



Reducing Mercury Emissions from Coal Combustion in the Energy Sector in Russia

Demonstration of Adding Chemical Reagents to Increase Mercury Capture



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The report can be found on UNEP Chemicals Branch website:

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Project manager in UNEP was Gunnar Futsaeter

Acronyms and Abbreviations

ACAP	Arctic Council Action Plan
DTIE	UNEP Division of Technology, Industry and Economics
EPA	United States Environmental Protection Agency
IOC	Institute of Organic Chemistry
ISTC	International Scientific and Technical Center
MATS	Mercury and Toxic Substances
PM	particulate matter
rpm	revolutions per minute
SSFA	Small Scale Funding Agreement
TPP	thermal power plant
UNEP	United Nations Environmental Programme
VTI	All-Russia Thermal Engineering Institute

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1 Background

Options for mercury (Hg) emission reductions are gaining an ever increasing level of attention since it has been universally accepted that these emissions are detrimental to human health and to the environment. In this respect, the most useful regulation is the Mercury and Toxic Substances (MATS) regulation developed by the U.S. Environmental Protection Agency (EPA), which specifies the limits for Hg emissions from coal-fired thermal power plants (TPP). This makes the United States the world's first country to mandate the control of Hg emissions with the existing air pollution control equipment or technology specifically installed to control Hg.

The most widely used types of particulate matter (PM) controls in Russia are wet centrifugal scrubbers with Venturi tube (wet PM scrubbers) (some 600 units operational), which are installed at more than 30 percent of coal-fired TPPs. A wet PM scrubber is shown in Figure 1.



Figure 1. Wet PM scrubber.

In Russia, attempts were undertaken by the All-Russia Thermal Engineering Institute (VTI) in the 1990s to measure Hg emissions from coal-fired TPPs, followed by the inventory activity under the Arctic Council Action Plan (ACAP) Program. The overall annual Hg emissions from coal-fired TPPs were estimated at 7 to 8 metric tons/year, with the greater amount of these emissions being attributed to the TPPs located in the industrial areas of the Urals, Western Siberia, and the European part of Russia. The Hg emissions problem is especially severe because of rather high background atmospheric pollution levels in these parts of the country. Despite this, no systematic approach has been considered to alleviate the problem, and the experimental work was rather uncommon.

VTI has previously evaluated means to improve PM capture efficiency in modified wet PM scrubbers. The modification was accomplished by introduction of the closed-cycle liquid spray system. The work was performed under a cooperative agreement between VTI and the Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences and was financed by the U.S. EPA through the International Scientific and Technical Center (ISTC). This report evaluates the possibility of further wet PM scrubber modification by addition of chemical reagent injection system for improved removal of Hg.

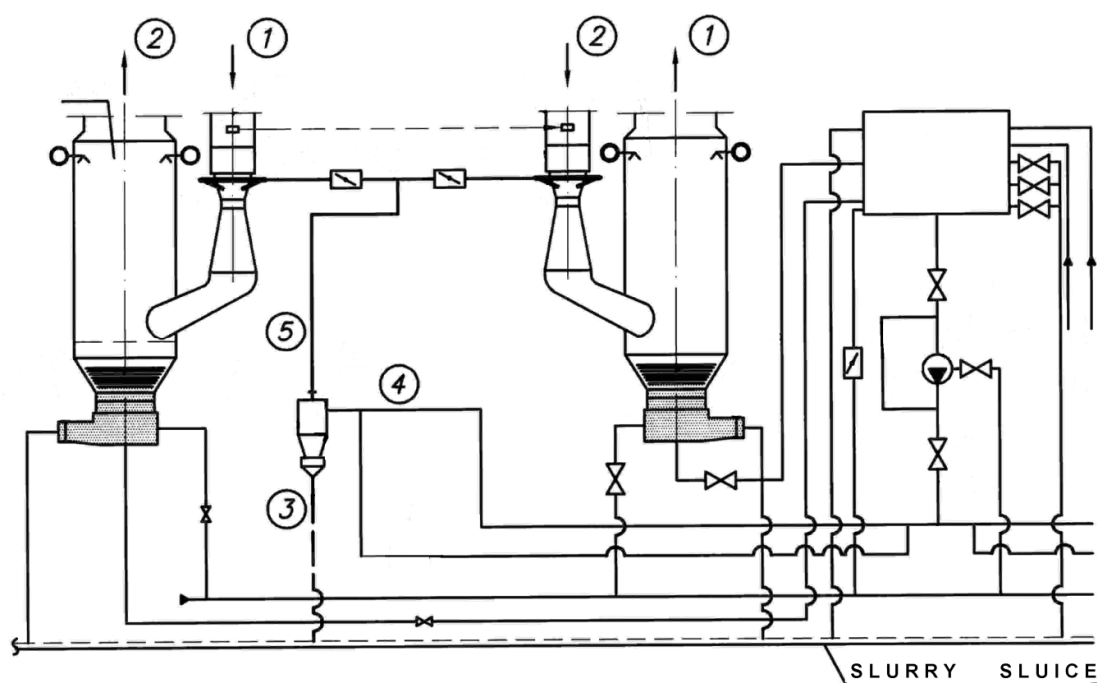
1.1 Objectives for this Project

This project will test adding chemical reagents (additives) to the previously modified wet PM scrubber liquor at Toliatti power plant to determine the extent of possible Hg removal once chemical additives are injected. Additives are expected to increase the extent of mercury oxidation. Oxidized mercury forms are water soluble and will be removed in wet PM scrubber sludge and thus increased efficiency of mercury removal from the flue gas stream will be accomplished. These additives will be tested at different concentrations in an attempt to find the optimum addition rate for maximization of mercury oxidation. Preliminary data of laboratory studies investigating the effectiveness of oxidizing additives on the extent of mercury oxidation demonstrated high mercury oxidation efficiency even at very low concentrations of additives.

2 Preliminary Experiments

Preliminary experiments focused on measuring the effect of increased water flow rate into wet PM scrubbers on the efficiency of PM removal and Hg removal from flue gas. The known method of improving the PM collection efficiency of wet PM scrubbers is to increase the flow of water sprayed into the throat of the tube. To satisfy higher water flow requirements, the closed-cycle system was previously installed during the project funded by the U.S. EPA. This modification enabled the spraying of water over a wide range of flows and the effective use of the reagents.

Preliminary experiments were carried out at the Toliatti TPP cogeneration plant. The plant is equipped with a TP-87, 420-ton per hour boiler, firing Kuznetsk coal and located in the area near the Volga River with rather unfavorable ecological conditions. The schematic of the closed-cycle water spray system for two wet scrubbers and sampling points for determination of fly ash load and Hg concentration in the flue gas is shown in Figure 2. The modification of the wet scrubbers was based on using the ash slurry previously clarified in the hydrocyclones. To accomplish this, the hydro-seals placed under the scrubbers were equipped with the on/off valves on the drain pipes to make it possible to deliver the slurry to the storage tank and further pump it to the hydrocyclone.



1. Fly ash sampling for determination of inlet ash load and Hg content in fly ash
2. Fly ash sampling for determination of outlet ash load and Hg content in fly ash
3. Pulp sampling from hydro cyclone drain for determination of Hg content in caught ash.
4. Pulp sampling for determination of Hg content in inlet of hydrocyclone.
5. Pulp sampling for determination of Hg content in closed-cycle liquid spray system

Figure 2. Schematic of sampling points for determination of PM loading and Hg concentration in flue gas.

In the hydrocyclone, the slurry is split into two streams – the clarified slurry stream and the dense slurry stream. The flow of dense slurry from the hydrocyclone is directed to the sluicing

system and that of the clarified slurry is fed to the annular headers arranged above the Venturi tube. From the annular headers, this clarified slurry is directed to the flue gases via eight specially designed nozzles. The flow of the clarified slurry fed for spraying into the Venturi tube is controlled by varying the pump motor revolutions per minute (rpm) using the frequency converter. The slurry flows were measured on the delivery pipes running from the pump to the hydrocyclone (measurement point 2 in Figure 2) and on the vertical liner section of the delivery pipe of the clarified slurry from the hydrocyclone to the Venturi tube nozzles (measurement point 1 in Figure2). Also, measurements of the service water flow were made (measurement point 4 in Figure 2).

