the analyses of the test fuels, an Eastern high volatile bituminous coal, and a Powder River Basin sub-bituminous coal. The chlorine content of the bituminous coal was 0.013%, which is low compared to many bituminous coals. In several tests with the bituminous coal, chlorine was injected at the burner to simulate a higher chlorine content coal. The coal ash compositions are shown in Table 3.

The furnace was fired at 3.7 million Btu/hr and 3% to 4% excess oxygen at the furnace exit. The flue gas oxygen content at the sodium sulfide injection point, upstream of the baghouse, was about 8%. For most tests, the temperature at the injection point was about 300°F, and the baghouse outlet temperature was 270°F. The residence time between the injection point and the baghouse inlet was about 2.3 seconds. Mercury concentrations were measured at the inlet and the outlet of the baghouse. The baghouse outlet temperature was varied from 245°F to 325°F during the tests with bituminous coal.

The sodium tetrasulfide was injected as a 5.5 wt% solution (diluted to 2.7% for some low injection rate tests) using an air-atomizing nozzle mounted on the duct centerline, co-current with flue gas flow. The highest rate of injection tested, 100 mg Na₂S₄/dscm flue gas, at 3% O₂, is equivalent to 13 ppmv. The mercury concentrations reported here are corrected to 3% oxygen, dry basis, in the flue gas. All mercury concentrations reported are vapor phase only. Particulate mercury was not measured. Without sorbent injection, the measured vapor phase mercury approximately corresponded to the mercury content of the coal. With sorbent injection, the measured concentration of mercury decreased at the baghouse inlet, because any mercury already reacted to a particulate form at that point was not measured. Additional reaction and removal of solids in the baghouse gave much lower measured concentrations at the outlet. In all cases, the baseline for reported percent removal is taken as the mercury concentration at the baghouse inlet, measured prior to sorbent injection.

SRI's semi-continuous mercury measurement method yields both elemental and total vapor phase mercury concentration. The concentration of oxidized mercury is taken as the

difference between measured elemental and total forms. The method incorporates an Apogee Scientific QSIS sampling probe, and a customized PSA 10.665 analyzer. The probe removes fly ash from the gas sample with minimal contact between the sample and the ash. SRI's method includes a spike and recovery system to correct for losses in the elemental train of the sample system. For most spike tests during injection of Na₂S₄ (i.e., other than the baseline tests), the spike recoveries were too low to permit meaningful correction of the elemental data. Therefore, we report only total vapor phase mercury for the injection tests.

Bituminous coal. Figure 1 shows mercury concentrations measured while firing bituminous coal. Figure 2 shows the results in terms of percent mercury removal. In a baseline test without sodium tetrasulfide injection, the measured a baghouse inlet mercury concentration was 8.1 µg/m³ in the flue gas. The elemental mercury concentration was 3.5 µg/m³ or 43% of the total. With no injection, the baghouse reduced the total mercury concentration by about 44% from the inlet. At the baghouse outlet without injection, all of the mercury was oxidized.

With sodium tetrasulfide injected at 100 mg/dscm, the flue gas mercury concentration at the inlet decreased from 8.1 µg/m³ to 5.4 µg/m³, while mercury at the baghouse outlet decreased to about 1.0 µg/m³. This result corresponds to 87% removal of mercury at the baghouse outlet with injection, compared to the no-injection inlet concentration. At an injection rate of 50 mg/dscm, the reduction at the outlet was 63%.

Injection temperature. Figure 3 shows the effect of temperature on mercury removal at a constant sodium tetrasulfide injection rate of 100 mg/dscm. Baghouse outlet mercury removal fell below 50% at 325 °F, compared to 87% at 270 °F. At 245 °F, mercury removal at the baghouse outlet reached 95%. Mercury removal at the inlet was 60% 245 °F, compared to 35% at 270 °F.