Test results of tests in the closed-cycle water spray mode demonstrated that the increase of the clarified slurry feed into Venturi tube nozzles up to 80 to 100 m³/h (which is equivalent of the 0.40 to 0.47 liter of water/Nm³ of flue gas) resulted in increased PM collection efficiency up to 98.67 to 98.85 percent (with the inlet flue gas PM concentration of 14.5 to 15.9 g/m³). In comparison, the PM collection efficiency under regular conditions is 86.7 percent. The improved PM collection efficiency results in a tenfold reduction of PM atmospheric release with no increase in the amount of fresh water fed to the facility.

Preliminary results of Hg removal as a function of spray water flow rate are shown in Figures 3 and 4. The results of measurement of Hg concentration in the coal-fired flue gas shown in Figure 3 are of particular interest as no such full-scope investigations were conducted on the Kuznetsk coal-fired power plants in Russia before.

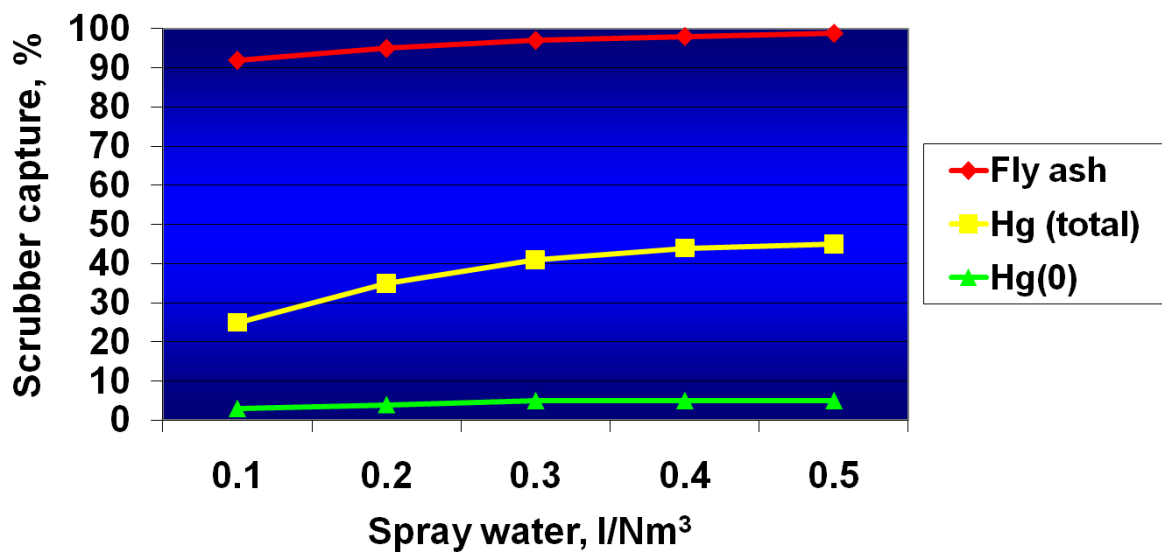


Figure 3. Efficiency of fly ash and Hg (total) removal for various scrubber operating modes.

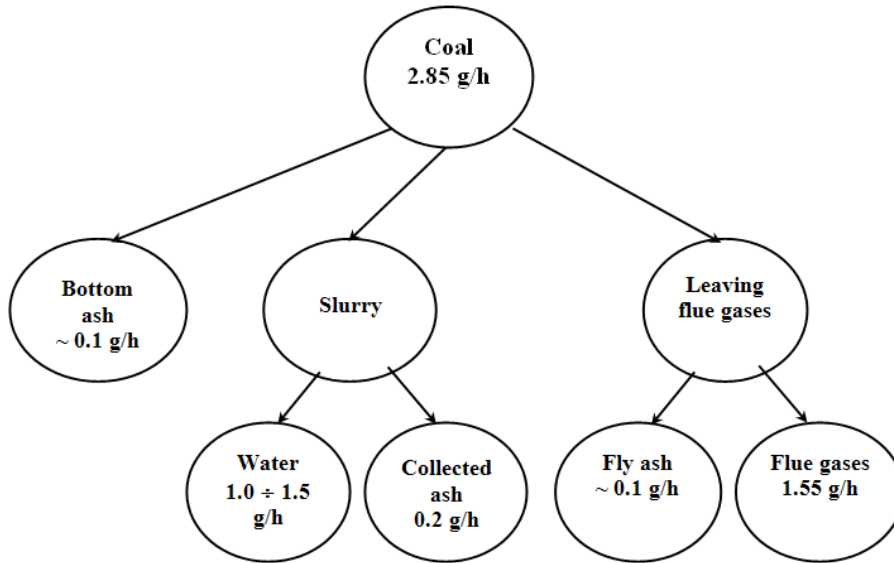


Figure 4. Calculation of Hg material balance for TP-87 boiler firing Kuznetsk coal.

As can be seen in Figure 3, the efficiency of fly ash removal (red curve in Figure 3) remains fairly constant at 90+%, while the efficiency of Hg (total) removal by wet PM scrubber is a function of spray water flow rate. Total Hg removal may be increased by 20 percentage points (from about 20% to about 40%) for scrubbers with the closed-cycle water spray system in comparison to normally used scrubber operating mode. However, one can see from the Figure 3 that mostly oxidized Hg (Hg^{2+}) is removed. Efficiency of elemental Hg (Hg^0) removal is low and does not depend on spray water flow rate.

Figure 4 illustrates the results of the calculation of the Hg material balance for Kuznetsk coal firing. Up to 60 percent of the total Hg contained in the coal were not removed in scrubbers and were released to the atmosphere. About 90 percent of this amount is Hg^0 vapor. Therefore, in order to improve the overall Hg capture by wet PM scrubber, Hg^0 vapor should be oxidized to Hg^{2+} .

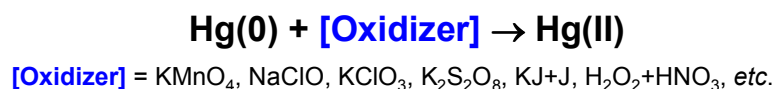
3 Additive Selection for Hg⁰ Oxidation in Flue Gas

Chemical oxidizers added to wet PM scrubbers can theoretically convert flue gas Hg⁰ to soluble Hg²⁺, thereby decreasing the release of Hg⁰ to atmosphere. The objective of laboratory tests presented in this section was to investigate Hg⁰ oxidation and to determine the extent of possible Hg removal in wet PM scrubbers of Toliatti TPP once chemical additives are added.

Bench-scale tests were conducted at the Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences investigating the possibility of oxidizing Hg⁰ in gases (in particular in air) by bubbling them through water solutions of oxidizing salts KMnO₄, KClO₃, and K₂S₂O₈. For additional oxidation and alkylation tests, HNO₃ and NaOH were used, respectively. The objective of the test is to demonstrate potential for capture of Hg vapor from flue gas of coal-fired power plants through injection of aqueous solutions of oxidizing agents into the flue gas. This procedure involves, first, the oxidation of Hg⁰ compounds to bivalent Hg and, secondly, their dissolution and subsequent removal.

The equipment for oxidizer injection can be mounted anywhere on the path of flue gases from the boiler furnace to the wet PM scrubber. It should be noted that fly ash components of flue gases may be potential reducing agents that could reduce the effectiveness of Hg oxidation. Another potential reducer may be carbon monoxide. This work targets coal-fired TPPs equipped with wet PM scrubbers as PM collectors. At these TPPs, it is most convenient to inject oxidizers into irrigation water of scrubbers.

For this purpose, laboratory studies, shown conceptually in Figure 5, were conducted on the interaction of solutions of oxidizers with the Hg vapor in the air, as well as the interaction of potassium permanganate and sodium hypochlorite with carbon monoxide. Detailed description of laboratory setup and analytical procedures is given in Appendix A: Laboratory Setup and Analytical Procedures.



- **Mercury concentration:**
40 ng/l
(2 to 4 ng/l in flue gases)
- **Oxidizer concentration:**
0.1 to 1% in water
- **pH:** 2 to 11
- **Temperature:** 20 to 95 °C

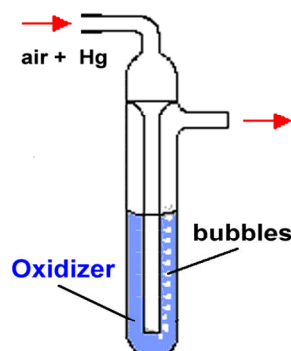


Figure 5. Testing concept for laboratory studies.

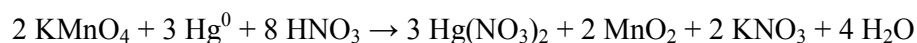
Concentration of Hg vapor in air before and after the aqueous oxidizer absorbent was measured using an RP-915+ Mercury Analyzer (Lumex). Description of the apparatus is given in Appendix A. For comparison, experiments were conducted by bubbling through 0.25-percent HNO₃ and through H₂O. Mercury concentration in the room before the experiment was measured at 25 ng/m³.

Initial Hg⁰ concentrations used under laboratory conditions were approximately 7 to 10 times higher than in the flue gas in Toliatti TPP (4 µg/m³ or 4,000 ng/m³). The results are shown in Table 1 giving Hg concentrations in simulated air before and after bubbling through aqueous solutions of various oxidants.

Table 1. Concentration of Hg vapor in the air before and after bubbling through oxidizers.

Oxidizer solution		Experiment duration, min.	Solution temperature, °C	Hg concentration, ng/m ³	
				Before	After
1.	1% KMnO ₄	30	20	35750	1840
		30	30	35750	1700
		30	50	35750	500
2.	1% KMnO ₄ , pH 2.5	30	20	22300	26
3.	1% KMnO ₄ , (pH 10)	30	20	27900	430
4.	0.1% KMnO ₄	30	20	26900	760
5.	0.1% KMnO ₄ , pH 3.0	30	20	42000	30
6.	0.1% KMnO ₄ , pH 10	30	20	42000	280
7.	1% KClO ₃	30	20	27000	4200
8.	1% KClO ₃	30	45	26000	2300
9.	1% K ₂ S ₂ O ₈	30	20	18000	3000
10.	1% K ₂ S ₂ O ₈	30	45	21000	1250
11.	1% K ₂ S ₂ O ₈ , pH 2	30	20	29000	1300
12.	0.02 M KJ+J ₂	30	20	41000	< 10
13.	0.25% HNO ₃	30	20	18000	1900
14.	0.25% HNO ₃	30	45	18800	1800
15.	H ₂ O	30	20	27500	26500

The highest Hg removal was observed for acidified solution of potassium permanganate (KMnO₄), even at a low concentration of 0.1 percent, and 20 °C (experiment number 5). The reaction taking place is shown below:



Based on results shown in Table 1, further studies have focused on the use of potassium permanganate as an oxidant.

3.1 Interaction of Carbon Monoxide with Potassium Permanganate

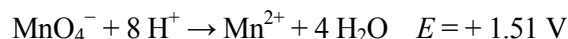
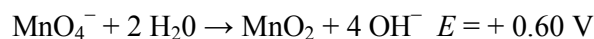
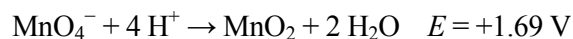
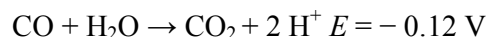
Interactions of carbon monoxide with potassium permanganate were investigated by monitoring the duration of CO bubbling, temperature, and pH of the KMnO_4 solution in the bubble flasks as well as KMnO_4 concentration following bubbling. The results are given in Table 2.

Table 2. Interaction of CO with KMnO_4 solution in water.

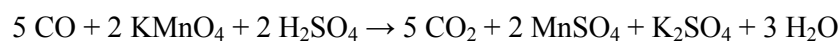
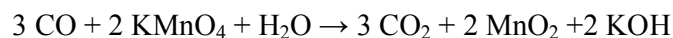
KMnO_4 concentration, %	Bubbling time	T °C	pH	KMnO_4 , concentration after bubbling, %	Note
0.001	40 s	20	7	0.00005	almost colorless
0.01	3 min	20	7	0.0013	yellowish-pink
0.1	5 min	20	7	0.05	brown
0.1	5 min	20	7	0.06	brown
0.001	60 s	20	2	0.00005	colorless
0.01	3 min	20	2	0	brown
0.04	5 min	20	0.3	0.013	1st bubbling
0.04	5 min	20	0.3	0.015	2nd bubbling
0.1	5 min	20	2	0.033	red-brown
0.1	5 min	65	7	0.053	red-brown
0.1	5 min	68	2	0.02	red-brown

The formation of brown manganese dioxide precipitate interfered with visual monitoring of the disappearance of KMnO_4 . Thus, control of KMnO_4 concentration after filtration of the precipitate MnO_2 was performed spectrophotometrically (spectrophotometer Hitachi U-1900, Japan) using calibration chart (see Appendix A).

Normal oxidation potentials are given below and were taken from literature (Lurie YY, *Handbook of Analytical Chemistry*, Moscow, Chemistry, 1971, s.271):



Reaction equations are given below:

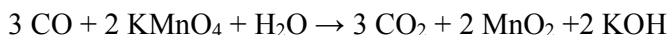


From the experiments described above, the following conclusions may be drawn:

- The rate of reaction of CO with KMnO_4 is extremely low

- No significant dependence of reaction rate on temperature and pH of the solution were found

As has been noted above, the rate of reaction of CO with KMnO₄ is low. As a result, difference in the flow rate of gaseous CO at the inlet and outlet of bubblers (two in a series) is practically non-detectable. Breakthrough of CO through a solution of KMnO₄ and low rate of its interaction is probably due to the low solubility of carbon monoxide in water. At the same time, as the equation below illustrates, under appropriate conditions the reaction can proceed to completion with precipitation of MnO₂:



This means that, theoretically, in Toliatti TPP, a huge and unacceptable expense for KMnO₄ (about 1700 kg/h) would be required for neutralizing a large amount of carbon monoxide (452 kg CO/h). The accurate answer as to the possibility of Hg emissions control by addition of potassium permanganate to a wet PM scrubber could only be obtained via experiments at the TPP.

3.2 Interaction of Mercury Vapor with the Sodium Hypochlorite

A solution of sodium hypochlorite (NaClO) was synthesized by electrolysis of NaCl. The concentration of NaClO was determined by iodometric titration with sodium thiosulfate. The initial solution contained 0.4-percent NaClO. More dilute solutions of 0.1 percent and 0.01 percent were prepared for tests of Hg absorption. The concentration of Hg vapor before and after the aqueous oxidizer absorbent was measured using RP-915+ Mercury Analyzer (Lumex). The Hg content in the room before the experiment was 150 ng/m³.

Data in Table 3 show high effectiveness of sodium hypochlorite for Hg oxidation, similar to potassium permanganate. Surprising and encouraging is the fact that 95 percent of Hg is oxidized even at very low concentrations of NaClO (0.01% NaClO, pH 8).

Table 3. Concentration of Hg vapor before and after bubbling through NaClO.