The results are plotted against baghouse outlet temperature. The flue gas temperature was varied using a heat exchanger upstream of the injection point, so the temperature varied at the injection nozzle as well. Injection/outlet temperatures for low, baseline, and high temperature cases were 257/245, 300/273, and 375/325 °F.

Chlorine injection. The chlorine content of the test bituminous coal was low relative to typical bituminous coals, with a fuel-chlorine of 0.013% equivalent to 9 ppm HCl in the flue gas. During injection of sodium tetrasulfide at 100 mg/dscm, chlorine gas was injected at the burner, at rates equivalent to a total HCl concentration in the flue gas of 45 and 85 ppm. This resulted in a reduction in apparent mercury removal efficiency. This was unexpected, since sodium tetrasulfide has been used successfully in waste-to-energy plants, where chlorine concentrations are typically higher. On initiation of chlorine injection, mercury concentration at the outlet spiked to well over the inlet baseline (no sodium sulfide or chlorine addition) value. This suggests that chlorine caused previously captured mercury to be released. This effect may exaggerate the negative influence of chlorine compared to a steady state process where there are no solids inventory accumulated under low-chlorine conditions.

PRB Coal. Figure 4 shows the mercury concentrations measured while firing the PRB coal. Figure 5 shows the results in terms of mercury removal at the outlet compared to the no-

injection inlet baseline. In the baseline test without sulfide injection, PRB coal combustion yielded $6.8\text{-}\mu\text{g}/\text{m}^3$ mercury concentration at the baghouse inlet. The portion of elemental mercury was higher than the bituminous coal, at 65% of the total. With no injection, the baghouse outlet concentration was reduced by 33% compared to the inlet, at $4.5\ \mu\text{g}/\text{m}^3$. About 44% of the outlet concentration was measured as elemental mercury.

With injection of sodium tetrasulfide at $100\ \text{mg}/\text{dscm}$, the total vapor phase mercury at the baghouse inlet decreased only about 25%, from $6.8\ \mu\text{g}/\text{m}^3$ to $5.2\ \mu\text{g}/\text{m}^3$. However, vapor-phase mercury was essentially eliminated at the baghouse outlet.

An intermediate injection rate of $50\ \text{mg}/\text{dscm}$ yielded an outlet concentration of only $0.9\ \text{mg}/\text{dscm}$, or about 87% removal. At the lowest injection rate tested, $25\ \text{mg}/\text{dscm}$, the outlet removal rate was about 65% compared to the no-injection baseline.

The reduced injection rate results cited above were measured after operating the system for about ten hours with no sorbent injection, and then injecting sodium tetrasulfide, first at 25 , and then at $50\ \text{mg}/\text{dscm}$.

In a separate test, the injection rate was reduced to $50\ \text{mg}/\text{dscm}$ after several hours of injection at $100\ \text{mg}/\text{dscm}$, and the outlet concentration remained at $0\text{-}0.1\ \mu\text{g}/\text{dscm}$ one hour after the rate reduction. Sorbent injection was then stopped, and after two hours, the outlet concentration was about half the pre-injection outlet value. This residual effect suggests that reaction in the filter cake is significant, and that in actual operations the required dose rate may be lower than the pilot plant test.

Hydrogen sulfide. A portable analyzer was used to sample baghouse inlet and outlet flue gas for hydrogen sulfide during each test. Hydrogen sulfide was not detected in any coal-firing tests. During preliminary tests with natural gas firing, low levels of H_2S consistent with partial decomposition of injected Na_2S_4 were detected. This indicated that the decomposition reaction suggested in Equation 3 may be important. Since there was no HCl with gas firing, the acid reactant for decomposition was probably CO_2 via Equation 3a. The absence of H_2S with coal firing may be a result of its reaction with other metals in the flue gas.