Oxidizer solution		Experiment time, min	Solution temperature, °C	Hg concentration, ng/m ³	
				Before	After
1.	H ₂ O	30	20	28400	21650
2.	0.01% NaClO, pH 8	30	20	39700	1910
3.	0.1% NaClO, pH 8	30	20	36200	640
4.	0.1% NaClO, pH 2	30	20	35600	303
5.	0.1% NaClO, pH 8	30	40	29900	1110

It should be noted that acidification of the solution leads to a significant change of the hypochlorite concentration due to its decomposition with simultaneous release of chlorine. This fact does not reduce the effectiveness of Hg control at a power plant, but can potentially improve it, if technology could be arranged so that the free chlorine would react with the Hg at the time of formation (*in situ*). Efficiency of Hg removal with various oxidants at pH=3 and temperature of 20 °C is shown in Figure 6 as a function of oxidant concentration. As can be seen in Figure 6, 100 % Hg capture was accomplished under laboratory conditions when either KMnO₄ or NaClO were added at 0.2% concentration. Two other additives tested, K₂S₂O₈ and KClO₃, were less effective and only improved Hg capture up to about 80 or about 75% when added at 0.5%.

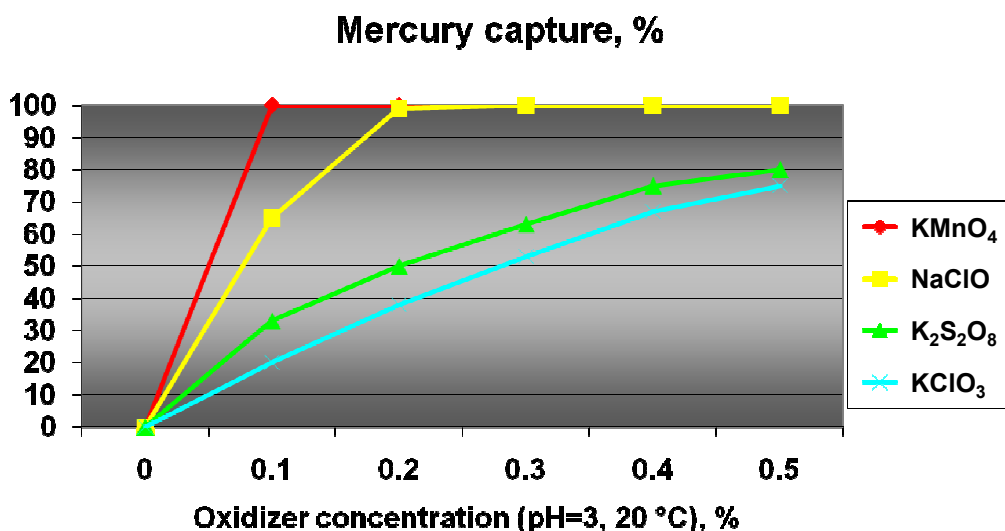


Figure 6. Efficiency of Hg removal with injection of various additives.

3.3 Interaction of Carbon Monoxide with Sodium Hypochlorite

A solution of NaClO was synthesized by electrolysis and its concentration was determined by iodometric titration with sodium thiosulfate. The initial solution contained 0.4-percent NaClO. More dilute solutions of 0.1 percent and 0.01 percent were prepared for experiments on absorption of Hg.

Acidification of solutions as a result of CO bubbling led to a noticeable change of hypochlorite concentration (concentration shown in brackets in the table) and evolution of chlorine. CO was bubbled at a standard flow, and the bubbling time was fixed. Flow rate was measured before and after the bubblers.

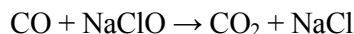
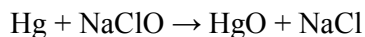
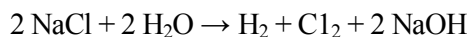
Table 4. Interaction of CO with NaClO solution.

NaClO concentration	Bubbling time, min.	T °C	pH	NaClO concentration after bubbling
0.01%	5	20	8	0.009%
0.01% (0.005)	5	20	2	0.0018%
0.01% (0.005)	5	20	2	1st bubbler 0.0018%
				2nd bubbler 0.0036%
0.01%	5	50	8	0.009%
0.1%	5	20	8	0.09%
0.1%	5	50	8	0.1%
0.1% (0.06)	5	20	2	0.004

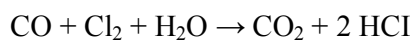
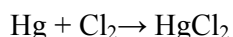
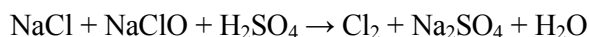
The experimental results shown in Table 4 indicate that NaClO has low activity in reaction with CO. As was the case of KMnO₄, the observed rate of reaction of CO with hypochlorite is

negligible. In the case of sodium hypochlorite, breakthrough of CO is also likely, due to low solubility of carbon monoxide in water. As expected, the increase of temperature of NaClO did not affect the reaction rate. Progress of reactions is given below:

at pH 8



at pH 2



3.4 Laboratory Study Conclusions and Recommendations

Laboratory studies confirmed that addition of KMnO_4 or NaClO into a wet PM scrubber can increase the degree of capture of Hg vapor from flue gas by converting Hg^0 into soluble Hg^{2+} compounds.

When considering the above two oxidizers, preference should be given to NaClO , for the following reasons:

- The disadvantage of KMnO_4 is that its distribution is regulated by State regulatory agencies. In addition, it is much more expensive than NaClO . Technological disadvantages include its very slow dissolution in water and inevitable appearance of manganese compounds in wastewater.
- The advantage of NaClO is that it can be generated with a flow-through electrolytic cell at the site. Thus, it is possible to exclude purchasing and transportation of concentrates as well as transportation and installation of additional containers and dispensers.
- For experiments at Toliatti TPP, it is recommended that 3.4 to 34 kg/h of sodium hypochlorite be added (or from 8.5 to 85 kg/h of 40% concentrate).
- Additional considerations related to oxidizing agents must take into account their cost, potential corrosive properties, safety issues, fire protection, etc.

4 Pilot Plant Tests at Toliatti TPP

Pilot plant verification of laboratory research results has been conducted at boiler TP-87 of Toliatti TPP equipped with wet PM scrubbers – the same unit that has been used previously for preliminary experiments during tests funded by the U.S. EPA. The pilot plant used for testing oxidation of Hg is shown schematically (top portion of the figure) and in a picture (bottom portion of the figure) in Figure 7. The main components of the pilot plant are oxidant tank, metering device for measuring oxidant addition rate, pump, and oxidant delivery tubing for injection of oxidant into the spray water pipe. As can be seen in Figure 7, the additive (NaClO) is pumped from the oxidizer tank and injected into the spray water pipe delivering spray water to the Venturi tube of the wet PM scrubber. The pilot plant shown in Figure 7 has been developed and installed specifically for testing of NaClO injection.

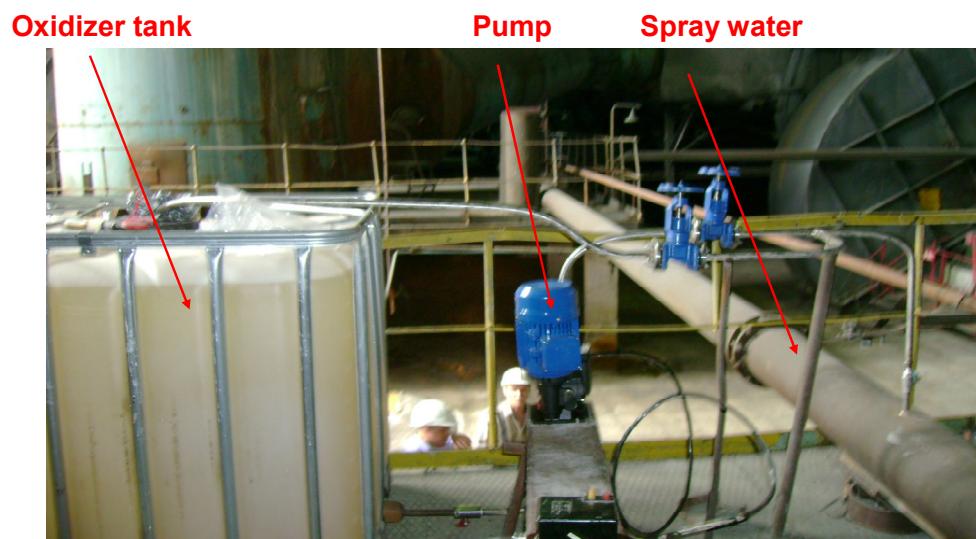
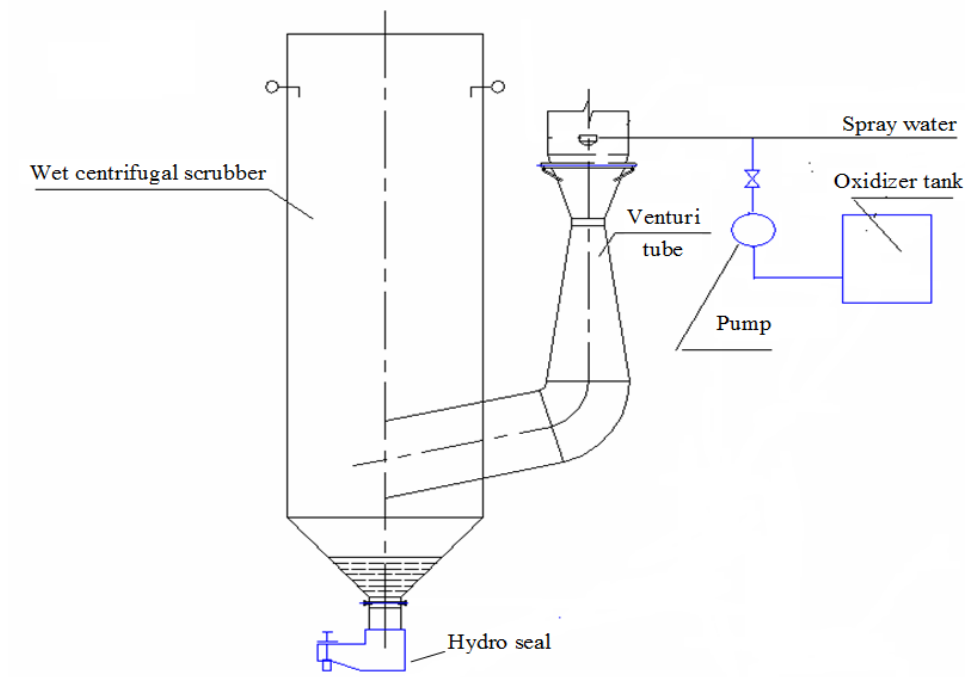


Figure 7. Pilot plant for injection of additives (top: schematic; bottom: actual).

4.1 Test Conditions

Pilot plant test conditions during tests at Toliatti TPP were as follows:

- Steam flow rate 420 t/h
- Spray water flow rate 60 t/h
- Flue gas flow rate 660,000 Nm³/h
- Oxidizer used 19% NaClO

Composition of coal fired during pilot tests was as follows:

- Heating value $Q_H^P = 23,540$ kJ/kg
- Ash content $A^P = 19.1\%$
- Moisture $W^P = 8.81\%$
- Volatility $V^P = 13.0\%$
- Sulfur content $S^P = 0.31\%$

Flue gas composition at the sampling point was:

- O₂ = 9.5 to 10.0%
- NO_x = 600 to 650 mg/m³
- CO = 20 to 25 mg/m³

Summary of pilot test conditions is given in Table 5.

Table 5. Pilot test conditions at TP-87 at Toliatti TPP.

Test no.	Flow of gases through the tube, l/min.	Total gas flow through sample under standard conditions, l	Sampling time, min.	Consumption of 19% sodium hypochlorite, l/h	Water consumption for wet PM scrubber, ton/h	Note
1	0.85	17.0	20	0	60	Sorbent Trap (yellow)
2	0.73	14.6	20	0	60	
3	0.65	13.0	20	0	60	
4	0.75	15.0	20	0	60	
5	0.90	18.0	20	0	60	
6	0.75	15.0	20	0	60	
7	0.50	15.0	30	0	60	Speciation Sorbent Trap (Red and Green)
8	0.50	15.0	30	0	60	
9	0.87	17.4	20	90	60	Sorbent Trap (yellow)
10	0.80	16.0	20	90	60	
11	0.68	10.2	15	90	60	
12	0.87	13.05	15	90	60	
13	0.90	18.0	20	172	60	
14	1.00	20.0	20	172	60	
15	0.75	15.0	20	172	60	
16	0.75	15.0	20	172	60	
17	1.00	20.0	20	172	60	
18	0.80	16.0	20	172	60	
19	0.89	26.7	30	250	60	
20	0.85	25.5	30	250	60	
21	0.85	17.0	20	250	60	
22	0.87	17.4	20	250	60	
23	0.90	18.0	20	250	60	
24	0.95	19.0	20	250	60	
25	0.50	15.0	30	250	60	Speciation Sorbent Trap (Red and Green)
26	0.40	12.0	30	250	60	

Regular and speciating sorbent traps were used, as shown in Table 5. Detailed analytical results are given in Appendix B: Results of Mercury Sampling with Sorbent Traps.

Generally, addition of an aqueous solution of NaClO into the wet PM scrubber's system reduced Hg content in flue gas. This trend is shown in Table 6 below for tests at TP-87 at Toliatti TPP.

Table 6. Effect of increasing sodium hypochlorite addition rate on Hg removal.

Sample number	Addition rate of 19% NaClO, l/h	Average Hg concentration in flue gas, ng / l
Tubes 1 through 8	0	1.886
Tubes 9 through 12	90	1.824
Tubes 13 through 18	172	1.623
Tubes 19 through 26	250	1.416

Interesting results were observed when comparing the results for tests number 7 and 8 with results for tests number 25 and 26 (both groups of tests shown in Table 5). For both groups of tests, unspiked speciating carbon traps were used. Tests number 7 and 8 did not have addition of NaClO; tests number 25 and 26 had sodium hypochlorite addition at a rate of 250 l/h.

For tests number 7 and 8 (without NaClO), significant amounts of Hg^{2+} were measured. It appears that these were forms of Hg^{2+} sparingly soluble in water. Addition of NaClO apparently led to chemical transformation of these forms of Hg into water-soluble forms and, as a consequence, negligible amounts of Hg^{2+} were measured in tests number 25 and 26.

Figure 8 summarizes Hg concentration measurements in flue gas of boiler TP-87 for various operating modes of wet PM scrubbers. As can be seen, up to about 60-percent total Hg capture was possible with addition NaClO to the wet PM scrubber system. Essentially all Hg^{2+} was captured at NaClO addition rate of 0.3 kg/metric ton of water/hour or higher.

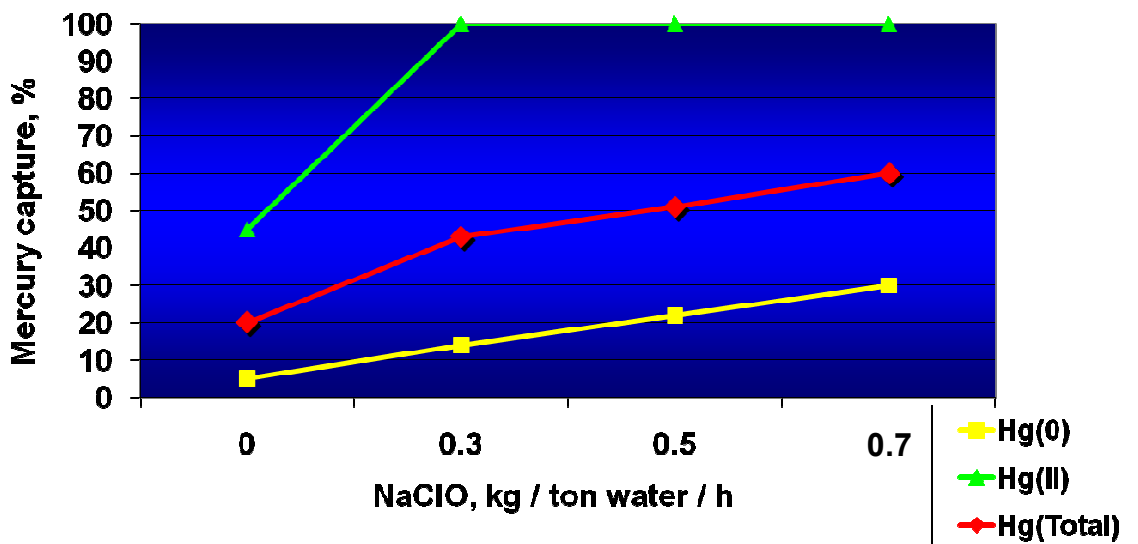


Figure 8. Effect of oxidizer injection rate on Hg removal.