IV. CONCLUSIONS

The tests showed that sodium tetrasulfide is effective for removing mercury in coal combustion when injected upstream of a baghouse. It reduced the mercury at the baghouse outlet by about 90% for the bituminous coal, and by over 98% for the PRB coal, when injected at 100 mg/dscm. This injection rate corresponds to about 1g Na₂S₄/kg bituminous coal, and 0.7 g/kg PRB coal. With the PRB coal, 65 and 87% removal rates were achieved with injection rates of 25 and 50 mg/dscm. The stated removals are based on baghouse outlet concentration with injection, compared to inlet concentration without injection. There was some removal across the baghouse without sorbent injection. Removal efficiency increased with decreasing temperature. Hydrogen sulfide was not detected in the flue gas when sodium tetrasulfide was injected during coal firing.

Since many coal-fired power stations use an electrostatic precipitator for particulate removal, we plan to test sodium tetrasulfide injection upstream of an ESP at the SRI Combustion Research Facility. Additional coal types, higher chlorine content coal, effects on ash handling and disposal, and impacts on operation of scrubbers, will be investigated. Babcock Power has developed plans to conduct a field test program at a 100 MW coal-fired facility next spring.

Sodium tetrasulfide is an alternative to carbon- based technologies for controlling mercury emissions from coal-fired plants. It appears to be especially promising for applications in which the elemental fraction of mercury is high, as is typical with PRB and lignite coals.

V. ACKNOWLEDGEMENTS

Babcock Power Environmental gratefully acknowledges the contributions of Southern Company and Southern Research Institute, who co-sponsored the tests; the US Department of Energy for providing funding for operation of the SRI facility under its program "Mercury Control with Calcium Based Sorbents and Oxidizing Agents (DE-PS26-02NT41183); and PPG Industries who contributed the sodium tetrasulfide for the tests, and provided advice on sulfide chemistry.

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Table 1
Properties of Mercury and Selected Compounds*

	Melting point, °C	Boiling point, °C	Sublim. point, °C	Decomp. point, °C	Solubility in water, mg/liter at ~20 °C
Hg	-39	357			i
HgO				500	53
HgCl ₂	276	302			69,000
HgS,β (black)	584				i
HgS,α (red)			584		0.01

*CRC Handbook of Chemistry and Physics, 53rd edition.

i = insoluble

Table 2
Bituminous and PRB coal analysis

	Choctaw American, High Volatile A Bituminous Coal	Black Thunder, Powder River Basin Sub-bituminous Coal
As-received basis		
Carbon, %	80.07	59.70
Hydrogen, %	4.84	3.83
Nitrogen, %	1.91	0.83
Sulfur, %	0.90	0.30
Oxygen, %	6.05	15.43
Moisture, %	2.04	14.00
Ash, %	4.19	5.92
Volatiles, %	31.76	37.57
Fixed Carbon, %	62.01	42.70
HHV, Btu/lb	14,019	9,969
Chlorine, %	0.0127	<0.010
Mercury, wt. ppm	0.065	0.068
Equivalent HCl in flue gas, ppm @3% O ₂ , dry	8.6	9.5
Equivalent mercury in flue gas, µg/dscm @ 3% O ₂ ,dry	6.5	9.5

Table 3
Coal Ash Analysis

wt. %	Choctaw America Bituminous	Black Thunder PRB Sub-bituminous
Li ₂ O	0.06	0.01
Na ₂ O	1.1	1.4
K ₂ O	2.0	0.5
MgO	1.1	4.3
CaO	2.5	22.0
Fe ₂ O ₃	13.8	6.0
Al ₂ O ₃	31.4	15.4
SiO ₂	42.6	35.4
TiO ₂	1.3	1.3
P ₂ O ₅	.16	0.7
SO ₃	2.8	11.5