5 Summary and Conclusions

The project has modified the wet PM scrubber installed on boiler #12 (TP-87 boiler) of Toliatti power plant (Toliatti TPP). The modification was by the means of the closed-loop liquid spray system allowing the addition of small amounts of oxidizing chemical into the main spray system of the wet PM scrubber to increase Hg removal. Laboratory studies carried out in the beginning of the project evaluated the addition of small quantities of oxidizing chemicals, such as for example, NaClO, KMnO₄, KClO₃, and K₂S₂O₈. The studies confirmed that addition of oxidizing chemicals into a wet PM scrubber could increase the capture of Hg vapor from flue gas by converting Hg⁰ into soluble Hg²⁺ compounds. The water soluble Hg²⁺ forms will be removed in wet PM scrubber and thus allowing for removal of the mercury from the gas stream. Following the laboratory screening of oxidizing chemicals, NaClO was selected for pilot tests at the power plant.

The oxidant delivery pilot plant for verification of laboratory research results has been installed at boiler TP-87 of Toliatti TPP firing Kuznetsk coal. The U.S. EPA Mercury Measurement Toolkit with a Lumex RA-915+ Mercury Analyzer with pyrolyzer PYRO-915, utilizing regular and speciated sorbent traps was used for Hg measurement. Addition of NaClO led to chemical transformation of Hg into water-soluble forms and, as a consequence, negligible amounts of Hg²⁺ were measured in flue gas downstream of the wet PM scrubber. Up to about 60-percent total Hg capture was possible with addition NaClO to the wet PM scrubber system, up from about 20-percent total Hg capture without the addition of chemicals. Speciated flue gas Hg measurements have shown that essentially all Hg²⁺ was captured by the wet PM scrubber, even with a very small addition rate of NaClO solution..

Analysis of pilot test results from Toliatti TPP demonstration leads to the following conclusions:

1. Wet PM scrubber is capable of removing about 20 percent of Hg without oxidizer addition.
2. Increasing the amount of spray water doesn't increase Hg⁰ removal, which is less than 5 percent. Even when utilizing impractically high water flow rates, about 40 percent of total Hg is removed.
3. Addition of NaClO into the wet PM scrubber system leads to significantly increased total Hg removal.
4. Hg⁰ removal increased up to about 25 to 30 percent with NaClO addition.
5. For tests when the addition rate of NaClO solution into wet PM scrubber system was increased up to 0.8 kg/metric ton of water/hour, total Hg capture was about 55 to 60 percent.
6. Nearly complete removal of Hg²⁺ was obtained even with very small addition rate of NaClO solution.

Appendix A: Laboratory Setup and Analytical Procedures

Laboratory setup described below was used to carry out experiments investigating oxidation of Hg^0 vapor in the air by bubbling it through aqueous solutions of oxidizers such as KMnO_4 and NaClO . Other oxidizers investigated during this study were KClO_3 , $\text{K}_2\text{S}_2\text{O}_8$, and $\text{KJ}+\text{J}_2$.

Apparatus

Experimental apparatus consisted of two impingers located in a fume hood. In the first impinger, high concentration of Hg vapor was produced by placing metallic Hg in it. Air with Hg vapor from the first impinger was bubbled (0.2 l/min) through 0.5 liters of oxidizer solution that was in the second glass impinger. Measurements of Hg concentration were made after 25 to 30 minutes from the start of each experiment to achieve a dynamic equilibrium concentration of Hg in air in both containers. The concentration of Hg in the first impinger was measured near the inlet of the pump and concentration of Hg in air was measured in the second impinger over saturated solution. Measurement was repeated 2 to 3 times. Solution temperature was varied from 20 to 50 °C. The contact time of air bubbles with a solution of oxidizer was approximately 0.5 sec.

KMnO₄+CO System Experiments

Carbon monoxide from a cylinder was used at a gas flow rate of 4 ml/s (40 ml per 10 seconds). The initial solution was prepared with 0.1-percent KMnO_4 concentration, solutions 0.04, 0.01, and 0.001-percent concentration of KMnO_4 were prepared by diluting the initial solution. In a bubbler filled with 10 ml of KMnO_4 and with a constant gas flow rate, the contact time was fixed. HNO_3 was added to acidify to pH 2 and 0.04-percent solution was adjusted to pH 0.3. After completing the bubbling of CO, the remaining amount of KMnO_4 in solution was determined spectrophotometrically. The precipitate of MnO_2 was filtered; more concentrated solutions were diluted.

The spectral data and calibration chart for concentration of KMnO_4 in reaction with carbon monoxide is given in Figure A1.

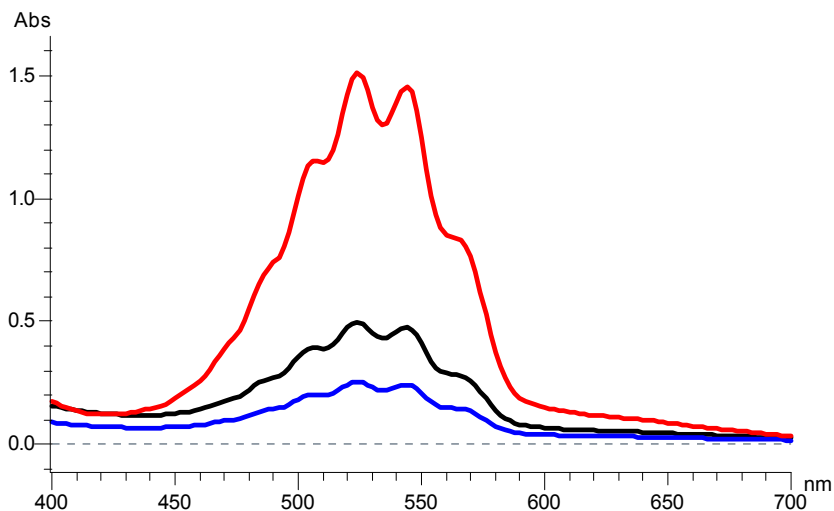


Figure A1. Spectral data and calibration chart for changing the concentration of KMnO_4 in the reaction with carbon monoxide.

Red - initial concentration KMnO_4 (0.1 % KMnO_4).

Black - final concentration KMnO_4 at pH 7 and 20 °C

Blue - final concentration KMnO_4 at pH 2 and 68 °C

Calibration curve for determining the concentration of KMnO_4 (optical density as a function of KMnO_4 concentration) is shown in Figure A2.