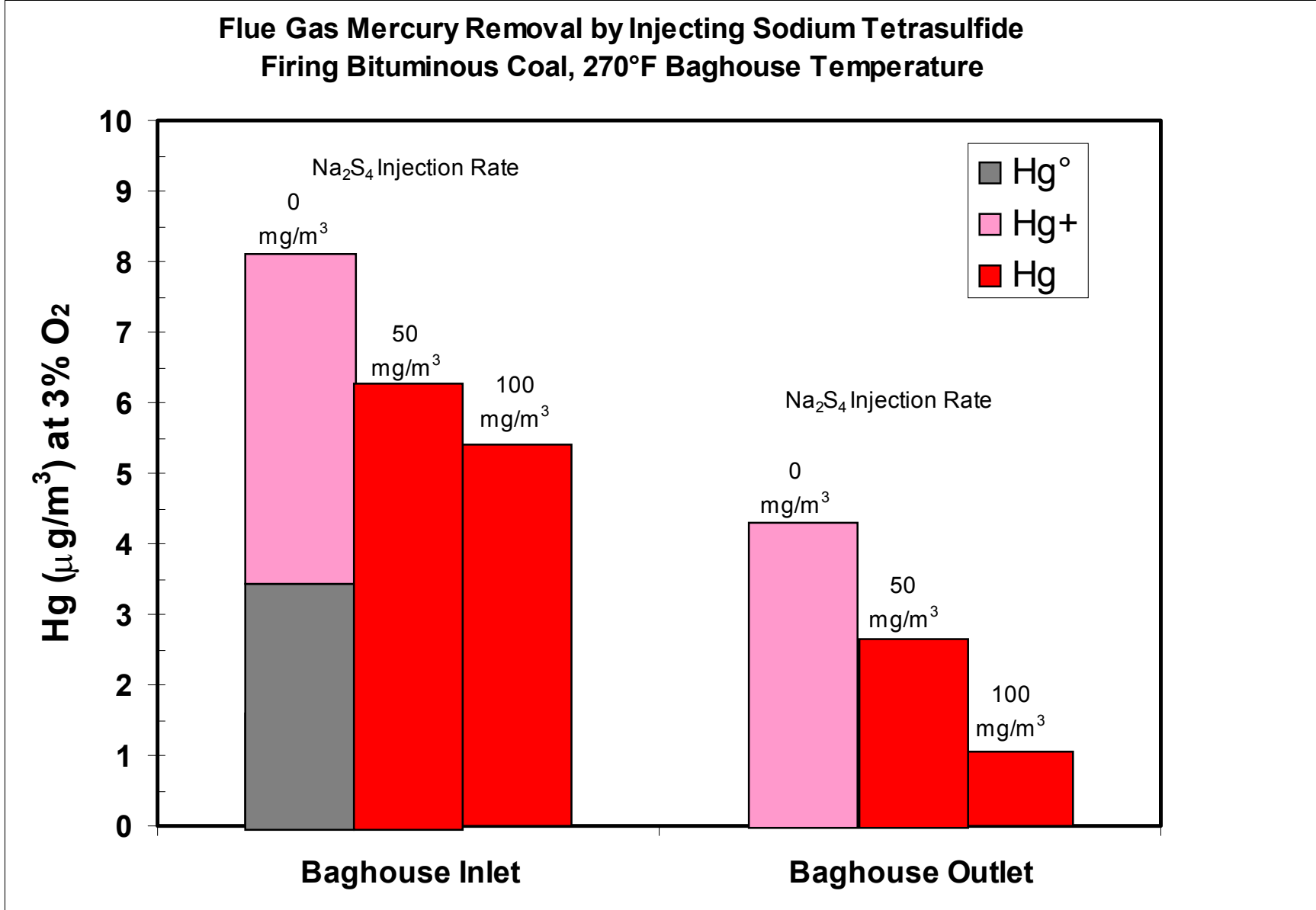


Figure 1. The effect of sodium tetrasulfide injection on flue gas mercury concentration firing bituminous coal.

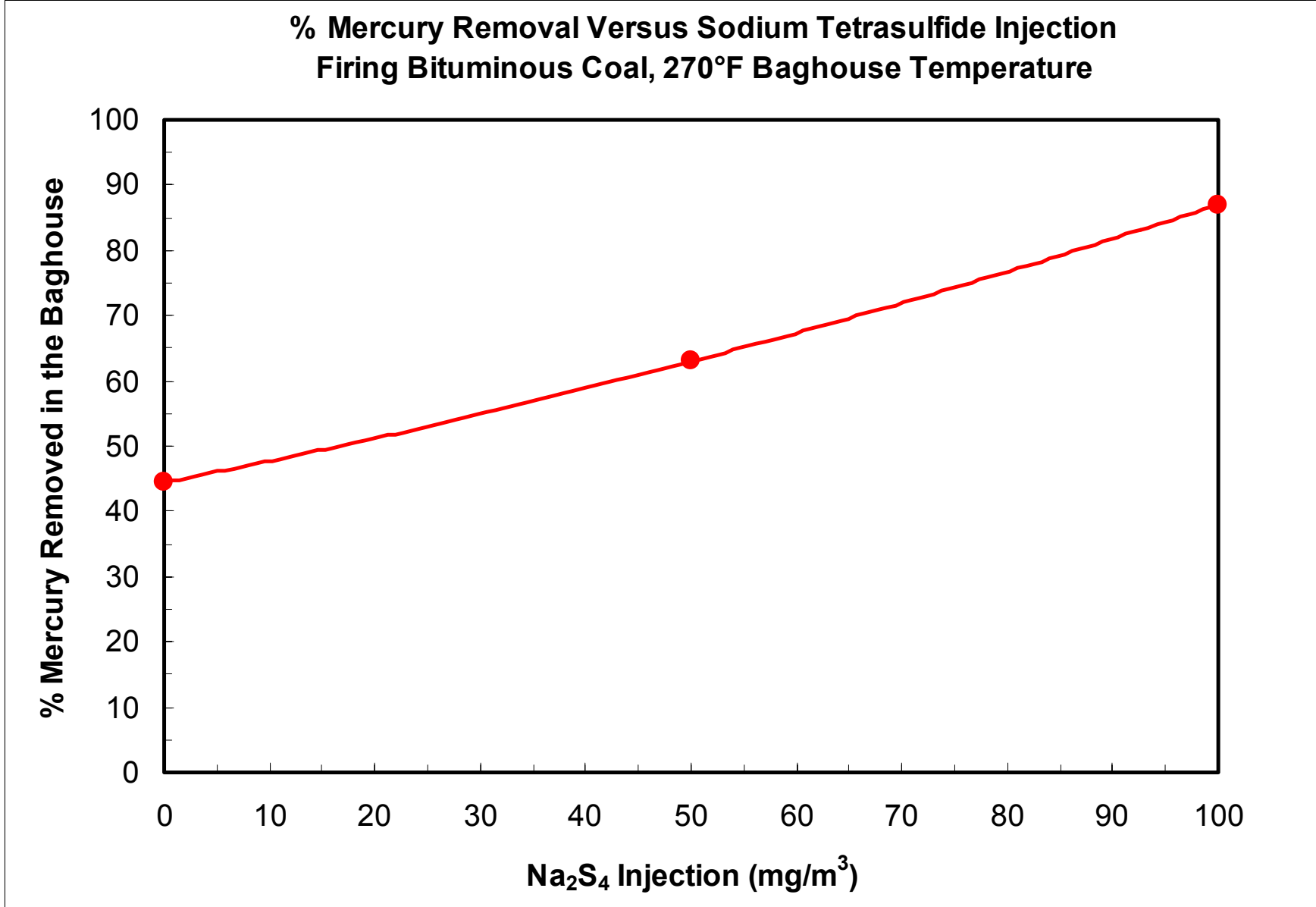


Figure 2. Mercury removal by injecting sodium tetrasulfide at the baghouse while firing bituminous coal.