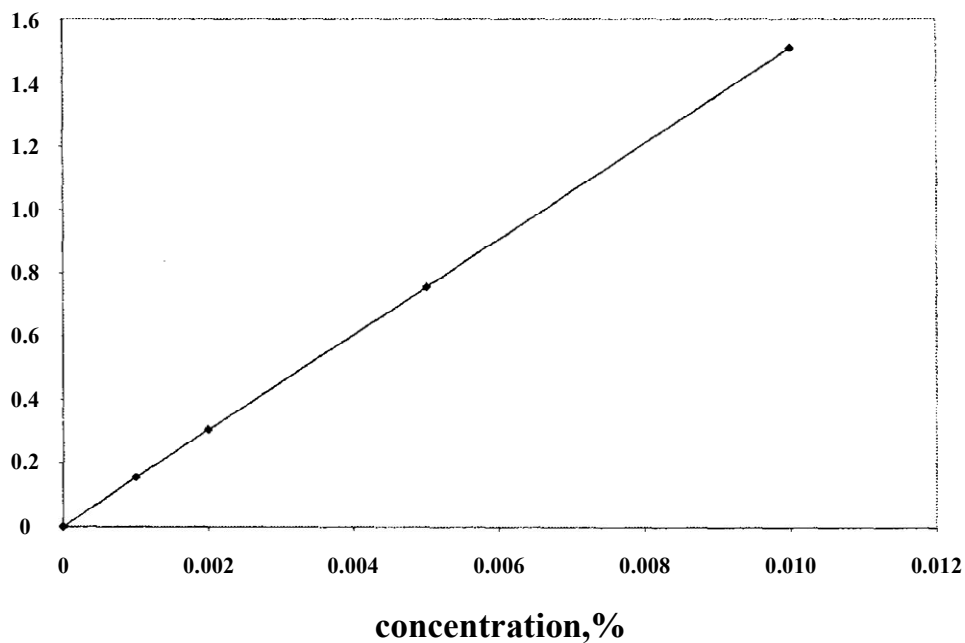


Figure A2. Calibration curve for KMnO_4 .

NaClO+CO System Experiments

First, 20 ml of NaClO was poured into impinger, CO was bubbled at a rate of 2.1 ml/s (40 ml per 19 seconds), and the contact time was fixed. The rate of bubbling monitored before and after the impinger (and after the second impinger in a separate experiment). Flow rate remained the same as before the impinger (2.1 ml/s) within the measurement error.

Titration was used for determination of “active chlorine” (Standard PNDF 14.1:2.113-97, Russia), based on the fact that free chlorine, hypochlorous acid, and hypochlorite ion react in an acidic medium with potassium iodide to release iodine that is titrated with sodium thiosulfate in the presence of starch.

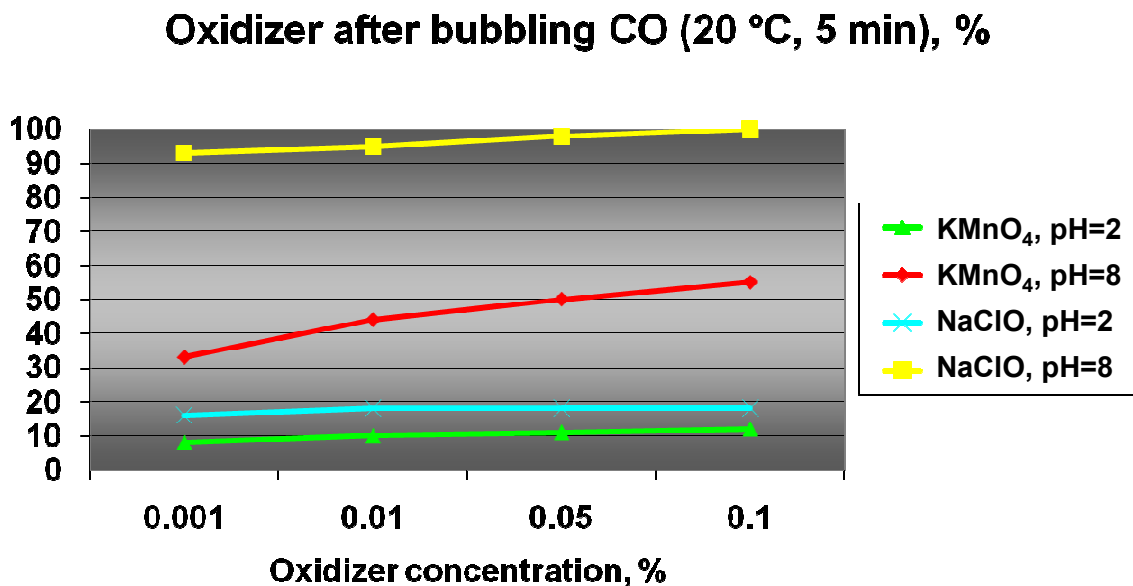


Figure A3. Efficiency of Hg removal for injection of various additives.

Analysis

In a conical flask equipped with a ground-glass stopper, 0.5 to 0.7 grams of potassium iodide is dissolved in 2 to 3 cm³ of distilled water; 12 cm³ acetic acid-acetate buffer (pH 4.5) is added, mixed, and placed for 5 minutes in a dark place. The liberated iodine is titrated with sodium thiosulfate (molar concentration 0.005 to 0.1 mol/dm³ depending on the content of “active chlorine” from 0.05 to 5.0 mg/dm³) until a light yellow color; 1 to 2 cm³ of starch solution is added and titration continued to the disappearance of the blue color of the solution.

Mass concentration of “active chlorine” (mg/l) is calculated by the formula below:

$$X = \frac{a \cdot K \cdot M \cdot 35,5 \cdot 1000}{V}$$

where

a – amount of sodium thiosulfate consumed in the titration of the sample, cm³

V – aliquot of sample, cm³

M – molar concentration of one equivalent of sodium thiosulfate, mol/dm³

K – correction factor for the titer of sodium thiosulfate

35.5 – equivalent molar mass of chlorine, g/mol

Appendix B: Results of Mercury Sampling Using Sorbent Traps

Analysis of Hg was performed according to U.S. EPA Mercury Measurement Toolkit's procedures using a Lumex RA-915+ Mercury Analyzer with pyrolyzer PYRO-915. The pyrolyzer has several modes of sample processing. Analysis of carbon was carried out in Mode 1, the temperature was 680 to 740 °C, and air flow rate was 0.8 to 1.2 l/min. Potassium chloride was analyzed in Mode 2 with processing temperature of 520 to 580 °C and air flow rate 0.8 to 1.2 l/min. In some cases, afterburning mode was used for additional heating of the evaporator with air flow increased to 3 l/min.

According to the guidelines on the use and analysis of sorbent traps, the first step of analysis was annealing of quartz boats.

The tube was cut in sections, close to carbon and fiberglass plugs. The first and subsequent plugs were weighed and then annealed in foil. In some cases (tubes 18, 20, 21, 22), all three plugs were burned at once. Phases with carbon or potassium chloride were weighed; depending on their weight, one to three samples were used and annealed. The results were summarized for each phase.

The results of analysis are presented in Table B1. Analyses of Hg in coal burned at the plant during tests is presented in Table B2.

Table B1. Results of analysis.

Trap number gas flow, l	Name of phase	Total weight of phase, g	Total Hg content in phase, ng	Total Hg content in tube, ng	Total Hg content, ng/l flue gas
No NaClO Average: 1.886 ng/l					
№ 1 17.0	Plug 21-1-3	0.1891	12.25	35.4	2.08
	Carbon 21-1	0.4298	22.11		
	Carbon 21-2	0.4108	1.04		
No NaClO Average: 1.886 ng/l					
№ 2 14.6	Plug 22-1-3	0.1952	8.206	25.716	1.76
	Carbon 22-1	0.4231	16.78		
	Carbon 22-2	0.2569	0.73		
No NaClO Average: 1.886 ng/l					
№ 3 13.0	Plug 23-1	0.0769	5.61	21.893	1.68
	Carbon 23-1	0.4168	13.09		
	Plug 23-2	0.0745	1.04		
	Carbon 23-2	0.4227	0.313		
	Plug 23-3	0.0708	1.84		
No NaClO Average: 1.886 ng/l					
№ 4 15.0	Plug 24-1	0.0673	6.595	26.04	1.74
	Carbon 24-1	0.4234	17.9		
	Plug 24-2	0.1279	0.396		
	Carbon 24-2	0.4169	0.77		
	Plug 24-3	0.0604	0.38		
No NaClO Average: 1.886 ng/l					
№ 5 18.0	Plug 25-1	0.0740	10.73	34.68	1.927
	Carbon 25-1	0.4235	22.32		
	Plug 25-2	0.0707	0.99		
	Carbon 25-2	0.4205	0.178		
	Plug 25-3	0.0611	0.46		
No NaClO Average: 1.886 ng/l					
№ 6 15.0	Plug 26-1	0.0907	7.89	26.9	1.79
	Carbon 26-1	0.4215	16.02		
	Plug 26-2	0.0720	0.58		
	Carbon 26-2	0.4284	1.83		
	Plug 26-3	0.0578	0.58		
No NaClO (tubes with KCL) Average: 2.055 ng/l					