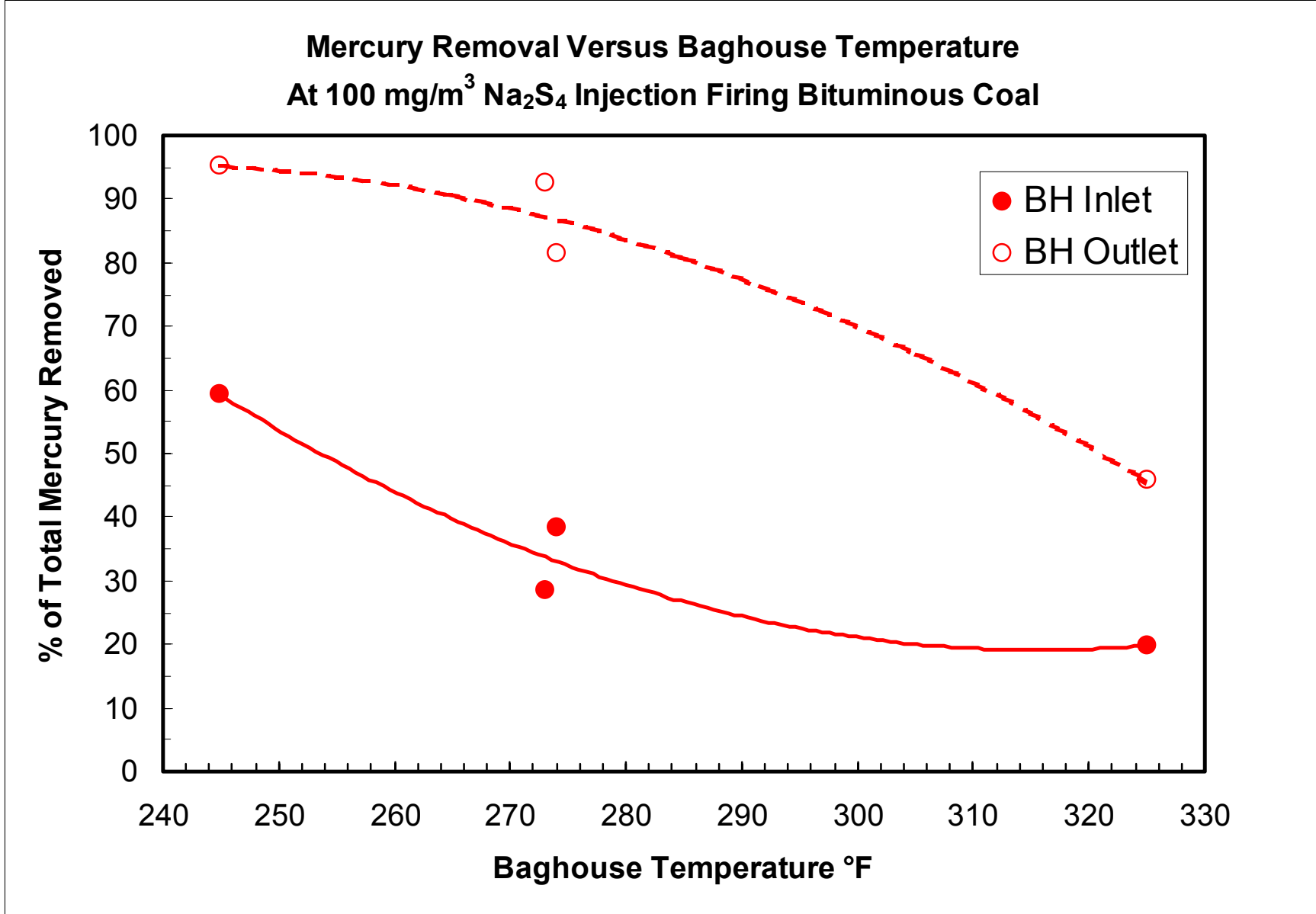


Figure 3. The effect of baghouse temperature on sodium tetrasulfide mercury removal for bituminous coal.

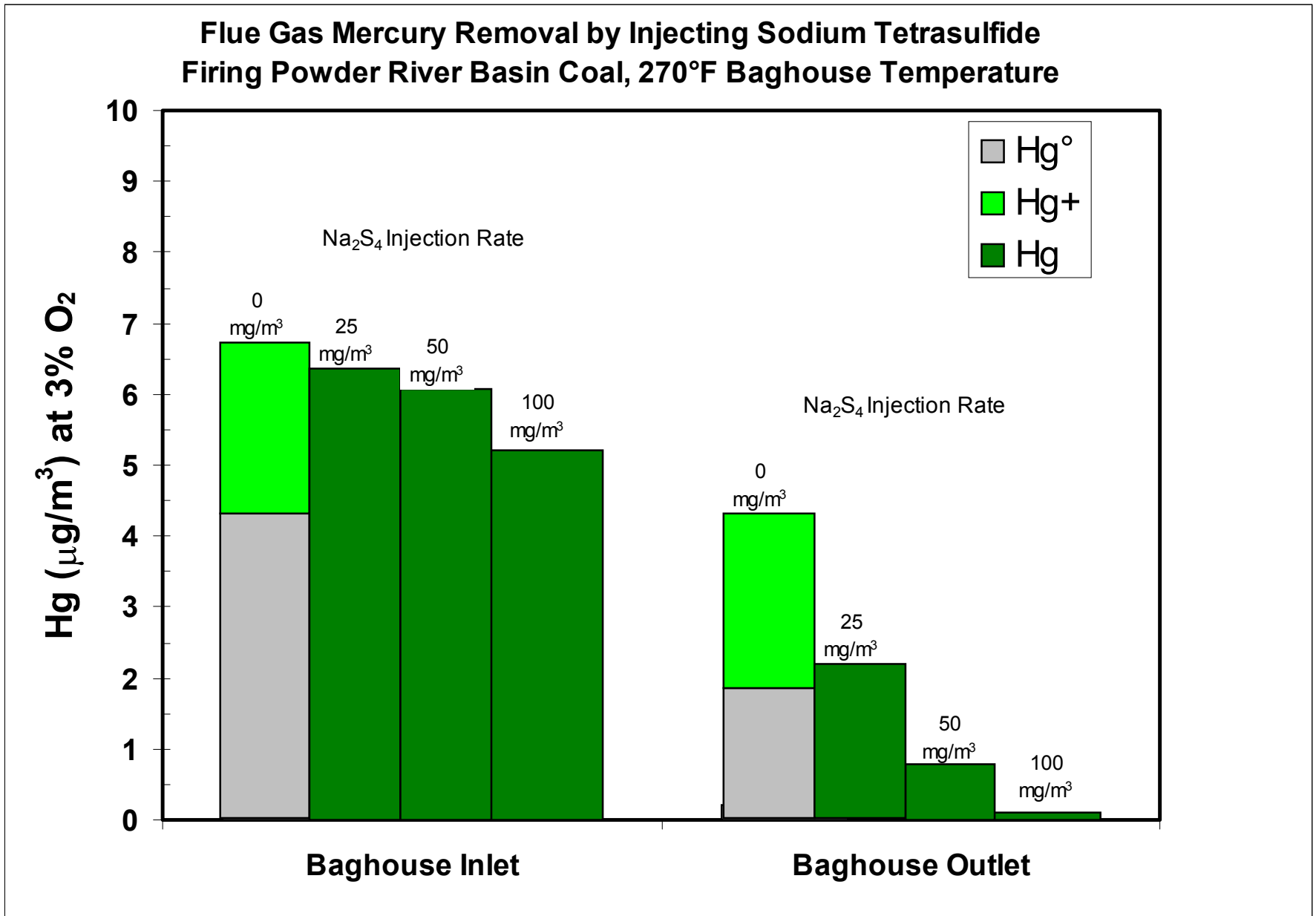


Figure 4. The effect of sodium tetrasulfide injection on flue gas mercury concentration firing Powder River Basin coal.