Trap number gas flow, l	Name of phase	Total weight of phase, g	Total Hg content in phase, ng	Total Hg content in tube, ng	Total Hg content, ng/l flue gas
№ 7 15.0	Plug 27-1	0.0954	7.250	28.555	1.904
	KCL 27-1	1.4575	7.814		
	Plug 27-2	0.0976	1.366		
	KCL 27-2	0.7555	0.866		
	Plug 27-3	0.0930	1.116		
	Carbon 27-3	0.4960	7.417		
	Plug 27-4	0.946	2.365		
	Carbon 27-4	0.4957	0.087		
	Plug 27-5	0.0609	0.274		
Addition of NaClO 90 l/h Average: 1.824 ng/l					
№ 9 17.4	Plug 17-1	0.0766	11.49	31.38	1.800
	Carbon 17-1	0.4245	17.39		
	Plug 17-2	0.0684	1.23		
	Carbon 17-2	0.4207	0.22		
	Plug 17-3	0.0584	1.05		
№ 10 16.0	Plug 18-1-3	0.1906	14.585	30.295	1.893
	Carbon 18-1	0.4160	15.275		
	Carbon 18-2	0.4263	0.435		
№ 11 10.2	Plug 19-1	0.0719	7.573	18.914	1.854
	Carbon 19-1	0.4154	9.516		
	Plug 19-2	0.0746	1.007		
	Carbon 19-2	0.4108	0.24		

Trap number gas flow, l	Name of phase	Total weight of phase, g	Total Hg content in phase, ng	Total Hg content in tube, ng	Total Hg content, ng/l flue gas
	Plug 19-3	0.0598	0.478		
Addition of NaClO 172 l/h Average: 1,623 ng/l					
№ 12 13.05	Plug 20-1-3	0.2051	9.049	22.892	1.75
	Carbon 20-1	0.4204	13.226		
Carbon 20-2	0.4278	0.557			
Addition of NaClO 172 l/h Average: 1,623 ng/l					
№ 13 18,0	Plug 11-1	0.0764	9.02	27.57	1.532
	Carbon 11-1	0.4240	16.49		
	Plug 11-2	0.0706	0.85		
	Carbon 11-2	0.4158	0.3		
	Plug 11-3	0.0056	1.01		
Addition of NaClO 172 l/h Average: 1,623 ng/l					
№ 14 20,0	Plug 12-1	0.0786	11.08	27.87	1.39
	Carbon 12-1	0.4241	15.03		
	Plug 12 -2	0.0715	0.77		
	Carbon 12-2	0.4267	0.12		
	Plug 12-3	0.00594	0.48		
Addition of NaClO 172 l/h Average: 1,623 ng/l					
№ 15 15,0	Plug 13-1	0.0787	9.36	24.42	1.628
	Carbon 13-1	0.4122	13.38		
	Plug 13-2	0.077	0.46		
	Carbon 13-2	0.4207	0.72		
	Plug 13-3	0.066	0.5		
Addition of NaClO 172 l/h Average: 1,623 ng/l					
№ 16 15,0	Plug 14-1	0.0775	10	28.03	1.87
	Carbon 14-1	0.4166	15.51		
	Plug 14-2	0.0797	0.8		
	Carbon 14-2	0.4191	0.99		
	Plug 14-3	0.0606	0.73		
Addition of NaClO 172 l/h Average: 1,623 ng/l					
№ 17 20,0	Plug 15-1	0.0738	11.88	32.9	1.645
	Carbon 15-1	0.4224	18.29		
	Plug 15-2	0.0676	0.95		
	Carbon 15-2	0.4158	0.28		

Trap number gas flow, l	Name of phase	Total weight of phase, g	Total Hg content in phase, ng	Total Hg content in tube, ng	Total Hg content, ng/l flue gas
	Plug 15-3	0.0601	1.5		
№ 18 16,0	Plug 16-1	0.0773	8.35	26.792	1.670
	Carbon 16-1	0.4167	16.7		
	Plug 16-2	0.0708	0.99		
	Carbon 16-2	0.4206	0.082		
	Plug 16-3	0.0577	0.66		
Addition of NaClO 250 l/h Average: 1.416 ng/l					
№ 19 26.7	Plug 3-1	0.0759	12.903	37.87	1.418
	Carbon 3-1	0.4223	22.493		
	Plug 3-2	0.0729	1.166		
	Carbon 3-2	0.4184	0.301		
	Plug 3-3	0.0597	1.015		
№ 20 25.5	Plug 4-1	0.0798	10.853	30.31	1.189
	Carbon 4-1	0.4236	18.564		
	Plug 4-2	0.0736	0.96		
	Carbon 4-2	0.4251	0.359		
	Plug 4-3	0.0644	0.534		
№ 21 17.0	Plug 5-1	0.0777	12.976	27.662	1.627
	Carbon 5-1	0.4244	12.179		
	Plug 5-2	0.0723	0.723		
	Carbon 5-2	0.4156	0.484		
	Plug 5-3	0.0619	1.300		
№ 22 17.4	Plug 6-1	0.0772	9.418	24.421	1.404
	Carbon 6-1	0.4249	12.884		
	Plug 6-2	0.0786	0.786		
	Carbon 6-2	0.4193	0.378		
	Plug 6-3	0.0620	0.955		
№ 23	Plug 7-1	0.0788	11.032	27.036	1.502
	Carbon 7-1	0.4224	15.229		

Trap number gas flow, l	Name of phase	Total weight of phase, g	Total Hg content in phase, ng	Total Hg content in tube, ng	Total Hg content, ng/l flue gas	
18.0	Plug 7-2	0.0746	0.440			
	Carbon 7-2	0.4268	0.365			
	Plug 7-3		0.410			
Addition of NaClO 250 l/h (tubes with KCL) Average: 1.474 ng/l						
№ 24	Plug 8-1	0.0758	9.788	24.508	1.290	
	Carbon 8-1	0.4251	13.000			
19.0	Plug 8-2	0.0727	0.872			
	Carbon 8-2	0.4269	0.203			
	Plug 8-3	0.0632	0.645			
№ 25	Plug 9-1	0.0918	6.334	19.538	1.306	
	KCL 9-1	1.5799	0.406			
	Plug 9-2	0.0931	3.910			
	KCL 9-2	0.9536	0.271			
	15.0	Plug 9-3	0.0959			1.343
		Carbon 9-3	0.4941			4.371
		Plug 9-4	0.0937			1.687
		Carbon 9-4	0.4913			0.157
		Plug 9-5	0.0623			1.059
№ 26	Plug 10-1	0.1004	6.426	19.056	1.588	
	KCL 10-1	1.5656	0.850			
	Plug 10-2	0.0917	3.301			
	KCL 10-2	0.9497	0.347			
	12.0	Plug 10-3	0.0928			1.485
		Carbon 10-3	0.5008			4.608
		Plug 10-4	0.0935			1.403
		Carbon 10-4	0.4941			0.023
		Plug 10-5	0.0613			0.613

Table B2. Analyses of Hg in coal burned at the plant during tests.

Coal sample weight, mg	Hg content in the sample, ng/g
89.8	102
86.9	100
61.9	120
90.3	85
67.6	77
128.9	104
132.6	116
83.9	122
93.6	109

Note: Average Hg content in coal – 104 ng/g

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