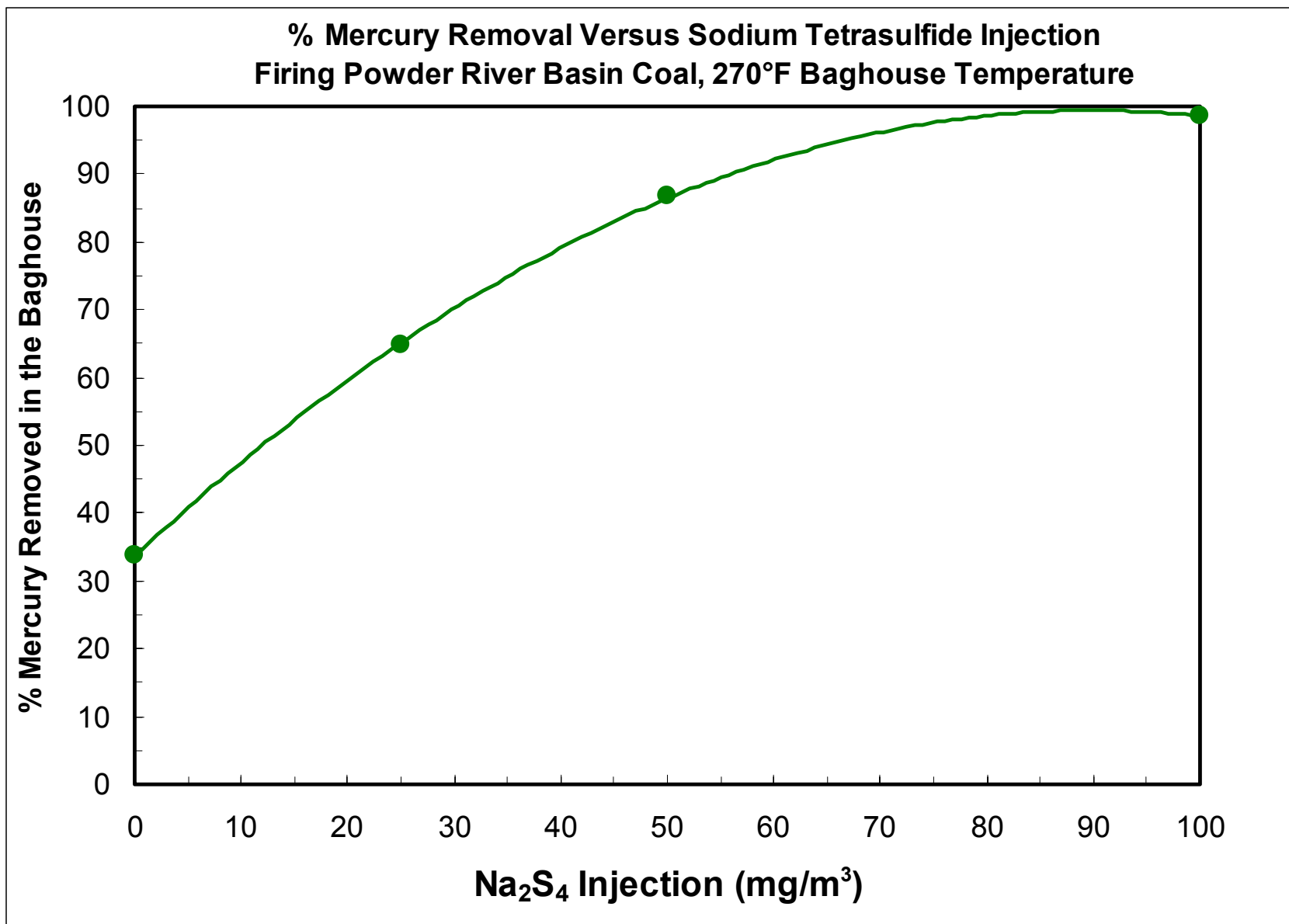


Figure 5. Mercury removal by injecting sodium tetrasulfide at the baghouse while firing PRB coal.